Anonyme. The Journal of physical chemistry. Published at Cornell university [3puis3 Published under the auspices of the American chemical society, the Chemical society and the Faraday society]. 1896 [I]-. 1931 . Oct.-dec..

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Journal of physical chemistry

Tome 35

Volume 40

Washington 1931

NUMERICAL EVALUATION OF INFINITE SERIES AND INTEGRALS WHICH ARISE IN CERTAIN PROBLEMS OF LINEAR HEAT FLOW, ELECTROCHEMICAL DIFFUSION, ETC.

BY W. LASH MILLER AND A. R. GORDON

In the Introduction to his *Théorie analytique de la chaleur*[1] Fourier points out that unless the solutions of the problems he considers are presented in a form that permits of numerical computation, they will be—for many purposes—valueless. He says:—

"Interprétation numérique des résultats du calcul est nécessaire et c'est un degré de perfection qu'il serait très important de donner à toutes les applications de l'Analyse au Sciences naturelles. On peut dire que, tant qu'on ne l'a pas obtenu, les solutions demeurent incomplètes ou inutiles, et que la vérité qu'on se proposait de découvrir n'est pas moins cachée dans les formules d'Analyse quelle ne l'était dans la question physique elle-même"[2].

Fourier's own contribution consisted in finding functions which satisfied the differential equations for the flow of heat and certain "boundary" and "initial" conditions as well. But in claiming[2] that these functions "are given in a form that is [always] convenient for numerical computation" he overstates his achievement; most of his solutions involve infinite series which except for special values of the constants converge too slowly to be summed. Subsequent writers seem to have lost sight altogether of Fourier's criterion; for instance the function given by Byerly[3] as the solution of the problem discussed in his *Art.* 51 *ex.* 4 involves integrals which are not only untabulated but which in general are not easily evaluated by the ordinary processes of graphical or tabular integration. The solutions obtained by Fourier's method for certain electrochemical problems on which we have been working in this laboratory, shared both defects; and in searching for methods by which the functions contained in them could be evaluated with the least expenditure of labour, we were led to study the whole question from a general point of view insofar as problems of linear flow are concerned.

Fourier's solutions, and the solutions obtained by his method for certain electrochemical problems,[4] are in general presented as infinite series; in Part II

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[1] Crowned by the Academy in 1812, printed in 1824-26. First published by Fermin Didot, Paris (1822). English edition: "The analytical theory of heat" (1878); See also Oeuvres de Fourier, Vol. I (1888), Vol. II (1890).

[2] Oeuvres de Fourier, Vol. I, p. 9.

[3] W. E. Byerly: Elementary Treatise on Fourier's series etc. (1893).

[4] T. R. Rosebrugh and W. Lash Miller: Mathematical theory of the changes of concentration at the electrode brought about by diffusion and by chemical action, J. Phys. Chem., 14, 816-884 (1912).

of the present paper we examine[1] the mathematical expressions for these series in the special case that the flow is linear, and shew that they fall into, or are closely related to, two groups for which we propose the names "Series of Φ_E Group" and "Series of the Λ_E Group" respectively. In Part I the initial and boundary conditions that give rise to series of these two groups are exemplified; other conditions[2] leading to solutions which do not involve series of these two groups are not considered. The examination brings out the relationship which the series of the Φ_E and Λ_E Groups bear to Jacobi's theta-functions; a relationship recognized by Jacobi[3] and formulated by Poincaré[4] and by Carslaw[5], but hitherto not exploited as a source of methods for evaluating the Groups in question.

These methods (Parts III and IV) are founded on the existence of pairs of series whose sums are equal but whose convergences are very differently affected by changes in the values of the constants they contain. The existence of such pairs was discovered by Jacobi in the case of his theta-functions; it is not however necessary to follow his argument in detail; for, as shewn in Sec. 5, Jacobi's classical results are only a special case of a formula due to Poisson[6] ("the Euler-Maclaurin Sum Formula with Poisson's Remainder") which in turn we shew to be merely a formulation of the Fourier's cosine-series for a series.[7]

The systematic plan based on this foundation for approximating to the sum of any series of the Groups here considered, must perforce take into account certain practical difficulties; one of these is the lack of numerical tables of certain integrals, another is the lack of finite expressions for certain

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[1] The examination is facilitated by the fact, noted by Fourier in a memoir of 1829 [Mémoire s.l. theorie d.l.chaleur: Mém. de l'Acad. roy.des Sciences 8, 581 (1829); Oeuvres de Fourier, Vol. II p. 149] that his general solution can be expressed as the sum of three quantities each of which (taken by itself) is the solution of a special case. This general solution, obviously an afterthought on the part of Fourier, is ignored by Byerly; probably because the *Mémoire* has been omitted from editions of the *Théorie*.

[2] See H. S. Carslaw: Introduction to the mathematical theory of the conduction of heat in solids, art. 36 p. 74 and art. 105 p. 213, (1921).

[3] "[Ces formulas] ne seront pas sans intérêt pour les célèbres géomètres qui s'occupent du mouvement de la chaleur; les numérateurs et les dénominateurs des fonctions par lesquelles on a exprimé les fonctions trigonométriques de l'amplitude étant souvent rencontrés dans ladite question." Letter from Jacobi to Legendre, April 1828 [C. G. L. Jacobi's gesammelte Werke, (1881), Vol. I p. 415]. The numerators and denominators there referred to are Jacobi's theta-functions.

[4] H. Poincaré: Théorie analytique de la propagation de la chaleur, p. 91, (1895).

[5] Carslaw: loc. cit., pp. 160, 161.

[6] Mém.s.l.calcul numérique des intégrales définies, Mém.d.l'Acad.roy.des Sciences, 6, 571 (1823).

Poisson barely escaped anticipation by Legendre [see A. M. LeGendre: Exercices de calcul intégral, Vol. II, Paris (1817) p. 150 Eq. g]. His deduction was based upon a theorem which has all but disappeared from mathematical literature, and whose validity has been attacked [see Carslaw: Introduction to the theory of Fourier's series and integrals, 2nd Ed., (1921), sec. 99, p. 230]. Boole deduced the formula by a method which the editor of the third edition [G. Boole: Treatise on the calculus of finite differences, 3rd Ed., sec. 16, p. 154 (1880)] rejected; on insufficient grounds it seems to us. The deduction given below involves but one assumption, viz. that the summand of the series to be transformed can be expanded in a cosine series, and thus supplies an answer to the question often raised "With what restrictions is the Poisson formula to be employed?".

[7] (See foot note page 2787.)

simpler series here called "Stationary". Where they exist, these obstacles restrict the choice of an approximation. Among the methods still available, the choice is based upon an *a priori* estimate of the amount of labour each procedure would require in order to obtain the sum with the degree of accuracy considered necessary by the computer; the fact that such an estimate can readily be made, renders the whole scheme practical.

Synopsis

Part I of the present paper gives examples of the problems[1] which can be solved in terms of series of the Groups whose summation is discussed below, and tabulates the "Original" (i.e. Fourier's) Forms of the solutions.

Part II classifies the series, defines the Families and Groups of which they are members, and explains the symbols used to represent them. It then deduces Poisson's Formula (assuming the validity of Fourier's expansion in a cosine-series) and uses it to obtain the "Poisson Forms" of all the series of the Families considered, including the series which occur in the Solutions of Part I.

Parts III and *IV* give labour-saving devices for evaluating all the series of the Φ_E and Λ_E Groups, and those related series which occur in the Solutions.

Part V uses the methods developed in Parts III and IV to evaluate certain integrals.

The Appendix discusses the integral $\int e^{z^2}.dz$ where z is complex. It contains numerical tables of $F(x) = e^{-x^2}\cdot\int_0^x e^{y^2}.dy$, Table XXVIII; $G(x) = \int_0^x e^{-\pi^2/y}.(1/\sqrt{y}).dy$ and $\int G(x).dx$, Table XXVII; and tables from which four-place values of the Fresnel Integrals may be obtained for all values of the argument without recourse to graphical interpolation (Table XXIV).

Readers whose sole wish is to find, as quickly as possible, the most suitable approximation to the series included in a Solution of Table I, must consult Table IV to find the symbol for the series; if this is not of the [*even*] or [*odd*]

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[7] Here Thomson was the pioneer [Quar. Jour. Math., I, 316 (1857)]. In 1857, without recognizing the functions with which he was dealing, he shewed that the "Original Form" of Jacobi's Θ_2 can be deduced from the "Poisson Form" (see below p. 2808) by developing the latter in a series of cosines. In a foot-note to this paper, Cayley pointed out that the relation found by Thomson had already been obtained by Jacobi and shewed how it might be deduced from known properties of the Elliptic Functions. From the point of view of the present paper, the chief service here rendered by Cayley was in reminding workers in this field that their functions are related to the Thetas; he apparently did not realize that Thomson's method might be made the starting point for a simplified treatment of the Elliptics themselves.

Carslaw [*Conduction of Heat*, loc. cit., p. 159] following essentially Thomson's procedure, shewed that when $f(y)$ is an "even" or "square" function

$$\sum_{-\infty}^{+\infty} f(b+n\omega) = \frac{2}{\omega}\cdot\int_0^\infty f(\lambda).d\lambda + \frac{4}{\omega}\cdot\sum_{n=1}^{\infty}\cos\frac{2n\pi b.}{\omega}\int_0^\infty f(\lambda)\cos\frac{2n\pi.d\lambda}{\omega}$$

Both Carslaw's and Thomson's equations are special cases of Poisson's Formula, see Table VII p. 2806.

[1] Thomson shews that the motion of a viscous fluid, closed electric current within a homogeneous conductor, and the electric potential in the conductor of a submarine cable when electromagnetic inertia can be neglected, can be dealt with similarly [B. A. Report, Sept. 1888; Math. and Phys. Papers Vol. III, p. 428].

type it must be replaced as shewn in the "Summary" of p. 2801. The form of $f(u)$ in the expression for Y at the head of Table I must then be noted, and the Class of the series found from Table X. The best approximation in view of the numerical values of at and gx is given in Table X. Sec. 9 furnishes examples of the use of each approximation, and a way to find an upper limit to the error involved in each.

If the series to be evaluated is contained in one of the Solutions of Table II, its symbol must be found from Table IV, and a suitable approximation from Part IV.

Readers who require approximations to an integral of the form $\int f(x^2).dx$ or $\int e^{\pm x^2}.f(x).dx$, should consult Part V; the approximations there given, however, are not in every case available, for they may involve integrals which themselves have not been tabulated.

Series of the Φ_F and Λ_F Groups do not occur in the Solutions of Part I; but because of their resemblance in form to those which do occur, they have been treated briefly, in brackets.

PART I

THE PROBLEMS AND THE ORIGINAL FORMS OF THE SOLUTIONS

The problems of heat flow and of diffusion which give rise to the series whose summation is discussed below may be grouped under four heads, the first second and third of which are solved by means of the differential equation (1) and the fourth by means of the differential equation (2).

Sec. 1: Problems leading to the differential equation (1).

(1) *Problems that have to do with the flow of heat* through a straight rod of uniform material and cross-section with the proviso that no heat can pass through the surface except at the ends:—In these the initial distribution of temperature along the axis is specified, and it is assumed that the two ends of the rod are maintained at arbitrary (constant or varied) temperatures throughout the experiment, or that they are impervious to heat, or that one end is impervious to heat while the temperature of the other is arbitrarily varied. Choosing as x-axis the direction of the rod ($x=0$ at one of its ends and $x=l$ at the other) using the letter z to denote the temperature and t to denote the time, the Initial Condition can be put in the form: [at $t=0$] $z=F(x)$; and the Boundary Condition at one end, e.g. [at $x=0$] is $z=f(t)$ if the temperature at the left hand end is arbitrarily controlled, or $\partial z/\partial x=0$ if that end is impervious to heat, while [at $x=l$] either $z=\psi(t)$ or $\partial z/\partial x=0$.

(2) *Problems of simple diffusion* through a solution contained in a cylindrical vessel:—Here the axis of the cylinder is taken as the x-axis, and z indicates the concentration of some selected constituent, supposed uniform throughout any given cross-section of the vessel. The initial distribution of concentration along the axis of the cylinder is specified, so that the Initial Condition is [at $t=0$] $z=F(x)$ as in the heat problem. The ends of the cylindrical mass of solution are taken to be impervious to the constituent

whose concentration is denoted by z—either because they are bounded by the material of which the vessel is composed, or (if one of them is a free surface) because the constituent in question is assumed to be non-volatile; so that the Boundary Condition both [at $x=0$] and [at $x=l$] is $\partial z/\partial x = 0$.

(3) *Problems of diffusion during electrolysis* when the ends of the cylindrical vessel are bounded by electrodes; with the proviso that no chemical reaction requiring appreciable time for its completion occurs between the products of electrolysis and the electrolyte:—Here z is used to indicate the concentration of some constituent (assumed uniform throughout each cross-section) which is formed or removed at either or both electrodes by electrolysis or migration or both combined; so that the rate of formation (or removal) of this constituent is proportional to the current. The Boundary Condition at an electrode at which the constituent appears or disappears will be $\partial z/\partial x = f(t)$; at one where it is neither formed nor destroyed and to or from which it is not transported by the current, the Condition will be $\partial z/\partial x = 0$. If the experimental conditions are such that during the electrolysis the concentration of the constituent to which z refers remains unaltered at some point between the electrodes, that point may be taken as the origin or as $x = l$ whichever is preferred; the Boundary Condition there will be z = *constant*, and the concentration changes between this point and either of the electrodes will obviously not be affected by any changes that may occur between it and the other. The same conditions hold in the case of a cylindrical electrode rotating in a uniform field; for the electrode may be regarded as surrounded by an adherent film of solution, uniform in thickness, through which diffusion occurs; and under ordinary experimental conditions this film is so thin that the difference between the areas of its inner and outer surfaces may be neglected.

Solutions of (1), (2) and (3):—In these three classes of problems the only Initial Condition that occurs is $z = F(x)$; and the only Boundary Conditions are $z = f(t)$ and $\partial z/\partial x = f(t)$, if the expressions $F(x)$ and $f(t)$ be taken to include zero and constants.[1] In solving them it is assumed that

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[1] The forms of $f(t)$ assumed in the conventional heat problems are: $f(t)$ = constant, $\sin \overline{b't+\alpha}$, $e^{b''t}$, $e^{Kt}.\sin \overline{v't+\alpha}$ – the last two in problems involving radiation; the same four forms occur in electrochemical problems. If when $t=t_1$, the temperature at which one end of the rod has been maintained is suddenly changed (see Byerly: loc. cit., Sec. 5^1, Ex. 2) or the current is abruptly varied, $f(t)$ is discontinuous (see p. 2833).

$F(x)$ is discontinuous in diffusion experiments where a layer of water is superposed on one of solution. If a change is made in the nature of the Boundary Conditions, i.e. if for $t > \vartheta$, z is specified while for $t < \vartheta$, $\partial z/\partial x$ had been specified (or vice versa), the Initial Condition of the new problem viz. $z = F(x)$ [at $t = \vartheta$], will be given by the Solution for $t = \vartheta$ of the problem for which the earlier Boundary Condition held, so that $F(x)$ will appear as an infinite series (see Tab. I and II). Such cases arise in electrolysis, for instance, when the concentration of copper at the cathode has been brought to zero by the current; up to that moment $\partial z/\partial x$ at the cathode has been fixed by the current, but the new condition will be $z = 0$. An analogous heat problem would arise if the end of a rod which had been maintained at constant temperature, should be thermally insulated. In these cases the Solution contains a double series, and every new change in the Boundary Conditions introduces an additional summation; examples are given in Part IV.

$$\partial z/\partial t = k.\partial^2 z/\partial x^2 \qquad (1)$$

where k is independent[1] of z, t and x.

Tables I and II give Solutions for certain of these problems[2], namely those in which two out of the three conditions have the form $z = 0$ or $\partial z/\partial x = 0$; solutions of all the others may be obtained by adding the expressions taken from the fourth columns of the tables, since the differential equation (1) is linear and therefore the sum of any number of solutions of it is itself a solution. For example, if the Initial Condition is [at $t = 0$] $z = F(x)$, and the Boundary Conditions are [at $x = 0$] $z = f(t)$ and [at $x = l$] $z = \psi(t)$, the solution is the sum of the Solutions Table I No. 1, Table I No. 1*a* in which $\psi(t)$ is to be written for $f(t)$, and Table II No. 1.

TABLE I[3]

[at $t = 0$] $z = 0$ for all values of x.

$$Y = \Sigma\Psi(N,gx).\int_0^t e^{-N^2a(t-u)}f(u).du;\ g = \pi/2l;\ a = g^2k.$$

No.	Boundary Conditions		Solution[4]	N	$\Psi(N,gx)$
	[at $x = 0$]	[at $x = l$]	$z =$		
1	$z = f(t)$	$z = 0$	$4aY/\pi$	$2n$	$2n.\sin 2ngx$
1a	$z = 0$	$z = f(t)$	$4aY/\pi$	$2n$	$(-1)^{n+1}2n.\sin 2ngx$
2	$z = f(t)$	$\partial z/\partial x = 0$	$4aY/\pi$	m	$m.\sin mgx$
2a	$\partial z/\partial x = 0$	$z = f(t)$	$4aY/\pi$	m	$(-1)^{n+1} m.\cos mgx$
3	$\partial z/\partial x = f(t)$	$z = 0$	$2kY/l$	m	$-\cos mgx$
3a	$z = 0$	$\partial z/\partial x = f(t)$	$2kY/l$	m	$(-1)^{n+1}.\sin mgx$
4	$\partial z/\partial x = f(t)$	$\partial z/\partial x = 0$	$\frac{2k}{l}(Y - \frac{1}{2}\int_0^t f(u).du)$	$2n$	$\cos 2ngx$
4a	$\partial z/\partial x = 0$	$\partial z/\partial x = f(t)$	$\frac{2k}{l}(Y + \frac{1}{2}\int_0^t f(u).du)$	$2n$	$-(-1)^{n+1}.\cos 2ngx$

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[1] The assumption that k depends on z (e.g. that the diffusion constant depends on the concentration) accords better with the facts; but if in Eq. 1, k be replaced by $\varphi(z)$, the resulting differential equation is not linear, and because of the mathematical difficulties involved, the general case has not been dealt with. An equation for the "Stationary State" (i.e. when $t = \infty$) has been deduced by Rosebrugh and Miller [loc. cit. p. 829] in the case of electrolysis with constant current.

[2] The Solutions given in Tab. II and those of Nos. 1, 1a, 2 and 2a of Tab. I are given in treatises on the conduction of heat [e.g. Byerly: loc. cit., Art. 61-63]. No. 3 of Tab. I is given by Rosebrugh and Miller: loc. cit. Eq. 44b.

[3] Here and throughout the paper, m is written as an abbreviation for $2n - 1$ and Σ for $\sum\limits_{n=1}^{\infty}$.

[4] The Solution given by Byerly (loc. cit.) for the conditions of Tab. I No. 2, after transliterating, is

$$z = f(t) - (4/\pi).f(t).\Sigma(\sin mgx)/m + 4aY/\pi \qquad \text{(A)}$$

He does not point out that the first and second members on the right of (A) are equal in magnitude and opposite in sign, and therefore cancel; the implication seems to be that at $x = 0$ the second and third terms on the right become zero (since $\sin mgx = 0$ if $x = 0$), leaving $z = f(t)$. This however is not the case; the Solution given in Tab. I No. 2 consists of the third term only on the right of (A) and may be written, after integrating by parts,

$$\begin{aligned} z = f(t).(4/\pi).\Sigma(\sin mgx)/m - f'(t).(4/\pi).\Sigma(\sin mgx)/m^3a + \dots \\ - f(0).(4/\pi).\Sigma(\sin mgx.e^{-m^2at})/m + \dots \end{aligned} \qquad \text{(B)}$$

When $x \rightarrow 0$, each of the series on the right of (B), except the first, approaches zero; while for all values of x no matter how small except for x identically zero, $(4/\pi).\Sigma(\sin mgx)/m = 1$; so that $z = f(t)$. Now in the physical phenomena which the mathematical formulas purport to represent, there is obviously no discontinuity at $x = 0$; so that if the formulas introduce a discontinuity there, it is the value when $x \rightarrow 0$ and not that when x is identically zero, that represents the physical condition at $x = 0$. The same remarks apply to Byerly's Solutions of Tab. I Nos. 1 and 1*a*.

Note: The condition common to all the Solutions in Table I, viz. "[at $t = 0$] $z = 0$", may be replaced by "[at $t = t_1$] $z = z_0$" by writing $(t-t_1)$ in place of t and $(z - z_0)$ in place of z throughout the Table.

Since it is obviously open to the computer to assign the value $x = 0$ to whichever end of the rod or cylinder he pleases (the other end then taking the value $x = l$), he can always choose freely between employing Solutions 1 or 1*a*, 2 or 2*a*, etc. The value of x corresponding to any given point on the rod will obviously be different in the two Solutions; but this is compensated for by the different forms of $\Psi(N,gx)$, and if the terms of Y be written out for any fixed point on the rod, they will be found to be identical in the two Solutions (cf.p. 2798). Thus if the series is to be summed directly i.e. if numerical values of the terms are to be computed and added, neither form has any advantage over the other; but if its sum is to be found by the use of approximations based on Poisson's Formula, 1*a*, 2*a*, 3*a* and 4*a* are not so convenient as the others.

TABLE II

[at $t = 0$] $z = F(x)$.

$$Y = \Sigma e^{-N^2at}.trig\ Ngx.\int_0^l F(\lambda).trig\ Ng\lambda.d\lambda;\ g = \pi/2l;\ a = g^2k.$$

No.	Boundary Conditions [at $x = 0$]	[at $x = l$]	Solution $z =$	N	*trig*
1	$z = 0$	$z = 0$	$2Y/l$	$2n$	*sin*
2	$z = 0$	$\partial z/\partial x = 0$	$2Y/l$	m	*sin*
2a	$\partial z/\partial x = 0$	$z = 0$	$2Y/l$	m	*cos*
3	$\partial z/\partial x = 0$	$\partial x/\partial x = 0$	$2Y/l + (1/l).\int_0^l F(\lambda).d\lambda$	$2n$	*cos*

Note: The condition common to all the Solutions of Table II, viz. "[at $t = 0$] $z = F(x)$," may be replaced by "[at $t = t_1$] $z - z_0 = F(x)$" by writing $(t - t_1)$ in place of t and $z-z_0$ in place of z throughout the Table.

Sec. 2: Problems leading to the differential equation (2).

(4) *Heat conduction problems* in which radiation is taken into account, *and diffusion problems* where the diffusing constituent is being destroyed simultaneously by reason of a chemical reaction whose rate is porportional to the concentration of that constituent:[1] Here the Initial and Boundary Conditions are those already established; but the differential equation is

$$\partial y/\partial t = k.\partial^2 y/\partial x^2 - Ky \tag{2}$$

in which y (instead of z) is written for the temperature or concentration, and both k and K are positive and independent of y, t and x.

Solutions of (4):—The solution of the differential equation (2) is

$$y = z.e^{-Kt} \tag{3}$$

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[1] For detailed discussion of electrochemical problems of this kind, see Rosebrugh and Miller: loc. cit. p. 864.

where z is a Solution of (1); and Tables I and II may be converted into tables of the Solutions of this second group of problems[1] by writing y instead of z, multiplying the entries headed "Solution" by e^{-Kt}, and replacing $f(u)$ wherever it occurs by $e^{Ku}.f(u)$. Thus the Solution of Eq. 2 which satisfies the conditions [at $t = 0$] $y = F(x)$, [at $x = 0$] $\partial y/\partial x = f(t)$, [at $x = l$] $\partial y/\partial x = 0$ is given by

$$y = \frac{-k.e^{-Kt}}{l}\cdot\left[2\sum \cos 2ngx.\int_0^t e^{-4n^2a(t-u)}.e^{Ku}.f(u).du + \int_0^t e^{Ku}.f(u).du\right]$$

$$+\frac{e^{-Kt}}{l}\cdot\left[2\sum e^{-4n^2at}.\cos\ 2ngx.\int_0^l F(\lambda).\cos\ 2ng\lambda.d\lambda + \int_0^l F(\lambda).d\lambda\right] \quad (4)$$

Sec. 3: "Solutions for the Infinite Rod".

In the text-books it is customary to discuss the flow of heat in an infinite rod (i.e. $l \rightarrow \infty$) as a problem apart, and to find Solutions directly from the differential equations[2]. Fourier shewed that this procedure is not necessary; and in the present paper we treat the problems of the infinite rod merely as special cases of those solved in Tables I and II, and their solutions as limiting cases of the Solutions of those tables. The solutions in question may be obtained from Table IX by deleting the last expression on each line of that table and writing ∞ instead of l as the upper limit of integration in Nos. II,1 to II,3; see Rule II, p. 2841.

The customary treatment of such problems obscures the fact that the "Solutions for the Infinite Rod" approach exactitude as kt/l^2 approaches zero; they are exact not only when l is infinite but also when l is finite if kt is infinitely small.[3] In practice the Solutions obtained as shewn above from Table IX may be employed with rods however short provided that kt is small enough; no matter how long the rod may be, they are not valid if the experiment be too prolonged; while for given values of kt and l, the error introduced by using them depends on x, i.e. on the position on the rod for which the temperature is sought. All this is dealt with in detail below; see Sec. 9 *approx. i.*

PART II

THE POISSON FORMS OF THE SOLUTIONS OF TABLES I AND II

From a purely mathematical point of view the Solutions given in Tables I and II are perfectly satisfactory; but from the point of view of a laboratory worker who wants numerical solutions for problems involving data supplied

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[1] Byerly gives the solutions of Eq. 2 for the conditions of Tab. I No. 1a and of Tab. II Nos. 1 and 3 [*loc. cit.* Art. 63].

[2] Byerly gives solutions valid for $l \rightarrow \infty$ of Eqs. 1 and 2 with the conditions of Tab. I. Nos. 1 and 2 and of Tab. II No. 1 [*loc. cit.* Art. 51]. The solution of Eq. 1 for the conditions of Tab. I No. 3 when $f(t)$ = constant has been dealt with by Weber [Wied. Ann., 7, 536 (1879)] and by Sand [Phil. Mag., 6 1, 45 (1901) and Z. physik. Chem., 35, 641 (1900)]; and when $f(t) = \sin\ (b^2t+\alpha)$ by Warburg [Wied. Ann., 67, 493 (1899)]. The solution of Eq. 2 for the same conditions has been deduced by Rosebrugh and Miller when $f(t)$ = constant [*loc. cit.* Eq. 81] and when $f(t) = \sin\ (b^2t+\alpha)$ [*loc. cit.* Eq. 109].

[3] Rosebrugh and Miller: *loc. cit.*, p. 828.

by his experiments, they will usually prove to be almost useless; for each of them involves at least one infinite series, and unless the data are specially selected with an eye to avoiding difficulties of computation, the labour involved in computing the terms of these series and adding them together will usually be prohibitively great. The question "How can these series be evaluated when direct summation is not practicable?" must therefore be answered if the Solutions of Tables I and II are to be put to practical use; the remainder of this paper will be devoted to a discussion of this question, which in its generality has not been dealt with in the text-books although they give finite expressions for the sums of a few of the series and supply solutions free from series for certain of the problems when l or t has the special value ∞.

The discussion of this question necessarily begins with an examination of the mathematical forms of the series to be evaluated; this leads to the formulation of relations between these series and certain others of simpler form to which we give the name "Series of the Θ-Family" because they include the series contained in Jacobi's four theta-functions. Now for each of his theta-functions Jacobi has found an equivalent expression (called by us its Poisson Form) which, like the theta-function itself, involves an infinite series; but the series in these Poisson Forms are rapidly convergent when certain of the quantities involved have values that make the series in the original theta-functions slowly convergent and therefore difficult to evaluate by direct summation. The present Part shews how analogous expressions may be obtained for all the series of the Θ-Family, and also for those of the Families to which the series of Tables I and II belong.

The discussion would have been shorter if Jacobi's formulas had been taken for granted and used as a starting point; our own experience has convinced us, however, that it is very difficult to apply these formulas in practice without such insight into their scope and meaning as follows from a clear apprehension of the arguments upon which they are based. Now the work of Jacobi is usually taken up in connection with Elliptic Functions and is not included in the mathematical courses ordinarily prescribed for students of Chemistry, nor is it easily "picked up" from the texts; the very clearly written treatise of Briot and Bouquet[1] for instance, the only text-book we know which bases the properties of the Elliptics on a preliminary study of the Thetas, takes hundreds of pages to arrive at the "Poisson Forms" referred to above. These same expressions, however, follow at once from a theorem generally known as the "Euler-Maclaurin Sum-Formula with Poisson's Remainder", which we call "Poisson's Formula" for short; the deduction is given in Sec. 6 below. Thus the discussion might have begun with Poisson's Formula instead of with Jacobi's; but unfortunately this formula, like the other, is omitted from the conventional courses; it was originally deduced from a theorem which is now unfamiliar, and nobody seems to have noticed that it is only a special case of Fourier's equation for expressing an arbitrary

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[1] Briot et Bouquet: "Fonctions elliptiques," 2nd Ed., (1875).

function as a cosine-series—the proof of this relationship is given in Sec. 5. Thus the "Poisson Forms" referred to above (including those originally obtained by Jacobi) are ultimately deducible from the formula known as "Fourier's cosine-series," and we have adopted that familiar formula as our starting point.

Because of the number of independent relations that have to be established, the Sections of this Part may at first sight seem somewhat unrelated; the order of the argument is:—(*Sec. 4*) Examination of the mathematical forms of the series of Tables I and II, which brings out their relations to the series of the Θ-Family; development of a system of symbols for the compact representation of individual series and groups of series; and discussion of the means whereby one expression for a given series may be replaced by another. (*Sec. 5*) Deduction of Poisson's Formula from Fourier's cosine-series. (*Sec. 6*) Application of Poisson's Formula to find the "Poisson Forms" of series of the Θ-Family. (*Sec. 7*) Combination of the results of Sec. 4 and 6 to find the Poisson Forms of series of the Φ-Family (including the series of Table I) and of the Λ-Family (including the series of Table II). Parts III and IV shew how the relations established in Part II may be used to find the sums of slowly converging series of the Φ-and Λ Families; and Part V employs them in the construction of convenient formulas for evaluating certain integrals.

Sec. 4: The mathematical forms of the series of Tab. I and II

Four[1] Families of series and their subdivision.

Forms of Table I: At the head of Table I there is given a general expression, Y, for the series involved in the Solutions collected in that table. In this expression the limits of the integration (viz. 0 and t) are independent of the variable of summation n, and the limits of summation (viz. 1 and ∞) are independent of the variable of integration, u; it is therefore permissible to change the order of integration and summation and to write

$$Y \text{ of Table I} = \int_0^t f(u).\{\Sigma e^{-N^2a(t-u)}.\Psi(N,gx)\}.du \qquad (5)$$

where N is either $2n$ or $2n-1$, and the forms of $\Psi(N, gx)$ are those given in the last column of Table I.

Series of the Θ-Family:—If now the name "Θ-Family of series" be used to include all series of the general form

$$\Theta = \Sigma e^{-N^2T}.(sin \text{ or } cos)NX \qquad (6)$$

(where N is any linear function of n, and N, T and X are all positive[2] and independent of one another), and also all series derivable from these by omitting terms and changing the signs of those retained according to any law,

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[1] The fourth, viz. the Ψ-Family, is defined on p. 2856; see also Tab. III No. 9. Special consideration of this Family is not necessary when discussing the series of Tables I and II, and the only references to it in Parts II and III are those needed to avoid repetition in Part V.

[2] If T were negative the series would not converge; if N or X were given negative values, the only effect would be to change the sign of $sinNX$.

examination of the last column of Tab. I will shew that all the series within { } of Eq. 5 are either members of the Θ-Family[1] or are derivatives with respect to $X = gx$ of members of that Family.

Series of the Φ-Family:— Every series of Tab. I may therefore be obtained from a series of the Θ-Family (or its derivative with respect to gx) by multiplying the latter by $f(u) . du$ and integrating between the limits o and t; any series so obtained will be spoken of as a member of "the Φ-Family of series" or as a derivative with respect to gx of a member of that Family, since (t being independent of g and of x) it is immaterial whether the differentiation with respect to gx be performed before or after the integration with respect to u. Tab. III No. 8 is an example of this Family.

Forms of Tab. II:— Applying the trigonometrical formula for the product of two sines or of two cosines to the series included in the Solutions of Tab. II, it will be seen that every one of them can be expressed as the sum or difference of two series of the form

$$\int_0^l F(\lambda) . \{\Sigma e^{-N^2at} . \cos Ng\,(x \pm \lambda)\} . d\lambda \qquad (7)$$

in which N stands for $2n$ or $2n-1$.

Series of the Λ-Family:— The series within { } of (7) are obviously members of the Θ-Family as defined above, and therefore all the series of Tab. II may be obtained from series of the Θ-Family by writing at for T, $g(x \pm \lambda)$ for X, multiplying by $F(\lambda) . d\lambda$ and integrating between the limits o and l. All the series so obtainable (whether the Θ-series involves $\sin NX$ or $\cos NX$) will be spoken of as "the Λ-Family of Series". Tab. III No. 10 is an example of this Family.

(4a) Subdivision of the Families: Symbols.

Of the four Families of Series defined above, two (viz. the Φ and Λ Families) are important from the point of view of the present paper because they (and their gx-derivatives) include the series of Tab. I and II; the third (viz. the Ψ-Family) occurs in the approximations of Part V; and the fourth (the Θ-Family) is introduced because the series of this Family are simple in form and are therefore easy to handle, while many of the relations needed in evaluating the series of the other three Families follow at once when those for the Θ-Family are known.

We have found it convenient, indeed necessary, to replace the conventional mathematical expressions for the series of these four Families by shorter symbols which emphasize the peculiarities of form important for the purpose of this paper. For instance, an italic *c* is used to indicate that the trigonometric factor is a cosine, and a subscript *s* that it is a sine. Thus:

$$\Theta c = \Sigma e^{-N^2T} . \cos NX \qquad \Theta s = \Sigma e^{-N^2T} . \sin NX \qquad (8)$$

---

[1] Since k, l, x and $(t-u)$ are all positive and independent of one another and of n, so must $gx = \pi x/2l$ and $a(t-u) = g^2k(t-u)$ be; and the substitution of gx for X and $a(t-u)$ for T involves no loss of generality. The condition common to all the problems of Part I viz. $0 \leqq x \leqq l$, fixes $\pi/2$ as the maximum value of $X = gx$ that can appear in the Solutions of Tab. I and II; but series with other values of X are also dealt with, see Tab. V p. 2799

The various "types of summation" are indicated by prefixes; thus [*all*] means that $N = n$ and that the + sign is prefixed to each term of the algebraic expression[1] for the series, as in the expansions for $[all]\Theta c$, $[all]\Theta s$, $[all]\Phi c$ etc. given in Table III; such expressions contain cosines or sines of all the multiples of X (or gx), and, in their exponents, the squares of all the integers. The prefix [*even*] means that the first, third, etc. terms of these expressions are

TABLE III: Definitions

1. $[all]\Theta c = \Sigma e^{-n^2T}.\cos nX = e^{-T}.\cos X + e^{-4T}.\cos 2X + e^{-9T}.\cos 3X + ..$
2. $[all]\Theta s = \Sigma e^{-n^2T}.\sin nX = e^{-T}.\sin X + e^{-4T}.\sin 2X + e^{-9T}.\sin 3X + \ldots$
3. $[even]\Theta c = \Sigma e^{-4n^2T}.\cos 2nX = e^{-4T}.\cos 2X + e^{-16T}.\cos 4X + \ldots$
4. $[odd]\Theta c = \Sigma e^{-m^2T}.\cos mX = e^{-T}.\cos X + e^{-9T}.\cos 3X + e^{-25T}.\cos 5X + \ldots$
5. $[alt]\Theta c = \Sigma(-1)^{n+1}.e^{-n^2T}.\cos nX = e^{-T}.\cos X - e^{-4T}.\cos 2X + - \ldots$
6. $[even\text{-}alt]\Theta c = \Sigma(-1)^{n+1}.e^{-4n^2T}.\cos 2nX = e^{-4T}.\cos 2X - e^{-16T}.\cos 4X + -$
7. $[odd\text{-}alt]\Theta s = \Sigma(-1)^{n+1}.e^{-m^2T}.\sin mX = e^{-T}.\sin X - e^{-9T}.\sin 3X + - \ldots$

For use in defining Φ, replace T by $a(t-u)$ and X by gx.

For use in defining Ψ, replace T by au and X by gx.

For use in defining Λ, replace T by at and X by $g(x \pm \lambda)$

Here and throughout this paper, $g = \pi/2l$, $a = g^2k$, $m = 2n - 1$, $\Sigma = \sum\limits_{1}^{\infty}$

8. $[all]\Phi c = \Sigma\cos ngx.\int_0^t e^{-n^2a(t-u)}.f(u).du$
9. $[all]\Psi c = \Sigma\cos ngx.\int_0^t e^{-n^2au}.f(u).du$
10. $[all]\Lambda c = \Sigma e^{-n^2at}.\int^l F(\lambda).\cos ng(x \pm \lambda).d\lambda$

TABLE IV

Symbols for the series of Tab. I and II.

Tab. I No. 1 $Y = -\,\partial/\partial(gx).[even]\Phi c$
" " 1a $= -\,\partial/\partial(gx).[even\text{-}alt]\Phi c$
" " 2 $= -\,\partial/\partial(gx).[odd]\Phi c$
" " 2a $= \partial/\partial(gx).[odd\text{-}alt]\Phi s$
" " 3 $= -\,[odd]\Phi c$
" " 3a $= [odd\text{-}alt]\Phi s$
" " 4 $= -\,[even]\Phi c$
" " 4a $= -\,[even\text{-}alt]\Phi c$

Tab.[2] II No. 1 $Y = [even]\Lambda c(x-\lambda) - [even]\Lambda c(x+\lambda)$
" " 2 $= [odd]\Lambda c(x-\lambda) - [odd]\Lambda c(x+\lambda)$
" " 2a $= [odd]\Lambda c(x-\lambda) + [odd\Lambda c(x+\lambda)$
" " 3 $= [even]\Lambda c(x-\lambda) + [even]\Lambda c(x+\lambda)$

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[1] It does not mean that the "absolute value" of each term is to be taken; for example, if $T = 1$ and $X = \pi/5$, the first three terms of $[all]\Theta c$ are: $0.297621 + 0.005660 - 0.000038$.

[2] $\Lambda c(x-\lambda)$ means that X in Θc is to be replaced by $g(x-\lambda)$.

omitted and only the even terms retained, as in [*even*]Θc of Table III; the meanings of four other prefixes are made clear by the examples given in that table. In Table IV, the series occurring in the Solutions of Tables I and II are rewritten using these symbols.

(4b) Alternative mathematical expressions for the same series. Two Groups within each Family.

One and the same numerical series may be represented by different algebraical expressions, and therefore by different symbols; this possibility has already been referred to in connection with Solutions 1 and 1*a* etc. of Table I. It will now be shewn that the use of expressions of alternating types (such as *alt*, *even-alt*, *odd-alt*) or with angles greater than $\pi/2$, is not compulsory in the case of series of the Θ Φ Ψ and Λ Families; as such expressions can always be replaced by others (for the same series) in which the type is non-alternating and the angle lies within the first quadrant. Also that in the Θ Φ and Ψ Families an expression of any other type can be replaced by a single expression of the *odd* or *even* type.

The replacements in question are effected by means of three Relations, and lead to the definition of two Groups. They consist merely in the replacement of one algebraical expression for a given series by another for identically the same series; the substitution of the "Poisson Form" (see Sec. 6 and 7) on the other hand, consists in the replacement of the given series by a wholly different series which has the same sum.

(*i*) *Relations arising from the convergence of the* [*odd*] *and* [*even*] *series*:— Any series that consists of a finite number of terms (which for the purpose of illustration is supposed to be even) may be represented by $\sum_{n=1}^{2k} f(n)$; and it is obvious that such a series can be divided into two other series, one of which viz. $\sum_{n=1}^{k} f(2n-1)$ consists of the first, third etc., or "odd" terms of the original series and the other viz. $\sum_{n=1}^{k} f(2n)$ of its second, fourth etc., or "even" terms; and that

$$\sum_{n=1}^{2k} f(n) = \sum_{n=1}^{k} f(2n-1) + \sum_{n=1}^{k} f(2n) \qquad (8)$$

Moreover, if an "alternating" series $\sum_{n=1}^{2k} (-1)^{n+1}.f(n)$ be formed by changing the signs of the even terms of the original series, then

$$\sum_{n=1}^{2k} (-1)^{n+1}.f(n) = \sum_{n=1}^{k} f(2n-1) - \sum_{n=1}^{k} f(2n) \qquad (9)$$

Briefly:

$$[\mathit{all}] = [\mathit{odd}] + [\mathit{even}] = [\mathit{alt}] + 2[\mathit{even}] \qquad (10)$$

$$[\mathit{alt}] = [\mathit{odd}] - [\mathit{even}] = [\mathit{all}] - 2[\mathit{even}] \qquad (11)$$

These relations hold for any finite value of k; and if the [*odd*] and [*even*] series be convergent, i.e. if in each of them the sum of all terms after the k'th be negligible, these same relations obviously hold when the upper limits of all four series are infinitely great[1] as they are in the series of the Families considered in this paper. But the condition that [*all*] should be convergent is not sufficient to ensure the validity of (10) and (11) when $k = \infty$; for this condition is consistent with the divergence of [*odd*] and [*even*], as is the case for example when $[\mathit{all}] = \Sigma(\cos n\pi)/n$.

As all the [*odd*] and [*even*] series of the present paper are convergent, the sums of the four series [*all*]Θc, [*even*]Θc, [*odd*]Θc, and [*alt*]Θc for any given values of T and X (the same for all of them) can be found if the sums of any two of them are known; similarly with the series of the other three Families.

(*ii*) *Relations valid for all series which fulfill* the condition (*i*) above and which are of the form

$$\text{Series} = \Sigma f(N).\cos \text{ or } \sin NX \qquad (12)$$

or

$$\text{Series} = \Sigma f(N).\int F(\lambda).\cos \text{ or } \sin NX.d\lambda \text{ where } X = \text{func}(\lambda) \qquad (13)$$

Series of the Θ Ψ and Φ Families are of the first form, those of the Λ Family are of the second.[2]

Table V*a* contains all the relations in question that are made use of in this paper; they may easily be obtained from Eqs. 10 and 11 and $\cos(B-X) = \cos(X-B) = \cos B.\cos X + \sin B.\sin X$. For example, the series represented by $\Sigma f(n).\cos nX$ is identical, term for term, with that represented by $-\Sigma(-1)^{n+1}.f(n).\cos n(\pi - X)$, so that these two expressions are merely two different ways of representing the same thing; in Tab. V*a* they have been abbreviated to [*all*]X and $-$[*alt*]$\pi - X$, since the sign, the type of summation and the angle are the only respects in which the two expressions differ.

Two Groups of series within each Family:— It is clear from Tab. V*a* that the series entered there (viz. those in which the trigonometric factor is a cosine and the type is [*all, even, odd, alt,* or *even-alt*], and that in which the factor is a sine and the type is odd-alternate) can all be represented by expressions of the [*odd*] and [*even*] types in which the angle lies within the first quadrant; i.e. that the sums of all these series, no matter what value might

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[1] If for instance the symbol [*all*]E be given to the series $1 + x + x^2/1.2 + x^3/1.2.3 + \ldots = e^x$, then $\sinh x$, $\cosh x$, e^{-x}, $\sin x$ and $\cos x$ would be represented by [*even*]E, [*odd*]E, [*alt*]E, [*even-alt*]E and [*odd-alt*]E respectively; the relations of Eqs. 10 and 11 obviously hold for these members of "the Exponential Family."

[2] Another example is furnished by Fourier's cosine series $F(X) - b_0/2 = \Sigma b_n.\cos nX$. If [*all*] be written for the series on the right, then $[\mathit{even}] = \Sigma b_{2n}.\cos 2nX$, etc.; and from Table V*a*, writing m for $2n-1$, $2\Sigma b_{2n}.\cos 2nX = F(X) + F(\pi - X) - b_0$; $2\Sigma b_m.\cos mX = F(X) - F(\pi - X)$; $\Sigma(-1)^n.b_n.\cos nX = F(\pi - X) - b_0/2$; $2\Sigma(-1)^n.b_{2n}.\cos 2nX = F(\pi/2 - X) + F(\pi/2 + X) - b_0$; $2\Sigma(-1)^{n+1}.b_m.\sin mX = F(\pi/2 - X) - F(\pi/2 + X)$.

TABLE V: Replacements

[all] = [even] + [odd] = $\Sigma f(n).\cos nX$.

[o-a *sin*] = $\Sigma\ (-1)^{n+1}.f(m).\sin mX$ where $m = 2n-1$; but in the other four expressions of the last line of Va, as elsewhere throughout the table, the trigonometric factor is a cosine.

TABLE VA: Valid for Θ_E, Φ_E, Ψ_E and Λ_E.

Angle = X	$0 < X < \pi/2$	$\pi/2 < X < \pi$	$\pi < X < 3\pi/2$	$3\pi/2 < X < 2\pi$.
[all]	[even+odd] X	[even−odd] $\pi - X$	[even−odd] $X - \pi$	[even+odd] $2\pi - X$
[even]	[even] X	[even] $\pi - X$	[even] $X - \pi$	[even] $2\pi - X$
[odd]	[odd] X	−[odd] $\pi - X$	−[odd] $X - \pi$	[odd] $2X - X$
[alt]	[odd−even] X	−[odd+even] $\pi - X$	−[even+odd] $X - \pi$	[odd−even] $2\pi - X$
[even-alt]	−[even] $\pi/2 - X$	−[even] $X - \pi/2$	−[even] $3\pi/2 - X$	−[even] $X - 3\pi/2$
[o-a sin]	[odd] $\pi/2 - X$	[odd] $X - \pi/2$	−[odd] $3\pi/2 - X$	−[odd] $X - 3\pi/2$

TABLE VB: Valid for Θ_E, Φ_E and Ψ_E only; for use with Θ_E, write T for a.

Angle = X	$0 < X < \pi$	$\pi < X < 2\pi$.
[all]	[even] $a/4$, $X/2$	[even] $a/4$, $(2\pi - X)/2$
[alt]	−[even] $a/4$, $(\pi - X)/2$	−[even] $a/4$, $(X - \pi)/2$

All the expressions given in any one line of Tab. V*a* represent identically the same series, if the same numerical value be given to X in each of them. If the value of X lies within the range indicated at the head of one of the columns, the angle involved in the expressions entered in that column lies between 0 and $\pi/2$; the table therefore shews how an expression involving an angle in the second third or fourth quadrant may be replaced by another expression (for the same series) whose angle lies in the first quadrant. The table also shews how to replace an expression of an alternating type by an expression or expressions of a non-alternating type for the same series; such replacements must be made before the approximations of Parts III and IV are used. Examples of the use of this table are given under *Summary*, p. 2801.

be assigned to X, could be computed from numerical tables[1] of [*even*] and [*odd*] for the same Family extending over the range $0 \leq X \leq \pi/2$, or from a table of [*all*] for $0 \leq X \leq \pi$. These series and all others[2] which can be expressed in terms of [*all*] or of [*odd*] and [*even*] by the methods used above, constitute a Group[3] within the Family which will be distinguished[4] by the subscript $_E$, thus: the Θ_E Group, the Φ_E Group, etc. A second set of Groups, viz. the Θ_F Φ_F Ψ_F and Λ_F Groups, includes all series for which (by means of Eqs. 10 and 11 and the trigonometrical expansion for $\sin \overline{X \pm B}$) expressions can be found in terms of [*all*]Θs, [*all*]Φs etc; the Θ_F Group, for instance, includes [*all, even, odd, alt,* and *even-alt*]Θs, [*odd-alt*]Θc, etc. As none of the series of this second set of Groups occur in the Solutions[5] of Tab. I and II (see Tab. IV), and as the methods of approximation developed for the first set of Groups are not applicable to the second, it is not necessary to

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[1] Complete tabulation of Φ Ψ or Λ would require triple-entry tables for each form of $f(u)$ or $F(\lambda)$, which is quite impracticable. For [*odd*]Θc and [*even*]Θc, double-entry tables are sufficient; values of these functions may be found from Houël's four-figure tables of $\theta_3 = 1 + 2$[*even*]Θc and $\theta_2 = 2$[*odd*]Θc which extend from $X = 0$ to $X = \pi/2$ at intervals of $\pi/20$ and for 10 values of T from $T = 0.381$ to $T = 1.618$ at intervals which increase with increase in T [see Jahnke und Emde: "Funktionentafeln" (1923)]. But four-figure values of these functions over the range of Houël's tables can be found by summing two terms at most of the series given in Table III; and six-figure values for any T and X can be obtained, as shewn on p. 2809 below, without looking up more than three exponentials in any case.

[2] For example $e^{-B} - e^{-9B} - e^{-25B} + e^{-49B} + \ldots = \sqrt{2}\,\{$[*all*]$\Theta c$ where $T = B$ and $X = \pi/4\} + \sqrt{2}\,\{$[*alt*]$\Theta c$ where $T = 16B$ and $X = 0\}$. If the signs run $+ + - -$, instead of $+ - - +$ as above, the series is a member of the Θ_F Group. Half the sum of the two, viz: $\Sigma(-1)^{n+1}.e^{-(4n-3)^2B}$, therefore belongs to neither Group, although it is a member of the Θ-Family.

[3] Jacobi's four Theta-Functions are closely related to our functions of the Θ_E Group; they are:—

$$\theta(X) = 1 - 2[\textit{even-alt}]\Theta c \qquad \theta_1(X) = 2[\textit{odd-alt}]\Theta s$$
$$\theta_2(X) = 2[\textit{odd}]\Theta c \qquad \theta_3(X) = 1 + 2[\textit{even}]\Theta c$$

The reason for the numerical term and the factor 2 when Jacobi's functions are expressed in our symbols is that his summations extend from $-\infty$ to $+\infty$ (see the first line of Tab. VIII) while in the series of our Θ-Family the limits are 1 and ∞.

The symbols $\theta(X)$ etc. defined above are those of Jacobi's later notation as used in his lectures [see Infinitesimal Calculus, Encycl. Brit. 9th Ed., Vol. 13, p. 71]. In Briot's notation our X is replaced by $\pi z/\omega$, but $\theta(X)$ by $\theta(z)$ instead of by $\theta(\pi z/\omega)$ [Briot and Bouquet: *loc. cit.* p. 115]. Jahnke and Emde [*loc. cit.* p. 48] write πv for X but use $\theta(v)$ instead of $\theta(\pi.v)$

In Cayley's treatise [A. Cayley: "Elliptic Functions," 2nd. Ed., (1895)] the Theta-Functions are given second place; Briot follows Jacobi in basing the theory of the Elliptics on a previous study of the Thetas. In transliterating Briot's Equations,

$$q = e^{-4T};\ p = e^{-\pi^2/4T};\ 1/C = \sqrt{\pi/4T};\ \pi z/\omega = X;\ \omega'/\omega = 4iT/\pi.$$

If X be replaced by $gx = \pi x/2l$, then $z = x$ and $\omega = 2l$. Briot's equations (13) [*loc. cit.* p. 267], e.g.

$$\vartheta_1/\theta_1 = C.e^{\pi z^2 i/\omega\omega'}$$

taken in conjunction with his definition of ϑ [*loc. cit.* p. 265] and C [*loc. cit.* Eq. 35, p. 320] give the Poisson Forms of Jacobi's four Theta-Functions, and correspond to four of the equations of our Tab. VIII.

[4] The names "Cosine-Group" and "Sine-Group" naturally suggest themselves; but it must not be forgotten that in certain series of the Cosine-Group, e.g. [*odd-alt*] Θs, the trigonometric factor is a sine, and vice versa. The symbols here employed have been chosen because the Poisson Forms of the series of the Θ_E Group are expressed as Exponentials (see Tab. VIII) while those of the Θ_F Group are expressed in terms of the function F (see p. 2811).

[5] Solutions of the differential equation (1) which involve Φ_F instead of Φ_E are not consistent with the Boundary Conditions of Part I.

go into details; but it must be emphasized that the two sets are mutually exclusive.[1]

(*iii*) *Relations valid for all series which fulfill* the conditions of (*i*) above, and are of the form

$$\text{Series} = \Sigma f(nb, nc) \qquad (14)$$

i.e. series in whose general terms b, c and n occur only in the combinations nb, nc. Series of the Θ-Family come under this head with $b = \sqrt{T}$ and $c = X$; so do series of the Φ and Ψ Families with $b = \sqrt{a}$ and $c = gx$; but series of the Λ-Family do not, since in the general term of [*all*]Λc, see Tab. III, g occurs both together with and apart from n.

In series of the kind considered, [*all*] $= \Sigma f(nb, nc)$ and [*even*] $= \Sigma f(2n.b, 2n.c) = \Sigma f(n.2b, n.2c)$; i.e. [*even*] with $b = B$ and $c = C$, and [*all*] with $b = 2B$ and $c = 2C$, are merely two expressions for the same series. From this it follows that a table of [*even*]Θc for angles in the first quadrant only, would serve to evaluate all members of the Θ_E Group; the same is true *mutatis mutandis* for series of the Φ_E and Ψ_E Groups but not for those of the Λ_E Group. See Table V*b*.

Summary:— By means of the Relations collected in Tab. V, any series of the Θ_E, Φ_E or Ψ_E Groups can be replaced by a single expression of the [*even*] or [*odd*] type with its angle in the first quadrant; in the case of series of the Φ_E Group such replacements must be made before the approximations of Part III can be used. For example, if the series to be summed be presented as [*odd-alt*]Φ*s* with $f(u) = 1$, $t = 0.108$, $a = 1$, $gx = \pi/10$, the replacement may be effected by entering Tab. V*a* at the line [*o-a sin*] and column $0 < X < \pi/2$, which gives [*odd*]$\pi/2 - X$; i.e. [*odd*]Φ*c* with $gx = \pi/2 - \pi/10 = 2\pi/5$ and all the other constants unchanged, is an expression for the given series which is suitable for use in Sec. 9 (see Ex. 3, p. 2825). As a second example, suppose that [*all*]Φc with $f(u) = 1$, $t = 0.1$, $a = 1$, and $gx = 7\pi/5$ is to be summed; Tab. V*b*, line [*all*], column $\pi < X < 2\pi$, gives $-$[*even*]$a/4, (gx-\pi)/2$; that is, $-$[*even*]Φc with $a = 0.25$, $gx = \pi/5$ and the other constants as given above, is the expression desired (see Ex. 1, p. 2825). Similarly, [*all*]Φc with $a = 1$ and $gx = 8\pi/5$ may be replaced by [*even*]Φc with $a = 0.25$ and $gx = \pi/5$ if the other constants be given the same values in both (see Ex. 1, p. 2825).

In the Θ_E, Φ_E and Ψ_E Groups it is possible to replace [*odd*] by the difference between two expressions of the [*even*] type; for instance [*odd*]Φc (with a and gx) = [*even*]Φc (with $a/4$ and $gx/2$) $-$ [*even*]Φc (with a and gx); but such replacements do not help with the approximations of Part III.

(4c) The Converging Exponential: Stationary and Evanescent Series

The reason for emphasizing the "Converging Exponential" e^{-N^2T} is that the rapidity with which any given series whose terms contain this factor converges, and therefore the ease of evaluating it by direct summation, depends on the value of T more than on any other single feature; when T is large, the

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[1] They are related by the equation

$$[all]\Theta c + i.\ [all]\Theta s = \Sigma e^{-n^2T}.e^{inX}$$

numerical values assumed by e^{-N^2T} in successive terms of the series (i.e. when n is given the successive values 1, 2, 3, etc.) diminish so rapidly that, generally speaking,[1] all except the first few terms may be neglected in computing the sum; while when T is very small, this source of rapid initial convergence disappears. By way of illustration, the values of e^{-n^2T} for successive values of n when $T = 1$ may be compared with those when $T = 0.01$:—

n	1	2	3	4	5
e^{-n^2}	.36788	.01832	.00012	.00000	.00000
$e^{-0.01n^2}$	.99005	.96079	.91393	.85214	.77880

Other things being equal, the least convergent series are obviously those in which $T = 0$; to evaluate these by direct summation would in many cases involve the computation of hundreds or even thousands of terms; on the other hand, their mathematical form is relatively simple, and for some of them finite expressions can be found which give their sums exactly. Such series arise when in the general expressions for Θ or Λ, the value *zero* is assigned to T; the Stationary Series (p. 2803) which play an important part in the numerical evaluation of series of the Φ-Family have another origin, but like the former lack the converging exponential.

Series of the Θ-Family when $T = 0$:— There are only two forms, viz. $\Sigma \cos NX$ and $\Sigma \sin NX$. Such series, strictly speaking, are not convergent and have no sum; but if they be regarded as the limits when $T \to 0$ of $\Sigma e^{-N^2T}.(\cos \text{ or } \sin)NX$, the sums of some of them may be found by setting $T = 0$ in the equations[2] of Table VIII and in Eqs. 35 and 36[3]; see Table VI.

TABLE VI

Series of the Θ-Family when $T \to 0$.

1. $\Sigma \cos nX = -1/2$. 2. $\Sigma \cos 2nX = -1/2$. 3. $\Sigma \cos mX = 0$
4. $\Sigma (-1)^{n+1}.\cos nX = 1/2$. 5. $\Sigma (1-)^{n+1}.\cos 2nX = 1/2$
6. $\Sigma (-1)^{n+1}.\sin mX = 0$. 7. $2\Sigma \sin nX = \cot (X/2)$.
8. $2\Sigma \sin 2nX = \cot X$. 9. $2 \Sigma \sin mX = \operatorname{cosec} X$.
10. $2 \Sigma(-1)^{n+1}.\sin nX = \tan (X/2)$. 11. $2\Sigma(-1)^{n+1}.\sin 2nX = \tan X$.
12. $2 \Sigma(-1)^{n+1}.\cos mX = \sec X$.

Series of the Λ-Family when $T = at = 0$:— Such series if derived from members of the Λ_E Group can be expressed as the sum or difference of two trigono-

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[1] There are exceptions, see p. 2823.

[2] When the value of X is such that the value of every term of the series is identically 1, or every term is identically zero, or is identically -1, the sum is ∞, 0 or $-\infty$ as the case may be; and these sums are to be accepted in place of those given in Table VI if there is any discrepancy; for in such cases, the substitution of 0 for T in the equations of Table VIII etc. gives rise to the indeterminate form 0/0. For instance $\Sigma \cos 2n\pi = \infty$ and not $-1/2$; $2\Sigma \sin 2n\pi = 0$ and not $\cot \pi$, which is infinite. This must be borne in mind when integrating expressions containing these series, if during the integration X passes through one of these singular values. Integrals of some of these series are given by L. B. W. Jolley: "Summation of Series," Nos. 266-9, 296-7, 317-8, (1925).

[3] Note that when $y \to \infty$, $F(y) \to 1/2y$; see Tab. XXV No. 3.

metrical series closely related to Fourier's "sine-series" and "cosine-series". For example

$$\Sigma\int_0^t F(\lambda).cos(2ng.\overline{x\pm\lambda}).d\lambda = \Sigma cos\ 2ngx.\int_0^t F(\lambda).cos\ 2ng\lambda.d\lambda$$

$$\mp\ \Sigma sin\ 2ngx.\int_0^t F(\lambda).sin\ 2ng\lambda.d\lambda \qquad (15)$$

See Table IV and Table II.

[If the series be derived from a member of the Λ_p Group, the trigonometrical series consist of cosines of multiples of gx multiplied by factors like those of Fourier's "sine-series" and vice versa.]

Series of the Φ-Family when $T = 0$:— The sum is zero in every case, for in the definition of Φ, T is replaced by $a(t-u)$; and if $a(t-u) = 0$, the upper as well as the lower limit of the integration must be zero.

Stationary and Evanescent Series of the Φ-Family:— The first step in computing the terms of any series of the Φ-Family is to perform the integration; that is to replace the integral whose upper and lower limits are t and 0 respectively, by an expression of the form $\varphi(t) - \varphi(0)$. By this replacement every series of the Φ-Family can be expressed as the difference between two other series, one (viz. S:Φ) arising from the upper and the other (viz. V:Φ) from the lower limit of the integration; thus

$$\Phi = S{:}\Phi - V{:}\Phi \qquad (16)$$

For example,[1] if $f(u) = e^{b^2u}$,

$$S{:}[even]\Phi c = e^{b^2t}.\Sigma(cos\ 2ngx)/(4n^2a+b^2)$$

$$V{:}[even]\Phi c = \Sigma(cos\ 2ngx.e^{-4n^2at})/(4n^2a+b^2) \qquad (17)$$

The name "Stationary Series" is given to S:Φ and the name "Evanescent Series" to V:Φ.

The expressions for S:Φ and V:Φ given in Eqs. 18 and 19 are obtained by integration-by-parts:—

$$S{:}\Phi = \Sigma trig\ Ngx.\left[\frac{f(t)}{N^2a} - \frac{f'(t)}{N^4a^2} + \ldots + \left(\frac{-1}{N^2a}\right)^p.e^{-N^2at}.\int_*^0 e^{N^2au}.f^p(u).du\right] \qquad (18)$$

$$V{:}\Phi = \Sigma trig\ Ngx.e^{-N^2at}.\left[\frac{f(0)}{N^2a} - \frac{f'(0)}{N^4a^2} + \ldots + \left(\frac{-1}{N^2a}\right)^p.\int_*^0 e^{N^2au}.f^p(u).du\right] \qquad (19)$$

The lower limits of the integrals contained in (18) and (19) are the same in both, and must be so chosen that on further integration-by-parts, each term arising from the lower limit will be identically zero.

It is obvious from Eq. 19 that when t is very large, $V{:}\Phi \rightarrow 0$ and Φ becomes practically equal to S:Φ; this is the origin of the names[2] Evanescent and Stationary. When $f(u)$ has any of the usual forms, the integral of $e^{-N^2a(t-u)}$.

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[1] For other examples see Note to Table XII p. 2818, also Ex. 10 p. 2830. Ex. 17 p. 2838, and Table XIII, p. 2818.

[2] These names were introduced by Rosebrugh and Miller: loc. cit. p. 847; the expression for which the symbol V is there used, would be indicated in the notation of the present paper by $-(2k/l)$. (V: [*odd*]Φ*c*). Where no uncertainty can result, the symbols S:Φ and V:Φ will be shortened to S and V.

$f(u).du$, which we shall name the "Original Integral", can be expressed in terms of tabulated functions; i.e. for any given value of N, the numerical value of the corresponding term of S or of V can be found.

As to the convergence of these series, it is obvious from Eqs. 18 and 19 that (because of the factor e^{-N^2at}) any Evanescent Series is more rapidly convergent than the Stationary Series arising from the same Φ. It is also obvious that the greater N is, the more important the first fraction will be in comparison with any of the others or with final integral; from which it follows that for large values of N the terms of the Stationary Series approximate in value to those of $\{f(t)/a\}.\Sigma(trig\ Ngx)/N^2$. In other words, the convergence of $S{:}\Phi$ after a considerable number of terms is that of $\Sigma 1/N^2$ and therefore direct summation of any Stationary Series is practically impossible. Finite expressions which give the exact sums of the Stationary Series for certain forms of $f(u)$ are known (see Sec. 10); in the case of the Evanescent Series no such expressions are known.

Neither Evanescent nor Stationary Series are members of the Φ-Family as defined on p. 2795; but because of their origin it is convenient to deal with them together with the series of that Family.

Stationary and Evanescent Series of the Ψ-Family:— In this Family (see Tab. III No. 9 and Part V, p. 2856) the Stationary Series arise from the lower limit of the integration, and the Evanescents (which contain the factor e^{-N^2at}) from the upper; but as the integrand is of the form $e^{-N^2au}.f(u).du$, $\Psi = S{:}\Psi - V{:}\Psi$. For example, if $f(u) = e^{b^2u}$,

$$S{:}[even]\Psi c = \Sigma(\cos 2ngx)/(4n^2a-b^2)$$
$$V{:}[even]\Psi c = e^{b^2t}.\Sigma(\cos 2ngx.e^{-4n^2at})/(4n^2a-b^2)$$

Sec. 5: Poisson's Formula

It is shewn in treatises on Fourier's Series[1] that when $\varphi(y)$ is finite single-valued and continuous for all values of y between $y = 0$ and $y = \pi$ (or if discontinuous has only finite discontinuities), and moreover has not an infinite number of maxima and minima in the neighbourhood of any point within that range, then for all values of y between $y = 0$ and $y = \pi$

$$\varphi(y) = 1/\pi.\int_0^{\pi}\varphi(\lambda).d\lambda + 2/\pi.\sum_{r=1}^{\infty}\cos ry.\int_0\varphi(\lambda).\cos r\lambda.d\lambda \qquad (20)$$

The expression on the right of Eq. 20 is known as the "cosine-series" for $\varphi(y)$.

There is a general method for replacing any given integral by another whose value is the same but whose limits are different; and under the title "extension to Fourier's series" the text-books[2] give the form assumed by the cosine-series when the integrals of Eq. 20 are replaced by others having the limits $-c$ and $+c$, or 0 and c. For the present purpose it is desirable to in-

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[1] For example, H. S. Carslaw: "Introduction to the Theory of Fourier's Series," Art. 96, pp. 215-216, (1921).

[2] For example, W. E. Byerly: loc. cit., Chap. II, Art. 31.

troduce integrals with the limits $n\omega$ and $(n+1)\omega$, where ω is any arbitrary constant and n is any arbitrary integer; this may be accomplished by substituting $\pi(z-n\omega)/\omega$ for y; if after this substitution $f(z)$ be written in place of $\varphi(y)$, Eq. 20 takes the form[1]

$$f(z) = (1/\omega).\int_{n\omega}^{(n+1)\omega} f(\lambda).d\lambda + (2/\omega).\sum_{r=1}^{\infty} \cos\frac{r\pi z}{\omega}.\int_{n\omega}^{(n+1)\omega} f(\lambda).\cos\frac{r\pi\lambda}{\omega}.d\lambda \qquad (21)$$

which is valid for $0 \leqq y \leqq \pi$, i.e. for $n\omega \leqq z \leqq (n+1)\omega$. Expressions for $f(n\omega)$ and for $f(\overline{n+1}.\omega)$ may be obtained by replacing the z of Eq. 21 by $n\omega$ and by $(n+1)\omega$ respectively; they are

$$f(n\omega) = (1/\omega).\int_{n\omega}^{(n+1)\omega} f(\lambda).d\lambda + (2/\omega).\sum_{r=1}^{\infty} \cos r\pi n.\int_{n\omega}^{(n+1)\omega} f(\lambda).\cos\frac{r\pi\lambda}{\omega}.d\lambda \qquad (22)$$

$$f(\overline{n+1}.\omega) = (1/\omega).\int_{n\omega}^{(n+1)\omega} f(\lambda).d\lambda + (2/\omega).\sum_{r=1}^{\infty} (-1)^r.\cos r\pi n.\int_{n\omega}^{(n+1)\omega} f(\lambda).\cos\frac{r\pi\lambda}{\omega}.d\lambda \quad (23)$$

Adding (22) and (23) term by term and dividing through by 2 gives Eq. 24; (note that when r is odd, the terms of the sums on the right of Eqs. 22 and 23 cancel; when r is even, $\cos r\pi n = 1$ for all integral values of n).

$$\tfrac{1}{2}f(n\omega) + \tfrac{1}{2}f(\overline{n+1}.\omega) = (1/\omega).\int_{n\omega}^{(n+1)\omega} f(\lambda).d\lambda + (2/\omega).\sum_{r=1}^{\infty} \int_{n\omega}^{(n+1)\omega} f(\lambda).\cos\frac{2r\pi\lambda}{\omega}.d\lambda \qquad (24)$$

If now in Eq. 24, n be given in succession the integral values c, $c+1$, $c+2$ … h, and the expressions so obtained for $\tfrac{1}{2}f(c\omega) + \tfrac{1}{2}f(\overline{c+1}.\omega)$, etc., be added together and multiplied by ω, there results

$$\omega.\{\tfrac{1}{2}f(c\omega) + f(\overline{c+1}.\omega) + f(\overline{c+2}.\omega) + \ldots + f(\overline{h-1}.\omega) + \tfrac{1}{2}f(h\omega)\} \qquad (25)$$

$$= (\omega/2)\,f(c\omega) + (\omega/2).f(h\omega) + \omega.\sum_{n=c+1}^{h-1} f(n\omega) = \int_{c\omega}^{h\omega} f(\lambda).d\lambda \text{ Thus } (\omega/2).f(c\omega)$$

$$+ 2\sum_{r=1}^{\infty} \int_{c\omega}^{h} f(\lambda).\cos\frac{2r\pi\lambda}{\omega}.d\lambda$$

Eq. 25 was first obtained by Poisson,[2] and includes the "Euler-Maclaurin Sum-Formula"; the argument just concluded shews that the expression on its right is nothing but the "cosine-series" for the expression on its left. For subsequent use it is convenient to have this same relation in other forms; those employed below are collected in Table VII.

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[1] The simplicity of this form is due to the definition of n as an integer, whence $\sin r\pi n = 0$ and $\cos r\pi n = \pm 1$; this last factor occurs twice, once in $\cos ry$ and again in the integrand, the product $(\cos r\pi n)^2 = 1$.

[2] Mém. de l'Acad. Roy. des Sciences de l'Institut de France, **6**, 571, (1823).

TABLE VII: Poisson's Formula

$$(25a)\quad \omega.\sum_{n=1}^{h-1} f(n\omega) = \int_0^{h\omega} j(\lambda).d\lambda - \frac{\omega}{2}.f(0) - \frac{\omega}{2}.f(h\omega) + 2\sum_{r=1}^{\infty}\int_0^{h\omega} f(\lambda).cos\frac{2r\pi\lambda}{\omega}.d\lambda$$

$$(25b)\quad \sum_{n=1}^{h-1} f(n\omega) = \int_0^{h} f(\lambda\omega).d\lambda - \frac{1}{2}f(0) - \frac{1}{2}f(h\omega) + 2\sum_{r=1}^{\infty}\int_0^{h} f(\lambda\omega).cos\ 2r\pi\lambda.d\lambda$$

$$(25c)\quad \sum_{n=P}^{Q} f(n\omega) = \int_P^{Q} f(\lambda\omega).d\lambda + \frac{1}{2}f(P\omega) + \frac{1}{2}f(Q\omega) + 2\sum_{r=1}^{\infty}\int_P^{Q} f(\lambda\omega).cos\ 2r\pi\lambda.d\lambda$$

$$(25d)\quad = \int_P^{Q} f(\lambda\omega).d\lambda + \frac{1}{2}f(P\omega) + \frac{1}{2}f(Q\omega) - \frac{\omega.B_1}{\lfloor 2}\Big[f'(P\omega) - f'(Q\omega)\Big] +$$

$$\frac{\omega^3 B_3}{\lfloor 4}\Big[f'''(P\omega) - f'''(Q\omega)\Big] - \frac{\omega^6 B_5}{\lfloor 6}\Big[f^{v}(P\omega) - f^{v}(Q\omega)\Big] + \text{etc.,}$$

[signs alternately + and − to include the $\overline{2s-1}$th deriv.] + R_s
where $B_1 = (1/\pi^2).\Sigma(1/n^2) = 1/6$; $B_3 = (3/\pi^4).\ \Sigma\ (1/n^4)$; etc.

and $R_s = 2(-1)^{s+1}.\sum_{r=1}^{\infty}\left(\frac{1}{2r\pi}\right)^{2s}.\int_P^{Q} cos\ 2r\pi\lambda.\left(\frac{d}{d\lambda}\right)^{2s} f(\lambda\omega).d\lambda$

$$(25e)\quad \Sigma f(n\omega) = \int_0^{\infty} f(\lambda\omega).d\lambda - \tfrac{1}{2}f(0) + 2\Sigma\int_0^{\infty} f(\lambda\omega).cos\ 2n\pi\lambda.d\lambda$$

$$= \quad (\text{P-approx.}) \quad + \quad (\text{Remainder})$$

$$(25f)\quad f(\overline{2n-1}.\omega) = \tfrac{1}{2}\int_{-1}^{\infty} f(\lambda\omega).d\lambda - \tfrac{1}{2}f(-\omega) + 2\Sigma\int_0^{\infty} f(\overline{2\lambda-1}.\omega)cos\ 2n\pi\lambda.d\lambda$$

$$(25g)\quad f(\overline{2n-1}.\omega) = \tfrac{1}{2}\int_0^{\infty} f(\lambda\omega).d\lambda + 2\Sigma\int_0^{\infty}\Big[f(\lambda\omega) - f(2\lambda\omega)\Big].cos\ 2n\pi\lambda.d\lambda$$

$$(25h)\quad = \tfrac{1}{2}\int_0^{\infty} f(\lambda\omega).d\lambda) - \Sigma(-1)^{n+1}.\int_0^{\infty} f(\lambda\omega).cos\ n\pi\lambda.d\lambda$$

$$= (\text{P-approx.}) \quad - \quad (\text{Remainder})$$

Setting $c = 0$, Eq. 25 becomes (25*a*). Replacing λ in (25*a*) by $\lambda\omega$ and dividing through by ω gives (25*b*), from which (25*c*) is readily obtained.[2] If the last term on the right of (25*c*) be expanded by repeated integration by parts, (25*d*) results; the R_s of this equation is often spoken of as "Poisson's Remainder to the Euler-Maclaurin Sum-Formula," while the rest of (25*d*) is the "Sum-Formula" itself. Setting $h = \infty$ in (25*b*) gives (25*e*) since $f(\infty)$ must be zero or the series will not converge; here the *r* of (25*b*) has been replaced by *n*, and following the convention of this paper Σ is written as an abbreviation for $\sum\limits_{n=1}^{\infty}$. Eq. 25*f* follows immediately from (25*e*) but is not convenient; since many of the integrals met with in practice are known only when the limits are 0 and ∞. The form for [*odd*] series given

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[1] $B_1/\lfloor 2 = 1/12$; $B_3/\lfloor 4 = 1/720$; $B_5/\lfloor 6 = 1/30240$; etc. Adams gives the values of the first 62 Bernoulli numbers in Brit. Ass. Reports, 1877, Notices, pg. 8.

[2] Add $f(h\omega)$ to both sides of (25*b*), which converts $\sum\limits_{n=1}^{h-1}$ into $\sum\limits_{n=1}^{h}$ and $-(1/2).f(h\omega)$ into $+(1/2).f(h\omega)$; then write (25*b*) with *P* instead of *h* and subtract.

in (25*g*) is free from this disadvantage; it may be obtained from (25*e*) by means of the relation |*odd*| = |*all*| − |*even*|, while the shorter form (25*h*) follows from (25*g*) by means of the relation 2 |*even*| − |*all*| = −|*alt*|. The form (25*h*) is that employed for |*odd*| series throughout this paper; and the terms "P-approximation" and "Remainder" must be understood to have the meanings indicated under Eqs. 25*e* and 25*h*.

If the "Remainder" of (25*e*) be expanded by integration-by-parts (cf. Eq. 25*d*), the derivatives of $f(\infty)$ are all zero and only the odd derivatives of $f(0)$ will remain. The form so obtained is in common use but is not available when $\Sigma f(n\omega) = \theta c$; for all the odd derivatives of $e^{-\lambda^2 T}.\cos \lambda X$ contain either λ or $\sin \lambda X$ as a factor and therefore vanish[1] when $\lambda = 0$.

Geometrical Illustration

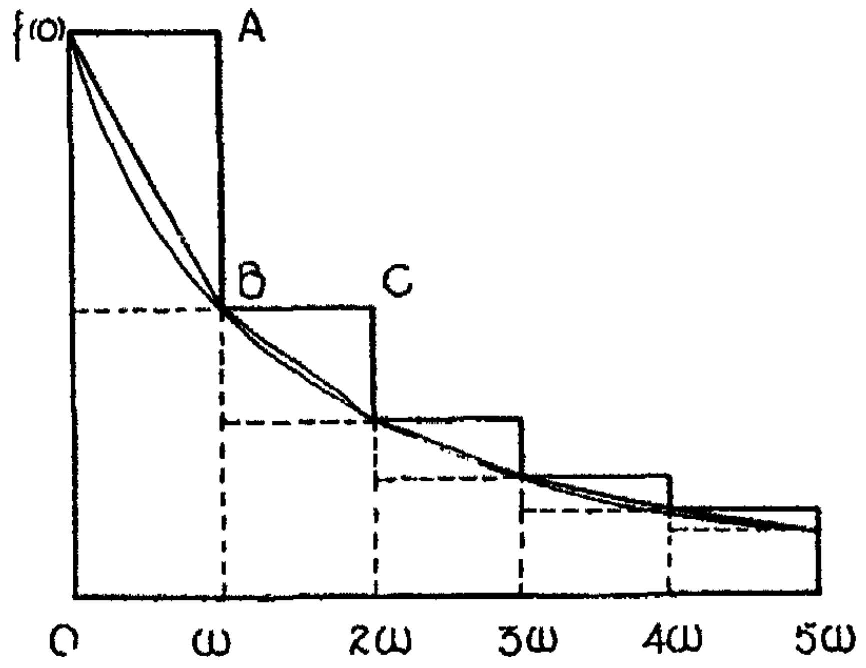

Fig. 1

The significance of Poisson's Formula and of the "P-approximation" is illustrated in Fig. 1. From the scales of ordinates and abscissas given in the Figure, it is obvious that the area of the rectangle $[0, f(0), A, \omega]$ is $\omega.f(0)$, the area of the rectangle $[\omega, B, C, 2\omega]$ is $\omega.f(\omega)$, and so on. Thus the area under the heavy stepped line is $\omega.\sum_{n=0}^{4} f(n\omega)$, and that under the dotted stepped line is $\omega.\sum_{n=1}^{5} f(n\omega)$, while the area under the smooth curve is $\int_0^5 f(\lambda).d\lambda$; finally the area under the jointed line lying just above the curve (the average of the areas under the two stepped lines) is $\omega/2.\{\sum_{n=0}^{4} f(n\omega) + \sum_{n=1}^{5} f(n\omega)\}$. Therefore

$$\omega.\sum_{n=1}^{4} f(n\omega) + \omega/2.f(0) + \omega/2.f(5\omega) =$$
$$\int_0^5 f(\lambda).d\lambda + \textit{area between jointed line and curve} \qquad (26)$$

Comparing Eq. 26 with Eq. 25, it appears that the sum on the right of the latter represents the area lying between the jointed line and the curve; and that the approximation to the value of the series arrived at by neglecting

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[1] Legendre [Traité des fonctions elliptiques, Paris, Vol. II, p. 578 (1826)] encountered a case like this before Poisson's Formula had been published, and (not to put too fine a point upon it) got lost. Poisson set him right [*loc. cit.*, p. 588].

this sum consists in identifying the area under the jointed line with that under the curve.[1] If ω be decreased, while $h\omega$ (and therefore the area under the curve) is kept constant,[2] it is evident that the jointed line will approach more closely to the curve; thus in the limit when $\omega \to 0$ the two will be identical, the Remainders of Eqs. 25*e* and 25*h* will be zero, and the P-approximations will be exact. But it does not follow from this that every decrease in the value of ω which leaves $h\omega$ constant must necessarily improve the approximation, unless $f(n\omega)$ be such that the curve has no point of inflexion (i.e. unless the jointed line lies always above or always below the curve). For where the line lies above the curve, the Series is greater than the Integral and the Remainder is positive, and where the line lies below the curve the Remainder is negative, so that if the curve has a point or points of inflexion the Remainder is the algebraic sum of positive and negative parts; and although every decrease in ω must bring the line everywhere nearer to the curve, and must therefore diminish the absolute value of every one of these parts, yet the net effect on their algebraic sum will obviously depend on whether the diminution of the positive parts or that of the negative parts predominates, i.e. it will depend on the form of the function $f(n\omega)$. See Rules II and II*a*, p. 2841.

Sec. 6:—The Poisson Forms[3] of Series of the Θ-Family.

(6a) Series of the Θ_E Group

The Poisson Form of $[all]\Theta c$ given in Table VIII may be obtained from Eq. 25*e* by setting $\omega = 1$ and $f(n\omega) = e^{-n^2T}.\cos nX$, and performing the integrations;[4] that for $[even]\Theta_c$ by setting $\omega = 1$ and $f(n\omega) = e^{-4n^2T}.\cos 2nX$ in the same equation; that for $[odd]\Theta c$ comes from Eq. 25*h*. Three different ways of writing the Poisson Form of $[all]\Theta c$ are given in the Table; the last of these is that employed throughout this paper.

To obviate the necessity of reprinting the expressions every time they are referred to, the following names and symbols will be employed:—The name "Remainder" and the symbol $Rem{:}\Theta_E$ (or the special symbols $Rem{:}[all]\Theta c$, etc.) for the quantities within { } in the Poisson Forms of $[all, even$ or $odd]\Theta c$; the name "P-approximation" and the symbol $P{:}\Theta_E$ for the other terms of the Poisson Form; the name "Approximation Integral" and the symbol $A{:}\Theta_E$ for the exponential term included in the P-approximation. In view of these definitions it is obvious that $P{:}[odd]\Theta c = A{:}[odd]\Theta c$, since in $[odd]\Theta c$ the P-approximation consists of the exponential term only. The n'th term of the

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[1] The same is true of the approximations arrived at by neglecting the sums on the right of Eqs. 25*b*, *c*, *e*, *f*. That obtained by neglecting the sum on the right of (25*h*) consists in identifying the area under the curve with that under the stepped line whose ordinates are: $f(\omega)$ for $0 < y < 2$, $f(3\omega)$ for $2 < y < 4$, $f(5\omega)$ for $4 < y < 6$ etc.

[2] It is obvious that this condition is fulfilled when $h = \infty$, which is the case with all the series dealt with in this paper; they however are functions of ω as well as of $n\omega$.

[3] This nomenclature possesses the essential quality of brevity, but it is open to the objection that the "Poisson Form" and the "Original Form" are wholly different series (see p. 2797). As the sums of the two series are the same, either "Form" can be employed in computations whose only object is to find that sum.

[4] See. D. Bierens de Haan: "Nouvelles Tables d'Intégrales définies," Table 263, Nos. 2 and 5, (1867).

series $Rem{:}\Theta_E$, disregarding the factor $(-1)^{n+1}$ if present,[1] will be indicated by the symbol $R_n{:}\Theta_E$; it may be split into two other terms each containing a single exponential, of these that containing $(n\pi - gx)$ in its exponent will receive the symbol $R_{na}{:}\Theta_E$, and the other the symbol $R_{nb}{:}\Theta_E$. Thus

$$[even]\Theta c = P{:}[even]\Theta c + Rem{:}[even]\Theta c = A{:}[even]\Theta c - \tfrac{1}{2} + Rem{:}[even]\Theta c \tag{27a}$$

$$= A{:}[even]\Theta c - \tfrac{1}{2} + \Sigma R_n{:}[even]\Theta c \tag{27b}$$

$$= A{:}[even]\Theta c - \tfrac{1}{2} + \Sigma R_{na}{:}[even]\Theta c + \Sigma R_{nb}{:}[even]\Theta c \tag{27c}$$

where
$$A{:}[even]\Theta c = (\sqrt{\pi}/4\sqrt{T}).e^{-X^2/4T} \tag{28}$$

$$R_{na}{:}[even]\Theta c = (\sqrt{\pi}/4\sqrt{T}).e^{-(n\pi - X)^2/4T} \tag{29}$$

$$R_{nb}{:}[even]\Theta c = (\sqrt{\pi}/4\sqrt{T}).e^{-(n\pi + X)^2/4T} \tag{30}$$

Similarly
$$[odd]\Theta c = P{:}[odd]\Theta c - Rem{:}[odd]\Theta c \tag{31}$$

$$= A{:}[odd]\Theta c - \Sigma(-1)^{n+1}.(R_{na}{:}[odd]\Theta c + R_{nb}{:}[odd]\Theta c)$$

where
$$A{:}[odd]\Theta c = A{:}[even]\Theta c, \qquad R_{na}{:}[odd]\Theta c = R_{na}{:}[even]\Theta c,$$

and
$$R_{nb}{:}[odd]\Theta c = R_{nb}{:}[even]\Theta c. \tag{32}$$

The expression given in Table VIII for the Poisson Form of $[all]\Theta c$ may be obtained by replacing X in the expression for $[all]\Theta c$ by $\pi - X$ and multiplying by -1; the expression for $[even\text{-}all]\Theta c$ and $[odd\text{-}all]\Theta s$ may be obtained in a similar manner by making the substitutions of Table Va. But as indicated by the omission of [ ], the terms included in these Forms will not be grouped into "Remainder" and "P-approximation," and in the applications of Parts III-IV no use will be made of them; for as is shewn in the "Summary" of p. 2801, no series of the Θ_E Group need necessarily be represented by an expression of an alternating type.

Choice between the Original Forms and the Poisson Forms of Series of the Θ_E Group:— Since the exponentials contained in the definitions of Θ_E given in Tab. III (viz. the Original Forms) are powers of e^{-T}, while those of Tab. VIII (the Poisson Forms) are powers of $e^{-1/T}$, it is obvious that when T is small (which makes evaluation of the Original Form by direct summation laborious) the Poisson Form will be rapidly convergent, while when T is large (which makes the Poisson Form slowly convergent) only a few terms of the Original Form need be computed and added in order to obtain a satisfactory approximation to the value of the series. Taking $[even]\Theta c$ as an example, when $T \geqq 0.4$ three terms of the Original Form suffice to ensure accuracy within a unit in the sixth decimal place, while when $T \leqq 0.4$ not more than three exponentials from the Poisson Form (viz. one from A and two from *Rem*) are needed to attain the same degree of accuracy. In practice, by making the proper choice between the two Forms, it is possible to evaluate any of the series listed in Tab. VIII within one unit in the sixth decimal place without looking up more than three exponentials at the outside; values of $[even]\Theta c$ or of $[odd]\Theta c$ are needed in *approx.vii-ix*, of Sec. 9.

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[1] In the applications only absolute values are involved; see "Safe Boundaries," p. 2822, and "Accuracy of the approximations," p. 2840.

TABLE VIII

Poisson Forms of certain Series of the Θ_E Group.

For use in defining Φ_E, replace T by $a(t-u) = g^2k(t-u)$ and X by gx.

For use in defining Ψ_E, replace T by au and X by gx.

For use in defining Λ_E, replace T by $at = g^2kt$ and X by $g(x \pm \lambda)$.

$$\sum_{-\infty}^{\infty} e^{-n^2T}.\cos nX = 1 + 2.[all]\Theta c = \sqrt{\frac{\pi}{T}}.\sum_{-\infty}^{\infty} e^{-(2n\pi+X)^2/4T}$$

$$[all]\ \Theta c = -\frac{1}{2} + \frac{1}{2}\sqrt{\frac{\pi}{T}}.\sum_{-\infty}^{\infty} e^{-(2n\pi+X)^2/4T}$$

$$= -\frac{1}{2} + \sqrt{\frac{\pi}{T}}.e^{-X^2/4T}\left(\frac{1}{2} + \sum e^{-n^2\pi^2/T}.\cosh\frac{n\pi X}{T}\right)$$

$$= \frac{1}{2}\sqrt{\frac{\pi}{T}}.e^{-X^2/4T} - \frac{1}{2} + \left\{\frac{1}{2}\sqrt{\frac{\pi}{T}}\sum\left(e^{-(2n\pi-X)^2/4T} + e^{-(2n\pi+X)^2/4T}\right)\right\}$$

$$[even]\ \Theta c = \frac{1}{4}\sqrt{\frac{\pi}{T}}.e^{-X^2/4T} - \frac{1}{2} + \left\{\frac{1}{4}\sqrt{\frac{\pi}{T}}\sum\left(e^{-(n\pi-X)^2/4T} + e^{-(n\pi+X)^2/4T}\right)\right\}$$

$$[odd]\Theta c = \frac{1}{4}\sqrt{\frac{\pi}{T}}.e^{-X^2/4T} - \left\{\frac{1}{4}\sqrt{\frac{\pi}{T}}\sum(-1)^{n+1}\left(e^{-(n\pi-X)^2/4T} + e^{-(n\pi+X)^2/4T}\right)\right\}$$

$$[alt]\ \Theta c = \frac{1}{2} - \frac{1}{2}\sqrt{\frac{\pi}{T}}\sum\left(e^{-(m\pi-X)^2/4T} + e^{-(m\pi+X)^2/4T}\right)$$

$$[enen\text{-}alt]\ \Theta c = \frac{1}{2} - \frac{1}{4}\sqrt{\frac{\pi}{T}}\sum\left(e^{-(m\pi-2X)^2/16T} + e^{-(m\pi+2X)^2/16T}\right)$$

$$[odd\text{-}alt]\ \Theta s = \frac{1}{4}\sqrt{\frac{\pi}{T}}\sum(-1)^{n+1}\left(e^{-(m\pi-2X)^2/16T} - e^{-(m\pi+2X)^2/16T}\right)$$

Euler-Maclaurin approximations to series of the Θ_E Group:— Approximate expressions involving Bernoulli numbers may be obtained from Eq. 25*d* by setting $P = 1$, $Q = \infty$, $\omega = 1$ and $f(n\omega) = e^{-N^2T}.\cos NX$, introducing the numerical values of the Bernoulli coefficients, and neglecting R_r; the resulting expression is extremely clumsy, and as shewn by actual computation[1] is less accurate than the convenient form given in Table VIII. In general, such Euler-Maclaurin approximations are of no practical value in dealing with the series of the Θ_E, Φ_E, Ψ_E and Λ_E Groups.

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[1] The following table gives the true value (found by direct summation of the Original Form), the P-approximation (Table VIII neglecting the Remainder) and the Euler-Maclaurin approximation (including the ninth derivative) for $[all]\Theta c$ when $X = 0$ and $T = 0.25$ 0.50 and 1.00.

	$T = 0.25$	$T = 0.50$	$T = 1.00$
True value	1.2724 53852	0.7533 14144	0.3863 18603
P-approx.	1.2724 53851	.7533 1414	.3862
E-M approx.	1.2724 5384	.7533 148	.3864

(6b) Poisson Forms of Series of the Θ_F Group

[Although it has been shewn (see Table IV) that series related to this Group do not occur in the Solutions of the problems enumerated in Part I, it may not be amiss to point out that Poisson Forms may be obtained for them as for the others. Thus from Eq. 25*e* by setting $f(n\omega) = e^{N^2T}.\sin nX$ and $\omega = 1$, and performing the integrations,[1] there results

$$[all]\Theta s = (1/\sqrt{T}).[F(X/2\sqrt{T}) - \Sigma\{F(\overline{2n\pi - X}/2\sqrt{T}) - F(\overline{2n\pi + X}/2\sqrt{T})\}] \quad (35)$$

Substituting $2X$ for X and $4T$ for T gives the Poisson Form of $[even]\Theta s$, whence by means of Eqs. 10 and 11 expressions for $[odd]\Theta s$ and $[all]\Theta s$ may be obtained. Substituting $\pi/2 - X$ for X in the expression for $[odd]\Theta s$ gives

$$[odd\text{-}all]\Theta c = \Sigma(-1)^{n+1}.\{F(\overline{m\pi - 2X}/4\sqrt{T}) + F(\overline{m\pi + 2X}/4\sqrt{T})\}/2\sqrt{T} \quad (36)$$

In evaluating series of this Group, where the Remainder is in general much less negligible than for the corresponding series of the Θ_E Group, approximations involving Bernoulli numbers might prove useful. Eq. 25*d* gives

$$\begin{aligned}[all]\Theta s \rightarrow (1/\sqrt{T}).F(X/2\sqrt{T}) + X/12 + (6TX - X^3)/720 \\ -(60T^2X + 20TX^3 + X^5)/30240 - \dots \quad (37)\end{aligned}$$

as an approximation to the sum of $[all]\Theta s$.]

Sec. 7: Poisson Forms of Series of the Φ_E and Λ_E Groups

On p. 2795 the series of the Φ-Family were defined to be those obtainable from series of the Θ-Family by writing $a(t-u)$ in place of T and gx in place of X, multiplying by $f(u).du$, and integrating between the limits 0 and t. The Poisson form of any series of the Φ-Family can therefore be obtained by multiplying the Poisson Form of the corresponding Θ series by $f(u).du$ and integrating after replacing T and X as before. Hence

$$\Phi c = P{:}\Phi c \pm Rem{:}\Phi c \quad (38)$$

(the sign prefixed to $Rem{:}\Phi c$ being that prefixed to $Rem{:}\Theta c$ in Table VIII) where

$$P{:}\Phi c = \int_0^t (P{:}\Theta c).f(u).du \quad (39)$$

$$Rem{:}\Phi c = \int_0^t (Rem{:}\Theta c).f(u).du \quad (40)$$

The examples of Eqs. 41-47 are important in what follows.

$$[even]\Phi c = A{:}[even]\Phi c - \tfrac{1}{2}\int_0^t f(u).du + Rem{:}[even]\Phi c \quad (41)$$

where $$A{:}[even]\Phi c = \frac{1}{4}\sqrt{\frac{\pi}{a}}.\int_0^t \frac{e^{-g^2x^2\,4a(t-u)}}{\sqrt{t-u}}.f(u).du \quad (42)$$

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[1] The symbol $F(x)$ is used for $e^{-x^2}.\int_0^x e^{y^2}.dy$, see p. 2874; numerical values of this function are given in Table XXVIII.

Since $\int_0^\infty e^{-\lambda^2T}.\sin\lambda X.d\lambda = i.\int_0^\infty e^{-\lambda^2T}.\cos\lambda X.d\lambda - \int_0^\infty e^{-\lambda^2T + i\lambda X}.d\lambda \qquad (i = \sqrt{-1}) \quad (33)$

where the first integral on the right is known and the second can be reduced to canonical orm by completing the square in the exponent, it is easy to shew that

$$A{:}[\text{all}]\Theta s = \int_0^\infty e^{-\lambda^2T}.\sin\lambda X.d\lambda = (1/\sqrt{T}).F(X/2\sqrt{T}) \quad (34)$$

$$Rem\colon[even]\Phi c = \Sigma R_n\colon[even]\Phi c = \Sigma R_{na}\colon[even]\Phi c + \Sigma R_{nb}\colon[even]\Phi c \tag{43}$$

$$R_{na}\colon[even]\Phi c = \frac{1}{4}\sqrt{\frac{\pi}{a}}\cdot\int_0^t \frac{e^{-(n\pi-gx)^2/4a(t-u)}}{\sqrt{t-u}}.f(u).du \tag{44}$$

$R_{nb}\colon[even]\Phi c$ = Similar expression in which $(n\pi-gx)$ is replaced by $(n\pi+gx)$. (45)

$$\text{Similarly } [odd]\Phi c = A\colon[odd]\Phi c - Rem\colon[odd]\Phi c \tag{46a}$$

$$= A\colon[odd]\Phi c - \Sigma(-1)^{n+1}.R_n\colon[odd]\Phi c \tag{46b}$$

$$= A\colon[odd]\Phi c - \Sigma(-1)^{n+1}\{R_{na}\colon[odd]\Phi c + R_{nb}\colon[odd]\Phi c\} \tag{46c}$$

where $A\colon[odd]\Phi c = A\colon[even]\Phi c,\ \ R_{na}\colon[odd]\Phi c = R_{na}\colon[even]\Phi c,$

$$R_{nb}\colon[odd]\Phi c = R_{nb}\colon[even]\Phi c. \tag{47}$$

Similarly, from the definition of series of the Λ-Family given on p. 2795

$$\Lambda c = P\colon\Lambda c \pm Rem\colon\Lambda c = \int_0^l (P\colon\Theta c).F(\lambda).d\lambda \pm \int_0^l (Rem\colon\Theta c).F(\lambda).d\lambda \tag{48}$$

The above relations serve to deduce from the expressions for Y given in Table IV, the "Poisson Forms" of the Solutions of Tables I and II given in Table IX. These can be converted into Solutions for infinite l by deleting the Remainders and writing ∞ where l occurs as the upper limit of the integration.

TABLE IX

The Poisson Forms of the Solutions of Tables I and II

No.	$z =$
I,1	$\frac{x}{2\sqrt{\pi k}}\cdot\int_0^t \frac{e^{-x^2/4k(t-u)}}{(t-u)^{3/2}}.f(u).du - \frac{2k}{l}\cdot\frac{\partial}{\partial x}(Rem\colon[even]\Phi c)$
I,2	ditto $+ \frac{2k}{l}\cdot\frac{\partial}{\partial x}(Rem\colon[odd]\Phi c)$
I,3	$-\sqrt{\frac{k}{\pi}}\cdot\int_0^t \frac{e^{-x^2/4k(t-u)}}{\sqrt{t-u}}.f(u).du + \frac{2k}{l}\cdot Rem\colon[odd]\Phi c$
I,4	ditto $- \frac{2k}{l}\cdot Rem\colon[even]\Phi c$
II,1	$\frac{1}{2\sqrt{\pi kt}}\cdot\int_0^l \{e^{-(x-\lambda)^2/4kt} - e^{-(x+\lambda)^2/4kt}\}.F(\lambda).d\lambda + (B-C)/l$
II,2	ditto $- (D-E)/l$
II,2a	$\frac{1}{2\sqrt{\pi kt}}\cdot\int_0^l \{e^{-(x-\lambda)^2/4kt} + e^{-(x+\lambda)^2/4kt}\}.F(\lambda).d\lambda - (D+E)/l$
II,3	ditto $+ (B+C)/l$

where $B = Rem\colon[even]\Lambda c,\ X = gx-g\lambda;$ $\quad C = Rem\colon[even]\Lambda c,\ X = gx+g\lambda$

$D = Rem\colon[odd]\Lambda c,\ X = gx-g\lambda;$ $\quad E = Rem\colon[odd]\Lambda c,\ X = gx+g\lambda$

The Poisson Forms of Table I Nos. 1a, 2a, 3a and 4a may be obtained from those of Table I Nos. 1, 2, 3 and 4 respectively by replacing x in the latter by $(l-x)$; this includes replacing $\partial/\partial x$ by $\partial/\partial(l-x) = -\partial/\partial x$.

PART III

THE EVALUATION OF SERIES OF THE Φ_E GROUP AND RELATED SERIES, INCLUDING THOSE OF TABLE I

In Part II, Sec. 7 it has been shewn how any series contained in the Solutions of Table I (or more generally any series of the Φ_E Group) can be replaced by another infinite series which we call the Poisson Form of the series in question; so that in evaluating the series, either the Original Form or the Poisson Form may be chosen as may prove convenient. In practice this choice is nearly always reduced to one between the Original Form and the P-approximation, and is determined by the necessity of avoiding difficulties of summation or of integration, which in turn depend on the value of at and of gx and on the form of $f(u)$; the present Part is devoted to a discussion of these matters in detail.

If the value of at is small, the Original Form is inconvenient because of the slow convergence of the Evanescent Series (see p. 2803), the infinite series in the Poisson Form on the other hand is rapidly convergent and if the integrals involved have been tabulated this Form is immediately available (*approx.i*); in general, however, these integrals have not been tabulated; *approx.ii*, *iii*, *iv* and *ix* are in effect methods for evaluating them. If on the other hand the value of at is large, the slow convergence of the Poisson Form and the consequent inaccuracy of the P-approximation is in itself a sufficient reason for avoiding it; the Evanescent Series $V{:}\Phi_E$ on the other hand is rapidly convergent, and if the integral involved in $V{:}\Phi_E$ (the Original Integral, p. 2804) has been tabulated, and a finite expression for the Stationary Series $S{:}\Phi_E$ is known, the employment of the Original Form is indicated (*approx. v*). In certain cases there is no finite expression for the sum of $S{:}\Phi_E$, and for a few forms of $f(u)$ the integral involved in $V{:}\Phi_E$ is untabulated; *approx.vi-ix* shew how these cases may be handled.

In Sec. 8 the influence of the numerical values of at and gx on the magnitude of $Rem{:}\Phi_E$ is discussed; this leads to a convenient method for finding the values of at and gx with which the *P-approx.* can be used without introducing errors greater than a quantity fixed in advance by the computer. In this Section also, relations are established which permit the evaluation of $P{:}\Phi_E$ in many cases where the integrals contained in it have not been tabulated. In Table X the series are classified according to the form of $f(u)$; and this table lists for each Class the approximations most suitable for given values of at and gx. In Sec. 9 the various approximations to Φ_E and to $\partial/\partial(gx).\Phi_E$ are considered in detail and illustrated by numerical examples[1];

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[1] These are intended to illustrate the accuracy of the mathematical methods, and are taken to a larger number of significant figures than is ordinarily necessary in laboratory computations. In many cases alternative methods of computation are used; these shew the great saving of labour that may be effected by following the methods recommended.

the evaluation of $S:\Phi_E$ is dealt with in Sec. 10; Rules for finding upper limits to the Remainders neglected in these approximations are given in Sec. 11.

Table X

Classification of Series of the Φ_E Group according to the form of $f(u)$; with the approximations recommended for each Class

Class	Definition				Approximation recommended for values of $\sqrt{at}$ and gx			
	A	A_0	V	S	above BE	below BE when $gx \neq 0$	above B	below B when $gx = 0$
A	+	+	+	+	*v*	*i*	*v*	*i*
B	.	+	+	+	*v*	OBJ,*ii*;OJH,*iii*;OHE,*iv*	*v*	*i*
C	.	.	+	+	*v*	OBJ,*ii*;OJE,*iii*	*v*	*ii*
D	.	+	+	.	*vii*	*ix*	*vi*	*i*
E	.	.	+	.	*vii*	*ix*	*vii*	*ix*
F	.	+	.	.	*ix*	*ix*	*viii*	*i*
G	.	.	.	.	*ix*	*ix*	*ix*	*ix*

Examples

A. u^p.

B. $u^p.e^{\pm b^2u}$; sin or $cos\ \overline{b^2u+\alpha}$.

C. $e^{Ku}.(sin$ or $cos)\ \overline{b^2u+\alpha}$.

D. $(b^2+u)^{-p}$; $(b^2\pm u)^{\pm p+0.5}$; $F(\sqrt{b^2u})$.

E. $e^{b^2u^2}$.

F. $1\sqrt{(b^2+u)(c^2+u)}$.

G. $1/(b^2+u^2)$.

Definitions of the Classes:—The Class to which a given series belongs depends upon the form of $f(u)$, and is based upon the existence or nonexistence of numerical tables from which the Approximation Integral (p. 2811) the Approximation Integral when $gx = 0$ or the Original Integral (p. 2804) can readily be computed, and upon the existence or nonexistence of a finite expression for the sum of the Stationary Series (p. 2803). The existence of such tables or of such an expression is indicated by a plus sign in the column headed A A_0 V or S respectively; their nonexistence by a dot. The approximation integrals for a number of forms of $f(u)$ are tabulated in Table XI, Original Integrals in Tables XII and XIII, finite expressions for S in Table XII.

The approximations are designated by the numbers *i-ix* (see Sec. 9). Table XVI shews that for each Class (except the last) more than one approximation is available; those given in Table X are recommended because they involve the least labour.

The range of values of $\sqrt{at}$ and gx for which an approximation is recommended is indicated by the position of the point representing the series in Fig. II (in which the ordinate of E is to be chosen with regard to the accuracy desired, see Table XIV). Thus "OBJ, *ii*" means that if the values of $\sqrt{at}$ and gx are those represented by any point within the triangle OBJ of Fig. II, *approx. ii* is recommended for series of Class B and Class C when gx is not zero.

The Examples include all those dealt with in Tables XI, XII and XIII, and are all that are met with in the literature (see foot-note p. 2789); the letter p denotes a positive integer or zero, b^2 c^2 and K are real positive quantities. The Class to which any form of $f(u)$ is assigned may obviously be altered by the publication of new tables; the appearance of numerical tables of H and K (see Appendix), for instance, would transfer $u^p.e^{-b^2u}$ from Class B to Class A, and $e^{Ku}.\overline{sin \text{ or } cos\ b^2u}$ from Class C to Class B.

Approximations to Φ'_E (see p. 2834) may also be chosen from this table; for this purpose *i-ix* must be replaced by *ia-ixa*, and when *approx. iv* is recommended in the table, *approx. iiia* must be employed.

TABLE XI

P-approximation to Φc; Nos. 1-3 valid when $0 \leq gx \leq \pi/2$, Nos. 4-14 valid when $gx = 0$

No.	$f(u)$	$P{:}[\text{odd}]\Phi c = A{:}[\text{odd}]\Phi c = A{:}[\text{even}]\Phi c = P{:}[\text{even}]\Phi c + \frac{1}{2}\int_0^t f(u).du.$
1.	1	$(gx/8a\sqrt{\pi}).\mathbf{G}(4\pi^2at/g^2x^2)$
2.[1]	u	$(t + g^2x^2/6a).B - (t\sqrt{\pi t/a}.e^{-g^2x^2/4at})/6$
3.[1]	u^2	$(2t + g^2x^2/10a).C - (t^2 + g^2x^2t/10a).B$ $+ (t^2\sqrt{\pi t/a}.e^{-g^2x^2/4at})/10$
4.	e^{b^2u}	$(\pi/4b\sqrt{a}).e^{b^2t}.\mathbf{P}(b\sqrt{t})$
5.	$b^2u.e^{b^2u}$	$(\pi/8b\sqrt{a}).(2b^2t - 1).\ \mathbf{P}(b\sqrt{t}) + \sqrt{\pi t}/4\sqrt{a}$
6.	e^{-b^2u}	$(\sqrt{\pi}/2b\sqrt{a}).\ F(b\sqrt{t})$
7.	$b^2u.e^{-b^2u}$	$(\sqrt{\pi}/4b\sqrt{a}).(2b^2t + 1).F(\sqrt{b^2t}) - \sqrt{\pi t}/4\sqrt{a}$
8.	$\sin \overline{b^2u+\alpha}$	$(\pi/b\sqrt{8a}).\{\sin \overline{b^2t+\alpha}.\mathbf{C}(\sqrt{2b^2t/\pi})$ $- \cos \overline{b^2t+\alpha}.\mathbf{S}(\sqrt{2b^2t/\pi})\}$
9.	$\cos \overline{b^2t+\alpha}$	$(\pi/b\sqrt{8a}).\ \{\cos \overline{b^2t+\alpha}.\mathbf{C}(\sqrt{2b^2t/\pi})$ $+ \sin \overline{b^2t+\alpha}.\mathbf{S}(\sqrt{2b^2t/\pi})\}$
10.	$1/(b^2 + u)$	$(\sqrt{\pi}/4\sqrt{ab^2+at}).\ \{\log(\sqrt{b^2+t} + \sqrt{t})$ $- \log(\sqrt{b^2+t} - \sqrt{t})\}$
11.	$1/\sqrt{b^2+u}$	$(\sqrt{\pi}/2\sqrt{a}).\sin^{-1}\sqrt{t/(b^2+t)}$
12.	$1/\sqrt{b^2-u}$	$(\sqrt{\pi}/2\sqrt{a}).\{\log(b + \sqrt{t}) - \log\sqrt{b^2-t}\}$
13.	$F(\sqrt{b^2u})$	$(\pi^{3/2}/8b\sqrt{a}).(1 - e^{-b^2t})$
14.	$1/\sqrt{(b^2+u)(c^2+u)}$	$(\sqrt{\pi}/2\sqrt{ab^2+at}).\mathbf{F}(\sin^{-1}\sqrt{(c^2+t)/(b^2+t)},$ $\sin^{-1}\sqrt{t/(c^2+t)})$

$$\mathbf{G}(x) = \int_0^x (e^{-\pi^2/y}/\sqrt{y}).dy;\mathbf{P}(x) = (2/\sqrt{\pi}).\int_0^x e^{-y^2}.dy;F(x) = e^{-x^2}.\int_0^x e^{y^2}dy;$$

$$\mathbf{S}(x) = \int_0^x \sin\tfrac{1}{2}\pi y^2.dy;\mathbf{C}(x) = \int_0^x \cos\tfrac{1}{2}\pi y^2.dy;\ \mathbf{F}(\alpha,\varphi) = \int_0^\varphi dy/\sqrt{1-\sin^2\alpha.\sin^2 y}.$$

For numerical values of the integrals involved in this Table, see:—
G(x):—Table XXVII, p. 2877.
$F(x)$:—Table XXVIII, p. 2878.
P(x):—J. Burgess: Trans. Edin. Roy. Soc., 39, 257 (1899).

S(x) and C(x):—Gilbert: Mém. cour. Acad. Bruxelles, 31 (1863); Ignatowsky: Ann. Physik (4) 23, 894 (1907); Brit. Ass. Report, 1926, p. 273; Jahnke und Emde: "Funktionentafeln," p. 23, (1923). See also Table XXIII and XXIV, pp. 2872 and 2873.

F(α, φ):—Legendre: "Exercices de calcul intégral," t. III, (1816); also Jahnke und Emde: loc. cit. p. 54.

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[1] For brevity in Nos. 2 and 3 of this Table, B is written for P: [*odd*] Φc when $f(u) = 1$, i.e. for $(gx/8a\sqrt{\pi})$. $\mathbf{G}(4\pi^2at/g^2x^2)$, and C for P: [*odd*]Φ*c* when $f(u) = u$, i.e. for the expression entered in the second line of this Table in the last column.

TABLE XII (see p. 2818)

No.	$f(u)$	$S{:}\Phi c$
1.	1	(XIIb,1)
2.	u	t.(XIIb,1) − (XIIb,2)
3.	u^2	t^2.(XIIb,1) − $2t$.(XIIb,2) + 2(XIIb,3).
4.	e^{b^2u}	e^{b^2t}.(XIIa,1)
5.	$b^2u.e^{b^2u}$	$e^{b^2t}.\{b^2t.$(XIIa,1) − (XIIa,7)$\}$
6.	e^{-b^2u}	e^{-b^2t}.(XIIa,2)
7.	$b^2u.e^{-b^2u}$	$e^{-b^2t}.\{b^2t.$(XIIa,2) − (XIIa,8)$\}$
8.	$\sin\overline{b^2u+\alpha}$	$\sin\overline{b^2t+\alpha}$.(XII$a$,3) − $\cos\overline{b^2t+\alpha}$.(XII$a$,4)
9.	$\cos\overline{b^2u+\alpha}$	$\cos\overline{b^2t+\alpha}$.(XII$a$,3) + $\sin\overline{b^2t+\alpha}$.(XII$a$,4)
10.	$e^{Ku}.\sin\overline{b^2u+\alpha}$	$e^{Kt}.\{\sin\overline{b^2t+\alpha}$.(XII$a$,5) − $\cos\overline{b^2t+\alpha}$.(XII$a$,6)$\}$
11.	$e^{Ku}.\cos\overline{b^2u+\alpha}$	$e^{Kt}.\{\cos\overline{b^2t+\alpha}$.(XII$a$,5) + $\sin\overline{b^2t+\alpha}$.(XII$a$,6)$\}$

TABLE XIIA

The Sums of certain series which occur in $S{:}\Phi c$ and the P-approximations to their Sums

Series = $\Sigma F(N).\cos Ngx$

No.	1. $F(N)$	2. N	3. Finite expression for $\frac{1}{2}F(0)+\Sigma F(2n).\cos 2ngx$ and for $\Sigma F(2n-1).\cos\overline{2n-1}gx$	4. P-approximation to expression of Col. 3
1	$\frac{1}{N^2a+b^2}$	$2n$	$M.C_1/S_2$	$M.e^{-r}$
		$2n-1$	$M.S_1/C_2$	"
2	$\frac{1}{N^2a-b^2}$	$2n$	$-M.c_1/s_2$	......
		$2n-1$	$M.s_1/c_2$	......
3	$\frac{N^2a}{N^4a^2+b^4}$	$2n$	$\frac{M}{\sqrt{2}}\{s_3S_3(s_4C_4+c_4S_4)-c_3C_3(s_4C_4-c_4S_4)\}/(C_4^2-c_4^2)$	$M.e^{-r/\sqrt{2}}.\cos\left(\frac{\pi}{4}+\frac{r}{\sqrt{2}}\right)$
		$2n-1$	$\frac{M}{\sqrt{2}}\{s_3C_3(c_4C_4+s_4S_4)+c_3S_3(c_4C_4-s_4S_4)\}/(C_4^2-s_4^2)$	"

TABLE XIIa (Continued)

	1.	2.	3.	4.
4.	$\frac{b^2}{N^4a^2+b^2}$	$2n$	$\frac{M}{\sqrt{2}}\left\{s_3S_3(s_4C_4-c_4S_4)+c_3C_3(s_4C_4+c_4S_4)\right\}/(C_4^2-c_4^2)$	$M.e^{-r/\sqrt{2}}.\sin\left(\frac{\pi}{2}+\frac{r}{\sqrt{2}}\right)$
		$2n-1$	$\frac{M}{\sqrt{2}}\left\{c_3S_3(c_4C_4+s_4S_4)-s_3C_3(c_4C_4-s_4S_4)\right\}/(C_4^2-s_4^2)$	"
5	$\frac{\Psi}{\Psi^2+b^4}$	$2n$	$Q\left\{C_6c_7(\alpha.S_8c_9-\beta.C_8s_9)+S_6s_7(\alpha.C_8s_9+\beta.S_8c_9)\right\}/(C_7^2-c_7^2)$	(See footnote 1)
		$2n-1$	$Q\left\{C_6s_7(\beta.C_8c_9+\alpha.S_8s_9)+S_6c_7(\alpha.C_8c_9-\beta.S_8s_9)\right\}/(C_7^2-s_7^2)$	"
6	$\frac{b^2}{\Psi^2+b^4}$	$2n$	$Q\left\{C_6c_7(\alpha.C_8s_9+\beta.S_8c_9)+S_6s_7(\beta.C_8s_9-\alpha.S_8c_9)\right\}/(C_7^2-c_7^2)$	(See footnote 2)
		$2n-1$	$Q\left\{S_6c_7(\beta.C_8c_9+\alpha.S_8s_9)-C_6s_7(\alpha.C_8c_9-\beta.S_8s_9)\right\}/(C_7^2-s_7^2)$	"
7	$\frac{b^2}{(N^2a+b^2)^2}$	$2n$	$\frac{M}{2}.\frac{1}{S_2}.\left\{C_1+r.S_1+\frac{\pi b.}{2\sqrt{a}}.\frac{C_5}{S_2}\right\}$	$\frac{M}{2}.e^{-r}.(1+r)$
		$2n-1$	$\frac{M}{2}.\frac{1}{C_2}.\left\{S_1+r.C_1-\frac{\pi b}{2\sqrt{a}}.\frac{C_5}{C_2}\right\}$	"
8	$\frac{b^2}{(N^2a-b^2)^2}$	$2n$	$\frac{M}{2}.\frac{1}{s_2}.\left\{c_1-r.s_1+\frac{\pi b}{2\sqrt{a}}.\frac{c_5}{s_2}\right\}$	......
		$2n-1$	$\frac{M}{2}.\frac{1}{c_2}.\left\{s_1+r.c_1-\frac{\pi b}{2\sqrt{a}}.\frac{c_5}{c_2}\right\}$	......

In this table only, the letters have the following meanings:—

$s = \sin$; $c = \cos$; $S = \sinh$; $C = \cosh$; $M = \pi/4b\sqrt{a}$; $Q = \pi/4\sqrt{a(K^2+b^4)}$

$\alpha^2 = (K+\sqrt{K^2+b^4})/2$; $\beta = b^2/2\alpha$; $r = bgx/\sqrt{a}$; $\Psi = N^2a+K$

Writing f for s, S, c or C, the subscripts have the following significance:—

$f_1 = f(b.\overline{\pi-2gx}/\sqrt{4a})$ $f_2 = f(b\pi/\sqrt{4a})$

$f_3 = f(b.\overline{\pi-2gx}/\sqrt{8a})$ $f_4 = f(b\pi/\sqrt{8a})$

$f_5 = f(bgx/\sqrt{a})$ $f_6 = f(\alpha.\overline{\pi-2gx}/\sqrt{4a})$

$f_7 = f(\beta.\overline{\pi-2gx}/\sqrt{4a})$ $f_8 = f(\alpha\pi/\sqrt{4a})$

$f_9 = f(\beta\pi/\sqrt{4a})$

---

[1] $Q.e^{-\alpha gx/\sqrt{a}}.\left\{\alpha.\cos\beta gx/\sqrt{a}-\beta.\sin\beta gx/\sqrt{a}\right\}$

[2] $Q.e^{+\alpha.gx/\sqrt{a}}.\left\{\alpha.\sin\beta gx/\sqrt{a}+\beta\cos\beta gx/\sqrt{a}\right\}$

TABLE XIIb

The Sums of certain series which occur in S:Φc.

Series = ΣF(N).cos Ngx

No.	$F(N)$	$\Sigma F(2n) . \cos 2ngx$	$\Sigma F(2n-1) . \cos \overline{2n-1}gx$
1	$\frac{1}{N^2a}$	$\frac{\pi^2}{24a}-\frac{\pi gx}{4a}+\frac{g^2x^2}{4a}$	$\frac{\pi^2}{8a}-\frac{\pi gx}{4a}$
2	$\frac{1}{N^4a^2}$	$\frac{\pi^4}{1440a^2}-\frac{\pi^2g^2x^2}{48a^2}+\frac{\pi g^3x^3}{24a^2}-\frac{g^4x^4}{48a^2}$	$\frac{\pi^4}{96a^2}-\frac{\pi^2g^2x^2}{16a^2}+\frac{\pi g^3x^3}{24a^2}$
3	$\frac{1}{N^6a^3}$	$\frac{\pi^6}{60480a^3}-\frac{\pi^4g^2x^2}{2880a^3}+\frac{\pi^2g^4x^4}{576a^3}$ $-\frac{\pi g^5x^5}{480a^3}+\frac{g^6x^6}{1440a^3}$	$\frac{\pi^6}{690a^3}-\frac{\pi^4g^2x^2}{192a^3}+\frac{\pi^2g^4x^4}{192a^3}$ $-\frac{\pi g^5x^5}{480a^3}$

TABLE XIII

The Original Integral (for use with *approx. vi* and *vii*).

No.	$f(u)$	The Original Integral $=\int^{u} e^{-N^2a(t-u)}.f(u).du$
1.	$1/(b^2+u)$	$e^{-N^2a(b^2+t)}.\int_{-\infty}^{N^2a(b^2+u)}\frac{e^y}{y}.dy$
2.	$1/\sqrt{b^2+u}$	$(2/N\sqrt{a}).e^{-N^2a(t-u)}.F(\sqrt{N^2ab+N^2au})$
3.	$1/\sqrt{b^2-u}$	$(2/N\sqrt{a}).e^{N^2a(b^2-t)}.\int_{\sqrt{N^2a(b^2-u)}}^{\infty}e^{-y^2}.dy$
4.	$\sqrt{b^2-u}$	$\sqrt{b^2-u}.\frac{e^{-N^2a(t-u)}}{N^2a}+\frac{e^{N^2a(b^2-t)}}{N^3a^{3/2}}.\int_{\sqrt{N^2a(b^2-u)}}^{\infty}e^{-y^2}.dy$
5.	$F(\sqrt{b^2u})$	$\frac{e^{N^2a(t-u)}}{N^2a-b^2}\cdot\left\{F(\sqrt{b^2u})-\frac{b}{N\sqrt{a}}\cdot F(\sqrt{N^2au})\right\}$
6.	$e^{b^2u^2}$	$\frac{e^{b^2u^2}}{b}.e^{-N^2a(t-u)}.F(\overline{N^2a+2b^2u}/2b)$
Note:	$F(x)$	$=e^{-x^2}.\int_0^x e^{y^2}.dy$

Examples illustrating the use of Tables XII, XIIa and XIIb.

These examples are necessary because of the compact form in which the information given in these Tables is presented; tables from which the results could be read directly, would take up too much space.

Example (*a*): To find a finite expression for the Stationary Series arising from [*even*]Φc when $f(u) = e^{b^2u}$. Look up $f(u) = e^{b^2u}$ in Table XII; line 4 reads $S = e^{b^2t}$. (*XIIa*, 1) which means $S = e^{b^2t}.\Sigma F(N).\cos Ngx$ with the value of $F(N)$ given in No. 1 of Table XII*a*. Hence $F(N) = 1/(N^2a + b^2)$ and therefore $F(0) = 1/b^2$; so that S:[*even*]$\Phi c = e^{b^2t}.\Sigma\cos Ngx/(N^2a+b^2)$, in which N is to be replaced by $2n$ since the series is of the [*even*] type. From Col. 3 of Table XII*a* No. 1 it appears that, when $N = 2n$, $\Sigma\cos Ngx/(N^2a+b^2) = M.C_1/S_2 - 1/2b^2$; replacing M, C_1 and S_2 by the expressions for which they are abbreviations (given at the foot of Table XII*a*) the final result is

$$S\text{:[}even\text{]}\Phi c = e^{b^2t}.\Sigma\cos 2ngx/(4n^2a+b^2) \qquad \text{(A)}$$

$$= e^{b^2t}.\left\{\frac{\pi}{4b\sqrt{a}}\cdot\frac{\cosh b(\pi-2gx)/\sqrt{4a}}{\sinh b\pi/\sqrt{4a}} - \frac{1}{2b^2}\right\} \qquad \text{(B)}$$

Example (*b*): To find the *P-approx.* to the Stationary Series arising from [*even*]Φc when $f(u) = e^{b^2u}$. Follow the procedure of Ex. (*a*) but use Col. 4 of Table XII*a* No. 1 instead of Col. 3. This gives

$$P{:}S = e^{b^2t}.\left\{\frac{\pi}{4b\sqrt{a}}.e^{-bgx\sqrt{a}} - \frac{1}{2b^2}\right\}$$

Example (*c*): To find the Evanescent Series arising from [*even*]Φc when $f(u) = e^{b^2u}$. The general rule is: In the expression for the Stationary Series (such as that given on the right of Eq. *A*, Ex. *a*) replace t by zero wherever it occurs, and insert the factor e^{-N^2at} immediately after the Σ sign. In the case chosen as example, this gives

$$V\text{:[}even\text{]}\Phi c = \Sigma(e^{-4n^2at}.\cos 2ngx)/(4n^2a+b^2)$$

Example (*d*)] To find the finite expression for the Stationary Series arising from [*odd*]Φc when $f(u) = 1$. Table XII line 1 reads S = (XII*b*, 1); No. 1 of Table XII*b* gives $F(N) = 1/N^2a$; as the series is of the [*odd*] type, $N = 2n-1$ and the last column of XII*b* must be used. Therefore $S = \Sigma\cos\overline{2n-1}.gx/(\overline{2n-1}^2.a) = \pi^2/8a - \pi gx/4a$.

Example (*e*): To find expressions for S, V and $P{:}S$ when the type of summation is neither [*even*] nor [*odd*] (see Table V, p. 2799). From the corresponding expressions for series of the [*even*] type those for series of the [*all*] type may be obtained by replacing a by $a/4$ and gx by $gx/2$; those for series of the [*all*] type by replacing a by $a/4$ and gx by $\pi - gx/2$; those for series of the [*even-all*] type by replacing gx by $\pi/2 - gx$. From the expressions for [*odd*]Φc those for [*odd-all*]Φs may be obtained by replacing gx by $\pi/2 - gx$. Thus (from Eq. *B* of Ex. *a*) when $f(u) = e^{b^2u}$

$$S\text{:[}all\text{]}\Phi c = e^{b^2t}.\left\{\frac{\pi}{2b\sqrt{a}}\cdot\frac{\cosh b(\pi-gx)/\sqrt{a}}{\sinh b\pi/\sqrt{a}}\right\} - \frac{1}{2b^2}$$

Sec. 8:—Relations between Series[1] of the Φ_E Group which differ only in the values of *at* and *gx*

Representation of a series by a point:—Any series of the Φ_E group is fully defined by its symbol (if the form of $f(u)$ and any constants contained in it be given) together with the numerical values of gx, a and t, or of gx, $\sqrt{at}$ and t. The value of gx and that of $\sqrt{at}$ may be given by the position of a point on a diagram such as Fig. 2, and in what follows the series will be spoken of as being represented by the point; this implies however that the symbol, the form of $f(u)$ with its constants, and the value of t (the same for every point on the diagram) are otherwise specified, for instance as a rubric to the figure.

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[1] Only series of the [*even*] and [*odd*] types are considered; see "Summary," p. 2801.

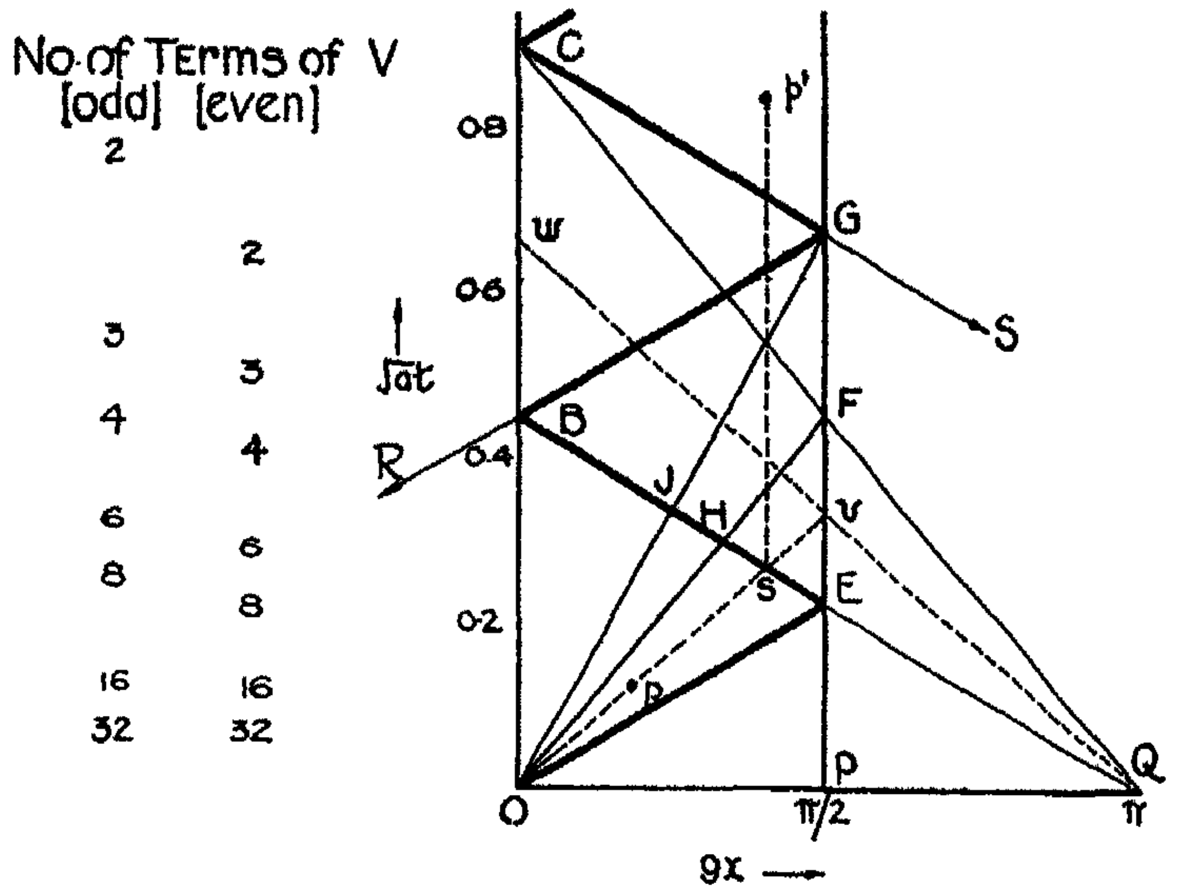

FIG. 2

In Fig. 2, 0.227 has been chosen as the ordinate of E; this gives "safe Boundaries" for [*even* or *odd*]Φc and for [*even* or *odd*]Ψc if quantities less than $10^{-6}.Mt$ may be neglected, and for [*even* or *odd*]$\Phi' c$ if quantities less than $8 \times 10^{-6}.Mt$ may be neglected. The Scales of "Number of terms of V" are safe if quantities less than $10^{-6}.t$ may be neglected and if $f(u)$ has one of the forms enumerated on page 2822.

Properties of the Diagram[1]

(*a*) If any line (such as OE, Ov, OF) be drawn upward and to the right from the point [$\sqrt{at} = 0$, $gx = 0$] of Fig. 2, the product[2] $\sqrt{a}.(A:\Phi c)$ will have the same value for all series represented by points on that line. *Approx. ii*, p. 2826, is based on this relation. (Proof:—This follows at once from Eqs. 42 and 47, since g^2x^2/a has the same value for all points on any line passing through the origin).

(*b*) If any line (such as EB, vw, FC) be drawn upward and to the left from the point Q of Fig. 2, the product $\sqrt{a}.(R_{1a}:\Phi c)$ will have the same value for all series represented by points on that line. (Proof:—This follows at once from Eqs. 44 and 47, since $(\pi - gx)^2/a$ has the same value for all points on any line passing through [$\sqrt{at} = 0$, $gx = \pi$].

(*c*) Similarly, $\sqrt{a}.(R_{1b}:\Phi c)$ will have the same value for all points on any line (such as BG) which passes through R; $\sqrt{a}.(R_{2a}:\Phi c)$ on any line (such as GC) passing through S, etc. The positions of R and S are merely indicated in Fig. 2; their ordinates are $\sqrt{at} = 0$; and their abscissas are $-\pi$ and $+2\pi$ respectively.

(*d*) If the line from O and the line from Q intersect on the ordinate passing through P, as at the points E, v and F of Fig. 2, the value of $\sqrt{a}.(A:\Phi c)$ charac-

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[1] Fig. 2 can be used as it stands for series of the Ψ_E Group (see p. 2856) as well as for series of the Φ_E Group. If used for Φ'_E (see p. 2834), $10^{-6}.Mt$ must be replaced by $8 \times 10^{-6}.Mt$ (see p. 2835) but $10^{-6}.Ct$ remains unaltered.

[2] The quantities $\sqrt{\bar{a}}.(A:\Psi c)$, $\sqrt{\bar{a}}.(R_{1a}:\Phi c)$ etc., are those which arise in evaluating Solutions 3 and 4 of Table I.

teristic of the first line will be identical with the value of $\sqrt{a}.(R_{1a}:\Phi c)$ characteristic of the second. (Proof:—This follows at once from Eqs. 42, 44 and 47, since when $gx = \pi/2$, $A = R_{1a}$). *Approx.iii*, p. 2827, is based on this relation.

Similarly, if a line through Q cuts a line through R on the ordinate $gx = 0$, the value of $\sqrt{a}.(R_{1a}:\Phi c)$ characteristic of the first line will be the same as the value of $\sqrt{a}.(R_{1b}:\Phi c)$ characteristic of the second (see Eqs. 44, 45 and 47); and so on. Thus $\sqrt{a}.A$ on OE $= \sqrt{a}.R_{1a}$ on EB $= \sqrt{a}.R_{1b}$ on BG $= \sqrt{a}.R_{2a}$ on GC, etc.

Boundaries

It is now convenient to discuss the properties of the set of lines OE, EB, BG . . (Fig. 2) which result when the ordinate of E is so chosen that the absolute value of R_{1a} for the series represented by that point is just negligible in view of the accuracy desired.

In the first place, it is obvious that R_{1a} must be negligible at all points on the line EB; since as has been shewn above, $\sqrt{a}.R_{1a}$ is constant for all points on that line and $\sqrt{a}$ increases from E to B. In the second place, if at be not too large,[1] and if $f(u)$ be one of those which retain their signs (which without loss of generality may be assumed to be positive) while u increases from 0 to t, then R_{1a} will decrease if a be decreased while t and gx remain unaltered; so that if R_{1a} is negligible along the line EB, it must be negligible at all points below it. Hence for functions of this kind, the line EB may be spoken of as the "Boundary[2] for R_{1a}." Similarly, BG is the Boundary for R_{1b}, GC for R_{2a}, etc.; but as OE runs downward (i.e. to smaller values of $\sqrt{a}$) from E, this line does not constitute a Boundary for $A:\Phi c$.

For all practical purposes, moreover, whenever the line EB is the Boundary for R_{1a}, it may also be taken as the Boundary for $Rem:\Phi c$; for the sum $(R_{1a}+R_{1b})$ at B is just equal to R_{1a} at E, while at every point on EB, R_{2a}, R_{2b}, etc., vanish in comparison with R_{1a}. From this it follows that *approx.i*, which assumes that $P:\Phi c$ is practically equal to Φc, may be employed only when the point representing the series lies on or below EB.

When the ordinate of E is fixed, the Boundaries can be drawn with ease:[3] this ordinate gives the value of $\sqrt{at}$ for which $R_{1a}:\Phi c$ is just negligible when $gx = \pi/2$. Table XIV gives the ordinates of E for [*even or odd*] Φc when $f(u) = 1$ and quantities ranging in magnitude from $10^{-10}.t$ to $10^{-3}.t$ are the largest considered negligible.[4] The only form of $f(u)$ other than $f(u) = 1$ for

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[1] For $\partial(R_{1a}:$ [*even or odd*] $\Phi c)/\partial a$ to be positive when $f(u)$ is positive, it is sufficient (see Eqs. 44 and 47) that $(\pi - gx)^2 > 2(at - au)$, i.e. $at < \pi^2/8$. Similarly, $\partial(R_{1b})/\partial a$ will be positive if $(\pi + gx)^2 > 2(at - au)$, i.e. $at < \pi^2/2$. In other words, the qualification in the text is equivalent to "if the ordinate of E is less than $\sqrt{\pi^2/8}$, i.e. is less than 1.11."

[2] It would be an *exact* Boundary for $\sqrt{a}.R_{1a}$, which is the quantity that arises in evaluating Solutions 3 and 4 of Table I, if the ordinate of E were chosen so that $\sqrt{a}.R_{1a}$ at $gx = \pi/2$ was just negligible. The *exact* Boundary for R_{1a} itself coincides with EB at E and elsewhere lies slightly above it; thus, strictly speaking, EB is a *safe* Boundary for R_{1a}, but this adjective is kept for Boundaries that are safer still.

[3] From their definitions, the ordinate of B is twice that of E, the ordinate of G is three times that of E, etc; so that OE and BG are parallel, and so are EB, GC, etc.

[4] When $f(u) = 1$, and $gx = \pi/2$, $(R_{1a}:$ [*even or odd*]$\Phi c)/t = (\sqrt{\pi}/16at).G(16at)$; see Table XXVI No. 2. The values of *log* (R_{1a}/t) for the values of at given in Table XXVII were computed and plotted against $\sqrt{at}$; whence the ordinates of E given in Table XIV were found by interpolation.

which the integrals needed in the construction of such a table have been tabulated is $f(u) = u^n$; but in the paragraph on "Safe Boundaries" it is shewn how the ordinates of Table XIV may be made generally useful.

TABLE XIV[1]

Ordinates of E for [*even* or *odd*]Φc when $f(u) = 1$.

R_{1a}/t	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}
$\sqrt{at}$	0.179	0.185	0.194	0.208	0.227	0.252	0.288	0.342

Fig. 2 is constructed on the assumption that when $f(u) = 1$, the quantity $10^{-6}.t$ is just negligible; if ten-thousand-fold greater accuracy had been required, the point E would have been lowered only 20%; if however quantities as great as $10^{-3}.t$ can be neglected, the point may be raised 50%.

"Safe" Boundaries:—By Rule I, p. 2840, $|R_{1a}:\Phi c| < M.\{R_{1a}:\Phi c(1)\}$ where M is the maximum absolute value attained by $f(u)$ in the interval $0 < u < t$, and $\Phi c(1)$ is a series identical in all respects with the given series except that the $f(u)$ of the given series is replaced by unity. Because of this relation, if the values of R_{1a} given in Table XIV be multiplied by M, the products will constitute upper limits to the quantities neglected by the assumption of various ordinates (viz. $\sqrt{at}$) for E, no matter what $f(u)$ may be, and in particular whether it changes sign in the interval $0 < u < t$ or does not. Put in another way, the assumption that $10^{-6}.Mt$ is the greatest quantity that may be neglected justifies the choice of 0.227 as the ordinate of E in Fig. 2; if $f(u) =$ *constant*, the Boundaries fixed by this choice are the highest possible, while if $f(u)$ has any other form the Boundaries are "safe," i.e. they are lower than is absolutely necessary.

Number of terms of V : Φc

Before deciding to adopt any particular method of approximation for evaluating a given series, it is important to have some idea of the number of terms of any Evanescent Series involved in it that would have to be computed. The following paragraphs shew how "safe[2]" Scales of the number of terms of V may be constructed. The Scales of Table XV (one of which has been plotted in Fig. 2) are safe for $V:\Phi c$, $V:\Phi'c$ (p. 2835) and $V:\Psi c$ (p. 2804), subject to certain restrictions as to the form of $f(u)$ explained below; and may also be used with Λc, see p. 2845.

The Scales of Fig. 2:—When $f(u)$ is 1, e^{b^2u}, $b^2u.e^{b^2u}$, $b/\sqrt{b^2-u}$ or $b.e^{b^2u^2}$, the absolute value of any term of the Evanescent Series $V:\Phi c$ is less[3] than that of

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[1] This Table also holds for [*even or odd*] Ψc (see p. 2856) when $f(u) = 1$. For $\Phi'c$ see Table XVII.

[2] Scales which give an upper limit to the number of terms needed.

[3] The general term of any Evanescent Series $V:\Phi c$ can be expressed in the form (e^{-N^2at}/a). $\cos Ngx \,.\, func(N)$, see Eq. 19; the forms of $func(N)$ corresponding to the forms of $f(u)$ given above can be found from Tables XII and XIII. If $|func(N)| < 1$ for any particular value of N, it is obvious that the absolute value of the term of $V:\Phi c$ which involves this N must be less than the corresponding term of $(\Sigma e^{-N^2at})/a$. For the first five forms of $f(u)$ given above $|func(N)| < 1$ for all values of N; for the next two, $|func(N)| < 1$ except possibly when $n = 1$.

TABLE XV[1]: Number of terms of V

Type	Accuracy	No. of terms =	1	2	3	4	5	6
[*odd*]	$10^{-6}.t$	$\sqrt{at}$ =	1.250	0.775	0.565	0.446	0.369	0.315
[*even*]	"	$\sqrt{at}$ =	0.955	.653	.498	.404	.340	.294
[*odd*]	$10^{-3}.t$	$\sqrt{at}$ =	0.928	.589	.435	.346	.289	.248
[*even*]	"	$\sqrt{at}$ =	0.719	.500	.385	.315	.267	.232
		No. of terms =	8	12	16	32		
[*odd*]	$10^{-6}.t$	$\sqrt{at}$ =	0.245	0.170	0.131	0.069		
[*even*]	"	$\sqrt{at}$ =	0.232	.164	.127	.068		

the corresponding term of the series $(\Sigma e^{-N^2at})/a$; and when $f(u)$ is either $b^2/(b^2+u)$ or $b/\sqrt{b^2+u}$ the same is true of all terms except the first. Fig. 2 shews the lowest value of $\sqrt{at}$ for which 1, 2, 3 etc. terms of $(\Sigma e^{-N^2at})/a$ give the sum of that series with an error not exceeding $10^{-6}.t$, and thus provides "safe" Scales for predicting in advance the number of terms of $V:\Phi c$ that must be computed in order to evaluate these Evanescent Series with an error not greater than $10^{-6}.t$ when $f(u)$ has one of the first five forms listed above; when $f(u)$ has either of the other two forms, the value of $\sqrt{at}$ for which a single term is said to be sufficient may be too low, the others are safe.

These same Scales are safe for use with either member of the pair of series into which $V:\Phi c$ is divided (see Table XII Nos. 8-11) when $f(u)$ is either (*sin* or *cos*) $\overline{b^2u+\alpha}$ or c^{Ku}. (*sin* or *cos*) $\overline{b^2u+\alpha}$.

If used when $f(u)$ is e^{-b^2u}, $b^2u.e^{-b^2u}$ or $F(\sqrt{b^2u})$, there are values of b^2/a for which one more term may be needed than the number given in the Scale; for with these forms of $f(u)$ the terms of the Evanescent Series consist of fractions with the denominator $N^2-(b^2/a)$, and if $b/\sqrt{a}$ is almost an integer, there will be one term (but only one) whose absolute value may exceed that of the corresponding term in the series on which these Scales are based.

The forms enumerated above include all those of Tables XII and XIII except $f(u)=u$ and $f(u)=u^2$. With these two, the Scales are safe only if the value of t is not too great; if $t \leqq 140$, they are safe when the number of terms predicted is not less than four.

It is obvious that if $f(u)$ be given as the product of one of the forms enumerated above into a constant C, the quantity neglected (when the number of terms computed is that called for by the Scales) will be less than $10^{-6}.Ct$. As the approximations of Sec. 9 obviate the necessity of computing $V:\Phi c$ when the series Φc is represented by a point below BE, it is never necessary to compute more than 9 terms of any Evanescent Series to arrive at the value of Φc with an absolute error not exceeding $10^{-6}.Mt$ or $10^{-6}.Ct$ as the case may be; always provided that $f(u)$ is one of the forms listed above

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[1] For practical purposes it is sufficient to compute n for a number of values of at from $e^{-n^2at}/at = 10^{-6}/2$, and obtain the values of at corresponding to integral values of n by graphical interpolation of these results. If for any reason more accurate values should be needed, the correction (C) to this approximate value (A) of at may be secured from $e^{-n^2(A+C)} = 10^{-6}(A+C)/2$ by taking logarithms and writing $\log(1+C/A) = C/A$. The n of these equations is the value of n in the first negligible term of $\Sigma e^{-n^2at}/at$; the next lower integer gives the number of terms of that series that must be retained.

(or C times it), and subject to the restrictions imposed above in certain cases on the values of $b/\sqrt{a}$ and of t.

[*Series of the* Φ_F *Group:*—As the Scales of "Number of terms of V" are based on the series $(\Sigma e^{-N^2at})/a$ (see p. 2823) they are as valid for Φ_F as for Φ_E; and as the theorem established for Φ_E in (b), p. 2820, holds equally for Φ_F (see Eq. 35), the Boundaries of Fig. 2 may be used unaltered. To bring the value of R_{1a}:[*even*]Φs below that entered in the first line of Table XIV, however, the ordinate of E must be very much less than that given in the second line of that Table (a formula for computing the proper value is given by Eq. 133, p. 2874); but as the other terms of *Rem*:Φs are not negligible in comparison with the first, E must be put still lower to ensure the accuracy desired. In Fig. 2 the ordinate of E, viz. $\sqrt{at} = 0.227$ for [*even*]Φc, ensures an accuracy of $10^{-6}.Mt$; if this same ordinate be used for [*even*]Φs, the error may reach $0.07Mt$, while to ensure an accuracy of $10^{-6}.Mt$, E must lie below $\sqrt{at} = 0.9\times10^{-3}$, i.e. a couple of thousand terms of V:[*even*]Φs might have to be computed. This slow convergence makes the Poisson Form of Φ_F almost useless for purposes of computation.]

Sec. 9: Approximations to Series of the Φ_E Group[1] and to their derivatives with respect to gx.

If the expression for the series to be summed is neither [*even*] nor [*odd*], it must be rewritten as shewn in the "Summary" of p. 2801; in all that follows it will be assumed that this replacement has been effected. The "Classes" are defined in Table X, p. 2814. Recommendations as to the choice of an approximation are made in that table. The Rules for estimating errors are those of Sec. 11, p. 2840. The sign→ means "is approximately equal to."

TABLE XVI

Synopsis of the Approximations of Sec. 9.

Approximation	Requisites A	A_0	V	S	Values of $\sqrt{at}$ and gx	Auxiliary Series
i	.	.	+	+	below BE	—
ii	.	.	+	+	below BE	on BE
iii	.	.	+	+	in OJE	on EG
iv	.	+	+	+	in OHE	on BC
v	.	.	+	+	above BE	—
vi	.	+	+	.	above B	at B
vii	.	.	+	.	above BE	on BE
viii	.	+	.	.	above B	at B
ix	.	.	.	.	all values	—

Requisites—If numerical values of the Approximation Integral, of the Approximation Integral when $gx = 0$, or of the terms of the Evanescent Series are made use of in the approximation, a plus sign is entered in the column headed A A_0 or V respectively; if the existence of a finite expression for the Stationary Series is presumed, a plus sign is entered under S. *In each case a dot signifies that the quantity or expression in question is not* needed.

The range of $\sqrt{at}$ and gx for which each approximation is designed is indicated by reference to the points lines and triangles of Fig. 2 (or of a similar figure in which the ordinate of E corresponds to the accuracy desired, see Table XIV).

The Auxiliary Series are defined under each approximation.

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[1] This Group is defined on p. 2800; a typical member viz. [*all*]Φc is written out in Table III No. 8; if in this expression n is replaced by $2n$ the prefix [*even*] is used, if by $m = 2n-1$, the prefix [*odd*], etc., as with series of the Θ-Family (see Table III). Where no uncertainty can result, S:Φc and V:Φc are abbreviated to S and V respectively.

Approx. i, viz. the P-approximation; and the Poisson Form.

This approximation, viz. $\Phi c \rightarrow P{:}\Phi c$, consists in neglecting $Rem{:}\Phi c$; it should be used wherever possible[1] if the position of the point representing the series in Fig. 2,[2] or the rules of Sec. 11, shew that its accuracy is sufficient (Ex. 1 and 2). If its accuracy is insufficient, and if the integrals involved in $Rem{:}\Phi c$ have been tabulated (Class A, see Table X) the Poisson Form may be used whenever the labour involved is less than that of computation by the Original Form (Ex. 3)

Example 1:—To evaluate $[even]\Phi c$ when $f(u) = 1$, $t = 0.1$, $a = 0.25$, $gx = \pi/5$. By Rule IV, p. 2843, the difference between the *P-approx.* and the true value is less than 4×10^{-15}, so that the question of accuracy does not arise. From Table XI No. 1, the *P-approx.* is $(gx/8a\sqrt{\pi}) \,.\, G(4\pi^2at/g^2x^2) - t/2$; Table XXVII gives G to eleven decimal places; hence the value of the series is $-0.04896\ 57913$ exact to the last figure. To attain the same accuracy by means of the Original Form (*Approx. v*), the finite expression for the Stationary Series must be looked up (Table XII, No. 1) and its value computed, besides which 13 terms of the Evanescent Series must be computed and summed; the result is $S - V = 0.06579\ 73627 - 0.11476\ 21540 = -0.04896\ 57913$. The saving of labour by the use of *approx. i* is obvious.

Example 2:—To evaluate $[odd]\Phi c$ when $f(u) = \sin \overline{b^2u + \alpha}$, $t = 0.09$, $a = 4$, $gx = 0$, $b^2 = 50\pi$, $\alpha = \pi/6$. By Rule I (see Eq. 72), the error of *approx. i* will in this case be less than 0.000024, which is sufficiently small for many purposes. The expression for $P{:}[odd]\Phi c$ is found in Table XI No. 8; after inserting the values of the constants, this gives 0.034239 as the value of the series with an error of at most 24 units in the sixth decimal place. Computation by means of the Original Form gives 0.034231, exact to the last place; but to attain this result, the complicated expression for S given in Table XIII No. 8 and three terms of the none too simple Evanescent Series had to be evaluated, in order to attain (as the result shews) an improvement in accuracy of 8 units in the sixth decimal place.

Example 3:—To evaluate $[odd]\Phi c$ when $f(u) = 1$, $t = 0.108$, $a = 1$, $gx = 2\pi/5$, Table XXVII shews that an error of 0.000004 will be introduced if the Remainder is neglected, while Table XI No. 1 (substituting the numerical value of the integral) gives $P{:}[odd]\Phi c = 0.00076\ 42252$; so that the result obtained by *approx. i* is more than one half percent in error. Since the series belongs to Class A, *approx. i* may be corrected by computing as many terms of the Remainder as may prove necessary; thus $R_{1a}{:}[odd]\Phi c = (0.075\sqrt{\pi}).G(1.2) = 0.00000\ 40679$, while $R_{1b}{:}[odd]\Phi c > 10^{-12}$, and all the other terms of the Remainder are smaller still. Hence $P{:}[odd]\Phi c - Rem{:}[odd]\Phi c = 0.00076\ 01573$, accurate to the tenth decimal. To attain this accuracy by the use of *approx. v*, the Stationary Series and eight terms of the Evanescent Series must be computed and added.

Approx. ii, iii and iv.

When the point p representing the series to be summed lies below BE of Fig. 2, $Rem{:}\Phi c$ may be neglected; so that $[even]\Phi c$ may be replaced by $A{:}[even]\Phi c - \frac{1}{2}\int_0^t f(u).du$, and $[odd]\Phi c$ may be replaced by $A{:}[odd]\Phi c$, see Eqs. 41 and 46. In *approx. i* it is assumed that the value of $A{:}\Phi c$ for the series represented by the point p can be found from tables; in *approx. ii, iii*

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[1] That is, whenever the integrals have been tabulated.

[2] The ordinate of E in the figure as printed is fixed by the assumption that $10^{-6}.Mt$ is the largest quantity that may be neglected; other assumptions lead to other ordinates for E, see Table XIV. If the point representing the series to be summed lies on or below BE, the error of *approx. i* cannot exceed the quantity assumed negligible in fixing the ordinate of E.

and *iv* it is shewn how its value may be computed from the sums of certain "auxiliary series," such as those represented by the points s, v and w respectively in Fig. 2. All these approximations are based on the relations established in (*a*) and (*d*) of p. 2820, viz.[1]

$$[\sqrt{a}.A:\Phi c]_p = [\sqrt{a}.A:\Phi c]_s = [\sqrt{a}.A:\Phi c]_v = [\sqrt{a}.R_{1a}:\Phi c]_w,$$

since p s and v lie on a straight line passing through the origin, and w lies on Qv.

An expression is given for the error[2] of each approximation, in this case the algebraic quantity that must be added to the value given by the approximation in order to secure the true value of the series. For lack of tables it is in general impracticable to compute the numerical values of these expressions, but approximations to their absolute values are given in terms of the quantity assumed negligible in fixing the ordinate of E; as shewn in the Examples, closer estimates may be arrived at by means of Rule I, p. 2840. In the case of *approx. iii* and *iv*, the constants of the auxiliary series depend only on those of the given series; and if the upper limit found for the error is too high, these approximations must be replaced by others. In the case of *approx. ii*, the constants of the auxiliary series depend also on the position of E, and although a slight lowering of E may have but little effect on the value of h (see Eqs. 49 and 50), Table XIV shews that it will greatly decrease the absolute value of the other factor of the error, viz. $[Rem:\Phi c]_s$.

Approx. ii:—At the point s where any line Op from the origin cuts BE, $Rem:\Phi c$ may be neglected (see Boundaries, p. 2821); so that at this point $\Phi c \rightarrow P:\Phi c$. Hence by means of (*a*), p. 2820, and Eqs. 41 and 46,

$$[even] \quad [\sqrt{a}.\{\Phi c + \tfrac{1}{2}\int_0^t f(u).du\}]_p \rightarrow [\sqrt{a}.\{\Phi c + \tfrac{1}{2}\int_0^t f(u).du\}]_s \tag{49a}$$

$$[even] \quad [\Phi c]_p \rightarrow h.[\Phi c]_s + \frac{h-1}{2}.\int_0^t f(u).du \tag{49b}$$

$$[odd] \quad [\Phi c)_p \rightarrow h.[\Phi c]_s \tag{50}$$

The quantity h, viz. the ratio $[\sqrt{a}]_s/[\sqrt{a}]_p$, is given by $h = 2E\pi/(\pi\sqrt{at} + 2Egx)$ in which E is the ordinate[3] of the point E in Fig. 2, and $\sqrt{at}$ and gx are to be given the values they have in the series represented by the point p.

To make (49*b*) and (50) exact, the quantity $h.[Rem:\Phi c]_s - [Rem:\Phi c]_p$ must be subtracted from the right of (49*b*) and added to the right of (50). In estimating the error introduced by neglecting this correction, $[Rem:\Phi c]_s$ may be replaced by $[R_{1a}:\Phi c]_E$, and (unless p is very close to BE) $[Rem:\Phi c]_p$ may be neglected; that is, the error of *approx. ii* is about h times the quantity assumed to be negligible in fixing the ordinate of E.

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[1] In this notation the values of $\sqrt{a}$ and gx are indicated by the subscript, all other constants are the same in the four series.

[2] *If p lies near the origin,* $[Rem:\Phi c]_s$ *will as usual be negligible; but* h *will be large* and so may be the errors of all three approximations. For such cases however the percentage error in $[A:\Phi c]_p$ will be the same as the percentage error in $[A:\Phi c]_{s \text{ or } v}$, or in $[R_{1a}:\Phi c]_w$ as the case may be.

[3] In Fig. 2, as printed, $E = 0.227$; but any other value might be chosen, see Table XIV.

The relations of Eqs. 49 and 50 hold for any point below s on Op, i.e. for values of h smaller than those given above; but the number of terms of V needed in evaluating the auxiliary series is least at s.

Approx. iii:—At the point v where Op cuts PH, $A{:}\Phi c = R_{1a}{:}\Phi c$, see ($d$) p. 2820; and if v lies below G, $R_{1a}{:}\Phi c \rightarrow Rem{:}\Phi c$, see Boundaries, p. 2821. If the series be of the [*even*] type, $Rem{:}\Phi c = \Phi c - A{:}\Phi c + \frac{1}{2}\int_0^t f(u).du$, see Eq. 41; hence if p lies below OG, $[A{:}\Phi c]_v \rightarrow [\Phi c - A{:}\Phi c]_v + \frac{1}{2}\int_0^t f(u).du$, i.e. $2[A{:}\Phi c]_v \rightarrow [\Phi c]_v + \frac{1}{2}\int_0^t f(u).du$; and by ($a$) of p. 2820

$$[even] \qquad [\Phi c]_p \rightarrow \frac{h}{2}.[\Phi c]_v + \frac{h-2}{4}.\int_0^t f(u).du \tag{51}$$

where $h = \pi/2gx$ in which gx is to be given the value it has in the series represented by the point p.

To make (51) exact, $[Rem{:}\Phi c]_p - (h/2).[Rem{:}\Phi c - R_{1a}{:}\Phi c]_v$, or in practice $[R_{1a}{:}\Phi c]_p - (h/2).[R_{1b}{:}\Phi c]_v$, must be added to the right. The absolute value of this correction cannot reach $(1 + h/3)$ times the quantity assumed to be negligible in fixing the ordinate of E. Similarly,

$$[[odd]\Phi c]_p \rightarrow (h/2.[[even]\Phi c]_v + (h/4).\int_0^t f(u).du \tag{52}$$

To make (52) exact, $[Rem{:}[odd]\Phi c]_p + (h/2).[Rem{:}[even]\Phi c - R_{1a}{:}[even]\Phi c]_v$ or in practice $[R_{1a}{:}[odd]\Phi c]_p + (h/2).[R_{1b}{:}[even]\Phi c]_v$ must be subtracted from the right. The absolute value of this correction cannot reach $(1 + h/3)$ times the quantity assumed to be negligible in fixing the ordinate of E.

Approx. iv:—At the point w where the line drawn from Q through v cuts OC, $[\sqrt{a}.R_{1a}{:}\Phi c]_w = [\sqrt{a}.A{:}\Phi c]_w$, by (d) p. 2820; and $[R_1{:}\Phi c]_w = 2[R_{1a}{:}\Phi c]_w$ since w is on the ordinate where $gx = 0$, see Eqs. 45 and 47. If w lies below C, $R_1{:}\Phi c \rightarrow Rem{:}\Phi c = \pm(\Phi c - P{:}\Phi c)$ all for the point w; the minus sign is to be taken when the series is of the [*odd*] type, see Eq. 46. Therefore if p lies below OF,

$$[even] \qquad [\Phi c]_p \rightarrow (h/2).[\Phi c - P{:}\Phi c]_w - \frac{1}{2}\int_0^t f(u).du \tag{53}$$

$$[odd] \qquad [\Phi c]_p \rightarrow (h/2).[P{:}\Phi c - \Phi c]_w \tag{54}$$

where $h = \pi/gx$ in which gx is to be given the value it has in the series represented by the point p.

To make (53) and (54) exact, $[Rem{:}\Phi c]_p \mp (h/2).[Rem{:}\Phi c - R_1{:}\Phi c]_w$, or in practice $[R_{1a}{:}\Phi c]_p - (h/2).[R_2{:}\Phi c]_w$, must be added to the right of (53) and subtracted from the right of (54). In the worst case the absolute value of this error cannot reach $(1 + h/4)$ times the quantity assumed to be negligible in fixing the ordinate of E.

If p lies below OE, w will lie below B, $[\Phi c - P{:}\Phi c]_w$ will be negligible, and Eqs. 53 and 54 become

$$[even] \qquad [\Phi c]_p \rightarrow -\frac{1}{2}\int_0^t f(u).du \tag{55}$$

$$[odd] \qquad [\Phi c]_p \rightarrow 0 \qquad (56)$$

The correction to be added to the right of (55) is practically $[R_{1a}:\Phi c]_p + (h/2).[R_1:\Phi c]_w$; the correction to be added to the right of (56) is practically $-[R_{1a}:\Phi c]_p + (h/2).[R_1:\Phi c]_w$; in neither case can its absolute value reach $(1 + h/2)$ times the quantity assumed to be negligible in fixing the ordinate of E.

Approx. ii.

Example 4:—To evaluate $[odd]\Phi c$ when $f(u) = \sin \overline{b^2u+\alpha}$, $t=0.05$, $a=0.0625$, $gx=\pi/160$, $b^2=50\pi$, $\alpha=\pi/6$. The given series is represented on Fig. 2 by the point $[\sqrt{at}=0.056, gx=\pi/160]$, which lies well below BE. The line drawn from the origin through this point cuts BE at $\sqrt{at}=0.43$, so that a safe value[1] for h is $0.43/0.056=7.6$, i.e. if h be given the value 7.6, the quantity neglected in (50) will be less than $10^{-6}.hMt=10^{-6}\times 7.6\times 1.0\times 0.05=3.8\times 10^{-7}$. The actual computation was made with $h=8$, i.e. the constants for the auxiliary series were $t=0.05$, $a=4$, $gx=\pi/20$, $b^2=50\pi$, $\alpha=\pi/6$; Rule I shews that the quantity neglected, viz. 8 times the Remainder of the auxiliary series, cannot exceed 6×10^{-7}. Setting $h=8$ in (50) gives 0.112463 as the sum of the given series; its true value, obtained by evaluating the expression for S given in Table XIII No. 8 and computing and adding 33 terms of V, is 0.112463.

In evaluating the right hand member of (50), Φc was replaced by $S-V$, see Eq. 16; four terms of the auxiliary Evanescent Series were needed instead of 33 of the Original Form. A further considerable saving of labour might be effected by computing the P-approximation to the auxiliary Stationary Series instead of the auxiliary Stationary Series itself; this substitution[2] is advantageous because of the relatively simple form of $P:S$; it is allowable in the present case because with the given values of the constants a, gx and b^2 and the value taken for h, the *sinh y* and *cosh y* of Sec. 10*b* p. 2837 are each equal to, $e^y/2$ within two parts per million. With this substitution the result is 0.112463.

Example 5: To evaluate $[odd]\Phi c$ when $f(u)=e^{Ku}.\sin \overline{b^2u+\alpha}$, $t=0.1$, $a=0.09$, $gx=0$ $K=0.05$, $b^2=0.12$, $\alpha=\pi/4$. This series is represented by the point $[\sqrt{at}=0.095, gx=0]$ on Fig. 2, which is well below BE. Hence if $h=0.455/0.095=4.8$, the quantity neglected in (50) will be less than $10^{-6}\times 4.8\times(M=0.72)\times 0.1=4.5\times 10^{-7}$; the value chosen for the computation was $h=5$, so that the constants of the auxiliary series have the values: $t=0.1$, $a=2.25$, $gx=0$, $K=0.05$, $b^2=0.12$, $\alpha=\pi/4$, and by Rule I the error (viz. 5 times the value of the Remainder of the auxiliary series) cannot exceed 1.0×10^{-6}. Eq. 50 gives $5(0.3702\,776 - 0.2366\,696) = 0.668040$ as the sum of the series; to obtain this result it was necessary to evaluate the expression for S given in Table XII No. 10 using the constants of the auxiliary series, and to compute and add 4 terms of the auxiliary Evanescent. The true value of the series, obtained by computing S and 17 terms of V, is 0.668041. In this example, with the numerical values assigned to the constants, the substitution of $P:S$ for S in evaluating the auxiliary series is inadmissible, because of the errors introduced by replacing the hyperbolic sines and cosines by single exponentials (see Ex. 4).

Approx. iii.

Example 6: To evaluate $[odd]\Phi c$ when $f(u)=e^{-b^2u}$, $t=0.018$, $a=1/9$, $gx=\pi/30$, $b^2=2.0$. The point p representing this series on Fig. 2 lies within the triangle OJH well below BE. In Eq. 52, $h=\pi/2gx=15$; so that the constants of the auxiliary series are: $t=0.018$, $a=25$, $gx=\pi/2$, $b^2=2.0$; as p is well below BE, $R_{1a}:[odd]\Phi c$ is completely negligible, and (from Rule I) 15 times $R_{1b}:[even]\Phi c$ for the auxiliary series cannot exceed 6×10^{-8}, which therefore constitutes an upper limit to the error of the approximation. In evaluating the right

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[1] See the expression for h given after Eq. 50.

[2] If this substitution be made, the quantity to be subtracted from the right of (49) and added to the right of (50) will be $h.\ [Rem:\Phi c - Rem:S]_t$; so that in certain cases, the approximation may actually be improved by the substitution.

of (52), Φc was replaced by $S-V=-0.0081205+0.0016848=-0.0064357$, see Table XII No. 6; whence $7.5(-0.0064357+0.0088399)=0.018032$ for the sum of the series; two terms of the auxiliary Evanescent were required.

This series was also summed by the use of *approx. ii*, using $h=7.5$ which is very close to the best value; five terms of this auxiliary Evanescent were required; when the Original Form (*approx. v*) was used, 34 terms of the Evanescent were needed; in both cases the result was the same as that obtained by *approx. iii*.

Approx. iv.

Example 7: To evaluate $[odd]\Phi c$ when $f(u)=e^{-b^2u}$, $t=0.02$, $a=1$, $gx=\pi/5$, $b^2=2$; this series is represented on Fig. 2 by the point $[\sqrt{at}=0.14, gx=\pi/5]$, which lies within OEH well below BE. In Eq. 54, $h=5$; so that the constants of the auxiliary series are: $t=0.02$, $a=25$, $gx=0$, $b^2=2$; by Rule I, the error (viz. 2.5 times $R_2:\Phi c$ for the auxiliary) is less than 5×10^{-11}. Employing the expression for $P:[odd]\Phi c$ given in Table XI No. 6 and those for S and V given in Table XII No. 6, Eq. 54 gives $2.5(0.02440842-0.05080042+0.02642072)=0.0000718$ as the sum of the series. Three terms of the auxiliary Evanescent were needed.

The use of *approx. ii* would require the computation of a Stationary Series and seven terms of an Evanescent to attain an accuracy of 2×10^{-8}. The computation was also carried out by means of the Original Form (*approx. v*), the Stationary and twelve terms of the Evanescent being required to ensure accuracy in the seventh decimal place; the result was the same as that obtained by *approx. iv*.

[*Example 8*:—To evaluate $[even]\Phi c$ when $f(u)=1/\sqrt{b^2+u}$, $t=0.36$, $a=0.25$, $gx=2\pi/5$, $b^2=1.44$; the point representing the series, viz. $[\sqrt{at}=0.3, gx=2\pi/5]$, lies below OF of Fig. 2 and a little above BE. In Eq. 53, $h=2.5$; so that the constants of the auxiliary series are: $t=0.36$, $a=1.5625$, $gx=0$, $b^2=1.44$. As (by Rule I) $1.25(R_2:\Phi c)$ for the auxiliary series is less than 10^{-11}, the only quantity that need be considered in estimating the error is $R_{1a}:\Phi c$ for the given series; by Rule I this cannot exceed 2×10^{-6}; it is positive and must be added to the approximate value.

It is not possible to evaluate Φc for the auxiliary (which appears on the right of Eq. 53) by the use of the Original Form (*approx. v*), since the series belongs to Class D (see Table X) and there is no finite expression[1] for S, but in Ex. 11 the sum of this series has been found to be 0.187839 by the use of *approx. vi*; the value of $P:\Phi c$ for the auxiliary (see Table XI No. 11) is 0.187076; so that the sum sought is $1.25(0.187839-0.187076)-0.141641=-0.140687$, to which something less than $+2\times10^{-6}$ must be added.

The series of this example was also evaluated by means of *approx. ix*, which gave -0.140686 exact to the last place; this method of evaluation is preferable to that described above, as it avoids the complicated computations of Ex. 11.]

Approx. v, viz. the Original Form.

The relation is $\Phi c = S - V$, see Eq. 16, p. 2803. Ex. 9 shews how convenient this approximation may be with favourable values of the constants, Ex. 1-7 how inconvenient with others. When $f(u) = e^{b^2u}$, $\overline{\sin \text{ or } \cos}\; b^2u$, or $e^{Ku}.\overline{\sin \text{ or } \cos}\; b^2u$, $P:S$ may sometimes be substituted for S (see Sec. 10*b*, p. 2837).

If $f(u)$ have one of the forms listed under D or E in Table X, *approx. v* may be used in spite of the fact that no finite expression is known for S, because in these cases an approximate value for S may be obtained by the method of Sec. 10*c*, p. 2837 (see Ex. 10); but this procedure usually involves more labour than does the evaluation of Φc by *approx. vi* or *vii*.

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[1] S might be evaluated by the method of Sec. 10*c*, illustrated in Ex. 17, but the computation is extremely laborious.

Example 9:—To evaluate [*even*]Φc when $f(u) = e^{b^2u}$, $t = 1$, $a = 1$, $gx = \pi/8$, $b^2 = 4$. From Table XII No. 4, [*even*]Φc $= S - V = 0.620782 - 0.002159 = 0.618623$. Only one term of the Evanescent Series is required to ensure accuracy in the sixth decimal place.

[*Example 10*—To evaluate [*even*]Φc when $f(u) = 1/\sqrt{b^2+u}$, $t = 1.44$, $a = 0.25$, $gx = 2\pi/5$, $b^2 = 0.36$. The expression for V may be found from the Original Integral entered in Table XIII No. 2 by setting $N = 2n$ and $u = 0$ in the latter, multiplying the resulting expression by $\cos 2ngx$, and prefixing the Σ sign. It is $V = (1/\sqrt{a}).\Sigma\cos 2ngx.e^{-4n^2at}.F(\sqrt{4n^2ab^2})/n = -0.181510$ (three terms needed); evaluation of S by the method of Sec. 10c gives $S = -0.695060$, see Ex. 17; hence $\Phi c = -0.513550$, exact to the last place. The method of *approx. vii* (see Ex. 12) is much to be preferred, because of the labour involved in evaluating S by the method of Sec. 10c.]

Approx. vi, vii and viii.

From the definition of the Φ-Family given on p. 2795, and those of $P{:}\Theta c$ and $Rem{:}\Theta c$ given in Eq. 27-31, there follows

$$\Phi c = \int_0^t \Theta c.f(u).du = \int_0^\tau \Theta c.f(u).du + \int_\tau^t \Theta c.f(u).du \tag{57a}$$

$$= \int_0^\tau \Theta c.f(u).du + \int_\tau^t (P{:}\Theta c).f(u).du + \int_\tau^t (Rem{:}\Theta c).f(u).du \tag{57b}$$

Approx. vi, vii and *viii* are based on Eq. 57*b* in which τ is to be given the smallest value that will permit the third term on the right to be neglected.

Third term of Eq. 57*b*:—An upper limit to the absolute value of this term is obviously given by $M^*.\int_\tau^t (Rem{:}\Theta c).du$ where M^* is the maximum absolute value attained by $f(u)$ in the interval $\tau < u < t$. In this the integrand is of the form $F(t-u).du$, see Table VIII; so that by changing the variable from u to $\tau + u$, the expression for the upper limit can be put in the form $M^*.\int_0^{t-\tau} F(t-\tau-u).du = M^*.\{Rem{:}\Phi^*c(1)\}$ where $\Phi^*c(1)$ is a series identical in all respects with Φc except that in it the t and $f(u)$ of Φc are replaced by $t-\tau$ and unity respectively. Thus if τ be so chosen that $\sqrt{a(t-\tau)}$ lies on BE or below it, the error introduced by neglecting the third term of (57*b*) cannot exceed $10^{-6}.M^*.(t-\tau)$, assuming that the ordinate of E is that of Fig. 2 as printed; and therefore must be less than $10^{-6}.Mt$, or in general than the quantity assumed negligible in fixing the ordinate of E.

The best value of τ is found by equating $\sqrt{a(t-\tau)}$ to the ordinate where BE cuts the perpendicular drawn downward from the point (such as p′ of Fig. 2) which gives $\sqrt{at}$ and gx for the series to be summed; because lower ordinates give larger values of τ, and the labour of evaluating the first term of (57*b*) increases with increase in τ (see below).

Second term of Eq. 57*b*:—Once τ has been chosen, the value of the second term of (57*b*) can be found at once if tables of the Approximation Integral $A{:}\Phi c$ have been constructed (*approx. vi, viii*); if they have not, computation by tabular integration (*approx. vii*) is best, for although evaluation by means of *approx. iv* is sometimes possible (see Ex. 13) it involves more labour.

First term of Eq. 57*b*:—If the Original Integral has not been tabulated, the first term of (57*b*) must be evaluated by tabular integration (*approx.*

viii). If the Original Integral has been tabulated, the term in question may be replaced by the difference between $V:\Phi c$ and a new series which also contains a converging exponential factor (*approx. vi* and *vii*), thus:—

$$\int_{0}^{\tau}\Theta c.f(u).du = \Sigma\cos Ngx.e^{-N^2a(t-\tau)}.\varphi(N,\tau) - V:\Phi c \qquad (58)$$

which follows at one from the expression given at the head of Table XIII for the indefinite integral. Expressions for $\varphi(N,\tau)$ may be obtained from Table XIII by writing τ instead of u; this table deals only with series of Classes D and E, but these are the only Classes for which *approx. vi* and *vii* are recommended. For use in Sec. 10c, it may be noted that the first series on the right of (58) becomes $S:\Phi c$ if τ be replaced by t; the greater $t-\tau$, the more rapid the convergence.

Approx. vi.

This approximation assumes that the first term of (57*b*) can be evaluated by (58); also that $A:\Phi c$ has been tabulated, which in practice means that $gx = 0$.

Example 11:—To evaluate $[\mathit{even}]\Phi c$ when $f(u) = 1/\sqrt{b^2+u}$, $t=0.36$, $a=1.5625$, $gx=0$, $b^2=1.44$. From Eqs. 57*b* and 58, by means of Table XIII No. 2 and Table XI No. 11,

$$[\mathit{even}]\Phi c \rightarrow \Sigma\{e^{-4n^2a(t-\tau)}.F(2n\sqrt{ab^2+a\tau}) - e^{-4n^2at}.F(2n\sqrt{ab^2})\}/n\sqrt{a}$$
$$+ (\sqrt{\pi}/2\sqrt{a}).\sin^{-1}\sqrt{(t-\tau)/(b^2+t)} - \sqrt{b^2+t} + \sqrt{b^2+\tau}$$

The best value for τ (see p. 2830) is given by $0.455=\sqrt{at-a\tau}$, whence $\tau=0.227$; the larger value $\tau=0.3024$ was chosen (although this necessitates the computation of two more terms of the first series on the right of Eq. 58) in order that $\sqrt{ab^2+a\tau}$ might be a two-figure number and interpolation in Table XXVIII might be avoided. The value $\tau=0.227$ corresponds to a possible error of $10^{-6}.M(t-\tau)=10^{-7}$; with $\tau=0.3024$, Rule I fixes the error as less than 10^{-12}.

Setting $\tau=0.3024$, the preceding equation becomes $[\mathit{even}]\Phi c \rightarrow 0.097003-0.015036+0.127513-1.341641+1.320000=0.187839$. Five terms of the first F series and two of the second had to be computed and added.

Approx. vii.

This approximation is identical with *approx. vi* except that tabular integration (*approx. ix*) is employed in evaluating the second term of (57*b*). The method illustrated in Ex. 13 is, strictly speaking, an independent approximation; in it the first term of (57*b*) is evaluated by (58) and the second by the method of *approx. iv*. As this procedure involves more labour than does *approx. vii* for the only Class of series with which it might be used, no number has been assigned to it.

Example 12:—To evaluate $[\mathit{even}]\Phi c$ when $f(u)=1/\sqrt{b^2+u}$, $t=1.44$, $a=0.25$, $gx=2\pi/5$, $b^2=0.36$. From $0.27=\sqrt{at-a\tau}$, $\tau=1.148$; with this value less than 0.5×10^{-6} is neglected (see p. 2822). The convenient value $\tau=1.08$ was chosen, which makes $\sqrt{ab^2+a\tau}=0.6$. With this value the quantity neglected in (57*b*) is less than 2×10^{-6} (see Rule I); as $f(u)$ and $Rem:\Theta c$ are positive, and the series is of the [*even*] type, the quantity neglected is positive.

Eqs. 57*b* and 58, and Table XIII No. 2 give

$$[\mathit{even}]\Phi c \rightarrow 2\,\Sigma\cos 4n\pi/5.\{e^{-0.36n^2}.F(1.2n) - e^{-1.44n^2}.F(0.6n)\}/n$$
$$+\int_{1.08}^{1.44}(A:[\mathit{even}]\Theta c).du/\sqrt{0.36+u} - \tfrac{1}{2}\int_{1.08}^{1.44}du/\sqrt{0.36+u} \qquad (59)$$

Five terms of the first F series and three of the second were needed, their algebraic sum is -0.372865; the value of the last expression on the right of (59) is -0.141641. The integrands of the remaining expression on the right of (59), viz.

$$(\sqrt{\pi}/2)\,.\,e^{-0.16\pi^2.(1.44-u)}/\sqrt{(1.44-u)(0.36+u)}$$

were computed[1] for $u = 1.08$, $u = 1.10$, . . $u = 1.44$ and differenced; taking account of third differences the formula of Ex. 15 p. 2833 gives 0.000955 as the value of the integral. Hence $[even]\Phi c \rightarrow -0.372865 + 0.000955 - 0.141641 = -0.513551$, to which something less than 2×10^{-6} must be added. Evaluation of the Original Form (Ex. 10) gives -0.513550 exact to the last place, but is much more laborious.

[*Example 13:*—To evaluate $[even]\Phi c$ when $f(u)$ and the constants are those of Ex. 12. Setting $\tau = 1.08$ as before, the values of the first and last expressions on the right of (59) are found as in Ex. 12; the remaining expression is identical with the $A{:}[even]\Phi c$ of Ex. 8 and may be evaluated by the method of *approx. iv* as in that example. The result is the same as that obtained in Ex. 12, but the method is not to be recommended; for although in Ex. 12 fourteen values of the integrand had to be computed, the operations involved are far simpler than those of Ex. 8 and accidental errors are immediately apparent; the method of Ex. 12 is far preferable to those of Ex. 10 and Ex. 13.]

Approx. viii.

This approximation is identical with *approx. vi* except that the first term of (57*b*) is to be evaluated by tabular integration (*approx. ix*) instead of by the method of Eq. 58. The assumption that $A{:}\Phi c$ is tabulated restricts the use of this approximation in practice to series in which $gx = 0$.

Example 14:—To evaluate $[odd]\Phi c$ when $f(u) = 1/\sqrt{(b^2+u)(c^2+u)}$, $t = 0.7$, $a = 1$, $gx = 0$, $b^2 = 1.7$, $c^2 = 0.5$, as accurately as four-place tables of the First Elliptic Integral permit. The error cannot reach $10^{-4}.M(t-\tau)$ if 0.288 be taken as the ordinate of E (see Table XIV); assuming this ordinate, the best value of τ is given by $2E = 0.576 = \sqrt{0.7-\tau}$, i.e. $\tau = 0.368$, the error corresponding to which is less than 0.4×10^{-4}. For convenience in the use of tables, the (safer) round number $\tau = 0.4$ was chosen; with this value the error is less than 10^{-5} (see Rule I).

With $\tau = 0.4$, the second term of (57*b*) becomes $(\sqrt{\pi}/9.6).\mathbf{F}(45°, 30°) = 0.3064$, see Table XI No. 14. To evaluate the first term of (57*b*), a table of the integrand

$$[odd]\Theta c.f(u) = \{e^{-(0.7-u)} + e^{-9(0.7-u)} + e^{-25(0.7-u)} .\,.\}/\sqrt{(1.7+u)(0.5+u)}$$

was computed and differenced for the nine values $u = 0.00, 0.05, 0.10 \ldots 0.40$. Taking account of third differences, the formula of Ex. 15, p. 2833, gives 0.2178 as the value of the integral; hence $[odd]\Phi c \rightarrow 0.2178 + 0.3064 = 0.5242$ exact within one unit in the fourth decimal place.

Approx. ix.

Whether or no any of the other approximations are available, any series of the Φ_E Group can be evaluated by tabular integration; in Ex. 15, the form of $f(u)$ is such that none of the other approximations can be used. To carry out such an integration, a table of the values of the integrand $\Theta c.f(u)$ must be computed and differenced (the values of Θc being found as shewn on p. 2809); since Θc changes very rapidly in value with change in u when u approaches t, it will usually be advantageous to divide this table into two, in the first of which (values of u near zero) the interval between successive values of u is greater than it is in the second (values of u near t). When the

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[1] For $u \geqq 1.36$ their values were negligible.

table or tables have been set up and differenced, the integration is effected by means of the formula[1] given in Ex. 15.

Example 15:—To evaluate $[odd]\Phi c$ when $f(u) = 1/(b^2+u^2)$, $t=0.24$, $a=1$, $gx=\pi/4$, $b^2=0.5$. With these values of the constants, $[odd]\Theta c$ may be replaced by $A:[odd]\Theta c - R_{1a}:[odd]\Theta c$ without introducing an error greater than 10^{-7}. The following table gives the values of the integrands for $u=0.00, 0.02 \ldots 0.12$ and their differences; the factor $\sqrt{\pi}/4$ is taken out to save labour.

$$(4/\sqrt{\pi}) \,.\, [odd]\Theta c.f(u) \rightarrow \frac{e^{-\pi^2/64(0.24-u)} - e^{-9\pi^2/64(0.24-u)}}{(\sqrt{0.24-u} \,.\, (0.5+u^2)} = F(u)$$

u	$F(u)$	Δ'	Δ''	Δ'''	Δ^{iv}	Δ^{v}
0.00	2.1346	−0.0287	−0.0197	−0.0045	−0.0014	−0.0006
.02	2.1059	.0484	.0242	.0059	.0020	−0.0006
.04	2.0575	.0726	.0301	.0079	−0.0026	
.06	1.9849	.1027	.0380	−0.0105		
.08	1.8822	.1407	−0.0485			
.10	1.7415	−0.1892				
0.12	1.5523					
	13.4589					

The value of the integral is computed from the sum of the entries in the second column and from the first and last entries of the last six columns of this table, as shewn in the following equation:

$$\int_0^{0.12} F(u).du = 0.02\Big\{13.4589 - \frac{1}{2}(1.5523+2.1346) - \frac{1}{12}(-0.1892+0.0287)$$
$$-\frac{1}{24}(-0.0485-0.0197) - \frac{19}{720}(-0.0105+0.0045) - \frac{3}{160}(-0.0026-0.0014)$$
$$-\frac{863}{60480}(-0.0006+0.0006)\Big\} = 0.232638$$

Here 0.02 is the common difference of the numbers in the first column, while the coefficients 1/2, 1/12, 1/24 etc. are deduced from the theory of interpolation, and are the same for all problems of tabular integration, without regard to the tabular interval or to the form of $F(u)$.

A similar table of the integrands for $u=0.12, 0.13, \ldots 0.24$, gives $\int_{0.12}^{0.24} F(u).du = 0.076549$. Hence $[odd]\Phi c \rightarrow (\sqrt{\pi}/4) \,.\, (0.232638 + 0.076549) = 0.13701$, exact to the fifth decimal place.

A more exact computation in which $F(u)$ was computed to the fifth decimal place for $u=0.00, 0.01, \ldots 0.19$ and for $u=0.190, 0.195 \ldots 0.240$, and in which fifth differences were taken into account, gave $[odd]\Phi c \rightarrow (\sqrt{\pi}/4) \,.\, (0.3048098 + 0.0043806) = 0.137007$, exact to the sixth decimal place. A rougher computation in which $F(u)$ was computed to the third decimal place for $u=0.00, 0.03, \ldots 0.24$, taking account only of first differences, gave $[odd]\Phi c = 0.1371$, a result which would be accurate enough for many laboratory computations.

Procedure to be followed when f(u) is discontinuous

Discontinuous forms of $f(u)$ occur in computations of the concentration-changes due to electrolysis with commutated or otherwise abruptly varied current. Let $f(u)$ have the successive values[2]: $f_1(u)$ from $u = 0$ to $u = t_1$,

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[1] See Boole: "Calculus of Finite Differences," 3rd Ed., p. 55 Eq. 28, (1880); also Rice: "Theory and Practice of Interpolation," p. 136 Eq. 235, (1899).

[2] The functions $f_1(u)$, $f_2(u)$ are by definition continuous within the ranges specified.

$f_2(u)$ from $u = t_1$ to $u = t_2$, . . . $f_r(u)$ from $u = t_{r-1}$ to $u = t_r = t$. Then

$$\Phi c = \Sigma \cos Ngx.\int_0^t e^{-N^2a(t-u)}.f(u).du$$

$$= \Sigma \cos Ngx.\left[e^{-N^2at}\int_0^{t_1} e^{N^2au}.f_1(u).du + e^{-N^2at}.\int_{t_1}^{t_2} e^{N^2au}.f_2(u).du + \; . \; . \; . \; . \right.$$

$$\left. . \; . \; . + e^{-N^2at}\int_{t_{r-1}}^{t} e^{N^2au}.f_r(u).du\right] \qquad (60a)$$

$$= \Sigma \cos Ngx.\left[e^{-N^2at}\int_0^{t} e^{N^2au}.f_1(u).du - e^{-N^2a(t-t_1)}.\int_0^{t-t_1} e^{N^2au}.f_1(t_1+u).du\right.$$

$$\left. + \; . - . \; . \; . + e^{-N^2a(t-t_{r-1})}.\int_0^{t-t_{r-1}} e^{N^2au}.f_r(t_{r-1}+u).du\right] \qquad (60b)$$

When the integrations have been performed, Eq. 60*a* gives Φc as the sum of a number of Evanescent Series plus one Stationary Series (arising from the last integration); this is the most convenient form when the intervals $t-t_1$, $t-t_2$, etc. are large. Eq. 60*b* expresses Φc as the sum of a number of series of the Φ_E Group; this is the most convenient form when the intervals are small, because it enables *approx. i-iv* to be employed. A number of special cases are dealt with by Rosebrugh and Miller: *loc. cit.*, p. 834-846 and 868-875.

Approximations to the Derivaties of Φ_E with respect to gx

Such series occur in Solutions Nos. 1 and 2 of Table I; the methods developed for evaluating Φ_E are available with certain modifications for these series as well.

Symbols:—For brevity, Φ' will be written instead of $\partial\Phi/\partial(gx)$. It can easily be verified that $\partial(P:\Phi c)/\partial(gx) = \partial(A:\Phi c)/\partial(gx)$, and this will be written $A:\Phi'c$; from Eqs. 42 and 46, it follows that

$$A:[even]\Phi'c = A:[odd]\Phi'c = -\frac{gx\sqrt{\pi}}{8a^{3/2}}\int_0^t \frac{e^{-g^2x^2/4a(t-u)}}{(t-u)^{3/2}}f(u).du \qquad (61)$$

Similarly, $R_{1a}:\Phi'c$ will be written for $\partial(R_{1a}:\Phi c)/\partial(gx)$, etc.

When $gx=0$:—By differentiating the expressions for $R_{na}:\Phi c$ and $R_{nb}:\Phi c$ given in Eqs. 44, 45 and 47 and then setting $gx = 0$, it can be shewn that when $gx = 0$, $R_{na}:\Phi'c = -R_{nb}:\Phi'c$ i.e. $R_n:\Phi'c = 0$, whence $Rem:\Phi'c = 0$ and therefore $\Phi'c = A:\Phi'c$; this eliminates *approx. iva*, see p. 2836. As shewn in the foot-note to Table I, when $gx = 0$, $[even]\Phi'c = [odd]\Phi'c = \pi.f(t)/4a$; the same results can be obtained by replacing the variable u by $y = gx/2\sqrt{at-au}$ in the expression for $A:\Phi'c$ given in Eq. 61, and then setting $gx=0$.

When $gx=\pi/2$:—It is apparent from the Original Form that when $gx = \pi/2$, $[even]\Phi'c = 0$. By differentiation of the Poisson Form, it can be shewn that when $gx = \pi/2$, $A:[even\ or\ odd]\Phi'c = -R_{1a}:[even\ or\ odd]\Phi'c$, a relation which is used in *Approx. iiia*, see p. 2835.

Boundaries:—From the expressions for $A:\Phi'c$ given under "Symbols" above, it follows that[1] $a.(A:\Phi'c)$ has the same value for all series represented by points on any line passing through the Origin of Fig. 2; similarly[1] $a.(R_{1a}:\Phi'c)$ has a constant value along any line through Q; etc. From this and the special relations when $gx = 0$ or $\pi/2$, it follows that $a.(A:\Phi'c)$ on OE $= -a.(R_{1a}\Phi'c)$ on EB $= a.(R_{1b}:\Phi'c)$ on BG $= -a.(R_{2a}:\Phi'c)$ on GC etc.

Ordinate of E:—The values of $\sqrt{at}$ for selected values of R_{1a}:[*even or odd*] $\Phi'c$ when $f(u) = 1$ and $gx = \pi/2$ are given in Table XVI. These are the ordinates of E for $\Phi'c$ when $f(u) = 1$ and the quantities $10^{-10}.t, \ldots 10^{-3}.t$ are regarded as negligible. In Fig. 2 as printed, the ordinate of E is 0.227; this corresponds to neglecting $10^{-6}.Mt$ when the Boundaries are those for [*even or odd*]Φc, and to neglecting $8\text{x}10^{-6}.Mt$ when the Boundaries are those for [*even or odd*]$\Phi'c$.

TABLE XVII

Ordinates of E for [*even* or *odd*]$\Phi'c$ when $f(u) = 1$.

$R_{1a}:\Phi'c/t$	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}
$\sqrt{at}$	0.167	0.173	0.181	0.193	0.209	0.229	0.257	0.300

Number of terms of V:—As the differentiation introduces an N into the numerator of each term of the Evanescent Series, $V:\Phi'c$ will be less rapidly convergent than $V:\Phi c$; but it is nevertheless more rapidly convergent than the series on which the Scales of "Number of terms of V" of Table XV are based; these therefore remain unaltered.

Errors of the approximations:—The equations given below are exact, the quantities neglected in the approximations are printed within { } and will be referred to as the "error"; upper limits to their values in any given case may be found by Rule I, in which Φc is to be replaced by $\Phi'c$.

Approx. ia:— $\Phi'c = A:\Phi'c \pm \{Rem:\Phi'c\}$. When $gx = 0$, $Rem: \Phi'c = 0$.

Approx. iia:— $[\Phi'c]_p = h^2.[\Phi'c]_s \pm \{h^2.[Rem:\Phi'c]_s - [Rem:\Phi'c]_p\}$

the plus sign to be taken when the series is [*odd*]. Here as in Eqs. 49 and 50 h^2 is the quotient of the value of a at the point s divided by its value at the point p. If the point s is on or below BE, the error can never reach h^2 times the quantity assumed to be negligible in fixing the ordinate of E.

Approx. iiia:—
$$[[odd]\Phi'c]_p = (h^2/2).[[odd]\Phi'c]_v \tag{62}$$
$$+ \{(h^2/2).[Rem:[odd]\Phi'c - R_{1a}:[odd]\Phi'c]_v - [Rem:[odd]\Phi'c]_p\}$$

here $h^2 = \pi^2/4g^2x^2$ where gx is to be given the value it has in the series at p. If v lies below G and p below BE, i.e. if p lies within OJE, the error, which is practically $h^2.[R_{1b}:[odd]\Phi'c]_v - [R_{1a}:[odd]\Phi'c]_p$, can never reach $(h^2/9 + 1)$ times the quantity assumed to be negligible in fixing the ordinate of E.

$$[[even]\Phi'c]_p = (h^2/2).[[odd]\Phi'c]_v + \{\text{see below}\} \tag{63}$$

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[1] These are the quantities that arise in evaluating Solutions Nos. 1 and 2 of Table I.

here $h^2 = \pi^2/4g^2x^2$ where gx is to be given the value it has in the series at p, and the quantity within { } is the same as in (62) except that $-[Rem{:}[odd]\Phi'c]_p$ is to be replaced by $+\ [Rem{:}[even]\Phi'c]_p$; so that if p lies below OJE the error cannot exceed that given for (62).

Example 16:—To evaluate $[even]\Phi'c$ when $f(u) = e^{-b^2u}$, $t = 0.02$, $a = 0.25$, $gx = \pi/10$, $b^2 = 2$. This series is represented on Fig. 2 by the point $[\sqrt{at} = 0.071, gx = \pi/10]$, which lies within OJE well below BE. In Eq. 63, $h^2 = 25$, so that the constants of the auxiliary series are: $t = 0.02$, $a = 6.25$, $gx = \pi/2$, $b^2 = 2$; and by Rule I (p. 2840) the error cannot reach 10^{-12}. To evaluate $[[odd]\Phi'c]_v$, the expressions for S and V given in Table XII No. 6 must be differentiated with respect to gx as the only variable, and then the values of the constants introduced; the result is $[[odd]S']_v - [[odd]V']_v = -0.1914878 + 0.1910678 = -0.0004200$ which (multiplied by 12.5) gives -0.005250 as the sum required; five terms of the auxiliary Evanescent were required. The same series was evaluated by the use of the Original Form (*approx. va*); this gives $[even]S' - [even]V' = -1.256014 + 1.250764 = -0.005250$ the same as before, but 24 terms of the Evanescent had to be computed.

[*Approx. iva*]:— *Approx. iv* to Φc was based on the computation of $R_{1a}{:}\Phi c$ from the difference between Φc and $P{:}\Phi c$ when $gx = 0$; since $\Phi'c = P{:}\Phi'c$ when $gx = 0$, it is not possible to make use of an auxiliary series at w in computing $\Phi'c$ for the point p. Thus if Table X is used in choosing an approximation to $\Phi'c$, *approx. iiia* should be used where the table says *approx. iv*.

Approx. va, the Original Form:— $\Phi'c = S' - V'$; these are found by differentiating with respect to gx the expressions for S and V given in Table XII.

Approx. via, viia, viiia:—The procedure is the same as in *approx. vi*, *vii* and *viii*, but in Eqs. 57 and 58, Φc, Θc, $P{:}\Theta c$ and $Rem{:}\Theta c$ must be replaced by $\Phi'c$, $\Theta'c$, $A{:}\Theta'c$ and $Rem{:}\Theta'c$ respectively, and $\cos Ngx$ on the right of (58) must be replaced by $-N.\sin Ngx$.

Approx. ixa:—The procedure is the same as in *approx. ix*, except that values of $\Theta'c$ are to be used instead of values of Θc.

Sec. 10: Evaluation of the Stationary Series[1] of the Φ-Family[2]

(a) Exact finite expressions for the sum of $S{:}\Phi_E$ when f(u) is of Class A, B or C

In these three Classes, $f(u) = u^p.e^{Bu}$ where B may be real, imaginary, complex or zero, and p is a positive integer or zero; with this $f(u)$, Poisson's Formula gives the exact value of $S{:}\Phi_E$ in finite form. A number of these exact expressions and their P-approximations are given in Table XII; all can be deduced from the expression for $S{:}[even]\Phi c$ where $f(u) = e^{b^2u}$ and b is real, by differentiation integration or appropriate substitutions.

(1) From Eq. 16, setting $f(u) = e^{b^2u}$, there follows

$$S{:}[even]\Phi c = e^{b^2t}\,.\,\Sigma(\cos 2ngx)/(4n^2a + b^2) \qquad (65)$$

The Poisson Form[3] can be found by setting $f(n\omega) = (\cos 2ngx)/(4n^2a + b^2)$ and $\omega = 1$, in Eq. 25*e* of Table VII. Thus

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[1] For definitions and symbols, see Eq. 16 and 18, p. 2803.
[2] For Stationary Series of the Ψ-Family, see p. 2804 and p. 2856.
[3] The definite integrals involved are given by de Haan, *loc. cit.*, Table 160 No. 5 and Table 163 No. 1.

$$S{:}[even]\Phi c = (\pi/4b\sqrt{a})\,.\,e^{b^2t}\,.\,e^{-bgx/\sqrt{a}} - e^{b^2t}/2b^2$$
$$+(\pi/4b\sqrt{a})\,.\,e^{b^2t}\,.\,\Sigma\{e^{-b(n\pi-gx)/\sqrt{a}} + e^{-b(n\pi+gx)/\sqrt{a}}\} \qquad (66)$$

Summing the geometrical series and rearranging gives (see Table XII, No. 4)

$$S{:}[even]\Phi c = \frac{\pi\,.\,e^{b^2t}}{4b\sqrt{a}}\,.\,\frac{\cosh b(\pi-2gx)/\sqrt{4a}}{\sinh b\pi/\sqrt{4a}} - \frac{e^{b^2t}}{2b^2} \qquad (67)$$

The two items on the right of the first line of (66) constitute the P-approximation ($P{:}S$) and the second line gives the Remainder ($Rem{:}S$) when $f(u) = e^{b^2u}$ and $\Phi_E = [even]\Phi c$. Expressions corresponding to Eqs. 66 and 67 when the type of summation is $[all]$, $[odd]$, etc., may be obtained as shewn in the "Summary" p. 2801, and in the note to Table XII.

(2) If b in Eq. 67 be replaced by ib where $i = \sqrt{-1}$, there results

$$[f(u) = e^{-b^2u}] \qquad S{:}[even]\Phi c = -\frac{\pi . e^{-b^2t}}{4b\sqrt{a}}\,.\,\frac{\cos b(\pi-2ngx)/\sqrt{4a}}{\sin b\pi/\sqrt{4a}} + \frac{e^{-b^2t}}{2b^2} \qquad \text{(Table XII No. 6)}$$

The expressions for $P{:}S$ and $Rem{:}S$ when $f(u) = e^{-b^2u}$ contain imaginary terms which cancel in the expression for S itself, and the real part of $P{:}S$ is not an approximation to the value of S when $g \to 0$.

(3) The expressions given in Table XII No. 5 for S and $P{:}S$ when $f(u) = u.e^{b^2u}$ can be obtained from Eqs. 66 and 67 by differentiating with respect to b^2; those when $f(u) = u^2.e^{b^2u}$, by differentiating twice, etc. When $f(u) = u^p$, $P{:}S$ and $Rem{:}S$ are infinite, but expressions for S may be obtained by taking the limits as $b \to 0$ of the expressions found for S when $f(u) = u^p.e^{b^2u}$; see Table XII Nos. 1-3.

(4) If b^2 in Eq. 67 be replaced by ib^2 and $-ib^2$ successively, half the sum of the resulting expressions gives S when $f(u) = \cos b^2u$ (Table XII No. 9) while their difference divided by $2i$ gives S when $f(u) = \sin b^2u$ (Table XII No. 8). The expressions given in Table XII Nos. 10 and 11 when $f(u) = e^{Ku}.\overline{\sin \text{ or } \cos}\, b^2u$, may be obtained in a similar manner by substituting $K+ib^2$ and $K-ib^2$ for b^2 in Eq. 67. Expressions for $P{:}S$ and $Rem{:}S$ may be obtained in like manner from Eq. 66; with all four forms of $f(u)$ the expressions for $P{:}S$ are real, and when $g \to 0$ approach those for S.

(10b) The P-approximation to $S{:}\Phi_E$ when f(u) is of Class B or C

The use of $P{:}S$ as an approximation to S, when permissible, is advantageous because of the relatively simple form of $P{:}S$; but as has been shewn in the preceding paragraphs, real and finite expressions for $P{:}S$ are known only for certain forms of $f(u)$, viz. Nos. 4, 5 and 8-11 of Table XII. Since this approximation consists in effect in replacing $\sinh y$ or $\cosh y$ by $e^y/2$, where y stands for the quantities bracketed in the definitions of f_1, f_2, etc. given at foot of Table XII*a*, it follows that the larger these quantities are, the less will be the error of the approximation. Comparison of the numerical value of the *sinh* or *cosh* with that of the exponential, usually gives a close enough estimate of the error introduced by the approximation (see Ex. 4, p. 2828); but since $Rem{:}S$ can be evaluated whenever $P{:}S$ can be evaluated, it is always possible to compute this error in any doubtful case.

(10c) Evaluation of $S{:}\Phi_E$ by means of semi-convergent series[1] when f(u) is of Class D or E.

When $f(u)$ has any of the forms listed in Table XIII or under Class D or E in Table X, each term of the series $S{:}\Phi c$ may be replaced by a semi-

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[1] There are cases in which it is easier to compute the value of S from $S = V + \Phi c$; but this procedure is obviously excluded when S is wanted only in order to find Φc.

convergent power-series which for large values of N may be used to compute the value of that term. To compute $S:\Phi c$, the terms with small values of N are evaluated individually, and by means of the power series an expression is found for the sum of all the others (Ex. 17). The values of $S:\Phi c$ so found may be used in computing the value of Φc itself, but this is not recommended, see Ex. 10, 12 and 13.

Example 17:—To evaluate $S:[even]\Phi c$ when $f(u) = 1/\sqrt{b^2+u}$, $t = 1.44$, $a = 0.25$, $gx = 2\pi/5$, $b^2 = 0.36$. The expression for S may be found from that for the Original Integral entered in Table XIII No. 2, by setting $u = t$ and $N = 2n$, multiplying by $\cos 2ngx$, and prefixing the sign of summation; this gives $S = \Sigma \cos 2ngx . F(2n\sqrt{ab^2+at})/n\sqrt{a}$. By Table XXV No. 3, when $y \geqq 10$, $F(y)$ may be replaced by $1/2y + 1/4y^3 + 3/8y^5$ without introducing an error greater than one unit in the seventh decimal place; hence if c^2 be written for $4ab^2+4at = 1.80$, $F(nc)$ may be replaced by the power series when $n \geqq 8$; therefore

$$S \rightarrow \sum_{n=1}^{7} \cos 2ngx . F(nc)/n\sqrt{a} + (1/2c\sqrt{a}) . \sum_{n=8}^{\infty} (\cos 2ngx)/n^2$$
$$+ (1/4c^3\sqrt{a}) . \sum_{n=8}^{\infty} \cos(2ngx)/n^4 + (3/8c^5\sqrt{a}) . \sum_{n=8}^{\infty} (\cos 2ngx)/n^6$$

The seven terms of the first series on the right were computed and added, using the values of F given in Table XXVIII. The second, third and fourth series on the right might have been evaluated by means of Eq. 25*d*, but except when $gx = 0$ or is very small, the labour of evaluation by this method is prohibitive because of the slow convergence of the successive derivatives; their values were found by means of the relation $\sum_{n=8}^{\infty} = \sum - \sum_{n=1}^{7}$ since exact expressions for the three sums from $n = 1$ to $n = \infty$ are given in Table XII*b*. The result is $S \rightarrow -0.6953506 + 0.0002880 + 0.0000029 + 0.0000001 = -0.695060$, exact to the sixth decimal place.

(10d) Evaluation of S: Φ_F and related series

[The Stationary Series arising from series of the Φ_F Group differ from those from the Φ_E Group only in the occurrence of $\sin NX$ in place of $\cos NX$ and vice versa. When $f(u)$ is of the form $u^p.e^{Bu}$ exact finite expressions can be found for the sum of $S:\Phi_F$ from those for $\Sigma(\overline{\cos \text{ or } \sin}\, nX)/(n+b)$, which in turn can be secured by expanding $\Sigma \overline{\cos \text{ or } \sin}\, (n+b)X$, introducing the values of $\Sigma \cos nX$ and $\Sigma \sin nX$ from Table VI, integrating between the limits π and X, and eliminating. But the expressions so obtained, though finite, involve the integrals of $\overline{\cos \text{ or } \sin}\, bx . \cot x/2 . dx$ which cannot be reduced to tabulated forms.[1]

The P-approximation to $\Sigma(\sin nX)/(n^2-b^2)$ can be expressed in terms of the Sine and Cosine Integrals, and an approximate expression can be found for the Remainder by using the expansion of Eq. 25*d* Table VII; but at best the result is clumsy, and if in it b be replaced by ib (to sum $\Sigma(\sin nX)/\overline{n^2+b^2}$) the resulting integrals are untabulated. The sum of $\Sigma \sin nX$ (Table XVIII No. 1) has already been found (p. 2802); by integration with respect to X between the limits π and X, that of $\Sigma(\cos nX)/n$ i.e. $S:[all]\Phi's$ when $f(u) = 1$, can be obtained (Table XVIII No. 2), but repetition of this procedure is useless because there are no tables of the requisite integrals. Finally although $\Sigma(\cos nX)/n^3$ and $\Sigma(\sin nX)/n^2$ can be evaluated as shewn in Ex. 18 and 19, the method there employed does not lend itself to generalization.

In the special case that $X = 0$, and $f(u) = 1 - u^p.e^{\pm b^2 u}$, the sums of the series $S:\Phi's$ (viz. those obtained from $S:\Phi s$ by differentiation with respect to $X = gx$) can be expressed

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[1] Legendre ["*Exercices de calcul intégral,*" Vol. 2, p. 163, (1817).] shews how one of these series viz. $\Sigma(-1)^n . (\sin nX)/(n+b)$ can be expressed in terms of the derivatives of *log* Γ; but his formulas are not convenient for purposes of computation.

in finite form by means of the logarithmic derivate of the Gamma-Function; one of these (Table XVIII No. 7) is required for use in Ex. 25, p. 2876. The relation entered as No. 3 of Table XVIII was established by Legendre, the inventor of the Gamma-Function. No. 4 can be deduced from Table VII Eq. 25*d* by setting $P=0$, $Q=\infty$, $\omega=1$, $f(n\omega)=-1/(n+b)$ and adding $\Sigma 1/n$ to the expression so obtained[1] (Legendre arrived at it through Euler's Integrals). No. 5 follows from No. 3 and the expression for $\Sigma 1/(n^2-b^2)$ given in Table XII*a* No. 2; No. 6 from Nos. 3 and 5 by addition. No. 8 may be obtained by substituting in turn ib and $-ib$ for b in No. 4, and subtracting; the expression so obtained is convenient when b is large, for small values of b it is better to sum a few terms of the series directly and use Table VII Eq. 25*d* to find an expression for the rest of them. The series of Table XVIII with the exception of No. 7 are of the [*all*] type; the sums of series of the other types can be found as explained in the "Summary," p. 2801.

TABLE XVIII*

1. $2.\Sigma \sin nX = \cot(X/2)$
2. $\Sigma \cos nX/n = -\log \sin(X/2) - \log 2.$
3. $b.\Sigma 1/n(n+b) = C + 1/b + \psi(b)$
4. $= C + \log b + 1/2b - B_1/2b^2 + B_3/4b^4 - B_5/6b^6 + \ldots$
5. $-b.\Sigma 1/n(n-b) = C + \pi.\cot b\pi + \psi(b)$
6. $-2b^2\Sigma 1/n(n^2-b^2) = 2C + 1/b + \pi.\cot b\pi + 2.\psi(b)$
7. $-2b^2\Sigma 1/m(m^2-b^2) = C - (\pi/2).\tan b\pi/2 + 2.\psi(b) - \psi(b/2)$
8. $b^2.\Sigma 1/n(n^2+b^2) = C + \log b + B_1/2b^2 + B_3/4b^4 + B_5/6b^6 + \ldots$

*Here C stands for Euler's Constant, viz. 0.5772 1566 49015, B_1 B_3 etc. for the Bernoulli coefficients (see p. 2806), and $\psi(\text{b})$ for $d.\log\Gamma(\text{b})/d\text{b}$. Tables of $\psi(\text{b})$ from b = 1 to b = 101 at intervals of 0.5 are given in the Brit. Ass. Report for 1916, p. 125-6; when b lies between 1 and 2, values of $\psi(\text{b})$ can be found by tabular differentiation of tables of log $\Gamma(\text{b})$, as in Example 25, p. 2876; when b = α + p (where α lies between 1 and 2 and p is a positive integer) the reduction formula $\psi(\alpha+\text{p}) = \psi(\alpha+\text{p}-1) + 1/(\alpha+\text{p}-1)$ must be used.

For purposes of differentiation, the 12-figure table of Legendre (*loc. cit.* Vol. 2, pg. 85-95) is best, since the tabular interval is only 0.001, and first second and third differences are printed; his logarithms however are to the base 10, in order to arrive at $\psi(\text{b})$ the result must be multiplied by 2.3025 8509 29940. Probably the most accessible table is the Brit. Ass. "Table of the logarithmic Gamma-Function" (1916 Report, pg. 123), natural logarithms, 10 figures, at intervals of 0.005.

Example 18:—To evaluate $\Sigma(\cos nB)/n^3$. If $f(u)=\sqrt{b^2-u}$,

$$[even]\Phi c = S - V \rightarrow \frac{1}{4}\sqrt{\frac{\pi}{a}}\cdot\int_0^t \sqrt{\frac{b^2-u}{t-u}}\cdot e^{-g^2x^2/4a(t-u)}.\,du - \frac{1}{2}\int_0^t \sqrt{b^2-u}\,.\,du \tag{68}$$

To obtain the S and V of (68), Σ must be prefixed to the integral of Table XIII No. 4 after writing $2n$ for N and multiplying by $\cos 2ngx$; u must then be replaced by t to give S and by zero to give V. By setting $2gx=B$ and giving b^2 the special value $b^2=t$ in the expressions[2] so obtained (and also in the two integrals on the right of Eq. 68) there results, after rearranging and multiplying through by $16a\sqrt{a/\pi}$,

$$\begin{aligned}\sum\frac{\cos nB}{n^3} = 4\sqrt{\frac{at}{\pi}}\cdot\sum\frac{\cos nB}{n^2}\cdot e^{-4n^2at} + \frac{2}{\sqrt{\pi}}\sum\frac{\cos nB}{n^3}\cdot\int_{2n\sqrt{at}}^{\infty} e^{-y^2}.\,dy \qquad (69)^3\\ + 4at\,.\,e^{-B^2/16at} + \frac{B^2}{4}\,.\,Ei(-B^2/16at) - \frac{16(at)^{3/2}}{3\sqrt{\pi}}\\ + (16a\sqrt{a/\pi})\,.\,\{Rem{:}[even]\Psi c \text{ with } f(u)=\sqrt{u} \text{ and } gx = B/2\}\end{aligned}$$

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[1] $\Sigma 1/n - \int_1^\infty dn/n = C =$ *Euler's Constant*; see Table XVIII.

[2] This substitution converts the two series into $S{:}\Psi c$ and $V{:}\Psi c$ respectively, and the expression on the right of (68) into $P{:}\Psi c$, in all of which $f(u) = \sqrt{u}$; see p. 2856.

[3] $Ei(-x) = \int_\infty^x (e^{-y}/y)\,.\,dy$, tabulated by J. W. L. Glaisher: Phil. Trans., 160, 367 (1875), and by W. Lash Miller and T. R. Rosebrugh: Trans; Roy. Soc. Can.

Since the left of (69) is independent of at, so must the right be; it is therefore allowable to select a value of at small enough to make the last line of (69) negligible, and yet large enough to permit ready evaluation of the two series. As the relations of Fig. 2 hold for Ψc as well as for Φc, the best value of at is given by the intersection of BE with the ordinate $gx = B/2$. If, for example[1], $B = \pi/4$, and the value $\sqrt{at} = 0.4$ be chosen, the quantity neglected cannot reach 0.6×10^{-6}, i.e. $(16a\sqrt{a/\pi}) \cdot 10^{-6} \cdot Mt$ where $t = 0.16/a$ and $M = 0.4/\sqrt{a}$. Eq. 69 with this value of $\sqrt{at}$, gives 0.663591 as the value of the series when $B = \pi/4$; only four terms from each of the two series on the right of (69) were required.

Example 19:—To evaluate $\Sigma(\sin nB)/n^2$. If both sides of (69) be differentiated with respect to B, the resulting equation will serve; if, for instance, $B = \pi/4$ and $at = 0.16$ as before, the result is $\Sigma(\sin nB)/n^2 = 0.98188$, exact within a unit of the fifth decimal place, since the quantity neglected is less than $(16a\sqrt{a/\pi}) \times 8 \times 10^{-6} \cdot Mt = 0.5 \times 10^{-5}$, see p. 2835.]

Sec. 11: The accuracy of approximations to Φ_E based on Poisson's Formula; the Φ_E Remainder[2]

Discussion of methods for finding an upper limit to $Rem{:}\Phi_E$ is necessary because all the approximations of Sec. 9 except *v* and *ix* involve neglecting at least one Φ_E Remainder; and as has been pointed out already, the integrals occurring in $Rem.\Phi_E$ are untabulated except for series of Class A. It is of course always possible to evaluate $Rem{:}\Phi_E$ by graphical integration or by the method of tabular integration illustrated in *approx. ix.*, and because of the rapid decrease of $Rem{:}\Theta_E$ with increase in u, this does not involve as much labour as might be expected; but in practice the use of Rules which give an upper limit to the absolute value of $Rem{:}\Phi_E$ is all that is necessary.

A very convenient Rule of this kind has been deduced in Sec. 8:—If the point representing the series in a diagram such as Fig. 2 lies below the line BE, the error introduced by neglecting $Rem{:}\Phi_E$ will be less than that specified by the diagram. If the point should lie a little above BE, Rules I, IV and V may be used to find an upper limit to its value. The remaining Rules shew for what forms of $f(u)$ and for what values of g or t, the upper limit computed for another $f(u)$ t and g may be relied on. Three of the Rules viz. I, II and III, hold for all forms of $f(u)$; the others are restricted, Rule VI most of all. Rules V and VI deal with relative errors, but in certain cases furnish upper limits to the absolute errors as well.

Rule I: The Max.f(u) Rule; valid for all forms of f(u).

If M be the greatest absolute value attained by $f(u)$ while u increases from o to t, it follows from the definitions given in Eqs. 44 45 and 47, that the absolute[3] value of $R_n{:}\Phi_E$ must be less than it would be if $f(u)$ were replaced

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[1] For $B = 0$, the series has long ago been evaluated by means of Eq. 25*d*; its value is 1.2020569.

[2] In the Rules enumerated in this Section, Ψ may be substituted for Φ (for the definition of $|all|\Psi c$, see Table III No. 9) if the following changes are made—Rules I-III*a* stand as printed, except that the restriction on the values of at in Rules III and III*a* must be deleted. In Rules IV and V, the subscript $u = 0$ in Eqs. 73 and 74 must be replaced by $u = t$. Rule VI becomes "*R_n/A for the series involving $f_1(u)$* will be *greater* than R_n/A for the series involving $f_2(u)$," so that the order in which the functions are arranged in the following paragraphs of the Rule must be reversed.

[3] The absolute value, i.e. the numerical value taken with the + sign, will be indicated in the usual manner by two perpendiculars.

by M; or in symbols $|R_n:\Phi_E| < M.\{R_n:\Phi_E(1)\}$, where $\Phi_E(1)$ stands for a series identical in every respect with the given series Φ_E except that in it the $f(u)$ of the given series is replaced by 1. As numerical values of $R_n:\Phi_E(1)$ may be found at once from Table XXVII, this Rule provides a convenient method for finding an upper limit to the absolute value of $R_n:\Phi_E$.

Since with series of the [*even*] type the terms of the Θ-Remainder are all of the same sign, it follows that

$$\left|Rem:[even]\Phi c\right| < M\{Rem:[even]\Phi c(1)\}$$

In the case of [*odd*]Φc where the terms of the Θ-Remainder alternate in sign, the Rule becomes: $\left|Rem:[odd]\Phi c\right| < M.\{Rem:[even]\Phi c(1)\}$, where [*even*]Φc(1) refers to a series identical in every respect with the given series except that $f(u)$ of the given series is replaced by 1 and the type of summation is [*even*] instead of [*odd*].

For instance, in Ex. 2, p. 2825, $M = 1$ (since the maximum absolute value of $\sin\overline{b^2u+\alpha}$ is 1); hence from Table XXVI, Nos. 2 and 3,

$$\left|Rem:[odd]\Phi c\right| < 1.\Sigma\{\overline{n\pi-gx}/8a\sqrt{\pi}).G(4\pi^2at/\overline{n\pi-gx}^2)$$
$$+ (n\pi+gx/8a\sqrt{\pi}).G(4\pi^2at/\overline{n\pi+gx}^2)\} \qquad (72)$$

Setting $t = 0.09$, $a = 4$, and $gx = 0$, the expression on the right of (72) becomes $\Sigma(n\sqrt{\pi}/16).G(1.44/n^2)$, and from Table XXVII the first term of this series is less than $(\sqrt{\pi}/16).G(1.5) = 0.000024$, the second term is less than 10^{-11}, and the other terms are smaller still. Thus by Rule I, the absolute value of the Remainder must be less than 24×10^{-6}; on p. 2825 its actual value was found to be 8×10^{-6}. Rule I is also used in Ex. 3-8, 11, 12, 14, 18, 19 and 24.

Rule II: The ∂/∂g Rule; valid for all forms of f(u).

Since in series of the Φ-Family, n always occurs in the combination ng, the quantity $g = \pi/2l$ may be identified with the ω of Eqs. 24-26; therefore, in the limit when $g \rightarrow 0$ (i.e. when $l \rightarrow \infty$), $Rem:\Theta_E$ and consequently $Rem:\Phi_E$ must vanish,[1] and the value of $P:\Phi_E$ must become identical with that of Φ_E itself. Thus the Solutions obtainable directly from the differential equations (1) and (2) by setting $l = \infty$, can also be obtained by substituting their P-approximations for the series contained in the Solutions of Table I.

Any decrease in g will decrease $Rem:\Theta_E$ and will therefore decrease $Rem:\Phi_E(1)$, provided that $a(t-u)$ lies below certain upper limits[2] which depend on the type of summation but which are sufficiently high to include all values of $a(t-u)$ for which the substitution of $P:\Theta_E$ for Θ_E is likely to prove useful. Therefore the upper limit to $|Rem:\Phi_E|$ found by Rule I for any given value of g, will be an upper limit for all smaller values of g; provided, of course, that the other constants in the series remain unaltered.

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[1] This follows at once from a consideration of the expressions for $Rem:\Theta c$ in Table VIII; all are of the form $(A/g) . e^{-B/g^2} . \cosh C/g$, and vanish in the limit when $g \rightarrow 0$.

[2] Safe limits may be found by differentiating $R_1:\Phi c$ with respect to g, and then imposing the condition that the integrand of the resulting integral must be positive for all values of u. These limits are:—for [*even or odd*]Φc, $at < \pi^2/2$ when $gx = 0$, $at < \pi^2/4$ when $gx = \pi/2$.

Rule II is useful in computing the concentrations at a rotating electrode; decreasing the rate of rotation increases l and therefore decreases g, so that if for any given rate of rotation Rule I has shewn that any one of the approximations *i-iv* is valid, that approximation must also be valid for all slower rates of rotation.

Rule IIa: The restricted ∂/∂g Rule; valid only if f(u) retains its sign in the interval $0 < u < l$.

If $f(u)$ retains its sign for $0 < u < l$, not only the upper limit to $|Rem:\Phi_E|$ but $|Rem:\Phi_E|$ itself will be lowered by decrease in g, subject of course to the restrictions as to the value of at stated in Rule II. This follows at once from the definition of $Rem:\Phi_E$ given in Eq. 40, as $Rem:\Theta_E$ is always positive.

Rule III: The ∂/∂t Rule; valid for all forms of f(u).

The value of the upper limit to $R_n:\Phi_E$ found by Rule I will be decreased by any decrease in t, provided that at lies below an assignable upper limit which depends on the type of summation.[1] In this statement, *Rem* may be substituted for R_n; in the case of *[even]*Φc, the limits of at are the same for *Rem* as for R_n, in the case of *[odd]*Φc they are lower[2] for *Rem*; but in every case they include all values of at for which *approx. i-iv* are useful.

As an example: In Ex. 2 p. 2825, Rule I shews that $|Rem:[odd]\Phi c|$ must be less than 24×10^{-6} when $t = 0.09$; hence by Rule III it must be less than 24×10^{-6} for all smaller values of t provided a, gx and $f(u)$ remain the same. This Rule like Rule II is of practical importance in electrochemical computations; for if Rule I should shew that any of the approximations *i-iv* may be used to compute the concentration at some instant during the electrolysis, Rule III shews that it may safely be used to compute the concentrations at any earlier instant.

This rule is also useful when *approx. vi, vii* and *viii* are employed; if Rule I shews that one of them is safe for a selected value of τ, then for all lower values of $t - \tau$ i.e. for all higher values of τ, it will be safer still (see Ex. 11 12 and 14).

Rule IIIa: The restricted ∂/∂t Rule; valid only if f(u) retains its sign in the interval $0 < u < t$.

If $f(u)$ retains its sign in the interval $0 < u < t$, the statements of Rule III as to the upper limits to $|R_n:\Phi_E|$ and $|Rem:\Phi_E|$ hold for $|R_n:\Phi_E|$ and $|Rem:\Phi_E|$ themselves. See foot-notes to Rule III.

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[1] If the expression for R_{1a}:*[even or odd]*$\Phi c(1)$ be differentiated with respect to t, the term arising from the differentiation with respect to the upper limit of the integration is zero, and for the other term to be positive it is sufficient that $(\pi - gx)^2 > 2a(t-u)$, i.e. if $gx = \pi/2$, $at < \pi^2/8$; if $gx = 0$, $at < \pi^2/2$. Similar differentiations shew that the limits just found for R_{1a} will also serve safely for R_{1b}, R_{2a}, etc.

[2] The derivative of Rem:*[odd]*Φc (1) with respect to t will be positive provided $at < 0.3$ if $gx = \pi/2$, and for higher values of at if $gx < \pi/2$, up to $at = 1.2$ when $gx = 0$; because for these values of at, the absolute value of the increment of each term of the Remainder for a given increment of t is less than that of the preceding term.

Thus if the current does not change its direction in the electrolytic experiments referred to under Rule III, the absolute values of $R_n:\Phi_E$ and $Rem:\Phi_E$ computed for any instant of the electrolysis will be less than those for any later instant; whereas if the current does change direction (sinusoidal current for example) all that can be said is, that the upper limits found by Rule I will be less (see Rule III). In Ex. 2 for example, 24×10^{-6} is an upper limit to the error when $t \leqq 0.09$; but the true value of that error, viz. 8×10^{-6}, is not necessarily so.

Rule IV: The Max. Exponential Rule; valid only if $f(u)$ retains its sign in the interval $0 < u < t$.

It is obvious from the equations of Tab. VIII that for given values of the constants at and gx, $\sqrt{t-u}.\mathrm{R}_n:\Theta_E$ will be greatest when $u = 0$; therefore, provided $f(u)$ retains its sign in the interval $0 < u < t$,

$$| R_n:\Phi_E | < t.(R_n:\Theta_E)_{u=0}. \left| \int_0^t \{f(u)/\sqrt{t-u}\}.du \right| \tag{73}$$

In the case of [*even*]Φc, *Rem* may be substituted for R_n in the statement of this Rule; while in the case of [*odd*]Φc, *Rem* may be substituted for R_n on the left of (73) and R_1 for R_n on the right.

This Rule is not of much practical use, since the upper limit it predicts is usually much higher than that given by Rule I; it can be useful only if $f(u)$ decreases very rapidly with increase in u; for example, if $a = 1$ $gx = 0$ $t = 0.05$ and $f(u) = e^{-50u}$, *Rem*:[*odd*]Φc is less than 0.0002 by Rule IV, and less than 0.0007 by Rule I.

Rule V: The R_n/A Rule; valid only if $f(u)$ retains its sign in the interval $0 < u < t$.

Since for given values of the constants a t and gx, the ratio $(R_n:\Theta_E)/(A:\Theta_E)$ has its greatest[1] value when $u = 0$, it follows that (provided $f(u)$ retains its sign in the interval $0 < u < t$)

$$(R_n:\Phi_E)/(A:\Phi_E) < [(R_n:\Theta_E)/(A:\Theta_E)]_{u=0} \tag{74}$$

as both sides of (74) are positive, the $||$ are omitted. In the case of [*even*]Φc, *Rem* may be substituted for R_n on both sides of (74); while in the case of [*odd*]Φc, *Rem* may be substituted on the left and R_1 on the right.

Rule V which provides an upper limit to the quotient $Rem:\Phi_E$ by $A:\Phi_E$ obviously provides an upper limit to $Rem:\Phi_E$ itself whenever the value of $A:\Phi_E$ can be found. The quantity on the right of (74) usually gives a rather high upper limit to the quantity on the left, especially when gx is small; but on the other hand, this limit is independent of the form of $f(u)$ and is easy to compute. For example, no matter what $f(u)$ may be (so long as it retains its sign), if $t = 7/90$, $a = 1$, and $gx = \pi/3$, the quotient *Rem*: [*odd*]Φc by A : [*odd*]Φc must (by Eq. 74) be less than 2.6×10^{-5}; from Tab. XXVII, when $f(u) = 1$ the true value of this quotient is 8×10^{-6}.

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[1] This is true if the series be of the [*even*] or [*odd*] type and gx lies between 0 and $\pi/2$; see Eqs. 27-32 p. 2809.

If the series be of the $[odd]$ type, the percentage error introduced by neglecting $Rem\!:[odd]\Phi c$ is almost exactly one hundred times the quotient $(Rem\!:[odd]\Phi c)/(A\!:[odd]\Phi c)$; and Eq. 74 states that this percentage error cannot exceed 200 times $e^{-\pi^2/4at}.\cosh\,(\pi gx/2at)$, no matter what $f(u)$ may be so long as it has the same sign between $u = 0$ and $u = t$. For an application of this Rule, see p. 2855, also *approx. c*, p. 2960, and "Boundaries for Eqs. 110-112," p. 2869.

Rule VI: The d.log f(u) Rule; valid only if f(u) retains its sign in the interval $0 < u < t$ and steadily increases or decreases during that interval.

If two series of the same type of summation and with the same values of the constants, $a\,t$ and gx, differ only in respect to $f(u)$ (assumed positive[1] over the whole range of integration in both cases), and if for every value of u between 0 and t, $d\log f_1(u)/du$ is greater than $d\log f_2(u)/du$, then $R_n\!:\Phi_E/A\!:\Phi_E$ for the series involving $f_1(u)$ will be less[2] than $R_n\!:\Phi_E/A\!:\Phi_E$ for the series involving $f_2(u)$.

From this Rule it is obvious that R_n/A when $f(u) = e^{b^2u}$ will decrease as b increases, while for $f(u) = e^{-b^2u}$, the opposite is true; also that R_n/A is less for $f(u) = b^2+u$ than for $f(u) = \sqrt{b^2+u}$; less for $f(u) = b^2+u$ than for $f(u) = 2b^2+u$, etc. Of course the type of summation in the series compared, and the values of $a\,t$ and gx, must be the same.

When the value of, or an upper limit to, R_n/A has been found for some particular $f(u)$, Rule VI defines a group of forms of $f(u)$ for which this is an upper limit. Thus the value of $R_1\!:[odd]\Phi c)/(A\!:[odd]\Phi c)$ when $f(u) = 1$, $a = 1$, $t = 7/90$ and $gx = \pi/3$, viz. 8×10^{-6}, (or the upper limit to it found by Rule V, viz. 2.6×10^{-5}), constitutes an upper limit for every series $[odd]\Phi c$ when $f(u)$ is such that $d\log f(u)/du$ is positive and the constants $a\,t$ and gx have the values given above; such functions are:—$f(u) = u$, u^2, b^2+u, e^{b^2u}, etc. Thus the error introduced by substituting $P\!:[odd]\Phi c$ for $[odd]\Phi c$ cannot exceed 8×10^{-4} percent of the sum of the series if $f(u) = e^{u}$, and will exceed 8×10^{-4} percent if $f(u) = e^{-u}$; but is obvious that the absolute error will be greater in the former case than in the latter.

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[1] This assumption does not involve any loss in generality; for so long as $f(u)$ retains its sign, changing this sign does not affect the absolute value of the sum of the series.

[2] This Rule may be established by the following argument:—Writing A as an abbreviation for $A\!:\Phi_E$ and A' for the quantity $(A\!:\Theta_E).f(u)$, it is obvious that the quantity $(A'/A).du$ *must always be a positive proper fraction no matter what* $f(u)$ *may be*; the sum of all these fractions is obviously unity; and the sum of the products of each one of them into the corresponding value of the ratio $R_n\!:\Theta_E/A\!:\Theta_E$ (viz. that taken for the same value of u as is the fraction) gives $(R_n\!:\Phi_E)/A$. If $d\log f_1(u)/du$ be greater than $d\log f_2(u)/du$ for every u between 0 and t, there must be some value of u in the range at which the two fractions are equal; at all higher values of u, every fraction for $f_1(u)$ will be greater than the corresponding fraction for $f_2(u)$, and vice versa. Now the values of the ratio $R_n\!:\Theta_E/A\!:\Theta_E$ into which these fractions are multiplied are independent of $f(u)$, i.e. they are the same for the two sets of fractions; moreover (see Rule V) the values of $R_n\!:\Theta_E/A\!:\Theta_E$ decrease as u increases. Therefore the series involving $f_2(u)$ which gives rise to the greater fractions at the lower values of u will have the greater R_n/A.

PART IV

EVALUATION OF SERIES OF THE Λ_E GROUP INCLUDING THOSE OF TAB. II

The general definition of the Λ-Family is given on p. 2795, see also Tab. III No. 10; the Λ_E Group is defined on p. 2800; the Poisson Form and the definition of $P{:}\Lambda$ and $Rem{:}\Lambda$ are given in Eq. 48, p. 2812. The Solutions of Table II (see Tab. IV) each consist of the sum or difference of two Λ's in one of which $X = g(x+\lambda)$, and in the other $X = g(x-\lambda)$, see Tab. III and VIII.

The Original Form (approx.vb):— As at remains constant during the λ-integration, there is nothing in this Family to correspond to the Stationary Series of Part III. Every series of the Λ-Family contains a converging exponential, and the "number of terms of V" in Tab. XV gives an upper limit[1] to the "number of terms of [*even or odd*]Λc."

The Poisson Form:— This is more generally useful for purposes of computation than is the case with series of the Φ-Family, because the integrals involved have been tabulated not only when $F(\lambda) = \lambda^p$ (p a positive integer), but also when $F(\lambda) = e^{B\lambda^2+C\lambda}$ if B and C are real. The untabulated forms which arise when B or C is imaginary or complex are dealt with in the Appendix, p. 2862 (see Table XXI p. 2865).

Boundaries:— If $F(\lambda) = 1$, a safe Boundary for $Rem{:}\Lambda c$ analogous to BE of Fig. 2 can be found from

$$R_{1a}{:}\,[\textit{even or odd}]\Lambda c = \tfrac{1}{4}\sqrt{\frac{\pi}{at}}\cdot\int_0^l e^{-(\pi-gx\mp g\lambda)^2/4at}.d\lambda = \frac{l}{2}\cdot\left\{\frac{2}{\sqrt{\pi}}\cdot\int_L^U e^{-y^2}.dy\right\} \quad (75)$$

the upper sign to be taken if $X = g(x+\lambda)$ and the lower if $X = g(x-\lambda)$. The quantity within brackets on the right of (75) is the difference between two Probability Integrals, viz. that in which the argument is U and that in which it is L, where $U = (\pi-gx)/2\sqrt{at}$ and $L = (\pi/2-gx)/2\sqrt{at}$ if $X = g(x+\lambda)$, and where $U = (3\pi/2-gx)/2\sqrt{at}$ and $L = (\pi-gx)/2\sqrt{at}$ if $X = g(x-\lambda)$. Safe upper limits to the values of $R_{1a}{:}\Lambda c$ are found by setting $U = \infty$ in Eq. 75. If $X = g(x-\lambda)$ these upper limits depend only on the values of l and of $(\pi-gx)/\sqrt{at}$, so that the upper limit of $(R_{1a})/l$ has the same value for all series represented by points on any line passing through Q of Fig. 2; the highest line for which this upper limit is negligible constitutes the Boundary for R_{1a} and also for *Rem.* Table XIX gives the values of $\sqrt{at}$ for the point at which the Boundary[2] cuts PH, when the "permissible error" (i.e. the greatest quantity assumed to be negligible) varies from $10^{-8}.l$ to $10^{-3}.l$. If $X = g(x+\lambda)$ the Boundary for R_{1a} runs upward through P; the ordinates of its intersection with OC are also given by the values of $\sqrt{at}$ in Table XIX.

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[1] If the Scales of Fig. 2 are used in estimating the number of terms of Λc, the error will not exceed $10^{-6}.Ml$ where M is the maximum absolute value attained by $F(\lambda)$ in the interval $0 < \lambda < l$.

[2] The line BE of Fig. 2 (in which $E = 0.227$) is the Boundary for $Rem{:}\Lambda c$ (with $X = gx - g\lambda$) which implies an accuracy of $6 \times 10^{-7}.Ml$, see Table XIX. The corresponding Boundary when $X = gx + g\lambda$ would be constituted by a line from P to meet OB at $\sqrt{at} = 0.227$.

TABLE XIX

Boundary for R_{1a}: [*even* or *odd*]Λc when $F(\lambda) = 1$.

Ordinates on OC for the Boundary when $X = g(x+\lambda)$; ordinates on PH for the Boundary when $X = g(x-\lambda)$.

$(R_{1a}$:[*even or odd*]$\Lambda c)/l$	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}
$\sqrt{at}$	0.197	0.212	0.232	0.260	0.299	0.359

Approx. ib, the P-approximation:— If the point representing the series lies below the Boundary, the error introduced by substituting $P{:}\Lambda c$ for Λc cannot exceed M times the quantity assumed to be negligible in fixing the ordinate(on OC or PH as the case may be) for $F(\lambda) = 1$; M being the maximum absolute value attained by $F(\lambda)$ in the interval $0 < \lambda < l$.

As the integral in $A{:}\Lambda c$ has the same form for all values of gx, the simplification introduced by setting $gx = 0$ in series of the Φ_E Group has no counterpart here.

Approx. ii, iii and *iv* of Part III cannot be adapted, because in this Family there are no relations corresponding to those developed in paragraphs (*a*) to (*d*) of Sec. 8.

Approx. vi-viii of Part III are not applicable because in this Family the integration is with respect to the angle, whereas in the Φ-Family it affects the exponential on which the convergence of the Original Form depends.

Approx. ixb:— In this Family the quantity to be tabulated is $\Theta c.F(\lambda)$; the values of Θc in such a table are all for the same value of $T = at$ and successive values of $X = g(x \pm \lambda)$.

Sec. 12: Evaluation of Multiple Series occurring in the Λ_E Group

Double Series:— It has been shewn in Tab. IV that the series printed at the head of Tab. II can always be expressed as the sum or difference of two series of the Λ_E Group, in one of which $X = g(x+\lambda)$ and in the other $X = g(x-\lambda)$. If now the $F(\lambda)$ of these series be one of the series occurring in the Solutions of Tab. I (in which ϑ must be written for t and λ for x) i.e. if $F(\lambda)$ be [*even or odd*]Φc or $\Phi' c$, the Λ-series so arising will contain a double summation; approximations to the values of these Double Series will now be considered.

Taking $F(\lambda) =$ [*even or odd*]Φc as an example,

$$\Lambda c = \left(\Sigma\int_0^t e^{-Q^2a(t-\vartheta)}.\cos Qg(x \pm\lambda)\right).\left(\Sigma\cos Ng\lambda.\int_0^\vartheta e^{-N^2a(\vartheta-u)}.f(u).du\right).d\lambda \quad (76)$$

in which Q stands for $2q$ or $2q - 1$ and N for $2n$ or $2n - 1$; since the two summations are independent it is necessary to use different symbols for the two variables of summation, but because of the brackets there is no ambiguity in writing Σ for $\sum\limits_{q=1}^{\infty}$ in the first and Σ for $\sum\limits_{n=1}^{\infty}$ in the second. The double sign is used in $\cos Qg(x \pm\lambda)$ to include both the Λc's; and where the double sign occurs in Eqs. 77-83, the upper is to be taken if + has been taken in (76).

Since in Eq. 76 Ac is presented as the product of two series, in one of which q is the only variable of summation and in the other n, its value must be independent of the order[1] in which the summations are effected. As moreover each of the quantities a ϑ gx and l is independent of all the others and of n and q, the four operations (viz. two summations and two integrations) indicated in Eq. 76, and also any differentiations with respect to a ϑ gx or l, may be performed in any order that may prove convenient; and at any stage either or both sums may be replaced by any suitable approximation.

In practice it is best to begin with the integration with respect to u, consulting Table XII and writing λ wherever x is printed in that Table. This replaces the second factor in the λ integrand of (76) by $S - V = S - \Sigma \cos N g\lambda . e^{-N^2 a\vartheta} . func\ N$ (see Eq. 16), and thus converts the right of (76) into the difference between two series; one of these, if S is known in finite form will only involve a single variable of summation viz. q, while the other is a double series. In this new double series all the factors of the integrand are free from λ (and are therefore to be treated as constants during the integration) except $\cos Qg(x \pm \lambda) . \cos Ng\lambda$ whose integral between the limits o and l is

$$[N = 2n,\ Q = 2q - 1] \quad (\pm Q . \sin Qgx + (-1)^{n+q} . Q . \cos Qgx)/g(N^2 - Q^2) \qquad (77)$$

$$[N = 2n - 1,\ Q = 2q] \quad (\pm Q . \sin Qgx - (-1)^{n+q} . N . \cos Qgx)/g(N^2 - Q^2) \qquad (78)$$

Thus whenever a finite expression is known for the sum of S, i.e. if Φ_E belongs to Class A, B or C of Tab. X, Eq. 76 can be put in the form[2]

$$\begin{aligned} \text{Ac} = \int_o^l S . \Sigma e^{-Q^2 a(t-\vartheta)} . \cos Qg(x \pm \lambda) . d\lambda \\ - \Sigma\Sigma \text{factor} . e^{-Q^2 a(t-\vartheta)} . e^{-N^2 a\vartheta}/g(N^2 - Q^2) \end{aligned} \qquad (79)$$

where the "factor" of the double sum is

$$(\pm Q . \sin Qgx - (-1)^{n+q} . N . \cos Qgx) . \text{func}\ N$$

if N is *odd* and Q is *even*, or a similar expression in the other case.

The single series in Eq. 79 will be rapidly convergent if $a(t - \vartheta)$ is large, and in such cases may be summed term by term; the integration of $S . \cos Qg(x \pm \lambda)$ presents no difficulty. If $a(t - \vartheta)$ be small, the series (which is a Θ_E) may be replaced by its P-approximation from Table VIII; the subsequent

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[1] This is important, for there are many repeated series whose values depend on the order of summation; for example $\Sigma\Sigma 1/(m^2 - 4q^2)$ in which m stands for $2n - 1$ and both n and q must be given all integral values from 1 to ∞. In such cases the order in which the summations are to be carried out is indicated by the relative position of the signs of summation, thus $\sum_q \sum_n$ indicates that the value of $\sum_n 1/(m^2 - 4q^2)$ is to be found for $q = 1, 2, \ldots$, and that the sum of all these values is to be taken as the value of the repeated series; since $\sum_n 1/(m^2 - 4q^2) = 0$ for every value of the integer q, it follows that $\sum_q \sum_n 1/(m^2 - 4q^2) = 0$, while $\sum_n \sum_q 1/(m^2 - 4q^2) = \sum_n -1/2m^2 = -\pi^2/16$. See Bromwich: "*Introduction to the Theory of Infinite Series*," p. 78-81.

[2] Since the value of Ac is independent of the order in which the summations are performed, the symbol $\Sigma\Sigma$ which leaves the order undetermined is used in Eq. 79.

integration will lead to tabulated forms only if $f(u) = constant$, u^p or $e^{\pm b^2 u}$, in other cases tabular integration (see *approx. ix*) must be employed.

The double series in Eq. 79 may be summed term by term if both $a\vartheta$ and $a(t-\vartheta)$ are large; in other cases it should be differentiated with respect to $a\vartheta$, which removes the denominator (N^2-Q^2); in the derivative viz.

$$-\Sigma\{\pm Q.sin\ Qgx.e^{-Q^2a(t-\vartheta)}\}.\Sigma\{e^{-N^2a\vartheta}.func\ N\} \qquad (80)$$
$$+\Sigma\{(-1)^q.cos\ Qgx.e^{-Q^2a(t-\vartheta)}\}.\Sigma\{(-1)^n.e^{-N^2a\vartheta}.func\ N\}$$

the variables are separated, and any or all of the single series may be replaced by suitable approximations.[1] After the replacements the derivative must be multiplied by $d(a\vartheta)$ and integrated with $a\vartheta$ as the upper limit, not forgetting the integration constant.

The foregoing is essentially the procedure followed in *Illustration I;* the double series of (85*a*) however involves two Λ's as must all that arise from the Solutions of Tab. II; for reasons of convenience it was combined with still another series to give the double series of (85*b*) before performing the differentiation and replacements. The series evaluated in this Illustration arises in problems discussed by Rosebrugh and Miller (*loc. cit.*, p. 862); to facilitate cross reference, their symbols have been retained and the [*odd-all*]Φs of the original has not been replaced by [*odd*]Φc.

The method just discussed for dealing with the sum on the right of (79) presumes the existence of a finite expression for S; it is moreover restricted by the assumption that if N is even Q will be odd and vice versa. The first limitation is unavoidable; the second is of no practical importance, for when N and Q are both odd or both even the physical problem reduces to one in which the Boundary Conditions remain unchanged except for a discontinuity in $f(t)$ at the moment $t = \vartheta$, and the Solution does not contain a double series. Examination of the integral of $cos\ Qg(x \pm \lambda).cos\ Ng\lambda$ when N and Q are both of the same type, and in particular of its form when $N = Q$ (which obviously cannot occur if one is odd and the other even), shews that in such cases the double series of Eq. 79 reduces to a single series; but for the purpose of the present paper detailed discussion of this transformation would be superfluous.

The difficulties which arise when putting this procedure in operation, are those of the integration with respect to $a\vartheta$; if the n-summation of the double series in (80) be replaced by its approximation while the q-summation is left as it stands, the integration leads to tabulated forms in all cases where a finite expression for S is known except when $f(u) = e^{Ku}.(sin\ or\ cos)\ b^2u$; but if the q-summation be replaced (whether the n-summation be replaced or not) the integrals are untabulated except for $gx = 0$. The form of the integration-constant must also be taken into consideration; the object of the replacement is to save labour of computation, and when the integration-constant is clumsy much of the advantage is lost.

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[1] The q-series are of the form Θ or Θ′, approximations to which may be found from Table VIII. The n-series are of the form $V = S - \Phi$ or $V' = S' - \Phi'$, all for $gx = 0$ and the $f(u)$ of Eq. 76; so that *approx. i*, *ii* and *ix* (or *ia*, *iia*, and *ixa*) are available.

Triple Series:—If in the Solutions of Table II, the $F(\lambda)$ be replaced by the double series of Eq. 79 (writing t_1 for t and λ for x), the A's will each contain a Triple Series. In the cases which occur in practice the type of the new summation will be odd if Q of Eq. 79 is even and vice versa, since both the sines and cosines of (77) and (78) are summed with respect to q; in all other cases the triple series will reduce to a double series and the physical problem to one whose solution does not involve a triple sum. This leads to a certain symmetry in the triple series with respect to the first and third variables of summation, which accounts for the choice of a special method for finding a "*q-approx.*" in Illustration II.

As with the double series of Eq. 76, the sum of the triple series is independent of the order in which the summations, integrations, differentiations and replacements are effected. Its form is such that, by introducing two differentiations, the method of Eq. 80 may be employed to separate the variables; this is essentially the procedure followed in Illustration II, except for the "*q-approx.*" where the integration constants[1] proved to be extremely clumsy.

There is another procedure which dispenses with the differentiations, and without separating the variables of summation at once replaces the q-summation by its approximation. This operation reduces the triple series to a double series in which each term contains functions of n and p (the third variable of summation), and in some cases may lead to a very useful approximation to the sum of the triple series. If P be written for $2p$ or $2p-1$, the triple series must have the form

$$\Sigma\Sigma\Sigma\text{factor}.e^{-N^2a\vartheta}.e^{-Q^2a(t_1-\vartheta)}.e^{-P^2a(t-t_1)}/(Q^2-N^2)(Q^2-P^2)g^2 \qquad (81)$$

where the "*factor*" depends on whether Q is even or odd. If the upper sign be taken in Eq. 76, these factors are

$$[Q\ even]\quad Q^2\{\pm(-1)^{p+q}.\sin Pgx-\cos Pgx\}+NP\{(-1)^{n+p}.\cos Pgx \pm(-1)^{n+q}.\sin Pgx\}$$

$$[Q\ odd]\quad -Q\{\pm(-1)^{p+q}.P.\sin Pgx+Q.\cos Pgx\}-Q\{(-1^{n+p}.Q.\cos Pgx \pm(-1)^{n+q}.P.\sin Pgx\}$$

If the lower sign in (76) be used, Q^2 outside the first bracket must be replaced by $-Q^2$, and $-Q$ outside the first bracket in the third line must be replaced by $+Q$. Since N and P are both even or both odd, in some terms of the summation they will be equal; for these terms, (81) becomes

$$\Sigma e^{-N^2a(\vartheta+t-t_1)}\mathit{func}\,N.\Sigma\mathit{factor}.e^{-Q^2a(t_1-\vartheta)}/(Q^2-N^2)^2g^2 \qquad (82)$$

For the terms in which N is not equal to P, (81) may be converted by the method of partial fractions into

$$\Sigma\Sigma\frac{e^{-N^2a\vartheta}\mathit{func}\,N.e^{-P^2a(t-t_1)}}{(N^2-P^2)g^2}\left\{\Sigma\frac{\mathit{factor}.e^{-Q^2a(t_1-\vartheta)}}{(Q^2-N^2)}-\Sigma\frac{\mathit{factor}.e^{-Q^2a(t_1-\vartheta)}}{(Q^2-P^2)}\right\} \qquad (83)$$

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[1] In the "*n-approx.*" and in the "*p-approx.*" only one differentiation is involved, and the integration constant is zero.

Approximations[1] to all the forms that can occur in these q summations, except such as can be found immediately from Table VIII, are given in Table XX. Some of them are complicated enough; whether in any given case direct summation of the triple series would be preferable to use of the formulas arrived at by this method, depends entirely on the values of the constants; in the comparatively simple series of *Illustration II*, this q-approximation is of real importance.

TABLE XX

Approximations for use with Eqs. 82 and 83

1.	$\Sigma Ee/De$	$\rightarrow 1/2m^2 - (\sqrt{\pi}/2m).F(\sqrt{m^2T})$
2.	$\Sigma(-1)^q.Ee/De$	$\rightarrow 1/2m^2 + (-1)^n.\pi.e^{-m^2T}/4m$
3.	$\Sigma Eo/Do$	$\rightarrow -(\sqrt{\pi}/4n).F(\sqrt{4n^2T})$
4.	$\Sigma(-1)^q.(2q-1).Eo/Do$	$\rightarrow (-1)^n.\pi.e^{-4n^2T}/4$
5.	$\Sigma Ee/(De)^2$	$\rightarrow (\sqrt{\pi}/4m^3).(2m^2T+1).F(\sqrt{m^2T})$ $- \sqrt{\pi T}/4m^2 + \pi^2.e^{-m^2T}/16m^2 - 1/2m^4$
6.	$\Sigma(-1)^q.Ee/(De)^2$	$\rightarrow -(-1)^n.\pi.(2m^2T+1).e^{-m^2T}/8m^3 - 1/2m^4$
7.	$\Sigma Eo/(Do)^2$	$\rightarrow (\sqrt{\pi}/32n^3).(8n^2T+1).F(\sqrt{4n^2T})$ $- \sqrt{\pi T}/16n^2 + \pi^2.e^{-4n^2T}/64n^2$
8.	$\Sigma(-1)^q.(2q-1).Eo/(Do)^2$	$\rightarrow (-1)^n.\pi T.e^{-4n^2T}/4$

In this table the following abbreviations are used: $\Sigma = \sum_{q=1}^{\infty}$; $Ee = e^{-4q^2T}$; $Eo = e^{-(2q-1)^2T}$; $De = 4q^2-m^2$; $Do = (2q-1)^2-4n^2$; n is a positive integer and $m = 2n-1$

Illustration I: Double Summation

(a) Origin of the Double Series

In the first problem dealt with by Rosebrugh and Miller in Part II of their paper, the Initial Condition is [at $t=0$] $z-z_0=0$; the Boundary Condition [at $x=0$] is $z-z_0=0$ for all values of t; the Boundary Condition [at $x=l$] changes at the moment $t=\vartheta$ from $\partial z/\partial x = C_1$ to $z-z_0 = \zeta-z_0$; z_0, C_1 and ζ are constants. Thus for $t \leqq \vartheta$, an expression for $z-z_0$ is given by Table I No. $3a$, after replacing z by $z-z_0$ and $f(t)$ by C_1. In particular

$$[\text{at } t=\vartheta]\ z-z_0 = (2k/l).\ \Sigma(-1)^{n+1}.\sin mgx.\int_0^{\vartheta} e^{-m^2a(\vartheta-u)}.C_1.du \qquad (84a)$$

$$= C_1x - (8C_1l/\pi^2).\ \Sigma(-1)^{n+1}.\sin mgx.e^{-m^2a\vartheta}/m^2 \qquad (84b)$$

If the Boundary Conditions of Table I No. $1a$ and Table II No. 1 be added, they give [at $x=0$] $z-z_0=0$, [at $x=l$] $z-z_0=f(t-\vartheta)$, [at $t=\vartheta$] $z-z_0 = F(x)$; so that if the $f(t-\vartheta)$ of Table I No. $1a$ be replaced by $\zeta-z_0$, and the

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[1] Series No. 1 of Table XX is V:[*even*|Φc with $f(u) = e^{-m^2u}$ and $gx = 0$; the approximation is $V\rightarrow S-P{:}\Phi c$. No. 2 is the same but with $gx = \pi/2$. No. 4 is $\partial/\partial(gx).V$:[*odd*]Φc with $f(u) = e^{-4n^2u}$ and $gx = \pi/2$. In Nos. 5 and 6, $f(u) = u.e^{-m^2u}$ and in Nos. 7 and 8, $f(u) = u.e^{-4n^2u}$.

$F(\lambda)$ of Table II No. 1 be replaced by the expression on the right of (84) in which λ is to be written for x, the sum of these two Solutions will give the values of $z-z_0$, when $t>\vartheta$. They are given in full in Eq. 85*a*; its first line is the Solution Table I No. 1*a*, the sum of the Stationary Series being obtained from Table XII; the second line is the Solution Table II No. 1, it is the difference between two Λ's, one with $X=g(x+\lambda)$ and the other with $X=g(x-\lambda)$, and is a Double Series.

$$[t>\vartheta]\ z-z_0 = \overline{\zeta-z_0}.x/l - 2(\overline{\zeta-z_0}/\pi).\ \Sigma(-1)^{q+1}.\sin 2qgx.e^{-4q^2a(t-\vartheta)}/q$$
$$+ (2/l).\int_0^l \Sigma\sin 2qgx.\sin 2qg\lambda.e^{-4q^2a(t-\vartheta)}.F(\lambda).d\lambda \qquad (85a)$$

Instead of evaluating the single series of (85*a*) by the methods of Sec. 9, and dealing with the double series as described on p. 2848, it is shorter in this case to convert the former into a double series,[1] add it to the latter, and deal with both at once; the compact form so obtained, Eq. 85*b*, is identical with Rosebrugh and Miller's Eq. 71.

$$[t>\vartheta]\ z-z_0 = \overline{\zeta-z_0}.x/l - (16C_1l/\pi^3).\ \Sigma\Sigma(-1)^{q+1}\frac{.e^{-m^2a\vartheta}.e^{-4q^2a(t-\vartheta)}}{q(m^2-4q^2)}.\sin 2qgx \qquad (85b)$$

If both sides of (85*b*) be differentiated with respect to gx, and then x be replaced by l, there results

$$[\text{at } x=l]\ \partial z/\partial x = (\zeta-z_0)/l - (16C_1/\pi^2).\Sigma\Sigma e^{-m^2a\vartheta}.e^{-4q^2a(t-\vartheta)}/(m^2-4q^2) \qquad (86)$$

Eq. 86 occurs in the solutions of certain problems of electrochemical polarization now being studied in this laboratory; an expression free from the restriction $x=l$ may be obtained by multiplying the quantity to the right of the sign of double summation by $(-1)^{q+1}.\cos 2qgx$.

(b) Evaluation of the Double Series

If $a\vartheta$ and $a(t-\vartheta)$ are not too small, the double series of (86) may be evaluated by direct summation. But the smaller $a\vartheta$ and $a(t-\vartheta)$ are, the greater the number of terms that must be computed and added; in such cases the methods of approximation already described may be employed. For brevity the letter H is written for the double series of (86) omitting its coefficient $(-16C_1/\pi^2)$, A is written for $a\vartheta$ and E for at.

Differentiating with respect to A,

$$\partial H/\partial A = -(\Sigma e^{-m^2A}).(\Sigma e^{-4q^2(E-A)}) \qquad (87)$$

Either or both of the factors on the right of (87) may now be replaced from Table VIII by its P-approximation, and if the result be multiplied by dA and integrated, it will give rise to an approximation to H. Three cases are possible:—

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[1] By replacing $\zeta-z_0$ by the expression obtained when x is set equal to l in Eq. 84b.

In Eq. 84, Σ stands for $\sum_{n=1}^{\infty}$ as usual, in (85*a*) for $\sum_{q=1}^{\infty}$; in (85*b*) both summations are from 1 to ∞ and the order of summation is immaterial.

q-approximation:—$a(t-\vartheta)$ small and $a\vartheta$ large.

$$\sum\sum\frac{e^{-m^2E}}{m^2-4q^2} - H = \int_A^E \frac{\partial H}{\partial A}.dA \rightarrow -\int_A^E \sum e^{-m^2A}.\left\{\tfrac{1}{4}\sqrt{\frac{\pi}{E-A}} - \tfrac{1}{2}\right\}dA \quad (88)$$

the q-summation on the right of (87) being replaced from Table VIII; from Table XIIa No. 2, the first double series on the left of (88) is equal to $-\Sigma e^{-m^2E}/2m^2$. Therefore

$$H \rightarrow (\sqrt{\pi}/2).\Sigma e^{-m^2A}.F(m\sqrt{E-A})/m \;-\; \Sigma e^{-m^2A}/2m^2 \quad (89)$$

n-approximation:—$a\vartheta$ small, $a(t-\vartheta)$ large.

$$H - \sum\sum e^{-4q^2E}/(m^2-4q^2) \rightarrow (\sqrt{\pi}/4).\sum\int_0^A e^{-4q^2(E-A)}.dA/\sqrt{A} \quad (90)$$

the n-summation on the right of (87) being replaced from Table VIII. From Table XIIa No. 2, the second double series on the left of (90) is zero. Hence

$$H \rightarrow (\sqrt{\pi}/4).\Sigma e^{-4q^2(E-A)}.F(2q\sqrt{A})/q \quad (91)$$

Double approximation:—both $a\vartheta$ and $a(t-\vartheta)$ small.

$$H - \sum\sum e^{-4q^2E}/(m^2-4q^2) \rightarrow (\pi/16).\int_0^A dA/\sqrt{A(E-A)} \;-\; (\sqrt{\pi}/8).\int_0^A dA/\sqrt{A} \quad (92)$$

The second double series on the left of (92) is zero (Table XIIa No. 2); hence

$$H \rightarrow \sqrt{\pi A}/4 - (\pi/8).sin^{-1}\sqrt{A/E} \quad (93)$$

Example 20:— $a\vartheta = A = 0.25$, $at = E = 0.34$.

Direct summation	$H = -0.183\,2412$	(18 terms needed)
q-approximation	$= -0.183\,2413$	(8 terms needed)
n-approximation	$= -0.183\,243$	(6 terms needed)
Double approximation	$= -0.1831$	(no summation.)

The approximations are not improved by computing more terms.

Illustration II: Triple Summation

(a) Origin of the Triple Series

If in the case dealt with as *Illustration I*, at some moment $t_1 > \vartheta$ the Boundary Conditions or one of them were to change again, the Solution would contain a triple series. The Boundary Conditions chosen for *Illustration II* are those of a problem in electrochemical diffusion now being studied in this laboratory; they are:— [at $t=0$] $z-z_0=0$; [at $x=0$] $z-z_0=0$; [at $x=l$] $\partial z/\partial x = C_1$ for $t<\vartheta$, $z=\zeta$ for $\vartheta<t<t_1$, $\partial z/\partial x = C_2$ for $t>t_1$; C_1 C_2 and ζ are constants.

When $t>t_1$ the solution is the sum of Solutions Table I No. 3a and Table II No. 2 after replacing[1] the m of Table II by $r = 2v-1$, t by $t-t_1$, $f(t)$ by

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[1] These are the letters used by R. and M.; $r = 2p - 1$ and $v = p$ of Eq. 81.

C_2, and $F(\lambda)$ by the expression on the right of (85*b*) in which t_1 is to be written for t and λ for x. Performing the integrations and collecting like terms, Eq. 94 follows immediately; it is identical with Eq. 72 of the paper by Rosebrugh and Miller.

$$[t>t_1]\; z-z_0 = C_2x + \frac{8l}{\pi^2}\left\{\frac{\zeta-z_0}{l} - C_2\right\}\cdot \Sigma \cos mg\,(l-x).e^{-m^2a(t-t_1)}/m^2$$
$$-\frac{128C_1l}{\pi^4}\sum\sum\sum\frac{e^{-m^2a\vartheta}.e^{-4q^2a(t_1-\vartheta)}.e^{-r^2a(t-t_1)}}{(m^2-4q^2)\;(r^2-4q^2)}.\cos\, rg(l-x) \qquad (94)$$

(b) Evaluation of the Triple Series

The triple series on the right of (94) may be evaluated by direct summation if all three quantities $a\vartheta$, $a(t_1-\vartheta)$ and $a(t-t_1)$ are large; as in *Illustration I*, the order of summation does not affect the result. The seven different approximations from which a choice is to be made when one or more of the three quantities is small are given below, for the special case that $x = l$. The letter H is used to indicate the triple series of (94) when $x=l$, omitting the factor $-128C_1l/\pi^4$; A is written for $a\vartheta$, B for at_1 and E for at.

v-approximation:—$a(t-t_1)$ small, the other two large.

$$\sum\sum\sum\frac{e^{-m^2A}.e^{-4q^2(E-A)}}{(m^2-4q^2)\;(r^2-4q^2)} - H = \int_B^E\frac{\partial H}{\partial B}.dB \rightarrow \sum\sum\frac{e^{-(m^2-4q^2)A}}{m^2-4q^2}.$$
$$\int_B^E e^{-4q^2B}\left(\tfrac{1}{4}\sqrt{\frac{\pi}{E-B}}\right).dB \qquad (95)$$

The sum of the first series on the left of (95) is zero (see Table XII*a*, No. 2); therefore

$$H \rightarrow -(\sqrt{\pi}/4).\Sigma\Sigma e^{-m^2A}.e^{-4q^2(B-A)}.F(2q\sqrt{E-B})/q(m^2-4q^2) \qquad (96)$$

n-approximation:—$a\vartheta$ small, the other two large. If in (96) r be written for m, $r^2(E-B)$ for m^2A, $2q\sqrt{A}$ for $2q\sqrt{E-B}$, the resulting expression will be the n-approximation to H.

q-approximation:—$a(t_1-\vartheta)$ small, the other two large.

$$H = \Sigma e^{-m^2(A+E-B)}.\Sigma e^{-4q^2(B-A)}/(4q^2-m^2)^2$$
$$+ \Sigma\Sigma e^{-m^2A}.e^{-r^2(E-B)}/(r^2-m^2).\Sigma e^{-4q^2(B-A)}\left\{\frac{1}{m^2-4q^2} - \frac{1}{r^2-4q^2}\right\}\text{when}^1\ m \neq r$$

see Eq. 82 and 83. Introducing the approximations of Table XX Nos. 5 and 1, there results

$$H\rightarrow\Sigma e^{-m^2(A+B-E)}.\{(\sqrt{\pi}/4m^3).(2m^2\overline{B-A}+1).F(m\sqrt{B-A})+\pi^2.e^{-m^2(B-A)}/16m^2$$
$$-\sqrt{\pi(B-A)}/4m^2-1/2m^4\} + \Sigma\Sigma e^{-m^2A}.e^{-r^2(E-B)}/(m^2-r^2).\{1/2m^2-$$
$$(\sqrt{\pi}/2m).F(m\sqrt{B-A}) - 1/2r^2 + (\sqrt{\pi}/2r).F(r\sqrt{B-A})\}\text{ when}^1\, m\neq r \quad (97)$$

Example 21:—If $A=0.50$, $B=0.59$, $E=1.09$, two terms of the single series are needed viz. $m=1$ and $m=3$; their sum is 0.0289211. The sum of two terms of the double series (viz. $m=1$, $r=3$ and $m=3$, $r=1$) is -0.0005958; the symmetry with respect to m and r of the last factor of Eq. 97 much facilitates their computation. This gives $H=0.0283253$; direct summation of the triple series (20 terms) gives 0.0283255.

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[1] In the double series of (97) and in the triple series of the preceding equation, terms in which $m = r$ are to be omitted.

q-v approximation:—$a(t-t_1)$ and $a(t_1-\vartheta)$ small, $a\vartheta$ large.

$$\int \frac{\partial^2 H}{\partial A.\partial B}.dA \to -\int (\Sigma e^{-m^2A}).\left\{\tfrac{1}{4}\sqrt{\frac{\pi}{B-A}}-\tfrac{1}{2}\right\}\left\{\tfrac{1}{4}\sqrt{\frac{\pi}{E-B}}\right\}.dA \qquad (98)$$

Choosing B as upper and A as lower limit of the integration, this gives

$$\Sigma\Sigma\Sigma\frac{e^{-m^2B}.e^{-r^2(E-B)}}{m^2-4q^2}-\Sigma\Sigma\Sigma\frac{e^{-m^2A}.e^{-4q^2(B-A)}.e^{-r^2(E-B)}}{m^2-4q^2}\to$$
$$-\frac{\pi}{8\sqrt{(E-B)}}\cdot\Sigma\frac{e^{-m^2A}}{m}.F(m\sqrt{B-A})+\frac{1}{8}\sqrt{\frac{\pi}{E-B}}\cdot\Sigma\frac{e^{-m^2A}-e^{-m^2B}}{m^2} \qquad (99)$$

From Table XIIa No. 2 and Table VIII, the sum of the first series on the left of (99) approximates to $-(\sqrt{\pi}/8).\ (1/\sqrt{E-B}).\ \Sigma e^{-m^2B}/m^2$. Therefore, multiplying through by dB and integrating between the limits B and E.

$$\Sigma\Sigma\Sigma\frac{e^{-m^2A}.e^{-4q^2(B-A)}}{(m^2-4q^2)\,(r^2-4q^2)}-H\to\frac{\pi}{8}\cdot\Sigma\frac{e^{-m^2A}}{m}\cdot\int_B^E\frac{F(m\sqrt{B-A}).}{\sqrt{E-B}}\cdot dB$$
$$-\frac{\sqrt{\pi(E-B)}}{4}\cdot\Sigma\frac{e^{-m^2A}}{m^2} \qquad (100)$$

The sum of the first series on the left of (100) is zero (see Table XIIa, No. 2), and the integral on the right can be evaluated by changing the variable of integration from B to $y = m\sqrt{E-B}$, and replacing $F(x)$ by $x(1 - 2x^2/3 + 4x^4/15 - + \ldots)$, see Table XXV No. 2. Therefore

$$H\to\frac{\sqrt{\pi(E-B)}}{4}\cdot\Sigma\frac{e^{-m^2A}}{m^2}-\left[\frac{\pi}{8}\cdot\Sigma\frac{e^{-m^2A}}{m^2}\cdot\left\{(1-e^{-W^2}).sin^{-1}\frac{U}{W}+\frac{U(W^2-U^2)^{1/2}}{W^2}\cdot\right.\right.$$
$$(1-e^{-W^2})+\frac{2U(W^2-U^2)^{3/2}}{3W^4}.(1-e^{-W^2}-W^2)+\frac{8U(W^2-U^2)^{5/2}}{15W^6}\cdot$$
$$\left.\left.\left(1-e^{-W^2}-W^2+\frac{W^4}{1.2}\right)+\ldots\right\}\right] \qquad (101)$$

in which $U = m\sqrt{E-B}$ and $W = m\sqrt{E-A}$.

Example 22:—If $A=0.50$, $B=0.60$ and $E=0.69$, the n, the n-v, the n-q and the n-q-v approximations are not appropriate; the value of the series obtained by direct summation, and the values given by the other three approximations are as follows:—

Direct summation	$H=0.029\,1760$	(40 terms needed)
v-approximation	$=0.029\,1760$	(10 terms needed)
q-approximation	$=0.029\,1759$	(10 terms needed)
q-v approximation	$=0.029\,1762$	(19 fractions needed)

From the point of view of labour involved, there is little to choose between the q-v approximation and direct summation; the other two are much shorter. If however $A=0.50$, $B=0.51$ and $E=0.52$, direct summation would be extremely laborious, while the q-v approximation would be much easier to compute than in the example given above.

n-q approximation:—$a\vartheta$ and $a(t_1-\vartheta)$ small, $a(t-t_1)$ large. If in the expressions on the right of (101) r be substituted for m, A for $E-B$, $E-B$ for A, and B for $E-A$, the resulting expression will be the n-q approximation to H.

n-v approximation:—$a\vartheta$ and $a(t-t_1)$ small, $a(t_1-\vartheta)$ large.

$$H = \int_O^A dA . \int_B^E dB \left(\frac{\partial^2 H}{\partial A . \partial B} \right) \rightarrow \frac{\pi}{16} . \sum \frac{e^{-4q^2(B-A)}}{q^2} . F(2q\sqrt{A}) . F(2q\sqrt{E-B}) \quad (102)$$

n-q-v approximation:—all three small.

$$H \rightarrow \frac{\pi^{3/2}}{64} . \int_O^A \int_B^E \frac{dA . dB}{\sqrt{A(B-A)(E-B)}} - \frac{\pi}{32} . \int_O^A \frac{dA}{\sqrt{A}} . \int_B^E \frac{dB}{\sqrt{E-B}}$$

$$= \frac{\pi^{3/2}}{16} . \int_O^{\sqrt{E-B}} \sin^{-1} \sqrt{A/(E-y^2)} . dy - \frac{\pi\sqrt{A(E-B)}}{8}$$

$$= (\pi^{3/2}/16) . \{ \sqrt{E-B} . \sin^{-1} \sqrt{A/B} + \sqrt{A} . \sin^{-1} \sqrt{(E-B)/(E-A)}$$

$$- \sqrt{E} . \tan^{-1} \sqrt{A(E-B)/E(B-A)} \} - \pi\sqrt{A(E-B)}/8 \quad (103)$$

Example 23:—If $A=0.10$, $B=0.20$ and $E=0.30$, any of the seven approximations may be employed; because of the values of the constants, the n-approximation is identical with the v-approximation. Some of the results are:

Direct summation	0.033 8027	(57 terms needed)
n- or v-approximation	0.033 8027	(22 terms needed)
n-v approximation	0.033 8027	(5 terms needed)
n-q-v approximation	0.033 794	(no summation)

Errors of the seven preceding approximations:— The error of the n- or q- or v-approximation depends primarily on the value of A, $B-A$ or $E-B$ respectively; an upper limit may be found by means of Rule V; the use of Rule I is not so convenient, as in these cases the $f(u)$ of that Rule appears in the form of a double series. As an illustration, the absolute error of the v-approximation in Ex. 22 cannot exceed $2H.e^{-\pi^2/0.36} = 2 \times 0.029 \times e^{-27.4} = 8 \times 10^{-14}$. An upper limit to the error of the n-v approximation can be found in the same way; in Ex. 23 for instance, it cannot exceed $4H.e^{-\pi^2/0.40} = 1.2 \times 10^{-11}$.

In the case of the q-v approximation, the error introduced by neglecting the v-Remainder is always numerically smaller than that introduced by neglecting the q-Remainder and is of the opposite sign. When Rule V is used to find an upper limit to the latter, the "Maximum Exponential" of the Rule involves the sum of $E-B$ and $B-A$, i.e. it is a function of $E-A$. Thus in Ex. 22 the error cannot exceed the product of $2.e^{-\pi^2/4(E-A)}$ into the expression in square brackets on the right of Eq. 101, viz. 6×10^{-7}; as shewn in the Example, its actual value is 2×10^{-7}.

Similarly, in the n-q-v approximation the only error which need be considered is that introduced by neglecting the q-Remainder. If Rule V be used to fix an upper limit to this quantity, the "Maximum Exponential" is a function of $A+B-A+E-B=E$; thus in Ex. 23, the absolute error of the n-q-v approximation cannot exceed $2(\pi^{3/2}/16).e^{-\pi^2/4E} \times$ (*Expression in* { } *on the right of Eq.* 103) $= 5 \times 10^{-5}$; the actual error is 9×10^{-6}.

PART V

SERIES FOR USE IN EVALUATING CERTAIN FAMILIES OF INTEGRALS

In the preceding sections it has been shewn how the sums of certain series may be found by the use of tables of integrals; here it will be shewn how integrals of certain families may be evaluated by the use of series[1] related to those of the Θ-Family—from Tables III and VIII

$$[all]\Theta c = \Sigma e^{-n^2T}.\cos nX = A:[all]\Theta c - 1/2 + Rem:[all]\Theta c \qquad (104)$$

where $A:[all]\Theta c = \sqrt{\pi}/2\sqrt{T}).e^{-X^2/4T}$

Of the five approximations discussed below, (*a*) is in effect an approximation to the integral of $(A:\Theta c).f(X).dX$, (*b*) to the integral of $(A:\Theta c).f(T).dT$ when $X=0$, and (*c*) to the same integral when $X\neq 0$; while for approx. (*d*), Eq. 104 is divided through by $A:\Theta c$ and the integral approximated to is that of $(1/2).f(X).(1/A:\Theta c).dX$; approx.(*e*) is in effect an extension of approx.(*c*). For practical reasons series of the [*odd*] type are to be preferred in *approx.*(*a*), (*b*) and (*c*); in (*d*) series of the [*all*] or [*even*] type must be used. All these approximations are based on series of the Θ_E Group; analogous formulas based on series of the Θ_F Group are of little practical importance because of the slow convergence of the Θ_F Remainder (see p. 2824).

The series employed in *approx.*(*b*) and (*c*) are members of the Ψ_E Group of the Ψ-Family, general expressions for which may be obtained by multiplying the corresponding Θ_E (in which T and X are to be replaced by au and gx respectively, see Tables III and VIII) by $f(u).du$ and integrating between the limits 0 and t. In series of the Φ-Family, $f(u)$ is by definition independent of t (p. 2795); if $f(t-u)$ be written instead of $f(u)$ the series is converted into one of the Ψ-Family, since

$$\int_0^t e^{-X^2a(t-u)}.f(t-u).du = \int_0^t e^{-X^2au}.f(u).du$$

An example of this conversion is given in the foot-note to p. 2839. If $f(u)=1$, the two series are identical, i.e. $\Psi(1) = \Phi(1)$; if $f(u) = e^{Bu}$, the relation[2] is $\Psi(e^{Bu}) = e^{Bt}.\Phi(e^{-Bu})$. All that has been said as to the "Boundaries" (p. 2821) and the "number of terms of V" (p. 2822) in connection with series of the Φ_E Group is applicable to series of the Ψ_E Group; but the Rules for finding upper limits to $Rem:\Phi_E$ must be modified as stated in the foot-note to p. 2840. The series of *approx.*(*a*) are members of the Λ_E Group in which $gx=0$; the series of *approx.*(*d*) are *sui generis.*

Sec. 13: Approximations to certain families of integrals

(a) Approx. to $\int e^{-x^2}.f(x).dx$ by series involving $\int \cos mx.f(x).dx$.

(Originally proposed[3] as a general method by W. Thompson in 1857). From Tables III and VIII, choosing $[odd]\Theta c$,

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[1] In this Part, as throughout, Σ stands for $\sum\limits_{n=1}^{\infty}$, and $m=2n-1$.

[2] The symbols $\Phi(1)$, $\Phi(e^{-Bu})$ etc. are used to indicate series of the Φ-Family in which $f(u) = 1$, $f(u) = e^{-Bu}$, etc.

[3] W. Thomson: Quar. J. Math., **1**, 316 (1857).

$$\Sigma e^{-m^2T}.\cos mX = (\sqrt{\pi}/4\sqrt{T}).e^{-X^2/4T} - Rem:[odd]\,\Theta c \qquad (105)$$

Replacing $X/2\sqrt{T}$ by x, multiplying through by $4\sqrt{T/\pi}.f(x).dx$, integrating between the limits o and K, and rearranging,

$$\int_0^K e^{-x^2}f(x).dx = 4\sqrt{\frac{T}{\pi}}.\sum e^{-m^2T}.\int_0^K \cos 2mx\sqrt{T}.f(x).dx + \text{a Remainder} \qquad (106)$$

The approximation consists in neglecting the "Remainder" on the right of (106); in order to facilitate the summation, the largest convenient value of T consistent with the accuracy desired should be chosen.

To find the error introduced by neglecting the "Remainder," the latter may be replaced by its first item, which if the maximum absolute value attained by $f(x)$ in the interval $0 < x < K$ be represented by M, is less than $M.\int_0^K e^{-(\pi - 2x\sqrt{T})^2/4T}.dx$, and this again is less than $M.\int_L^\infty e^{-y^2}.dy$ where L is written for $(\pi - 2K\sqrt{T})/2\sqrt{T}$. This last expression becomes identical with the product of $M\sqrt{\pi}$ into the "$(R_{1a}$: [*even or odd*] $\Lambda c)/l$" of Table XIX if the $\sqrt{at}$ of that table be replaced by $\sqrt{T}$ and the gx by $2K\sqrt{T}$; so that if the quotient of the "permissible error" by $M\sqrt{\pi}$ be looked up (interpolated) in the top line of Table XIX, the corresponding figure in the second line will be the ordinate for E in Fig. 2, i.e. it will fix the position of the Boundary BE; the point at which the ray (i.e. line passing through the origin) with slope $1/2K$ cuts[1] this Boundary gives the desired maximum value of $\sqrt{T}$. This relation is expressed analytically (writing E for the ordinate of the point E of Fig. 2) by $\sqrt{T} = 2\pi E/(\pi + 4KE)$; for instance, if $K = 2$ and if $10^{-6}.M\sqrt{\pi}$ be considered negligible (whence $E = 0.232$) the desired value is $\sqrt{T} = 0.29$. If the permissible error be $10^{-6}.M\sqrt{\pi}$, an upper limit to the number of terms of the series that must be computed is given by the point on the "odd" scale (as printed in Fig. 2) whose ordinate is that of the intersection of the ray with BE (or with the perpendicular PE if it does not cut BE); for other assumptions, see Table XV. With $E = 0.232$, the number of terms increases with increase in K from a minimum of 4 terms to 9 terms when $K = 3.35$ (where the ray passes through E) after which it mounts rapidly; if $K = 10$, 30 terms might have to be evaluated and summed to ensure an accuracy of $10^{-6}.M\sqrt{\pi}$.

Thomson suggested that this approximation might be used, setting $f(x) = 1$, to compute the Probability Integral,[2] but *approx.*(*b*) is better. An approximation to the integrals of $e^{-x^2}.\overline{\sin \text{ or } \cos}\; bx.dx$ may be found by setting $f(x) = \overline{\sin \text{ or } \cos}\; bx$; at least four terms of the series are needed to ensure an accuracy of $10^{-6}.\sqrt{\pi}$ no matter how small K may be, and the number increases with increase in K; when $K = 1.37$ seven terms are necessary, and for larger values it is easier to evaluate the integral by computing $H(b/2, K)$ and $\mathrm{K}(b/2, K)$ as shewn in the Appendix p. 2869.

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[1] If the intersection lies to the right of PE, the ordinate at which the ray cuts PE gives the desired values.

[2] Thomson (*loc. cit.* p. 319) estimated that for upper limits below 6.47/2 seven terms at most would be needed to give results exact to four decimal places; by the method explained above it can be shewn that with this number of terms the error could not exceed 2 units at the sixth decimal place. The fifteen-place table of Jas. Burgess [Trans. Roy. Soc. Edin. 39, 257 (1896)] was computed by an altogether different method.

(b) Approx. to $\int f(x^2).dx$ by series involving $\int e^{-m^2x} f(x).dx$

(Used in computing $F(x)$ Table XXVIII, see p. 2874). Replacing X by o in Eq. 105 and T by ax, multiplying through by $2\sqrt{a/\pi}.f(x).dx$, integrating between the limits o and K^2, and rearranging

$$\int_0^K f(x^2).dx = \tfrac{1}{2}\int_0^{K^2} \frac{f(x)}{\sqrt{x}} \cdot dx = 2\sqrt{\frac{a}{\pi}} \cdot \sum \int_0^{K^2} e^{-m^2ax} f(x).dx + \text{a Remainder} \qquad (107)$$

The approximation consists in neglecting the "Remainder" of Eq. 107. If $f(x)$ is of the form e^{Bx} (where B may be positive or negative, real imaginary or complex) a finite expression may be found in Table XII*a* for the sum of the series arising from the lower limit of the integral on the right of (107); with other forms of $f(x)$ the evaluation of this series may be so troublesome as to render the approximation undesirable.

The error introduced by neglecting the "Remainder" of (107) is for practical purposes given by the value of its first item viz.

$$\int_0^{K^2} e^{-\pi^2/4ax} f(x)/\sqrt{x}.dx \ < \ (M/2\sqrt{a}).G(4aK^2) \qquad (108)$$

where M is the maximum absolute value attained by $f(x)$ in the interval $0 < x < K^2$. Thus for given values of M and K, and any assumed value of a, an upper limit to the absolute error of the approximation can be found from Table XXVII; the largest convenient value of a consistent with the accuracy desired should be employed, as the number of terms of the series arising from the upper limit of the integral (in Eq. 107) that must be summed decreases with increase in $K\sqrt{a}$. If a be so chosen that the permissible error is $2 \times 10^{-6}.M\sqrt{a/\pi}$ or $2 \times 10^{-3}.M\sqrt{a/\pi}$, an upper limit to this number may be found from Table XV by writing $K\sqrt{a}$ in place of $\sqrt{at}$ and entering on the line [*odd*]. A great advantage that this approximation enjoys over all the others is, that the number of terms to be summed increases very slowly with increase in K; the reason is, that a slight lowering of the point E (Fig. 2) corresponds to a great increase in accuracy but only to a slight increase in the number of terms to be summed. For example, if $10^{-6}.M$ be considered negligible, four terms of the Evanescent Series will be sufficient when $K = 1$, and five at most when $K = 10$; if $a = 0.2$ be chosen in the first case and $a = 0.0016$ in the second.

(c) Approx. to $\int e^{-b^2/x^2} f(x^2).dx$ by series involving $\int e^{-m^2x} f(x).dx$

(Used in computing G(x), Table XXVII; see also p. 2869). Replacing X by $2b\sqrt{a}$ and T by ax in Eq. 105, multiplying through by $2\sqrt{a/\pi}.f(x).dx$ integrating between the limits o and K^2, and rearranging

$$\int_0^K e^{-b^2/x^2} f(x^2).dx = 2\sqrt{\frac{a}{\pi}} \cdot \sum \cos 2mb\sqrt{a}. \int_0^{K^2} e^{-m^2ax} f(x).dx + \text{a Remainder} \qquad (109)$$

The approximation consists in neglecting the "Remainder" of (109); the series may be summed by the methods of *approx.ii iii* or *iv* (p. 2825) depending on the value of $K/2b$; all are available if $f(x)$ is a member of Class A or B as defined in Table X, and all but *approx.iv* if it belongs to Class C.

When $f(x) = e^{Cx}$ integrals of the type here considered cannot be evaluated by means of *approx.*(*b*), as the $f(x)$ of that approximation would be $e^{Cx-b^2/x}$ and the integrals required are untabulated. In this case, according as the series is to be evaluated by the method of *approx. ii iii* or *iv*, *approx.*(*c*) gives Eqs. 110, 111 and 112 respectively as expressions for the integral.

$$\int_0^K e^{Cx^2-b^2/x^2}.dx \rightarrow \tfrac{1}{2}\sqrt{\frac{\pi}{C}}\cdot\frac{\sin\{\sqrt{C}(\pi-4b\sqrt{a})/\sqrt{4a}\}}{\cos(\pi\sqrt{C/4a})} - 2\sqrt{\frac{a}{\pi}}\cdot e^{CK^2}.\sum\frac{\cos 2mb\sqrt{a}}{m^2a-C}.e^{-m^2aK^2} \qquad (110)$$

In Eq. 110 (to be used when $6E/\pi < K/2b < \infty$), $\sqrt{a}$ is to be given the largest convenient value not exceeding $2\pi E/(\pi K+4bE)$ where E is the ordinate assigned to the point E in Fig. 2. If $E=0.227$, from 4 to 6 terms of the Evanescent Series are needed to give the value of the integral with an error not exceeding $2 \times 10^{-6}.MK^2\sqrt{a/\pi}$.

$$\int_0^K e^{Cx^2-b^2/x^2}.dx \rightarrow (\sqrt{\pi}/4b).e^{CK^2}\sum(-1)^{n+1}.e^{-n^2\pi^2K^2/4b^2}/(n^2\pi^2/4b^2-C) - (\sqrt{\pi/16C}).\mathrm{cosec}\ 2b\sqrt{C} + (\sqrt{\pi}/8bC).e^{CK^2} \qquad (111)$$

In Eq. 111 (to be used when $4E/\pi < K/2b < 6E/\pi$), if $E=0.227$ three or four terms of the Evanescent Series must be computed to evaluate the integral with an error not exceeding $10^{-6}.MK^2.\sqrt{\pi}/2b$.

$$\int_0^K e^{Cx^2-b^2/x^2}.dx \rightarrow (1/2\sqrt{C}).e^{CK^2}.F(\sqrt{CK^2}) - (\sqrt{\pi/16C}).\tan\sqrt{b^2C} + (\sqrt{\pi}/2b).e^{CK^2}.\sum e^{-m^2\pi^2K^2/4b^2}/(m^2\pi^2/4b^2-C) \qquad (112)$$

In Eq. 112 (to be used when $2E/\pi < K/2b < 4E/\pi$), if $E=0.227$ from two to four terms of the Evanescent Series must be computed to evaluate the integral with an error not exceeding $10^{-6}.MK^2.\sqrt{\pi}/2b$.

Eqs. 110-112 were obtained from Eqs. 50, 52 and 54 respectively; the value $E=0.227$ is that of Fig. 2 as printed. Eq. 110 may be used for $2E/\pi < K/2b < \infty$ without exceeding the error stated above, nine terms being required when $K/2b = 2E/\pi = 0.145$; Eq. 111 may be used for $2E/\pi < K/2b < 6E/\pi$ with a maximum of nine terms; Eq. 112 on the other hand is valid only within the range stated after that equation. Thus no matter what the values of K and b may be, not more than nine terms of the Evanescent Series need be computed (six if the best formula be used) in order to ensure the postulated accuracy; values of E for other degrees of accuracy can be found from Table XIV. Eq. 112 cannot be used when C is complex; all the others are valid whether C be positive or negative, real imaginary or complex. If $C=0$ and $b=\pi$ the integral is $(1/2).\mathbf{G}(K^2)$, while if $C=1$ the integral is $H(K, b/K)$, see Table XXII, No. 1.

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[1] If the approximation be based on [*even*]θc instead of on [*odd*]θc, the terms on the right of (112) must be modified as follows:—Change the signs of the first and third terms, replace *tan* by *cot* in the second term and *m* by *2n* in the third, and add a fourth term viz. $\sqrt{\pi}.e^{CK^2}/4bC$. The equation so modified is referred to on p. 2861 and p. 2877 as Eq. 112*a*.

The expression given after each equation for the upper limit to the error is deduced from Rule I, p. 2840; M stands for the maximum absolute value of e^{Cx} when x lies between 0 and K^2. When C is a positive constant $M=e^{CK^2}$, and if CK^2 is large, Rule I much overestimates the possible error; in such a case Rule V (p. 2843) is more useful, it shews that for all three equations, no matter what the value of CK^2 may be or the form of $f(x)$ (so long as it retains its sign in the interval $0<x<K^2$) the error cannot exceed one fifty-thousandth of the value of the integral if $E = 0.227$, while if the value $E = 0.18$ be chosen (which involves the computation of at most two additional terms of the Evanescent Series) the error cannot exceed one millionth part of the value of the integral. For an example of this application of Rule V to a special case, see p. 2869.

(d) Approx. to $\int e^{x^2}.f(x).dx$ by series involving $\int cosh\ nx.f(x).dx$

(Used by H. G. Dawson[1] in 1898 to compute the integral of $e^{x^2}.dx$). From the expression for $[all]\Theta c$ in the second line of Table VIII, replacing X by $2x\sqrt{T}$, multiplying through by $2e^{x^2}.f(x).dx$, integrating between the limits 0 and K, and rearranging:

$$\int_0^K e^{x^2}.f(x).dx = \sqrt{\frac{\pi}{T}}.\int_0^K f(x).dx + 2\sqrt{\frac{\pi}{T}}.\sum e^{-n^2\pi^2.T}.\int_0^K cosh\ (2n\pi x/\sqrt{T})\times$$
$$f(x).dx - 2\sum e^{-n^2T}.\int_0^K e^{x^2}.cos\ 2nx\sqrt{T}.f(x).dx \quad (113)$$

The approximation consists in neglecting the series in the second line of (113); in order to facilitate the summation of the series in the first line, the smallest convenient value of T consistent with the accuracy desired should be chosen. To find an approximate upper limit to the absolute error, the series neglected may be replaced by its first term, the cosine by unity, and $f(x)$ by M viz. the greatest absolute value attained by $f(x)$ while x increases from 0 to K; this gives $2M.e^{K^2-T}.F(K)$. An upper limit to the number of terms of the series in the first line of (113) that must be computed, is the n found from

$$2M.e^{K^2-T}.F(K) = (M/n\sqrt{\pi}).e^{-n^2\pi^2/T}.sinh(2n\pi K/\sqrt{T}) \quad (114)$$

after giving T the smallest value that will make the expression on the left of (114) negligible in view of the accuracy desired. This approximation resembles *approx.(a)* in that the number of terms that must be computed increases very rapidly with increase in the value of K.

Setting $f(x) = 1$, the integral becomes that of $e^{x^2}.dx$, and for $K=2$ the value $T=20$ ensures accuracy in the sixth decimal place (i.e. eight significant figures) when nine terms are computed; Dawson used $T = 4\pi^2$ which (for $K=2$) required 13 terms to attain the same accuracy. By the use of *approx. (b)* nine-figure values of this integral, no matter what the value of K may be, can be secured without computing more than seven terms of the Evanescent series of Eq. 134, see p. 2874.

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[1] H. G. Dawson: Proc. London Math. Soc., **29**, 519 (1898).

By setting $f(x)$ = *sin or cos* bx, an approximation to the integral of $e^{x^2}.sin$ *or cos* $bx.dx$. may be found; the number of terms required to hold the error below $10^{-6}.e^{K^2}.F(K)$ increases with increase in K from three when K is very small to five when $K = 0.9$ and seven when $K = 1.1$; for larger values of K, it is easier to evaluate these integrals by computing $H(K,b/2)$ and $K(K,b/2)$ as shewn in the Appendix.

(e) Use of the approximations in the construction of a Table

In discussing the foregoing approximations it has been tacitly assumed that the object of the computer is to find the numerical value of some single integral whose limits etc. have been specified; this is not quite the point of view when a Table of the integral in question is being constructed. In the latter case an endeavour would no doubt be made to proceed by means of Taylor's Series, or the methods of tabular integration, and the approximations would be employed only to furnish the relatively small number of accurate values needed to prevent accumulation of errors; thus it might be well worth while to secure additional accurate values by recombining the terms of Evanescent Series already computed even although the limits etc. of these new integrals can not be arbitrarily selected but are fixed by the procedure used in evaluating them.

The absolute values of the individual terms of the Evanescent Series of Eq. 112*a* would be identical with those of the corresponding series of Eq. 111 if in the latter b^2 were replaced by $b^2/4$ while C and K^2 had the same values in both; thus the Evanescent terms which had already been used to evaluate the integral of $e^{Cx^2-b^2/x^2}.dx$ by (112*a*) could be used over again to evaluate the integral of $e^{Cx^2-b^2/4x^2}.dx$ by (111). For examples, see p. 2870 and p. 2877. No such device is available with *approx.*(*a*) or *approx.* (*d*); and if it be adapted to *approx.*(*b*) the second integral will be of a different form from the first.

If *approx.*(*c*) is being used in the construction of a Table, there is another way by which labour already expended can be utilized again. Like all the others of this Part, this approximation is based on the neglect of a Remainder; and the range over which each of its three subdivisions is valid, has been fixed by the assumption that the absolute value of the appropriate Remainder is unknown (but that it lies below some predetermined limit). The first item of the Remainder of (110), however, viz. $2\sqrt{a/\pi}.R_{1a}:[odd]\Psi c$, is numerically equal to the integral itself for the same values of C and K but another value of b; so that if the portion of the Table already constructed includes the value of the integral for this value of b, an approximation may be employed which neglects only R_{1b} and subsequent terms of the Remainder of (110) and requires the computation of fewer terms of the Evanescent Series than does the approximation of (110). This modification corresponds to choosing an auxiliary series (see *approx. ii*, p. 2826) on BG of Fig. 2 instead of on BE. Examples of the use of this method and of corresponding methods based on (111) and (112) are given on p. 2870 and p. 2877; no similar device is available in the case of *approx.*(*a*) and *approx.*(*d*); in the case of *approx.*(*b*) the information needed cannot be secured from the table under construction.

APPENDIX

ON THE INTEGRAL $\int e^{z^2}.dz$ AND RELATED INTEGRALS

The group of integrals here to be considered includes the Probability Integral, the Fresnel Integrals, the Integral of $e^{x^4}.dx$ and others illustrated in Table XXI and Eqs. 128 and 129; it will be shewn that all can be expressed in terms of two functions to which the symbols U and V are given, and that all could be evaluated by means of two double-entry tables. As the tables in question have not been constructed, methods are described for evaluating the integrals in the absence of such tables. The practical advantages possessed by one particular pair of tables (viz. H and K) in comparison with any other pair are then established, and are illustrated by the construction of Tables from which four-place values of the two Fresnel Integrals can be obtained for any value of the argument between 0 and ∞ without recourse to graphical interpolation.

Sec. 14: The functions *U* and *V*

If $z = x + iy$ (where x and y are real and $i = \sqrt{-1}$), then

$$\int_0^{p+iq} e^{z^2}.dz = U(p,q) + i.V(p,q) \tag{116}$$

where

$$U(p,q) = \int_0^p e^{x^2-y^2}.\cos 2xy.dx - \int_0^q e^{x^2-y^2}.\sin 2xy.dy \tag{117}$$

and

$$V(p,q) = \int_0^p e^{x^2-y^2}.\sin 2xy.dx + \int_0^q e^{x^2-y^2}.\cos 2xy.dy \tag{118}$$

Since the integral on the left of (116) is a single-valued function of p and q, its real part viz. $U(p,q)$ and its imaginary part viz. $i\,V(p,q)$ must each of them be single-valued functions of p and q. This conclusion, on which all the subsequent argument depends, may be verified by differentiating[1] the expressions on the right of (117) and (118), since the expressions for $\partial^2U/\partial p.\partial q$ and for $\partial^2V/\partial p.\partial q$ will be found to be independent of the order of differentiation. The only reason for introducing the complex quantity (116) is that it gives rise to functions of the real variables p and q, viz. $U(p,q)$ and $V(p,q)$ which possess this property.

Without assuming some relation between x and y, neither of the integrals on the right of (117) can be evaluated; any assumption may be made that permits x during the integration to assume all values between 0 and p, and y all values between 0 and q; it is obvious that the value of each integral taken by itself will depend on the assumption made, but since for given p and q $U(p,q)$ has but one value, the difference between the values of the two integrals must be the same no matter what the assumption may be. If, for instance, it be assumed that $y=0$ while x increases from 0 to p, and that then y increases from 0 to q while x retains the constant value p,

---

[1] $\partial U(p,q)/\partial p = e^{p^2-q^2}.\cos 2pq$; $\partial^2U(p,q)/\partial p.\partial q = -2.e^{p^2-q^2}(q.\cos 2pq + p.\sin 2pq)$.

$$U(p,q) = \int_0^p e^{x^2}.dx - e^{p^2}.\int_0^q e^{-y^2}.sin\ 2py.dy \qquad (119)$$

$$V(p,q) = e^{p^2}.\int_0^q e^{-y^2}.cos\ 2py.dy \qquad (120)$$

while if it be assumed that $x = 0$ while y increases from 0 to q, and that then x increases from 0 to p while $y = q$,

$$U(p,q) = e^{-q^2}.\int_0^p e^{x^2}.cos\ 2qx.dx \qquad (121)$$

$$V(p,q) = \int_0^q e^{-y^2}.dy + e^{-q^2}.\int_0^p e^{x^2}.sin\ 2qx.dx \qquad (122)$$

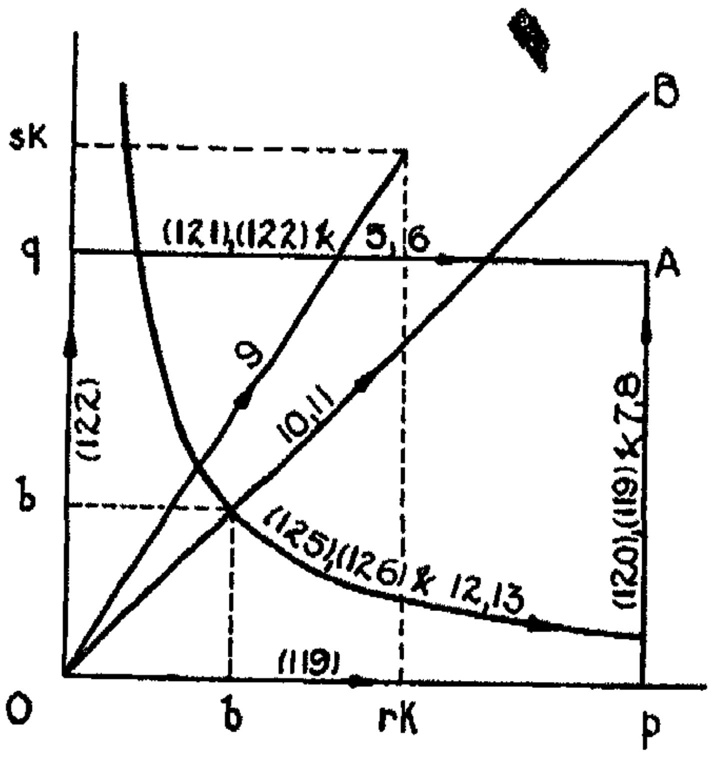

FIG. 3

Paths of Integration:—The numbers 5, 6 etc. are those of Tab. XXI; numbers in brackets are equation numbers. The letters are those of the text p. 2862-2868 except *rK* and *sK* which are those of Tab. XXI No. 9.

and the conclusion to be drawn from the preceding argument is that the expression on the right of (119) may be equated to that on the right of (121), and that the right of (120) may be equated to the right of (122).

If the successive values assumed by x and y during the integrations be represented by points on Fig. 3, the first assumption corresponds to the line OpA and the second to OqA; these lines are often spoken of as "paths of integration," and the statement that $U(p,q)$ is "independent of the path" is only another way of saying that for any given p and q, $U(p,q)$ has but one value.

By integrating along different paths the differences (or sums) of a large number of integrals may be expressed in terms of U and V; for any line on Fig. 3 defines some relation between x and y, and the algebraic sum of the integrals defined by this relation gives the difference between the values of U (or of V, as the case may be), at the points denoted by the extremities of the line. In general, if the relation be $y = f(x)$,

$$\int_\alpha^p e^{x^2-(fx)^2}.cos\ (2x.f\,x).dx - \int_\alpha^p e^{x^2-(fx)^2}.sin\ (2x.f\,x).f'x.dx$$
$$= U(p, fp) - U\ (\alpha, f\alpha) \qquad (123)$$

$$\int_\alpha^p e^{x^2-(fx)^2}.sin\ (2x.f\,x).dx + \int_\alpha^p e^{x^2-(fx)^2}.cos\ (2x.f\,x).f'x.dx$$
$$= V(p, fp) - V(\alpha, f\alpha) \qquad (124)$$

Eqs. 123 and 124 contain between them four integrals; there are two forms of $f(x)$ for which it is possible to eliminate[1] two of these integrals and combine the other two, these are:—

1. *The first form for which elimination is possible is* $x.f(x) = b^2$; for this form $f'(x) = -b^2/x^2$ and the trigonometric factor of the integrand is either *sin* $2b^2$ or *cos* $2b^2$ i.e. is independent of x. The path of integration in this case is a rectangular hyperbola cutting the diagonal OB of Fig. 3 at the point $x = y = b$ Elimination gives

$$\int_\alpha^p e^{x^2-b^4/x^2}.dx = \{U(p, b^2/p) - U(\alpha, b^2/\alpha)\}.cos\ 2b^2$$
$$+ \{V(p, b^2/p) - V(\alpha, b^2/\alpha)\}.sin\ 2b^2 \qquad (125)$$

$$\int_\alpha^p \frac{b^2}{x^2}.e^{x^2-b^4/x^2}.dx = \{U(p, b^2/p) - U(\alpha, b^2/\alpha)\}.sin\ 2b^2$$
$$- \{V(p, b^2/p) - V(\alpha, b^2/\alpha)\}.cos\ 2b^2 \qquad (126)$$

2. *The second form for which elimination is possible is* $f(x) = \beta x + \gamma$; this form corresponds to any straight line on Fig. 3. Here $f'(x) = \beta$, and elimination gives

$$(1 + \beta^2).e^{-\gamma^2}.\int_\alpha^p e^{(1-\beta^2)x^2-2\beta\gamma x}.cos\ (2\beta x^2+2\gamma x).dx$$
$$= U(p, \beta p+\gamma) - U(\alpha,\beta\alpha+\gamma) + \beta.V(p, \beta p+\gamma) - \beta.V(\alpha,\beta\alpha+\gamma) \qquad (127)$$

and a similar equation for the integral containing *sin* instead of *cos* in its integrand. In these integrals the coefficients of x^2 and x in the sine or cosine depend on those in the exponent; expressions in terms of U and V for analogous integrals where all four coefficients are independent of one another and of the limits of integration may be found by substituting $\omega x+\alpha$ for x and eliminating by means of the trigonometric formulas for the sines and cosines of sums. These expressions are

$$\int_o^p e^{Rx^2+2Sx}.cos\,(2Tx^2+2Wx).dx = \frac{(cos\,M-\beta.sin\,M)\Delta U+(\beta.cos\,M+sin\,M)\Delta V}{\text{Denominator}} \qquad (128)$$

$$\int_o^p e^{Rx^2+2Sx}.sin\,(2Tx^2+2Wx).dx = \frac{(cos\,M-\beta.sin M)\Delta V-(\beta.cos\,M+sin\,M)\,\Delta U}{\text{Denominator}} \qquad (129)$$

where to save printing the following abbreviations are used:

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[1] In general, of course, this is not possible; for instance no elimination is possible if $y^2 - x^2 = b^2$, the path corresponding to which is a rectangular hyperbola asymptotic to OB of Fig. 3.

$\Delta U = U(p,\beta p+\gamma) - U(\alpha,\beta\alpha+\gamma)$; $\Delta V = V(p,\beta p+\gamma) - V(\alpha,\beta\alpha+\gamma)$
$P = (p-\alpha)/\omega$; $R = (1-\beta^2)\omega^2$; $S = (1-\beta^2)\alpha\omega-\beta\gamma\omega$; $T = \beta\omega^2$; $W = (2\alpha\beta+\gamma)\omega$;
$M = 2\alpha(\alpha\beta+\gamma)$; *Denominator* $= \omega(1+\beta^2).e^{(1-\beta^2)\alpha^2-2\alpha\beta\gamma-\gamma^2}$.

By giving special values to α β γ and ω, the relatively simple forms of Table XXI may be obtained. On the other hand, if an integral of the most general form of Eqs. 128 and 129 be presented for evaluation, the numerical values of p, α, β, γ, and ω needed on the right of Eqs. 128 and 129 can be found from the numerical values of P, R, S, T and W in the given integral by means of the following equations[1]:

$$2\omega^2 = \sqrt{R^2+4T^2} + R \qquad 2T.\beta = \sqrt{R^2+4T^2} - R$$
$$(\beta^2 + 1)\omega.\alpha = \beta W + S \qquad \omega.\gamma = W - 2\alpha\beta\omega \qquad p = \omega P + \alpha \tag{130}$$

TABLE XXI: The functions U and V

1. $U(p,q) = -U(-p,q) = -U(-p,-q) = U(p,-q)$
2. $V(p,q) = V(-p,q) = -V(-p,-q) = -V(p,-q)$
3. $U(0,0) = V(0,0) = U(0,q) = V(p,0) = 0$
4. $U(p,0) = \int_0^p e^{x^2}.dx$; $U(p,\infty) = 0$; $V(0,q) = \int_0^q e^{-x^2}.dx$; $V(p,\infty) = \sqrt{\pi}/2$
5. $\int_0^K e^{x^2}.\cos 2Bx.dx = e^{B^2}.U(K,B)$
6. $\int_0^K e^{x^2}.\sin 2Bx.dx = e^{B^2}.V(K,B) - e^{B^2}.\int_0^B e^{-x^2}.dx$
7. $\int_0^K e^{-x^2}.\cos 2Bx.dx = e^{-B^2}.V(B,K)$
8. $\int_0^K e^{-x^2}.\sin 2Bx.dx = e^{-B^2}.\int_0^B e^{x^2}.dx - e^{-B^2}.U(B,K)$
9. $\int_0^K e^{x^2}.\cos 2Bx^2.dx = \{r.U(rK,sK) + s.V(rK,sK)\}/\sqrt{4B^2+1}$

   where $2r^2 = \sqrt{4B^2+1} + 1$, and $2s^2 = \sqrt{4B^2+1} - 1$.
10. $2\sqrt{B}.\int_0^K \cos 2Bx^2.dx = U(K\sqrt{B}.K\sqrt{B}) + V(K\sqrt{B},K\sqrt{B})$
11. $2\sqrt{B}.\int_0^K \sin 2Bx^2.dx = V(K\sqrt{B}.K\sqrt{B}) - U(K\sqrt{B}.K\sqrt{B})$
12. A: [*odd or even*] Φc ($f.u = e^{\pm Cu}.\sin$ or $\cos \overline{b^2u+\alpha}$) when $gx = 0$ can be reduced to the algebraic sum of the two integrals of Eqs. 128 and 129, each multiplied by a factor; in both of them $P = \sqrt{l}$, $R = C$, $S = W = 0$, $T = b^2/2$. The Remainder integrals cannot be so reduced. See also Tab. XXII Nos. 5 and 6.

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[1] Valid except when $R = T = 0$, which gives $\omega = 0$, so that α β and γ are indeterminate.

TABLE XXI: The functions U and V (Continued)

13. A: [*odd* or *even*]Λc ($F.\lambda = e^{b\lambda^2+c\lambda}.\sin$ or $\cos \overline{e\lambda^2+h\lambda}$) can be similarly reduced; here $P=l$, $R=b-1/4kt$, $2S=c+x/2Kt$, $2T=e$, $2W=h$; the Remainder integrals can be handled similarly, using the substitutions of Tab. XXII No. 6.

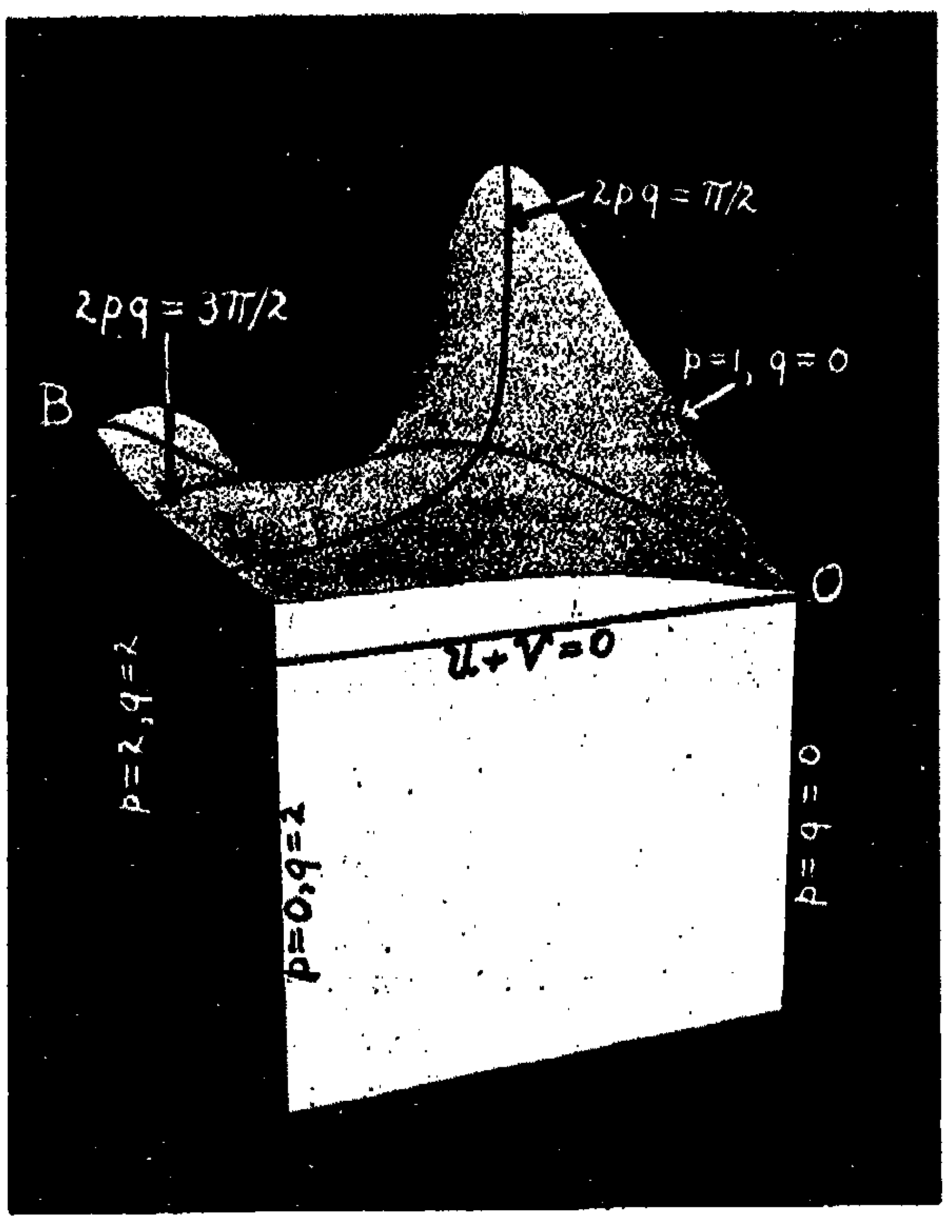

FIG. 4

Unsuitability of $U(p,q)$ and $V(p,q)$ for purposes of tabulation

If at the point [$x=p$, $y=q$] of Fig. 3, a line were erected perpendicular to the (x,y) plane and of length proportional to $U(p,q)$, and similarly at all other points of the figure, the summits of all these lines would lie in the U-surface; the V-surface, the $(U+V)$ surface, etc. might be constructed similarly. Fig. 4 shews a portion of the $(U+V)$ surface, viz. that for values of p and q within the dotted lines of Fig. 5; this surface was chosen for illustration rather than the U-surface or the V-surface because $U(p,q) + V(p,q)$ along the line of intersection of the surface with the plane $x = y$ (see OB of Fig. 4) is equal to $2\int_0^p \cos 2x^2.dx$, one of the Fresnel Integrals. As is apparent in Fig. 4 the $(U + V)$ surface is characterized by rapid changes of level; for small q's, and p's larger than those included in the figure, these changes soon became too great for graphical representation; but the differential equation for the contour lines viz. $dq/dp = -\sec. 4pq - \tan 4pq$ (from $d.U(p,q) + d.V(p,q) = 0$) gives some idea of the form of the surface. The U-surface, the V-surface and the $(U-V)$ surface have the same mountainous character; so that double-entry tables of any of these functions, which obviously describe the corresponding surface in detail, would have to contain a tremendous number of entries if interpolation were to be possible.

The line of intersection of the U-surface (or the V-surface) with any plane perpendicular to the (x,y) plane, will in general[1] cut through hills and valleys; the elevations along this line give the values of the integral whose path of integration is a straight line on the (x,y) plane, viz. the projection of the intersection; such integrals are therefore in general unsuitable for tabulation, and so are the integrals of Eqs. 128 and 129 (e.g. Nos. 6-13 of Table XXI) which are linear functions of the others. The Fresnel Integrals are the only members of this group for which tables have been constructed, and except the Brit. Ass. Table[2] of 1926 which contains 200 entries for the first three cycles, none of them can be interpolated without the use of a graph (Cornu's Spiral).

On the other hand, if the projection of the intersection be an hyperbola for which $xy = constant$, the line of intersection (e.g. Fig. 4, $2pq=\pi/2$ and $2pq=3\pi/2$) will lie in the general direction of the ridges and valleys; and the corresponding integrals viz. $H(p,q)$ and $K(p,q)$ will be free from the property that makes tabulation of $U(p,q)$ and $V(p,q)$ impracticable.

Sec. 15: The functions $H(p,q)$ and $K(p,q)$

The first of the two expressions for $H(p,q)$ or $K(p,q)$ given in Table XXII corresponds to a double-entry table in which pq is constant for each column and p for each line; the values of both functions are positive throughout, both increase down the columns and $H(p,q)$ decreases to the right along the lines. Consideration of the second derivatives[3] (see Table XXII) shews that $H(p,q)$ can have no point of inflexion within a column, none in the lines for which $p<0.92$, and one in every line for which $p>0.92$; while $K(p,q)$ must have a maximum in every line for which $p>0.92$, and one point of inflexion in every line for which $pq = p\sqrt{1-p^2}$, none in the others. The second expressions given in Table XXII for the functions correspond to tables in which pq is constant for each column, and p/q for each line; thus in both

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[1] That is, except when $p = 0$ or $q = 0$.

[2] Brit. Ass. Report, 1926, pg. 273.

[3] For instance, the second derivative of H with respect to q while p remains constant is proportional to $2pH - E$ (Table XXII), and the point to be settled is whether this quantity will pass through zero while p remains constant and q increases. If $p = 0.92$ and $q = 0$, $E = 2pH$ (Tab. XXV No. 9); as q increases both E and H decrease, but the percentage decrease in H is greater than in E as is obvious from the form of the integral in the first expression for H in Table XXII. Therefore for all values of $q > 0$, while $p = 0.92$, $E > 2pH$, and in general there cannot be more than one value of q for each p at which $E = 2pH$. Since $E - 2pH$ has the same sign at $q = 0$, and at $q = p$ when $p < 0.92$, there can be no point of inflexion for this value of p; above $p = 0.92$ the signs are different, therefore there must be one point of inflexion and it has just been shewn that there cannot be more than one.

TABLE XXII: The functions H and K

1. $H(p,q) = \int_0^p e^{x^2 - p^2q^2/x^2}.dx = \sqrt{pq}.\int_0^* e^{pq(x^2-1/x^2)}.dx$
$= U(p,q).\cos 2pq + V(p,q).\sin 2pq - (\sqrt{\pi}/2).\sin 2pq$

2. $K(p,q) = pq.\int_0^p (1/x^2).e^{x^2-p^2q^2/x^2}.dx = \sqrt{pq}.\int_0^* (1/x^2).e^{pq(x^2-1/x^2)}.dx$
$= U(p,q).\sin 2pq - V(p,q).\cos 2pq + (\sqrt{\pi}/2).\cos 2pq$

where the upper limit* stands for $\sqrt{p/q}$.

3. $H(0,q) = K(0,q) = 0$; $H(p,0) = \int_0^p e^{x^2}.dx$; $K(p,0) = \sqrt{\pi}/2$.

4. $H(K, B^2/K) = \int_0^K e^{x^2 - B^4/x^2}.dx$
$= \cos 2B^2.U(K, B^2/K) + \sin 2B^2.V(K, B^2/K) - (\sqrt{\pi}/2).\sin 2B^2$

5. A:[*odd or even*] Φc $(f.u = e^{-b^2u}) = (\sqrt{\pi/4b^2a}).e^{-b^2t}$ times the right of No. 4 where $K = b\sqrt{t}$ and $2B^2 = bgx/\sqrt{a}$.

6. R_{na} may be substituted for A in No. 5 if gx be replaced by $n\pi - gx$; R_{nb} may be substituted for A in No. 5 if gx be replaced by $n\pi + gx$.

7. Derivatives:— Here E is written for $e^{p^2-q^2}$, H for $H(p.q)$ and K for $K(p,q)$. The quantity kept constant during the differentiation is printed as a subscript.

$(\partial H/\partial p)_q = E - 2qK$; $(\partial H/\partial q)_p = -2pK$; $(\partial H/\partial p)_{pq} = E$
$(\partial K/\partial p)_q = 2qH$; $(\partial K/\partial q)_p = 2pH - E$; $(\partial K/\partial p)_{pq} = qE/p$
$(\partial^2 H/\partial q^2)_p = -2p(2pH - E)$; $(\partial^2 K/\partial q^2)_p = 2qE - 4p^2K$
$(\partial^2 H/\partial p^2)_{pq} = 2(p^2+q^2)E/p$; $(\partial^2 K/\partial p^2)_{pq} = 2q(p^2+q^2-1)E/p^2$

pairs of tables the columns correspond to the hyperbolas of Fig. 5, in the first pair the lines correspond to perpendiculars in the figure and in the second to rays from the origin.

But although by tabulating H and K instead of U and V, the violent oscillations characteristic of the latter would be avoided, nevertheless the rapid increase in $H(p,q)$ and $K(p,q)$ with increase in p would introduce another difficulty for the interpolator; for instance in the column $pq = 4\pi$ the value of $H(p,q)$ would be 0.0691 for $p = q = 3.55$ and 1.23×10^7 for $p = 5.01$. The best way to overcome this difficulty would be to tabulate the products of $H(p,q)$ and $K(p,q)$ into $e^{q^2-p^2}$ instead of the functions themselves, at all events for $p > q$; in such a table the entries 0.0691 for $p = 3.55$ and 0.0800 for $p = 5.01$ would replace those given above. This device may be illustrated by the case of $F(x)$, Tab. XXVIII; of course to find the values of the integral of $e^{x^2}.dx$ from the $F(x)$ table, e^{x^2} must be found by interpolation of a table of exponentials[1], but by means of the multiplication theorem for exponentials interpolation in the latter table can be effected as closely as de-

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[1] J. W. L. Glaisher: [Camb. Phil. Soc. Trans., 13, 243 (1883)] nine figures from $x = 0$ to $x = 500$; G. F. Becker and C. E. van Orstrand: [*Hyperbolic Functions*, Smithsonian Inst. (1909)] seven to nine figures from $x = 0$ to $x = 100$; F. W. Newman, see p. 2874 f. note.

sired. Similarly, by using tables of H and K to find[1] values of U and V, the difficulty of interpolating the latter functions would be avoided; as there are addition theorems for sines and cosines and excellent tables[2] of those functions.

Methods of evaluating $H(p,q)$ and $K(p,q)$ and for delimiting the values of p and q for which each method is available will now be explained; these are based on *approx.(c)* p. 2858, and *approx.(b)* p. 2858; the use of *approx.* (*a*) and *approx.(d)* is in general not advisable, although for very small values of p the latter might prove useful (see p. 2861 and Table XXI Nos. 6 and 7). By means of the relations given in Table XXII, any one of the four methods (viz. one based on *approx.b* and three on *approx.c*) can also be used to evaluate $U(p,q)$ and $V(p,q)$ and the integrals of Table XXII and Eqs. 128 and 129. The semi-convergent series obtained in the usual way by "integration-by-parts" are too clumsy for practical use, except in the special cases that $p=0$ (Probability Integral), $p=q$ (Fresnel Integrals, see Table XXIII) or $q=0$ (the Integral of $e^{x^2}.dx$, see Table XXV).

Evaluation of H(p,q) and K(p,q) by means of approx. (c) and (e)

To use *approx.*(*c*), K must be replaced by p, C by 1, and b^2 by p^2q^2 in Eqs. 110-112; the left hand member of each of these equations then becomes $H(p,q)$. If both sides of these equations be differentiated with respect to b as sole variable before the summations are made, the left hand member becomes twice $K(p,q)$; as the differentiation leaves all the exponentials unchanged, the statements as to relative error and maximum number of terms made below hold for $K(p,q)$ as well as for $H(p,q)$. Lower Boundaries for Eqs. 111 and 112 are found by Rule V, p. 2843, assuming that the error must not exceed one three-millionth part of the quantity to be computed, and are entered in Fig. 5.

Upper Boundary:—The hyperbola $q^2-p^2=15$ of Fig. 5 runs through values of p and q for which $e^{p^2-q^2}=0.3 \times 10^{-6}$. Since for $q \geqq p$, both $H(p,q)$ and $K(p,q)$ are less than $e^{p^2-q^2}$, this line constitutes a safe Boundary above which the values of both functions will be negligible if 0.3×10^{-6} is the accuracy postulated in fixing the other Boundaries of the figure.

Boundaries for (112):—In this equation, $H(p,q)$ is regarded as $\sqrt{\pi}/2pq$ times $R_1{:}[odd]\Psi c$ where $gx=0$, $l=p^2$ and $a=\pi^2/4p^2q^2$; Eq. 74 fixes $(R_2{:}\Theta c)/(R_1{:}\Theta c)$ as an upper limit to the relative error. Introducing the values of the constants, and noting that $e^{-15}=0.3 \times 10^{-6}$, this gives $e^{-3q^2} \leqq e^{-15}$, i.e. $q=2.24$ as the lowest value of q with which Eq. 112 can be relied upon to give the accuracy postulated. With this value of q only two terms of the Evanescent Series need be computed; with larger values of q the accuracy increases but so does the number of terms; when $q=4.5$, five terms may be needed, and for $q>4.5$ the approximations of (131) and (132) are preferable.

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[1] From Table XXII Nos. 1 and 2,

$$U(p, q) = \cos 2pq.\ H(p, q) + \sin 2pq.\ K(p, q).$$
$$V(p, q) = \sin 2pq.\ H(p, q) - \cos 2pq.\ K(p, q) + \sqrt{\pi}/2.$$

[2] The most complete are the fifteen-figure tables at intervals of 10 sec. by H. Andoyer: 'Nouvelles tables trigonométriques," 3 vols., (1916).

Boundaries for (111):—Here $H(p,q)$ is regarded as $\sqrt{\pi}/2pq$ times A: $[even]\Psi c$ where $gx=\pi/2$, $t=p^2$ and $a=\pi^2/16p^2q^2$; and Eq. 74 gives $e^{-8q^2}=e^{-15}$, i.e. $q=1.37$, as the lowest value permissible. Three terms are needed when $q=1.37$ and five when $q=2.24$; for $q>2.24$ the approximation of Eq. 112 is preferable.

Boundaries for (110):— Here $H(p,q)$ is regarded as $2\sqrt{a/\pi}$ times $A:[odd]\Psi c$ where $gx=2pq\sqrt{a}$, and $t=p^2$. To keep down the number of terms of the Evanescent Series that must be computed, a should be given the largest convenient value consistent with the accuracy desired. Eq. 74 gives $e^{-\pi^2/4p^2a}.e^{\pi q/p\sqrt{a}}=e^{-15}$; whence $p\sqrt{a}=\pi(\sqrt{q^2+15}-q)/30$ is the largest admissible value of $p\sqrt{a}$. With this value, five terms are needed if $q=0$, and seven if $q=1.37$; if $q>1.37$ the approximation of (111) is preferable.

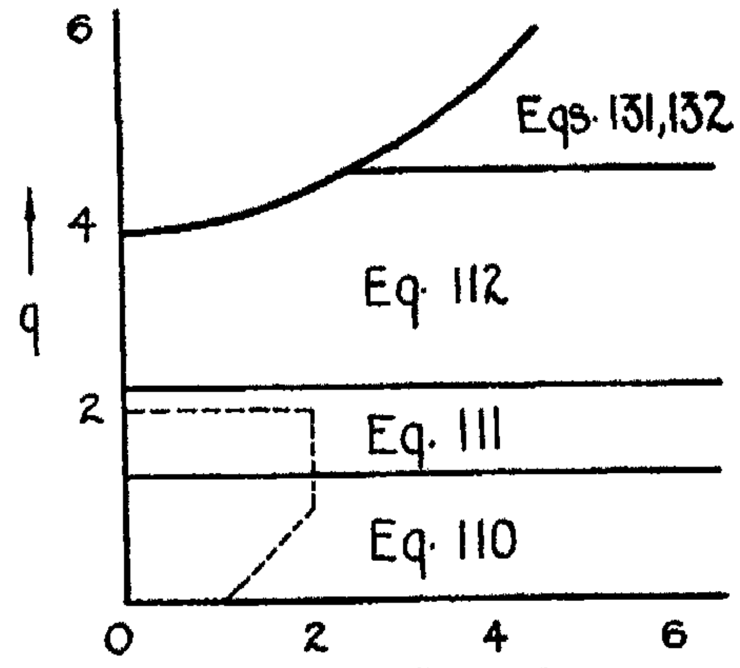

FIG. 5

Extension of the Boundaries (see *approx.e*, p. 2861):— The Remainder neglected in (112) is $(\sqrt{\pi}/2pq).(-R_2:[odd]\Psi c+R_3:[odd]\Psi c-+\ldots)$, and the quantity computed viz. $H(p,q)$, is $(\sqrt{\pi}/2pq).R_1:[odd]\Psi c$, in all of which $gx=0$, $t=p^2$, $a=\pi^2/4p^2q^2$ and $f(u)=e^u$. But since, by Tab. VIII, $R_2:[odd]\Psi c$ would be equal to $(1/2).R_1:[odd]\Psi c$ if in the latter q were replaced by $2q$, the first item of the Remainder neglected in (112) is nothing but $H(p,2q)$. If a table were being constructed, and $H(p,2q)$ had already been computed, its value might be added to the approximate value of $H(p,q)$ given by (112), thus reducing the error to that involved in the neglect of $(\sqrt{\pi}/2pq).(R_3.:[odd]\Psi c-R_4:[odd]\Psi c+-\ldots)$. For practical purposes this last expression may be replaced by its first term, which is nothing but $H(p,3q)$, and by Rule V this cannot exceed one three-millionth part of $H(p,q)$ if $q\geqq 1.37$. Thus if a table of $H(p,q)$ were being constructed beginning with high values of q, the entries already computed might be used to correct the erroneous values given by Eq. 112 when $q<2.24$, so that this eqation might be utilized for values of q as low as $q=1.37$. Thus the use of (111) might be dispensed with altogether, and the computation of five, four or three terms of the Evanescent of (111) might be replaced by that of two or one terms of the Evanescent of (112).

The Boundary of (111) can be extended in a similar manner from $q=1.37$ to $q=0.80$; in this case the saving may be considerable, since one to three terms of the Evanescent of (111) take the place of five to seven terms of the Evanescent of (110). The procedure consists in subtracting $H(p,3q)$ from the value of $H(p,q)$ given by (111).

The corresponding correction to (110) replaces the Evanescent Series of which five to seven terms must be computed by one of which three to five terms suffice. This it does by assigning to $\sqrt{a}$ a value fixed by $p\sqrt{a} = \pi(\sqrt{q^2+15} + q)/30$ instead of the value stated to be permissible under "Boundaries for (110)," and then correcting the erroneous value so obtained for $H(p,q)$ by adding $H(p, \pi - 2pq\sqrt{a}/2p)$ to it.

Evaluation of H(p,q) and K(p,q) by means of approx. (b)

To use *approx.*(*b*), the K of Eq. 107 must be replaced by p; if then the $f(x^2)$ be replaced by $e^{(1-\eta^2)x^2}.(\cos 2\eta x^2 - \eta.\sin 2\eta x^2)$ where $\eta=q/p$, the left hand member becomes $U(p,q)$; while if the $f(x^2)$ be replaced by $e^{(1-\eta^2)x^2}.(\eta.\cos 2\eta x^2 + \sin 2\eta x^2)$, it becomes $V(p,q)$.

Boundaries[1] *for* (131) *and* (132):—If the value allotted to the constant a be such that $p\sqrt{a}=0.45$, Rule I shews[2] that the error of the approximation cannot exceed $10^{-6}.(pq+p^2).e^{p^2-q^2}$, and Fig. 2 that not more than four terms of the Evanescent Series need be computed no matter what the values of p and q may be. A small decrease in the value allotted to a, which involves the computation of an extra term or two, greatly increases the accuracy (see Table XIV); for instance, if $p\sqrt{a}=0.30$ the possible error is one hundredth of that when $p\sqrt{a}=0.45$, and six terms will do.

The expression for the Stationary Series, however, is so complicated that in practice the use of *approx.*(*b*) is to be recommended only for values of p and q such that both the cosh and sinh of $q\pi/2p\sqrt{a}$ or $\pi/2\sqrt{a}$ (whichever is the smaller) may be replaced by the exponential; the error introduced by this replacement will not exceed one three-millionth part of the *cosh* or *sinh* if $p\sqrt{a} = 0.45$ and both p and q are greater than 2.15. The line $q=2.15$ and the line $p=2.15$ thus constitute a Boundary below and to the left of which the simplified form of *approx.*(*b*) is excluded if the postulated accuracy is to be attained; in practice, however, the Upper Boundary and the line $q=4.5$ may be taken, since it is at least as easy to compute five terms of the Evanescent of (112) as four terms of the Evanescent here considered.

Assuming that p and q are large enough to permit the substitution of exponentials for the hyperbolic sines and cosines (see above), the approximations to $H(p,q)$ and $K(p,q)$ which arise from *approx.*(*b*) are as given in (131) and (132). These equations were obtained as explained above from

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[1] For upper Boundary see p. 2869.

[2] Rule V is inapplicable, since $f(u)$ changes sign during the integration.

(107) by using the last column of Table XII*a* Nos. 5 and 6, and the relations between U, V, H and K given in Table XXII; the maximum error cannot exceed that given for $U(p,q)$ and $V(p,q)$ under "Boundaries for (131) and (132)."

$$H(p,q) \rightarrow 2\sqrt{\frac{a}{\pi}}\,.\,e^{p^2-q^2}\,.\sum\frac{(q^2/p^2+1-m^2a)\,.\,e^{-m^2ap^2}}{(m^2a+q^2/p^2-1)^2+4q^2/p^2} \qquad (131)$$

$$K(p,q) \rightarrow \frac{2q}{p}\sqrt{\frac{a}{\pi}}\,.\,e^{p^2-q^2}\,.\sum\frac{(q^2/p^2+1+m^2a)\,.\,e^{-m^2ap^2}}{(m^2a+q^2/p^2-1)^2+4q^2/p^2} \qquad (132)$$

Sec. 16: Three special cases

(a) The Fresnel Integrals[1]

In a table of C(x) or S(x) proceeding by equal increments of x, interpolation is quite impossible after the first few entries, for as one goes down the table the maxima and minima succeed each other with increasing frequency; in Ignatowski's Table, for example, the last two entries viz. C(8.4) = 0.4709 and C(8.5) = 0.5142 correspond to angles 152 degrees apart, and give no hint that C(8.426) = 0.4621. In tables proceeding by equal increments of the angle, i.e. of $\pi x^2/2$, the maxima and minima are equidistant throughout; and if the tabular difference is small enough interpolation is possible, as in the B.A. six-figure Table which contains 200 entries for the first three cycles.

TABLE XXIII: The Fresnel Integrals

$$\mathbf{C}(x) = \int_0^x \cos\tfrac{1}{2}\pi y.dy = \frac{1}{\sqrt{2\pi}}\int_0^{\pi x^2/2}\frac{\cos y}{\sqrt{y}}.dy = \tfrac{1}{2} + \frac{\mathbf{K}+\mathbf{H}}{\sqrt{\pi}}.\sin\frac{\pi x^2}{2} - \frac{\mathbf{K}-\mathbf{H}}{\sqrt{\pi}}.\cos\frac{\pi x^2}{2}$$

$$\mathbf{S}(x) = \int_0^x \sin\tfrac{1}{2}\pi y^2.dy = \tfrac{1}{2} - \frac{\mathbf{K}-\mathbf{H}}{\sqrt{\pi}}.\sin\frac{\pi x^2}{2} - \frac{\mathbf{K}+\mathbf{H}}{\sqrt{\pi}}.\cos\frac{\pi x^2}{2}$$

where $\mathbf{K} = K(x\sqrt{\pi}/2, x\sqrt{\pi}/2)$ and $\mathbf{H} = H(x\sqrt{\pi}/2, x\sqrt{\pi}/2)$; for numerical values of **H** and **K**, see Table XXIV.

In the tables of Gilbert and Ignatowski the value of C(x) is entered against the argument x; in Lommel's table and the B. A. table, the value of C($\sqrt{2x/\pi}$) is entered against x, i.e. C(x) is entered against $\pi x^2/2$.

Gilbert: Mém. cour. Acad. Brux. **31** (1863); Ignatowski: Ann. Physik, (4) **23**, 894 (1907); Lommel: Abh. Münch. Akad. (2) **15**, 120 (1886); Brit. Ass. Report, p. 273 (1926).

Table XXIV gives $(\mathbf{K}+\mathbf{H})/\sqrt{\pi}$ and $(\mathbf{K}-\mathbf{H})/\sqrt{\pi}$ to four places as functions of x from $x=0$ to $x=13$, i.e. for the first forty-two cycles; after $x=2$, linear interpolation is sufficient to ensure the fourth decimal. For values of x greater than 13, $(\mathbf{K}-\mathbf{H})/\sqrt{\pi}=0$ and $(\mathbf{K}+\mathbf{H})/\sqrt{\pi} = 1/\pi x$ exact to the fourth place. From this Table, by means of the relations given in Table XXIII, four-place values of C(x) and S(x) may be obtained for all values of x. This Table was computed from Gilbert's and Ignatowski's values of C(x) and S(x) by means of the relations given in Table XXIII; errors[2] in the original tables

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[1] The symbols *C S* H and K are defined in Table XXIII.

[2] Some of these, especially in Jahnke and Emde, are misprints. The true values are:— C(0.1) = 0.1000; C(0.8) = 0.7229; C(1.1) = 0.7638; C(1.6) = 0.6389; C(1.8) = 0.3337; C(4.5) = 0.5260; C(5.1) = 0.4998; C(7.3) = 0.5190.

TABLE XXIV; see Table XXIII

x	$\frac{(K+H)}{\sqrt{\pi}}$	$\frac{(K-H)}{\sqrt{\pi}}$	x	$\frac{(K+H)}{\sqrt{\pi}}$	$\frac{(K-H)}{\sqrt{\pi}}$	x	$\frac{(K+H)}{\sqrt{\pi}}$	$\frac{(K-H)}{\sqrt{\pi}}$
0.00	0.5000	0.5000	2.00	0.1566	0.0117	5.50	0.0578	0.0006
.05	.4982	.4520	2.10	.1495	.0104	5.60	.0568	.0006
.10	.4931	.4078	2.20	.1429	.0091	5.70	.0559	.0005
.15	.4855	.3674	2.30	.1369	.0081	5.80	.0549	.0005
.20	.4760	.3306	2.40	.1315	.0071	5.90	.0540	.0005
.25	.4649	.2972	2.50	.1264	.0062	6.00	.0531	.0005
.30	.4528	.2671	2.60	.1217	.0055	6.10	.0522	.0004
.35	.4399	.2398	2.70	.1172	.0050	6.20	.0514	.0004
.40	.4265	.2154	2.80	.1131	.0045	6.30	.0506	.0004
.45	.4129	.1934	2.90	.1093	.0041	6.40	.0498	.0004
.50	.3992	.1736	3.00	.1057	.0037	6.50	.0490	.0004
.55	.3856	.1560	3.10	.1023	.0033	6.60	.0482	.0004
.60	.3723	.1402	3.20	.0992	.0030	6.70	.0475	.0004
.65	.3593	.1261	3.30	.0962	.0027	6.80	.0468	.0004
.70	.3466	.1135	3.40	.0933	.0025	6.90	.0461	.0003
.75	.3343	.1022	3.50	.0907	.0023	7.00	.0455	.0003
.80	.3225	.0922	3.60	.0883	.0021	7.10	.0449	.0003
.85	.3112	.0833	3.70	.0859	.0019	7.20	.0443	.0003
.90	.3003	.0753	3.80	.0836	.0018	7.30	.0437	.0003
0.95	.2899	.0682	3.90	.0815	.0017	7.40	.0431	.0003
1.00	.2800	.0618	4.00	.0795	.0016	7.50	.0425	.0002
1.05	.2705	.0561	4.10	.0776	.0015	7.60	.0420	.0002
1.10	.2614	.0510	4.20	.0757	.0014	7.70	.0414	.0002
1.15	.2528	.0464	4.30	.0740	.0013	7.80	.0408	.0002
1.20	.2446	.0423	4.40	.0723	.0012	7.90	.0403	.0002
1.25	.2368	.0386	4.50	.0707	.0011	8.00	.0398	.0002
1.30	.2295	.0353	4.60	.0691	.0010	8.10	.0393	.0002
1.35	.2225	.0323	4.70	.0675	.0009	8.20	.0388	.0002
1.40	.2158	.0296	4.80	.0662	.0009	8.30	.0384	.0002
1.45	.2094	.0272	4.90	.0649	.0009	8.40	.0379	.0002
1.50	.2034	.0250	5.00	.0636	.0008	8.50	.0375	.0002
1.60	.1922	.0213	5.10	.0624	.0008	9.00	.0354	.0001
1.70	.1820	.0182	5.20	.0612	.0008	9.50	.0335	.0001
1.80	.1727	.0156	5.30	.0601	.0007	10.00	.0318	.0001
1.90	0.1643	0.0135	5.40	0.0589	0.0007	10.50	.0303	.0001
						11.00	.0289	.0001
						11.50	.0277	.0001
						12.00	.0265	.0001
						12.50	.0255	.0001
						13.00	0.0245	0.0000

For larger values of x,

$$\frac{K+H}{\sqrt{\pi}} = 1/\pi x; \quad \frac{K-H}{\sqrt{\pi}} = 0$$

are exact to four places.

were found by differencing **H** and **K** (to find them by differencing the original tables was of course quite impossible) and were corrected by computation as explained below; from $x=0$ to $x=1.5$ Gilbert's tabular interval was halved, partly by interpolation and partly by independent computation of the series.

For the first three cycles the B.A. Table gives six-place values; ten-figure values might be obtained, if needed, from the twelve-place Bessel Functions (B.A. Report for 1925 p. 221) as explained on p. 273 of the Report for 1926. For higher values of x, Eqs. 131 and 132 may be used; for this purpose both p and q must be replaced by $x\sqrt{\pi}/2$, whereupon the left hand members become the **H** and **K** respectively of Tables XXIII and XXIV.

Example 24:—The last entry in the B.A. Table gives $C(\sqrt{40\cdot\pi})=0.580389$ and $S(\sqrt{40\cdot\pi})=0.461646$. Choosing $a=0.01$, seven terms of (131) give $\mathbf{H} = 0.0769\ 5320\ 488$ and seven terms of (132) give $\mathbf{K} = 0.0808\ 7033\ 962$ with a possible error well under 10^{-11}. From these, $C(\sqrt{40\cdot\pi})=0.58038\ 89720$ and $S(\sqrt{40\cdot\pi}) = 0.46164\ 57788$, which agree to the last place with the figures obtained by adding (in each case) twenty-two 12-figure Bessel Functions.

(16b) The function $F(\mathbf{x})=e^{-x^2}.\int_0^x e^{y^2}.dy$

The advantage which a table of $F(x)$ has over one of the integral[1] of $e^{x^2}.dx$ consists in the facility with which the former may be interpolated, as has already been pointed out. The function $F(x)$ occurs in the P-approximations to Φ_E when $gx=0$ and $f(u)=e^{-b^2u}$ (see Table XI Nos. 6 and 7, and Ex. 7) and in the Original Integral when $f(u) = 1/\sqrt{b^2+u}$, $F(\sqrt{b^2u})$ or $e^{b^2u^2}$ (see Table XIII Nos. 2, 5 and 6, and Ex. 11, 12 and 17); also in the Poisson Form of Θ_F (see Eqs. 35 and 36) and in the Poisson Form of Λ_F when $F(\lambda)$ is any odd integral power of λ. The integral of $F(x).dx$ occurs in the Poisson Form of Λ_F when $F(\lambda)$ is any even integral power of λ; it cannot be reduced to known forms and is untabulated. The integral of Eq. 133, viz. twice $A:[even]\Phi s(1)$, needed in finding the error of the P-approximation to Φ_F (see p. 2824) may be evaluated by replacing $F(x)$ by the semiconvergent series of Table XXV No. 3, since only small values of T need be considered; this gives:

$$\int_0^T F(X/2\sqrt{t})/\sqrt{t}.dt \longrightarrow T/X + T^2/X^3 + 4T^3/X^5 + 30T^4/X^7 + \ldots \quad (133)$$

The numerical values of $F(x)$ given in Table XXVIII were obtained as follows:— From $x=0$ to $x=2$ from Dawson's six-figure Table[2] of the integral of $e^{x^2}.dx$ and Newman's Table[3] of e^{-x}. From $x=2$ to $x=4$ nine-figure values at intervals of 0.2, and from $x=4$ to $x=6$ ten-figure values at intervals of 0.5, were computed by Eq. 134.

$$F(x)\rightarrow(\sqrt{\pi}/2).e^{-x^2}.\tan\,\pi/2\sqrt{a} - 2\sqrt{a/\pi}.\Sigma e^{-m^2ax^2}/(m^2a-1) \quad (134)$$

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[1] For tables to convert the first function into the other, see footnote p. 2868.

[2] H. G. Dawson: Proc. London Math. Soc., 29, 519 (1898).

[3] F. W. Newman: Camb. Phil. Soc. Trans., 13, 145 (1883); 12-18 decimal places; intervals of .001 from x = 0 to 15.35, of .002 to 17.30, of .005 to 27.64, of .01 to 37.0.

TABLE XXV: The function F

1. $F(x) = e^{-x^2}.\int_0^x e^{y^2}.dy = \frac{1}{2}e^{-x^2}.\int_0^{x^2}\frac{e^y}{\sqrt{y}}.dy$

2. $\quad = x(1 - 2x^2/3 + 4x^4/15 - 8x^6/105 + 16x^8/945 - \ldots)$

3. $\quad = 1/2x + 1/4x^3 + 3/8x^5 + 15/16x^7 + 105/32x^9 + \ldots$ (semi-convergent)

4. $F(ix) = i.e^{x^2}.\int_0^x e^{-y^2}.dy$ 5. $d.F(x)/dx = 1 - 2x.F(x)$

6. $\int F(\sqrt{x}).dx = \sqrt{x} - F(\sqrt{x})$

7.[1] $\int_0^t \{F(\sqrt{x}).dx/\sqrt{t-x}\} = (\pi/2).(1 - e^{-t})$

8. $\iint F(x).dx.dx = F(x) - x + 2x.\int F(x).dx$

9. At $x = 0.9241\ 3887$, $F(x)$ has its maximum value viz. $1/2x = 0.5410\ 4422$.

10. At $x = 1.501976$, $F(x)$ has a point of inflexion; here $F(x) = x/(2x^2 - 1) = 0.427686$.

which may be obtained from Eq. 107 by writing y for x and x for K and then replacing $f(y^2)$ by $e^{-(x^2-y^2)}$. In each computation a was given the value $0.1/x^2$, so that the error of the approximation was always less than 5×10^{-12}; seven terms of the Evanescent Series were needed to ensure accuracy in the tenth decimal place. From $x=6$ to $x=10$ at intervals of 0.5, and for $x=11$ and $x=12$, ten-figure values were computed by the semi-convergent series of Table XXV No. 3; at $x=6$ the value given by ten terms of the series agreed to the tenth decimal place with that obtained from (134), at $x=12$ only six terms were needed.

Intermediate values were obtained by means of Eq. 135, which is nothing but Taylor's theorem,

$$F(x+0.01) - F(x) = 0.01[d\,F(x)/dx] + 0.0005[d^2F(x)/dx^2] + \ldots \qquad (135)$$

$$= (10^{-9}/3).(29998000 - 299975x + 2000x^2 - 10x^3)$$

$$- (10^{-9}/3).F(x).(299985 + 59994000x - 599940x^2 + 4000x^3 - 20x^4)$$

and similar equations for $F(x+0.05)$ etc. when $x>4$. The two power-series were computed from their differences, on the adding machine; Eq. 135 proved a rapid means of interpolation as well as an independent check on the accuracy of the nine and ten-figure numbers.

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[1] This form occurs as P:[*odd*]Φc with $f(u) = 16C/\pi^2$ times the H of Eq. 89, in computing the concentration of hydrogen dissolved in the catholyte during the electrolysis of acid copper sulphate solutions by currents above the limiting current. The relation given above may be established by expanding $F(\sqrt{x})$ by No. 2, integrating term by term and replacing the definite integrals so obtained by their known values from de Haan: loc. cit., Table VII).

The integral of $F(x).dx$ might be obtained by tabular integration of Table XXVIII, computing as a check a few points by the integral of Table XXV No. 2 or No. 3, or by Eq. 136. For large values of the upper limit K, the integral approaches infinity; for these high values it would be better to tabulate $\int F(x).dx - (1/2).\log K$ which becomes constant.

$$\int_0^K F(x).dx \rightarrow \sqrt{\frac{\pi}{2}}.\tan\frac{\pi}{2\sqrt{a}}.\int_0^K e^{-y^2}.dy + \frac{2}{\sqrt{\pi}}.\sum\frac{1}{m(m^2a-1)}.\int_{mK\sqrt{a}}^{\infty} e^{-y^2}.dy - \sum\frac{1}{m(m^2a-1)} \qquad (136)$$

Eq. 136 was obtained by integrating (134); its error (see Eq. 108) is less than $(1/8a).\int_0^{2K\sqrt{a}} \mathrm{G}(y^2).dy$ which in turn, if $2K\sqrt{a} \leqq 1$, is less than $(1/8a).\int_0^{2K\sqrt{a}} \mathrm{G}(y).dy$; Table XXVII shews that if $K\sqrt{a} \leqq 0.5$, this latter quantity is less than $2 \times 10^{-7}.K^2$. If a be given the value $0.25/K^2$, four terms of the Evanescent Series (viz. the first on the right of Eq. 136) are sufficient to ensure accuracy in the sixth decimal place; the sum of the other series may be found from Table XVIII No. 7.

Example 25:—To evaluate $\int_0^1 F(x).dx$. Choosing $a = 0.16$ the error of the approximation will be less than 10^{-6}. The value of the first term on the right of (136) is 0.66185 5656; the sum of six terms of the Evanescent Series is −0.61222 7917. By Table XVIII No. 7, the *sum of the other series is given by* $C/2-(\pi/4).\tan 5\pi/4+\psi(2.5)-0.5\psi(1.25) = 0.32009\text{-}3076$; the value of $\psi(2.5)$ viz. 0.70315 6641, was taken from the B.A. table of the logarithmic derivate of the Gamma-Function; that of $\psi(1.25)$ viz. −0.22745 3532, was obtained from Legendre's table of $\log_{10}\Gamma$ (tabular difference 0.005) by means of the formula

$$0.005\psi(1.25) = 2.30258\ 5093(\Delta-\Delta^2/2+\Delta^3/3-\Delta^4/4)$$

The value so found for the integral is 0.3697 2082, which is the same as that obtained by integrating Table XXV No. 2 between the limits 0 and 1. By choosing the value 1/9 for a, interpolation in the $\log\Gamma$ table might have been avoided, but two more terms of the Evanescent would have had to be computed.

(16c) The functions $\mathrm{G}(x)$ and $\int \mathrm{G}(x).dx$ (defined in Tab. XXVI, No. 1)

Table XXVI Nos. 2 and 3 follow from Eqs. 44, 45 and 47 if in the latter $f(u) = 1$. No. 4 was obtained by integrating by parts the integral on the right of No. 1; it is useful in computing $\mathrm{G}(x)$ when x is small. Nos. 5 and 6

TABLE XXVI: The Function G

1. $\mathrm{G}(x) = \int_0^x \frac{e^{-\pi^2/y}}{\sqrt{y}}.dy = 2\sqrt{x}.e^{-\pi^2/x} - 4\pi.\int_{\pi/\sqrt{x}}^{\infty} e^{-y^2}.dy$
2. R_{na}: [*odd or even*]$\Phi c(1) = (\overline{n\pi-gx}/8a\sqrt{\pi}).\mathrm{G}(4\pi^2at/\overline{n\pi-gx}^2)$
3. R_{nb}: [*odd or even*]$\Phi c(1) = (\overline{n\pi+gx}/8a\sqrt{\pi}).\mathrm{G}(4\pi^2at/\overline{n\pi+gx}^2)$
4. $\mathrm{G}(x) = (x^{3/2}/\pi^2).e^{-\pi^2/x}.(1-3x/2\pi^2+3.5.x^2/4\pi^4-3.5.7.x^3/8\pi^6+\ldots)$
5. $\sqrt{\pi}.\mathrm{G}(x) = x/2 + \pi^2/6 - \sqrt{\pi x} - \sum e^{-n^2x}/n^2 - \sqrt{\pi}.\sum_{n=1}^{\infty} n.\mathrm{G}(x/n^2)$
6. $\sqrt{\pi}.\mathrm{G}(4x) = x - \pi^2/6 + 2.\sum(-1)^{n+1}.e^{-n^2x}/n^2 - \sqrt{\pi}.\sum_{n=2} m.\mathrm{G}(4x/m^2)$

are special cases of (112*a*) and (111) respectively; to obtain No. 5 from (112*a*) replace K^2 by x and b^2 by π^2, and then take the limit when $C \rightarrow 0$, noting that when $y \rightarrow 0$ $F(y) \rightarrow y$; to obtain No. 6 from (111) replace K^2 by x and b^2 by $\pi^2/4$, and then let $C \rightarrow 0$.

From Table XXVI No. 4 it follows that for $x \leqq 0.4$, $G(x) < 0.5 \times 10^{-13}$; so that for $x/4 \leqq 0.4$, the last series on the right of No. 5 may be neglected in computing $G(x)$ without affecting the twelfth decimal. Similarly, if $4x/9 = 0.4$, values of $G(4x)$ may be found with the same degree of accuracy from No. 6 without taking account of the last series on the right of that equation. As pointed out in Part V, p. 2861, the other series in Nos. 5 and 6 consist of the same terms with different signs; advantage was taken of this to lessen the labour of computing Table XXVII.

For values of the argument (viz. $4x$) above 3.6, the first terms of the last series of No. 6 must be taken into account; up to $4x/9 = 0.6$, i.e. arguments up to 5.4, this term may conveniently be computed by No. 4, for higher values No. 5 may be used; it is not practical to attempt to find it by interpolating in the table of $G(x)$.

The Table of the Integral of $G(x).dx$ has been used to find an upper limit to the error of Eq. 136, see p. 2876. The approximations used in computing this Table were obtained by integrating Table XXVI Nos. 5 and 6 term by term.

TABLE XXVII; see Table XXV

x	$G(x)$	$\int_0^x G(y) \, . \, dy$
0.4	0.00000 000000	0.00000 000000
.5	.00000 000009	.00000 000000
.6	.00000 000311	.00000 000009
.7	.00000 004060	.00000 000164
.8	.00000 028555	.00000 001469
0.9	.00000 132598	.00000 008436
1.0	.00000 459578	.00000 035270
1.1	.00001 285787	.00000 116795
1.2	.00003 060092	.00000 323816
1.3	.00006 425453	.00000 781629
1.4	.00012 219418	.00001 689656
1.5	.00021 456279	.00003 340114
1.6	.00035 296323	.00006 134233
1.7	.00055 008046	.00010 595024
1.8	.00081 928415	.00017 376096
1.9	.00117 424853	.00027 266581
2.0	.00162 861296	.00041 192438
2.1	.00219 569515	.00060 214629
2.2	.00288 826095	.00085 524702
2.3	.00371 834885	.00118 438351
2.4	.00469 714441	.00160 387475
2.5	0.00583 489801	0.00212 911208

TABLE XXVIII; see Table XXV

x	F(x)	x	F(x)	x	F(x)
0.00	0.000 000	0.35	0.322 770	0.70	0.510 503
.01	.009 999	.36	.330 451	.71	.513 286
.02	.019 995	.37	.338 010	.72	.515 926
.03	.029 981	.38	.345 447	.73	.518 428
.04	.039 957	.39	.352 759	.74	.520 789
.05	.049 917	.40	.359 943	.75	.523 013
.06	.059 857	.41	.366 999	.76	.525 100
.07	.069 771	.42	.373 924	.77	.527 050
.08	.079 660	.43	.380 717	.78	.528 866
.09	.089 516	.44	.387 375	.79	.530 549
.10	.099 336	.45	.393 899	.80	.532 101
.11	.109 117	.46	.400 285	.81	.533 523
.12	.118 854	.47	.406 533	.82	.534 816
.13	.128 545	.48	.412 641	.83	.535 981
.14	.138 185	.49	.418 609	.84	.537 021
.15	.147 769	.50	.424 436	.85	.537 937
.16	.157 297	.51	.430 120	.86	.538 732
.17	.166 762	.52	.435 662	.87	.539 406
.18	.176 162	.53	.441 059	.88	.539 960
.19	.185 492	.54	.446 311	.89	.540 399
20	.194 751	.55	.451 418	.90	.540 724
21	.203 933	.56	.456 380	.91	.540 934
.22	.213 037	.57	.461 195	.92	.541 034
.23	.222 058	.58	.465 864	.93	.541 025
.24	.230 993	.59	.470 386	.94	.540 910
.25	.239 839	.60	.474 763	.95	.540 688
.26	.248 593	.61	.478 993	.96	.540 363
.27	.257 253	.62	.483 076	.97	.539 938
.28	.265 814	.63	.487 013	.98	.539 414
.29	.274 275	.64	.490 803	.99	.538 793
.30	.282 631	.65	.494 448	1.00	.538 080
.31	.290 882	.66	.497 947	1.01	.537 272
.32	.299 023	.67	.501 303	1.02	.536 375
.33	.307 054	.68	.504 513	1.03	.535 388
0.34	0.314 970	0.69	0.507 580	1.04	0.534 317

TABLE XXVIII (Continued)

x	$F(x)$	x	$F(x)$	x	$F(x)$
1.05	0.533 162	1.40	0.456 507	1.75	0.359 436
1.06	.531 925	1.41	.453 718	1.76	.356 865
1.07	.530 609	1.42	.450 918	1.77	.354 313
1.08	.529 216	1.43	.448 107	1.78	.351 780
1.09	.527 748	1.44	.445 286	1.79	.349 266
1.10	.526 207	1.45	.442 458	1.80	.346 773
1.11	.524 595	1.46	.439 624	1.81	.344 299
1.12	.522 915	1.47	.436 785	1.82	.341 846
1.13	.521 169	1.48	.433 942	1.83	.339 413
1.14	.519 359	1.49	.431 096	1.84	.337 001
1.15	.517 487	1.50	.428 249	1.85	.334 609
1.16	.515 555	1.51	.425 401	1.86	.332 239
1.17	.513 566	1.52	.422 555	1.87	.329 891
1.18	.511 521	1.53	.419 710	1.88	.327 563
1.19	.509 423	1.54	.416 869	1.89	.325 258
1.20	.507 273	1.55	.414 032	1.90	.322 974
1.21	.505 075	1.56	.411 199	1.91	.320 712
1.22	.502 829	1.57	.408 373	1.92	.318 471
1.23	.500 537	1.58	.405 554	1.93	.316 253
1.24	.498 202	1.59	.402 742	1.94	.314 057
1.25	.495 827	1.60	.399 940	1.95	.311 883
1.26	.493 412	1.61	.397 146	1.96	.309 730
1.27	.490 960	1.62	.394 364	1.97	.307 600
1.28	.488 472	1.63	.391 592	1.98	.305 491
1.29	.485 950	1.64	.388 832	1.99	.303 405
1.30	.483 397	1.65	.386 085	2.00	.3013 4039
1.31	.480 814	1.66	.383 351	2.01	.2992 9770
1.32	.478 203	1.67	.380 630	2.02	.2972 7683
1.33	.475 566	1.68	.377 925	2.03	.2952 7771
1.34	.472 904	1.69	.375 234	2.04	.2933 0025
1.35	.470 219	1.70	.372 559	2.05	.2913 4438
1.36	.467 513	1.71	.369 900	2.06	.2894 0998
1.37	.464 787	1.72	.367 258	2.07	.2874 9696
1.38	.462 043	1.73	.364 633	2.08	.2856 0519
1.39	0.459 283	1.74	0.362 026	2.09	0.2837 3456

TABLE XXVIII (Continued)

x	$F(x)$	x	$F(x)$	x	$F(x)$
2.10	0.2818 8494	2.45	0.2290 2237	2.80	0.1935 5072
2.11	.2800 5618	2.46	.2278 0728	2.81	.1927 1599
2.12	.2782 4815	2.47	.2266 0607	2.82	.1918 8940
2.13	.2764 6069	2.48	.2254 1854	2.83	.1910 7083
2.14	.2746 9364	2.49	.2242 4449	2.84	.1902 6015
2.15	.2729 4686	2.50	.2230 8372	2.85	.1894 5724
2.16	.2712 2016	2.51	.2219 3605	2.86	.1886 6198
2.17	.2695 1338	2.52	.2208 0128	2.87	.1878 7427
2.18	.2678 2634	2.53	.2196 7922	2.88	.1870 9398
2.19	.2661 5886	2.54	.2185 6968	2.89	.1863 2100
2.20	.2645 1076	2.55	.2174 7248	2.90	.1855 5523
2.21	.2628 8185	2.56	.2163 8743	2.91	.1847 9656
2.22	.2612 7194	2.57	.2153 1434	2.92	.1840 4488
2.23	.2596 8084	2.58	.2142 5305	2.93	.1833 0009
2.24	.2581 0834	2.59	.2132 0337	2.94	.1825 6208
2.25	.2565 5426	2.60	.2121 6512	2.95	.1818 3075
2.26	.2550 1839	2.61	.2111 3814	2.96	.1811 0602
2.27	.2535 0053	2.62	.2101 2225	2.97	.1803 8777
2.28	.2520 0048	2.63	.2091 1727	2.98	.1796 7592
2.29	.2505 1802	2.64	.2081 2305	2.99	.1789 7037
2.30	.2490 5296	2.65	.2071 3942	3.00	.1782 7103
2.31	.2476 0508	2.66	.2061 6622	3.01	.1775 7781
2.32	.2461 7418	2.67	.2052 0328	3.02	.1768 9063
2.33	.2447 6005	2.68	.2042 5046	3.03	.1762 0940
2.34	.2433 6247	2.69	.2033 0758	3.04	.1755 3403
2.35	.2419 8125	2.70	.2023 7451	3.05	.1748 6443
2.36	.2406 1616	2.71	.2014 5109	3.06	.1742 0054
2.37	.2392 6701	2.72	.2005 3716	3.07	.1735 4226
2.38	.2379 3358	2.73	.1996 3260	3.08	.1728 8952
2.39	.2366 1567	2.74	.1987 3724	3.09	.1722 4225
2.40	.2353 1306	2.75	.1978 5095	3.10	.1716 0036
2.41	.2340 2554	2.76	.1969 7359	3.11	.1709 6378
2.42	.2327 5292	2.77	.1961 0502	3.12	.1703 3244
2.43	.2314 9499	2.78	.1952 4511	3.13	.1697 0627
2.44	0.2302 5154	2.79	0.1943 9372	3.14	0.1690 8519

TABLE XXVIII (Continued)

x	$F(x)$	x	$F(x)$	x	$F(x)$
3.15	0.1684 6914	3.50	0.1496 2159	3.85	0.1347 9616
3.16	.1678 5806	3.51	.1491 4969	3.86	.1344 1797
3.17	.1672 5186	3.52	.1486 8097	3.87	.1340 4202
3.18	.1666 5050	3.53	.1482 1539	3.88	.1336 6826
3.19	.1660 5390	3.54	.1477 5294	3.89	.1332 9669
3.20	.1654 6200	3.55	.1472 9357	3.90	.1329 2729
3.21	.1648 7474	3.56	.1468 3724	3.91	.1325 6003
3.22	.1642 9206	3.57	.1463 8393	3.92	.1321 9490
3.23	.1637 1390	3.58	.1459 3361	3.93	.1318 3187
3.24	.1631 4021	3.59	.1454 8623	3.94	.1314 7092
3.25	.1625 7091	3.60	.1450 4177	3.95	.1311 1204
3.26	.1620 0597	3.61	.1446 0020	3.96	.1307 5521
3.27	.1614 4532	3.62	.1441 6149	3.97	.1304 0041
3.28	.1608 8890	3.63	.1437 2561	3.98	.1300 4762
3.29	.1603 3668	3.64	.1432 9252	3.99	.1296 9682
3.30	.1597 8858	3.65	.1428 6221	4.00	.1293 4800
3.31	.1592 4457	3.66	.1424 3463	4.05	.1276 3291
3.32	.1587 0458	3.67	.1420 0977	4.10	.1259 6466
3.33	.1581 6858	3.68	.1415 8759	4.15	.1243 4125
3.34	.1576 3651	3.69	.1411 6807	4.20	.1227 6082
3.35	.1571 0833	3.70	.1407 5117	4.25	.1212 2159
3.36	.1565 8398	3.71	.1403 3688	4.30	.1197 2192
3.37	.1560 6343	3.72	.1399 2517	4.35	.1182 6023
3.38	.1555 4662	3.73	.1395 1601	4.40	.1168 3504
3.39	.1550 3351	3.74	.1391 0937	4.45	.1154 4494
3.40	.1545 2406	3.75	.1387 0524	4.50	.1140 8861
3.41	.1540 1822	3.76	.1383 0358	4.55	.1127 6478
3.42	.1535 1596	3.77	.1379 0437	4.60	.1114 7227
3.43	.1530 1722	3.78	.1375 0759	4.65	.1102 0993
3.44	.1525 2198	3.79	.1371 1322	4.70	.1089 7668
3.45	.1520 3019	3.80	.1367 2122	4.75	.1077 7151
3.46	.1515 4180	3.81	.1363 3158	4.80	.1065 9343
3.47	.1510 5679	3.82	.1359 4428	4.85	.1054 4151
3.48	.1505 7511	3.83	.1355 5929	4.90	.1043 1487
3.49	0.1500 9672	3.84	0.1351 7659	4.95	0.1032 1266

TABLE XXVIII (Continued)

x	$F(x)$	x	$F(x)$	x	$F(x)$
5.00	0.1021 34075	6.50	0.0778 67819	8.50	0.0592 39372
5.05	.1010 78338	6.55	.0772 58604	8.60	.0585 40837
5.10	.1000 44714	6.60	.0766 58970	8.70	.0578 58698
5.15	.0990 32499	6.65	.0760 68689	8.80	.0571 92381
5.20	.0980 41020	6.70	.0754 87541	8.90	.0565 41338
5.25	.0970 69629	6.75	.0749 15314	9.00	.0559 05047
5.30	.0961 17708	6.80	.0743 51800	9.10	.0552 83008
5.35	.0951 84665	6.85	.0737 96800	9.20	.0546 74744
5.40	.0942 69931	6.90	.0732 50120	9.30	.0540 79801
5.45	.0933 72961	6.95	.0727 11573	9.40	.0534 97743
5.50	.0924 93232	7.00	.0721 80975	9.50	.0529 28153
5.55	.0916 30242	7.05	.0716 58150	9.60	.0523 70632
5.60	.0907 83507	7.10	.0711 42927	9.70	.0518 24800
5.65	.0899 52563	7.15	.0706 35139	9.80	.0512 90290
5.70	.0891 36965	7.20	.0701 34625	9.90	.0507 66751
5.75	.0883 36283	7.25	.0696 41228	10.00	.0502 53847
5.80	.0875 50104	7.30	.0691 54795	10.20	.0492 58670
5.85	.0867 78032	7.35	.0686 75179	10.40	.0483 02328
5.90	.0860 19682	7.40	.0682 02235	10.60	.0473 82583
5.95	.0852 74686	7.45	.0677 35825	10.80	.0464 97363
6.00	.0845 42689	7.50	.0672 75812	11.00	.0456 44752
6.05	.0838 23347	7.60	.0663 74453	11.20	.0448 22974
6.10	.0831 16331	7.70	.0654 97146	11.40	.0440 30378
6.15	.0824 21320	7.80	.0646 42932	11.60	.0432 65432
6.20	.0817 38007	7.90	.0638 10903	11.80	.0425 26708
6.25	.0810 66094	8.00	.0630 00199	12.00	0.0418 12876
6.30	.0804 05295	8.10	.0622 10002		
6.35	.0797 55332	8.20	.0614 39539		
6.40	.0791 15936	8.30	.0606 88074		
6.45	0.0784 86849	8.40	0.0599 54907		

CONTENTS

ABBREVIATIONS:—$m = 2n - 1$; $a = g^2k$; $g = \pi/2l$; $\Sigma = \sum_1^\infty$; → means "is approximately equal to"

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THE DEFINITION AND EVALUATION OF THE FUGACITY OF AN ELEMENT OR COMPOUND IN THE GASEOUS STATE

BY G. TUNELL

The purpose of this paper is to show that in reality the definition of the fugacity function of Lewis depends on a physical hypothesis (experimental fact) in addition to the hypothesis that the volume of unit mass, e.g. one mol or one gram, of the element or compound in the gaseous state is a single-valued continuous function of the temperature and the pressure. The additional physical hypothesis is well founded experimentally and the fugacity defined on the basis of it is undoubtedly a useful function.

The fact that the definition of fugacity presupposes a hypothesis not presupposed in the definition of Lewis's free energy (Gibbs's zeta function) has been concealed, however, by Lewis and Randall's derivations in which they step over the limitation that division by zero is not a process defined in algebra and thus are apparently able to present as a theorem from their definition of fugacity a relation that cannot be proved from their definition of fugacity; in reality the relation in question must be taken as the definition of fugacity, and from it the relation called by Lewis and Randall the first part of their definition of fugacity follows as a theorem.

Lewis has stated his aim as follows:

"In . . . . more exact investigations the old approximate equations of thermodynamic chemistry will no longer suffice. We must either turn to the precise, but rather abstruse, equations of entropy and the thermodynamic potential, or modify the methods which are in more common use, in such a way as to render them exact. . . . The aim. . . . is to develop by familiar methods a systematic set of thermodynamic equations entirely similar in form to those which are now in use, but rigorously exact."[1]

"The great utility of this new quantity will be shown to lie in the fact that the approximate equations containing the vapor pressure and developed rigorously except for the assumption that the vapor pressure obeys the gas law, may be replaced by exact equations of the same form or of equal simplicity containing the fugacity instead of the vapor pressure."[2]

Lewis's aim was good and the function that he invented on the basis of his wide experience in chemical thermodynamics is undoubtedly valuable, but the derivations of Lewis and Randall discussed in this paper have caused confusion and perplexity in the minds of many readers. The definition and derivations given in the following pages are exactly consistent with Lewis and

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[1] G. N. Lewis: Outlines of a new system of thermodynamic chemistry, Proc. Am. Acad., 43, 260 (1907).

[2] G. N. Lewis: The law of physico-chemical change, Proc. Am. Acad., 37, 55 (1901).

Randall's physical hypotheses,[3] and this definition gives to the fugacity the properties that, it is evident from their writings, Lewis, and Lewis and Randall intend it to have, at the same time removing the difficulties introduced by Lewis and Randall's erroneous derivations. The definition of fugacity given in this paper shows how the physical hypothesis (experimental fact) in addition to the hypothesis that the volume of unit mass of the element or compound in the gaseous state is a single-valued continuous function of the temperature and the pressure contributes to the fugacity the properties found by Lewis although he does not make clear how it comes to have them.

Lewis and Randall[4] say: "We may partially define the fugacity, f, in terms of the molal free energy, F, through the equation

$$F = RT \ln f + B, \tag{1}$$

where B is defined no further than by the statement that it is a function of temperature only, or in other words, that it is a constant at a single temperature." R denotes the gas constant; T, the absolute thermodynamic temperature; ln f, the natural logarithm of f. "Between two isothermal states this equation becomes

$$F_B - F_A = RT \ln \frac{f_B}{f_A}. \tag{2}$$

"We see that these equations do not determine the numerical value of the fugacity, but only determine the ratio of the fugacities of a substance in two isothermal states. We may therefore complete the definition *by assigning at each temperature a numerical value to the fugacity in some one state.*" (Italics by the author of this paper.)

"We have found .... the difference in free energy of a perfect gas between two different pressures, at the same temperature, namely,

$$F_B - F_A = RT \ln \frac{P_B}{P_A},$$

and comparing this with Equation 2, we see that the fugacity of a perfect gas is proportional to its pressure.

"Now, at least theoretically, every substance can be brought isothermally into the state of a perfect gas. For, if we admit that every substance at a finite temperature has a finite vapor pressure, then if the pressure upon a substance is decreased without limit the substance will eventually vaporize, and with further diminution in pressure the vapor will approach nearer and nearer to the condition of a perfect gas.

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[3] One of the physical hypotheses made by Lewis and Randall is now known to be in error. Cf. L. J. Gillespie, J. Am. Chem. Soc., 48, 30 (1926). The definitions and derivations of the author of this paper, however, apply both to real gases and to hypothetical gases fulfilling the erroneous hypothesis of Lewis and Randall. In other words the necessary change in this hypothesis does not affect the theory of the fugacity, and this hypothesis need not be discussed at length in this paper, although the true situation in respect to it is indicated.

[4] G. N. Lewis and M. Randall: "Thermodynamics and the Free Energy of Chemical Substances," p. 191 (1923).

"Therefore instead of completing our definition of fugacity by assigning to it some arbitrary value in a chosen state, such as the liquid state at one atmosphere, it is better to complete the definition by making the fugacity of a perfect gas equal to the pressure. Fugacity will be regarded as having the same dimensions as pressure, and the unit of fugacity will be the atmosphere."

The statement of Lewis and Randall that their partial definition of the fugacity, f, by the equation

$$\text{(A)} \qquad \mathrm{F}(\mathrm{T},\mathrm{P}) - \mathrm{F}(\mathrm{T},\mathrm{P}') = \mathrm{RT} \ln \frac{\mathrm{f}(\mathrm{T},\mathrm{P})}{\mathrm{f}(\mathrm{T},\mathrm{P}')},$$

where P′ denotes any constant pressure greater than zero, can be completed by making the fugacity of a perfect gas equal to the pressure, that is, by assigning the value zero to the fugacity at zero pressure at each temperature, will now be examined.

It should be noted that Lewis and Randall do not assume that any real gas becomes perfect at any pressure above zero, but explicitly assume the contrary. Thus they write:[5] "We find in plotting the isotherm of an imperfect gas. . . . that $\alpha[\alpha \equiv \mathrm{RT}/\mathrm{P} - \mathrm{v}]$ always approaches a constant value at low pressures. In other words, at constant temperature and at low pressures there is a constant difference between the actual volume and the volume calculated by the gas law." In accordance with these statements of Lewis and Randall, the following physical hypothesis is made in this paper:

$$\text{(I)}^{6} \qquad \lim_{\mathrm{P} \doteq 0} \left(\frac{\mathrm{RT}'}{\mathrm{P}} - \mathrm{v} \right) = \mathrm{K}(\mathrm{T}'),$$

where T′ denotes any constant temperature greater than absolute zero; P, the pressure; v, the volume; K(T′), at each constant temperature greater than absolute zero a constant different from zero except at the Boyle temperature (not the same constant at different temperatures). Lewis and Randall[7] and the author also assume that

$$\text{(II)} \qquad \lim_{\mathrm{P} \doteq 0} \frac{\mathrm{Pv}}{\mathrm{T}'} = \mathrm{R}.$$

Lewis and Randall[8] write: "the molal free energy of a gas approaches an infinite negative value as the pressure approaches zero." As applied to a real gas this statement is a theorem derived mathematically from the first and second laws of thermodynamics and the additional physical hypothesis of Lewis and Randall that

$$\lim_{\mathrm{P} \doteq 0} \left(\frac{\mathrm{RT}'}{\mathrm{P}} - \mathrm{v} \right) = \mathrm{K}(\mathrm{T}').$$

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[5] Lewis and Randall: Op. cit., p. 197.

[6] Equations with Arabic numbers are Lewis and Randall's equations and the Arabic numbers are Lewis and Randall's numbers; equations with capital letters are equations used in the critical analysis of Lewis and Randall's definition and evaluations; equations with Roman numbers are steps in the rigorous derivations of the results of Lewis and Randall worked out by the author of this paper.

[7] Op. cit., p. 197.

[8] Idem, p. 190.

A proof of this theorem by the author of this paper is as follows. Lewis's molal free energy, F, (Gibbs's zeta function for one mol) is defined by the equation

$$\mathrm{F} = \mathrm{E} + \mathrm{P}\mathrm{v} - \mathrm{T}\mathrm{s},$$

where E denotes the molal internal energy; P, the pressure; v, the molal volume; T, the absolute thermodynamic temperature; s, the molal entropy. Thus

$$\left(\frac{\partial \mathrm{F}}{\partial \mathrm{P}}\right)_{\mathrm{T}} = \left(\frac{\partial \mathrm{E}}{\partial \mathrm{P}}\right)_{\mathrm{T}} + \mathrm{P}\left(\frac{\partial \mathrm{v}}{\partial \mathrm{P}}\right)_{\mathrm{T}} + \mathrm{v} - \mathrm{T}\left(\frac{\partial \mathrm{s}}{\partial \mathrm{P}}\right)_{\mathrm{T}}.$$

The first law of thermodynamics for reversible processes (continuous series of equilibrium states) in one-component systems of one phase is embodied in the following equation

$$\text{(III)}\quad \mathrm{E}(\mathrm{T},\mathrm{P}) - \mathrm{E}(\mathrm{T}_0,\mathrm{P}_0) = \int_{(\mathrm{T}_0,\mathrm{P}_0)}^{(\mathrm{T},\mathrm{P})} \left(\mathrm{C_P} - \mathrm{P}\left(\frac{\partial \mathrm{v}}{\partial \mathrm{T}}\right)_{\mathrm{P}}\right) d\mathrm{T} + \left(\mathrm{L_P} - \mathrm{P}\left(\frac{\partial \mathrm{v}}{\partial \mathrm{P}}\right)_{\mathrm{T}}\right) d\mathrm{P},$$

which is also written in the more familiar but less explicit form

$$\text{(IV)}\qquad \mathrm{E}(\mathrm{T},\mathrm{P}) - \mathrm{E}\ (\mathrm{T}_0,\mathrm{P}_0) = \int_{(\mathrm{T}_0,\mathrm{P}_0)}^{(\mathrm{T},\mathrm{P})} d\mathrm{Q} - d\mathrm{w},$$

the integral in each of the equations, (III) and (IV), being extended over any path in the domain, $0<\mathrm{T}<\infty$, $0<\mathrm{P}\leqq\phi(\mathrm{T})$, connecting the points $(\mathrm{T}_0,\mathrm{P}_0)$ and (T,P); where Q denotes the heat received (heat of the path); w, the work done (work of the path); $\mathrm{C_P}$, the molal heat capacity; $\mathrm{L_P}$,[9] the molal latent heat of change of pressure at constant temperature; E, the molal internal energy; and $\mathrm{P}=\phi(\mathrm{T})$, $0<\mathrm{T}<\infty$, is the equation of the boundary of the stability field of the gas separating it from the stability fields of solid and liquid. The physical hypothesis (experimental fact) embodied in each of the equations, (III) and (IV), may be stated in words as follows: The value of the integral in each of the equations, (III) and (IV), is independent of the choice of the path of integration in the domain, $0<\mathrm{T}<\infty$, $0<\mathrm{P}\leqq\phi(\mathrm{T})$, that is, it depends only on the limits of integration, and the integral may therefore be used to define a function, the molal internal energy, of the independent variables, T and P. By the definition of Q for this system

$$\text{(V)}\qquad \mathrm{Q} = \int_{(\mathrm{T}_0,\mathrm{P}_0)}^{(\mathrm{T},\mathrm{P})} d\mathrm{Q} = \int_{(\mathrm{T}_0,\mathrm{P}_0)}^{(\mathrm{T},\mathrm{P})} \mathrm{C_P}\, d\mathrm{T} + \mathrm{L_P}\, d\mathrm{P},$$

the values of the integals in (V) depending on the choice of the path of integration. By the definition of w for this system

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[9] The latent heat of change of pressure at constant temperature is denoted by l_p by several authors but is denoted here by $\mathrm{L_P}$ in conformity with Lewis and Randall's denotation of molal quantities by small capital letters. $\mathrm{L_P}$ must not be confused with Lewis and Randall's L, which denotes the molal relative heat content.

$$\text{(VI)} \qquad w = \int_{(T_o,P_o)}^{(T,P)} dw = \int_{(T_o,P_o)}^{(T,P)} P dv = \int_{(T_o,P_o)}^{(T,P)} P\left(\frac{\partial v}{\partial T}\right)_P dT + P\left(\frac{\partial v}{\partial P}\right)_T dP,$$

the values of the integrals in (VI) depending on the choice of the path of integration. Thus equation (IV) may be brought readily into the form (III) by means of (V) and (VI). From (III) it follows directly[10] that

$$\left(\frac{\partial E}{\partial P}\right)_T = L_P - P\left(\frac{\partial v}{\partial P}\right)_T.$$

The second law of thermodynamics for reversible processes (continuous series of equilibrium states) in one-component systems of one phase is embodied in the following equation

$$\text{(VII)} \qquad s(T,P) - s(T_o,P_o) = \int_{(T_o,P_o)}^{(T,P)} \frac{C_P}{T} dT + \frac{L_P}{T} dP, \text{[11]}$$

which is also written in the more familiar but less explicit form

$$\text{(VIII)} \qquad s(T,P) - s(T_o,P_o) = \int_{(T_o,P_o)}^{(T,P)} \frac{dQ}{T},$$

the integral being extended over any path in the domain, $o < T < \infty$, $o < P \leqq \phi(T)$, connecting the points, (T_o,P_o) and (T,P); where s denotes the molal entropy. The physical hypothesis (experimental fact) embodied in each of the equations, (VII) and (VIII), may be stated in words as follows: The value of the integral in each of the equations, (VII) and (VIII), is independent of the choice of the path of integration in the domain, $o < T < \infty$, $o < P \leqq \phi(T)$, that is, it depends only on the limits of integration, and the integral may therefore be used to define a function, the molal entropy, of the independent variables, T and P. Equation (VIII) may be brought readily into the form (VII) by means of (V). From (VII) it follows directly that

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[10] W. F. Osgood: "Lehrbuch der Funktionentheorie," 5. Aufl., Bd.1, S. 138-150 (1928); "Advanced Calculus," pp. 228-230 (1925).

[11] The first and second laws of thermodynamics are expressed in this form, which is the standard mathematical form for the representation of a line integral that is independent of the path, first because the physical law is thus exhibited explicitly, and second because it is from these two equations that all of the thermodynamic relations for the system in question are deduced. A necessary and sufficient condition for (III) is

$$\text{(III')} \qquad \left[\frac{\partial\left(C_P - P\left(\frac{\partial v}{\partial T}\right)_P\right)}{\partial P}\right]_T = \left[\frac{\partial\left(L_P - P\left(\frac{\partial v}{\partial P}\right)_T\right)}{\partial T}\right]_P.$$

Likewise a necessary and sufficient condition for (VII) is

$$\text{(VII')} \qquad \left[\frac{\partial\left(\frac{C_P}{T}\right)}{\partial P}\right]_T = \left[\frac{\partial\left(\frac{L_P}{T}\right)}{\partial T}\right]_P.$$

From these two equations, (III') and (VII'), all of the relations for this system summarized in P. W. Bridgman's "Condensed Collection of Thermodynamic Formulas" (1925) are obtained.

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{L_P}{T}.$$

Substituting the values of $(\partial E/\partial P)_T$ and $(\partial S/\partial P)_T$ in the equation for $(\partial F/\partial P)_T$ obtained by differentiating with respect to the pressure the equation of definition of F, one therefore obtains the equation

$$\text{(IX)} \qquad \left(\frac{\partial F}{\partial P}\right)_T = v.$$

Integrating this equation with respect to the pressure, one obtains

$$\begin{aligned} F(T,P) - F(T,P') &= \int_{P'}^{P} v\,dP \\ &= \int_{P'}^{P} \left\{\frac{RT}{P} - \frac{RT}{P} + v\right\} dP \\ &= RT \ln\frac{P}{P'} - \int_{P'}^{P} \left(\frac{RT}{P} - v\right) dP. \end{aligned}$$

Now let P approach zero as a limit[12] in the equation

$$F(T',P) - F(T',P') = RT' \ln\frac{P}{P'} - \int_{P'}^{P} \left(\frac{RT'}{P} - v\right) dP,$$

where T' denotes a constant greater than zero and P' denotes a constant greater than zero. Then the first term of the right hand member of this equation becomes negatively infinite and the last term of the right hand member approaches a limit since $(RT/P - v)$ is continuous in the domain, $0 < T < \infty$, $0 < P \leqq \phi(T)$, and

$$\text{(I)} \qquad \lim_{P \doteq 0} \left(\frac{RT'}{P} - v\right) = K(T').$$

Therefore $F(T',P)$ becomes negatively infinite when P approaches zero as a limit.

Lewis and Randall's equation of definition of the ratio of the fugacities in two isothermal states may be set in the following form,

$$f(T,P) = f(T,P')e^{\frac{F(T,P) - F(T,P')}{RT}}$$

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[12] The fact that v becomes infinite is not sufficient to prove that

$$\int_{P'}^{P} v\,dP$$

becomes negatively or positively infinite when P approaches zero as a limit. An example of an integral that approaches a limit when the upper limit of integration approaches zero as a limit although the integrand becomes infinite is the following

$$\lim_{x \doteq 0} \int_{1}^{x} \frac{dx}{\sqrt{x}} = -2.$$

and P allowed to approach zero as a limit. Then from the fact stated by Lewis and Randall and proved above that the molal free energy becomes negatively infinite when the pressure approaches zero as a limit, it follows that

$$\lim_{P \doteq 0} f(T',P) = f(T',P') \left\{ \lim_{P \doteq 0} e^{\frac{\mathrm{F}(T',P) - \mathrm{F}(T',P')}{RT'}} \right\}$$
$$= 0,$$

where T′ denotes a constant greater than zero and P′ denotes a constant greater than zero. Thus the fugacity may be defined on the boundary, $P = 0,\ 0 < T < \infty$, by the equation

$$\text{(B)} \qquad f(T,0) = 0.$$

Suppose that the standard state at any temperature be chosen as the state of zero pressure. Lewis and Randall[13] state that: "in the limit, when P^* [P of this paper] $= 0$, we know that f^* [f(T,P) of this paper] $= P^*$ by the definition of fugacity," and according to them this choice of the standard state together with their equation of definition of the ratio of the fugacities in two isothermal states

$$\text{(A)} \qquad \mathrm{F}(T,P) - \mathrm{F}(T,P') = RT \ln \frac{f(T,P)}{f(T,P')}$$

determines the value of f in any other state, that is, for any other values of T and P. This is plainly not the case. In the first place Lewis and Randall's equation of definition of the ratio of the fugacities in two isothermal states will not give the ratio of the fugacities in the two isothermal states, (T′,P′) and (T′,0), T′, a constant greater than zero, P′, a constant greater than zero, since the molal free energy becomes negatively infinite when the pressure approaches zero as a limit and thus the molal free energy is not defined in the state, (T′,0). In the second place the equations

$$\frac{f(T',0)}{f(T',P')} = 0,$$

and

$$f(T',0) = 0$$

do not fix the value of f(T′,P′).

From Lewis and Randall's equation of definition of the ratio of the fugacities in two isothermal states and the relation

$$\left(\frac{\partial \mathrm{F}}{\partial P}\right)_T = v,$$

they conclude[14] that

$$\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{v}{RT},$$

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[13] Op. cit., p. 193.

[14] Lewis and Randall: Op. cit., p. 192.

and hence[15]

$$\mathrm{RT}\ \ln\frac{f(T,P')}{f(T,P)} = \int_{P}^{P'} v\mathrm{dP}.$$

Lewis and Randall[16] define the function, α, by the equation

$$\alpha = \frac{RT}{P} - v.$$

Thus

$$\mathrm{RT}\ \ln\frac{f(T,P')}{f(T,P)} = \int_{P}^{P'}\left\{\frac{RT}{P} - \alpha\ (T,P)\right\}\mathrm{dP}$$

$$= \mathrm{RT}\ \ln\frac{P'}{P} - \int_{P}^{P'}\alpha\ (T,P)\ \mathrm{dP}.$$

Hence

$$\mathrm{RT}\ \ln f(T,P') = \mathrm{RT}\ \ln P' + \mathrm{RT}\ \ln\frac{f(T,P)}{P} - \int_{P}^{P'}\alpha\ (T,P)\ \mathrm{dP}$$

Lewis and Randall allow P to approach zero as a limit. Thus

$$\mathrm{RT'}\ \ln f(T',P') = \mathrm{RT'}\lim_{P \doteq 0}\ln\frac{f(T',P)}{P}$$

$$+ \mathrm{RT'}\ \ln P' - \lim_{P \doteq 0}\int_{P}^{P'}\alpha\ (T',P)\ \mathrm{dP},$$

where T′ denotes a constant greater than zero and P′ denotes a constant greater than zero. From the fact stated by Lewis and Randall that: "in the limit, when P* [P of this paper] = 0, we know that f* [f(T,P) of this paper] = P* by the definition of fugacity," they conclude[17] that

$$\mathrm{RT}\ \ln f(T,P) = \mathrm{RT}\ \ln P - \int_{0}^{P}\alpha\ (T,P)\ \mathrm{dP}. \tag{14}$$

This equation, however, does not follow mathematically from the definition laid down and the hypotheses made explicitly by Lewis and Randall. The ratio

$$\frac{f(T,P)}{P}$$

is not defined when P = 0, since division by zero is not a process defined in algebra. Nor does the theorem that the limit of the quotient of two variables is equal to the quotient of the limits of the two variables apply when the

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[15] Idem, p. 193.

[16] Idem, p. 194.

[17] Lewis and Randall: Op. cit., p. 195.

limit of the variable in the denominator is zero. When numerator and denominator both approach zero as a limit, their ratio may approach any limit whatever, or it may increase beyond all limit, or finally, although remaining finite, that is, always lying between two fixed numbers, it may jump about and so fail to approach a limit. Lewis and Randall[15] make no attempt to prove that the limit of the indeterminate form is one

$$\text{(C)} \qquad \lim_{P \doteq 0} \frac{f(T',P)}{P} = 1.$$

As a matter of fact there is no way of proving that the limit of the indeterminate form is one

$$\text{(C)} \qquad \lim_{P \doteq 0} \frac{f(T',P)}{P} = 1.$$

from Lewis and Randall's equation of definition of the ratio of the fugacities in two isothermal states

$$\text{(A)} \qquad \mathrm{F}(T,P) - \mathrm{F}(T,P') = RT \ln \frac{f(T,P)}{f(T,P')}$$

and assignment of the value zero to the function f(T,P) when P = 0,

$$\text{(B)} \qquad f(T,0) = 0$$

and therefore it does not follow mathematically from equations (A) and (B) that

$$\text{(D)} \qquad RT \ln f(T,P) = RT \ln P - \int_0^P \alpha\,(T,P)\,dP.$$

The reason why it is impossible to prove equations (C) and (D) from equations (A) and (B) is that equations (A) and (B) would be satisfied by an infinite number of possible continuous functions of the temperature, T, and pressure, P, that would not satisfy equations (C) and (D). For example, the function, f′, defined by the equations

$$RT \ln f'(T,P) = K' + RT \ln P - \int_0^P \alpha\,(T,P)\,dP$$

and

$$f'\,(T,0) = 0,$$

where K′ denotes any constant not equal to zero, satisfies equations (A) and (B) when f′ is substituted for f, but does not satisfy equations (C) and (D). Thus equations (A) and (B) are not sufficient conditions to establish the truth of equations (C) and (D).

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[15] In their chapter entitled "The Fugacity" (Thermodynamics and the Free Energy of Chemical Substances, pp. 190-202), which is devoted to the definition and evaluation of the fugacity and its partial derivatives, Lewis and Randall do not even state that the limit of the indeterminate form, f(T′,P)/P, is one,

$$\lim_{P \doteq 0} \frac{f(T',P)}{P} = 1.$$

Of all the possible functions that would satisfy equation (A), the one that has the properties it is evidently the intention of Lewis[19] and of Lewis and Randall[20] that the fugacity should have is the function, f(T,P) defined by the equation

$$\mathrm{RT} \ln f(\mathrm{T},\mathrm{P}) = \mathrm{RT} \ln \mathrm{P} - \int_0^{\mathrm{P}} \left(\frac{\mathrm{RT}}{\mathrm{P}} - v\right) d\mathrm{P},\ 0 < \mathrm{T} < \infty,\ 0 < \mathrm{P} \leqq \phi(\mathrm{T}),$$

where $\mathrm{P} = \phi(\mathrm{T})$, $0 < \mathrm{T} < \infty$, is the equation of the boundary of the stability field of the gas separating it from the stability fields of solid and liquid. It is possible to define a function of the temperature and pressure by this equation because of the physical hypothesis (experimental fact) that

$$\text{(I)} \qquad \lim_{\mathrm{P} \doteq 0} \left(\frac{\mathrm{RT}'}{\mathrm{P}} - v\right) = \mathrm{K}(\mathrm{T}'),$$

where T′ denotes any constant temperature greater than absolute zero, and K(T′) denotes at a given temperature a constant different from zero except at the Boyle temperature. This physical hypothesis (experimental fact) of course is not presupposed in the definition of Lewis's free energy.

In this paper the author therefore adopts as the definition of the fugacity, f, the equation

$$\text{(X)} \quad \mathrm{RT} \ln f(\mathrm{T},\mathrm{P}) = \mathrm{RT} \ln \mathrm{P} - \int_0^{\mathrm{P}} \left(\frac{\mathrm{RT}}{\mathrm{P}} - v\right) d\mathrm{P},\ 0 < \mathrm{T} < \infty,\ 0 < \mathrm{P} \leqq \phi(\mathrm{T}),^{21}$$

It follows immediately from this definition of fugacity that

$$\lim_{\mathrm{P} \doteq 0} f(\mathrm{T}',\mathrm{P}) = 0,$$

where T′ denotes a constant greater than zero, and that

$$\lim_{\mathrm{P} \doteq 0} \frac{f(\mathrm{T}',\mathrm{P})}{\mathrm{P}} = \lim_{\mathrm{P} \doteq 0} e^{-\frac{1}{\mathrm{RT}'} \int_0^{\mathrm{P}} \alpha(\mathrm{T}',\mathrm{P})\, d\mathrm{P}};$$

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[19] In "The law of physico-chemical change" (Proc. Am. Acad., 37, 68 (1901)) Lewis writes

$$\mathrm{RT} \ln \psi = \mathrm{RT} \ln \mathrm{P} - \mathrm{A}_{\infty}$$

where ψ denotes the fugacity, and "A_{∞} represents the total area bounded by the line MN [the isobar of the pressure P] and the curves MM′ [the isotherm of the imperfect gas] and NN′ [the hyperbola the equation of which is $\mathrm{P}v = \mathrm{RT}'$] each produced to infinity." He does not write this equation as the definition of fugacity, however.

[20] Lewis and Randall (Op. cit., p. 195) also write

$$\mathrm{RT} \ln f = \mathrm{RT} \ln \mathrm{P} - \int_0^{\mathrm{P}} \alpha\, d\mathrm{P}$$

although they do not give this equation as the definition of fugacity.

[21] It may be noted in passing that

$$f(\mathrm{T},\mathrm{P}) \neq e^{F/(\mathrm{RT})};$$

the function $e^{F/(\mathrm{RT})}$ depends on the integration constants of energy and entropy whereas the fugacity, f(T,P), does not; moreover f(T,P) has the dimensions of pressure whereas $e^{F/(\mathrm{RT})}$ is a pure number.

(XI) $$\lim_{P \doteq 0} \frac{f(T',P)}{P} = 1.$$

Since the volume of one mol of the element or compound in the gaseous state is assumed to be a single-valued continuous function of the temperature, T, and pressure, P, in the domain, $0<T<\infty$, $0<P\leqq\phi(T)$, therefore the fugacity is also a single-valued continuous function of the temperature, T, and pressure, P, in this domain. This conclusion is based on two additional physical hypotheses that are obviously true physically, and on two theorems. These hypotheses and theorems will be stated in this paragraph. The first theorem is as follows. The difference of two functions each of which is continuous in a domain is continuous in the same domain.[22] Thus $\alpha(T,P)$ is continuous in the domain, $0<T<\infty$, $0<P\leqq\phi(T)$. The physical hypothesis has already been made that

$$\lim_{P \doteq 0} \alpha\,(T',P) = K(T'),$$

where T′ denotes any constant temperature greater than absolute zero and K(T′) denotes at a given temperature a constant different from zero except at the Boyle temperature, and therefore α may be defined on the boundary, $P=0$, $0<T<\infty$, by the equation,

$$\alpha(T,0) = K(T),$$

where K(T) is some single-valued function of the temperature, T. The two additional physical hypotheses will now be made that K(T) is a continuous function of the temperature, T, in the interval, $0<T<\infty$, and that $\alpha(T,P)$ is a continuous function of the temperature, T, and pressure, P, in the domain, $0<T<\infty$, $0\leqq P\leqq\phi(T)$. The second theorem is as follows. If $\alpha(T,P)$ is a continuous function of the two independent variables, T and P, in the domain, $0<T<\infty$, $0\leqq P\leqq\phi(T)$, then the integral

$$\int_0^P \alpha(T,P)dP$$

is a continuous function of the two independent variables, T and P, in the same domain.[23] Therefore the fugacity, f, is a single-valued continuous function of T and P in the domain, $0<T<\infty$, $0<P\leqq\phi(T)$.

The definition of the fugacity may be extended over the boundary, $P=0$, $0<T<\infty$, by the equation

(XII) $$f(T,0) = 0,\ 0<T<\infty.$$

The fugacity is then continuous on the boundary, $P=0$, $0<T<\infty$.

The equation of definition of the fugacity may thus be given also in the following slightly different form

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[22] W. F. Osgood: "Lehrbuch der Funktionentheorie," 5. Aufl., Bd. 1, S. 12.

[23] W. F. Osgood: "Lehrbuch der Funktionentheorie," 5. Aufl., Bd. 1, S. 123.

$$\text{(XIII)}\qquad f(T,P)=Pe^{-\frac{1}{RT}\int_0^P \alpha(T,P)\,dP},\ 0<T<\infty,\ 0\leqq P\leqq \phi(T).$$

When $P=0$, this equation reduces to $f(T,0)=0$, $0<T<\infty$, which is equation (XII).

Differentiating $f(T,P)$ with respect to P holding T fast, one obtains

$$\text{(XIV)}\qquad RT\left(\frac{\partial \ln f}{\partial P}\right)_T = v.$$

It has already been proved that

$$\text{(IX)}\qquad \left(\frac{\partial F}{\partial P}\right)_T = v.$$

Therefore from the definition of fugacity adopted in this paper it follows that

$$\text{(XV)}\quad F(T,P)-F(T,p)=RT\ln\frac{f(T,P)}{f(T,p)},\ 0<T<\infty,\ 0<P\leqq\phi(T),\ 0<p\leqq\phi(T),$$

where P and p denote the pressures constituting the limits of integration. Thus equations (XV) and (XII) are necessary conditions, although, as has already been proved in this paper, they are not sufficient conditions,[24] to establish the truth of equation (XIII). In equation (XV), T, P, and p are independent variables; therefore one may differentiate both sides with respect to T holding P and p fast.

The partial derivative with respect to temperature of the logarithm of the fugacity, $(\partial \ln f/\partial T)_P$, will next be evaluated by two methods, the first method being a completion of the incomplete derivation of Lewis and Randall, the second a shorter and entirely independent method. In the first method use is made of certain points proved in the second method. The second method is, however, complete in itself and does not depend on any results obtained in the first method.

First method of evaluation of $(\partial \ln f/\partial T)_P$. In the attempt to evaluate $(\partial \ln f/\partial T)_P$ by the method of Lewis and Randall let the differentiation just mentioned be carried out. Thus

$$\left(\frac{\partial F(T,P)}{\partial T}\right)_P-\left(\frac{\partial F(T,p)}{\partial T}\right)_p = RT\left(\frac{\partial}{\partial T}\ln\frac{f(T,P)}{f(T,p)}\right)_{P,p}+R\ln\frac{f(T,P)}{f(T,p)}$$
$$=RT\left(\frac{\partial \ln f(T,P)}{\partial T}\right)_P-RT\left(\frac{\partial \ln f(T,p)}{\partial T}\right)_p+\frac{F(T,P)-F(T,p)}{T}.$$

From the definition of Lewis's free energy it follows that

$$\left(\frac{\partial F}{\partial T}\right)_P=\left(\frac{\partial E}{\partial T}\right)_P+P\left(\frac{\partial V}{\partial T}\right)_P-T\left(\frac{\partial S}{\partial T}\right)_P-S.$$

From equation (III) it follows directly that

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[24] It was proved that equations (A) and (B) are not sufficient conditions to establish the truth of equations (C) and (D); this is equivalent to proof that equations (XV) and (XII) are not sufficient conditions to establish the truth of equation (XIII).

$$\left(\frac{\partial \mathrm{E}}{\partial \mathrm{T}}\right)_{\mathrm{p}} = \mathrm{c_p} - \mathrm{P}\left(\frac{\partial \mathrm{v}}{\partial \mathrm{T}}\right)_{\mathrm{p}},$$

and from equation (VII) that

$$\left(\frac{\partial \mathrm{s}}{\partial \mathrm{T}}\right)_{\mathrm{p}} = \frac{\mathrm{c_p}}{\mathrm{T}}.$$

Hence

$$\left(\frac{\partial \mathrm{F}}{\partial \mathrm{T}}\right)_{\mathrm{p}} = -\,\mathrm{s}.$$

Thus

$$-\mathrm{s}(\mathrm{T},\mathrm{P}) + \mathrm{s}(\mathrm{T},\mathrm{p}) = \mathrm{RT}\left(\frac{\partial \ln \mathrm{f}(\mathrm{T},\mathrm{P})}{\partial \mathrm{T}}\right)_{\mathrm{P}} - \mathrm{RT}\left(\frac{\partial \ln \mathrm{f}(\mathrm{T},\mathrm{p})}{\partial \mathrm{T}}\right)_{\mathrm{p}} + \frac{\mathrm{F}(\mathrm{T},\mathrm{P}) - \mathrm{F}(\mathrm{T},\mathrm{p})}{\mathrm{T}}.$$

And, since

$$\mathrm{F} = \mathrm{H} - \mathrm{Ts},$$

where H denotes Lewis's molal heat content (Gibbs's chi function for one mol, molal enthalpy, molal total heat, molal enkaumy), therefore

$$\frac{-\,\mathrm{H}(\mathrm{T},\mathrm{P}) + \mathrm{H}(\mathrm{T},\mathrm{p})}{\mathrm{RT}^2} = \left(\frac{\partial \ln \mathrm{f}(\mathrm{T},\mathrm{P})}{\partial \mathrm{T}}\right)_{\mathrm{P}} - \left(\frac{\partial \ln \mathrm{f}(\mathrm{T},\mathrm{p})}{\partial \mathrm{T}}\right)_{\mathrm{p}}.$$

Since the natural logarithm of zero is not defined, and since $\mathrm{f}(\mathrm{T},0) = 0$, therefore

$$\left(\frac{\partial \ln \mathrm{f}(\mathrm{T},\mathrm{p})}{\partial \mathrm{T}}\right)_{\mathrm{p}}$$

is not defined when $\mathrm{p} = 0$. Moreover the fact that

$$\left(\frac{\partial\, \mathrm{f}(\mathrm{T},\mathrm{p})}{\partial \mathrm{T}}\right)_{\mathrm{p}}\Bigg|_{\substack{\mathrm{T}=\mathrm{T}'\\ \mathrm{p}=0}} = 0$$

affords no help here, because

$$\left(\frac{\partial \ln \mathrm{f}(\mathrm{T},\mathrm{p})}{\partial \mathrm{T}}\right)_{\mathrm{p}} = \frac{1}{\mathrm{f}(\mathrm{T},\mathrm{p})}\left(\frac{\partial\, \mathrm{f}(\mathrm{T},\mathrm{p})}{\partial \mathrm{T}}\right)_{\mathrm{p}}$$

and the right hand member of the last equation is also not defined when $\mathrm{p} = 0$. However, p may be allowed to approach zero as a limit. Thus

$$\lim_{\mathrm{p}\doteq 0}\left\{\frac{-\,\mathrm{H}(\mathrm{T}',\mathrm{P}) + \mathrm{H}(\mathrm{T}',\mathrm{p})}{\mathrm{RT}'^2}\right\} = \lim_{\mathrm{p}\doteq 0}\left\{\left(\frac{\partial \ln \mathrm{f}(\mathrm{T},\mathrm{P})}{\partial \mathrm{T}}\right)_{\mathrm{P}}\Bigg|_{\mathrm{T}=\mathrm{T}'} - \left(\frac{\partial \ln \mathrm{f}(\mathrm{T},\mathrm{p})}{\partial \mathrm{T}}\right)_{\mathrm{p}}\Bigg|_{\mathrm{T}=\mathrm{T}'}\right\}.$$

Now $\mathrm{H}(\mathrm{T},\mathrm{P})$ and

$$\left(\frac{\partial \ln \mathrm{f}(\mathrm{T},\mathrm{P})}{\partial \mathrm{T}}\right)_{\mathrm{P}}$$

do not depend on p and may be taken out of the braces:

$$\frac{-\,\mathrm{H}(\mathrm{T}',\mathrm{P})}{\mathrm{RT}'^2} + \lim_{\mathrm{p}\doteq 0}\frac{\mathrm{H}(\mathrm{T}',\mathrm{p})}{\mathrm{RT}'^2} = \left(\frac{\partial \ln \mathrm{f}(\mathrm{T},\mathrm{P})}{\partial \mathrm{T}}\right)_{\mathrm{P}}\Bigg|_{\mathrm{T}=\mathrm{T}'} - \lim_{\mathrm{p}\doteq 0}\left(\frac{\partial \ln \mathrm{f}(\mathrm{T},\mathrm{p})}{\partial \mathrm{T}}\right)_{\mathrm{p}}\Bigg|_{\mathrm{T}=\mathrm{T}'}.$$

It will be proved further on that

$$\lim_{p \doteq 0} \mathrm{H}(T',p) = h(T'),$$

where h(T) denotes a function of the temperature, T, continuous in the interval, $0 < T < \infty$. Hence

$$\frac{-\mathrm{H}(T',P) + h(T')}{RT'^2} = \left(\frac{\partial \ln f(T,P)}{\partial T}\right)_P \Bigg|_{T=T'} - \lim_{p \doteq 0} \left(\frac{\partial \ln f(T,p)}{\partial T}\right)_p \Bigg|_{T=T'}.$$

It remains to be proved that

$$\lim_{p \doteq 0} \left(\frac{\partial \ln f(T,p)}{\partial T}\right)_p \Bigg|_{T=T'} = \lim_{p \doteq 0} \frac{1}{f(T',p)} \left(\frac{\partial f(T,p)}{\partial T}\right)_p \Bigg|_{T=T'} = 0.$$

The first factor of the product

$$\frac{1}{f(T',p)} \left(\frac{\partial f(T,p)}{\partial T}\right)_p \Bigg|_{T=T'}$$

becomes infinite; therefore it is not obvious that the product approaches zero as a limit, and this must be proved. Differentiating the equation of definition of f

$$RT \ln f(T,p) = RT \ln p - \int_0^p \alpha(T,p)\,d\,p$$

with respect to T holding p fast, one obtains

$$R \ln f(T,p) + RT\left(\frac{\partial \ln f(T,p)}{\partial T}\right)_p = R \ln p - \left(\frac{\partial}{\partial T}\int_0^p \alpha(T,p)dp\right)_p;$$

$$R \ln \frac{f(T,p)}{p} + RT\left(\frac{\partial \ln f(T,p)}{\partial T}\right)_p = -\left(\frac{\partial}{\partial T}\int_0^p \alpha(T,p)dp\right)_p.$$

Now

$$\int_0^0 \alpha(T,p)dp = 0$$

and

$$\left(\frac{\partial}{\partial T}\int_0^p \alpha(T,p)dp\right)_p \Bigg|_{p=0} = 0.$$

In a second method of evaluation of $(\partial \ln f/\partial T)_P$, presented at the conclusion of this method, it will be proved that

$$\left(\frac{\partial}{\partial T}\int_0^p \alpha(T,p)dp\right)_p$$

is continuous on the boundary, $p = 0, 0 < T < \infty$. Therefore

$$\lim_{p \to 0}\left(\frac{\partial}{\partial T}\int_0^p \alpha(T,p)dp\right)_p\Bigg|_{T=T'} = 0.$$

It has already been proved from the equation of definition of f given in this paper that

$$\lim_{p \to 0}\frac{f(T',p)}{p} = 1.$$

Therefore allowing p to approach zero as a limit holding T fast, one has

$$RT' \lim_{p \to 0}\left(\frac{\partial \ln f(T,p)}{\partial T}\right)_p\Bigg|_{T=T'} = -R \lim_{p \to 0} \ln \frac{f(T',p)}{p}$$

$$-\lim_{p \to 0}\left(\frac{\partial}{\partial T}\int_0^p \alpha(T,p)dp\right)_p\Bigg|_{T=T'};$$

$$RT' \lim_{p \to 0}\left(\frac{\partial \ln f(T,p)}{\partial T}\right)_p\Bigg|_{T=T'} = 0.$$

Hence finally

$$\text{(XVI)} \qquad \left(\frac{\partial \ln f(T,P)}{\partial T}\right)_P = \frac{h(T) - H(T,P)}{RT^2}.$$

This method of evaluation of $(\partial \ln f/\partial T)_P$ has been carried out in accordance with the plan of the incomplete proof of Lewis and Randall. The proof given by Lewis and Randall is incomplete because they make no attempt to prove that

$$\lim_{p \to 0}\left(\frac{\partial \ln f(T,p)}{\partial T}\right)_p\Bigg|_{T=T'} = 0,$$

but simply drop the term

$$RT\left(\frac{\partial \ln f^*}{\partial T}\right)_P$$

from their equation (28)

$$(28) \quad \left(\frac{\partial F^*}{\partial T}\right)_P - \left(\frac{\partial F}{\partial T}\right)_P = R \ln \frac{f^*}{f} + RT\left(\frac{\partial \ln f^*}{\partial T}\right)_P - RT\left(\frac{\partial \ln f}{\partial T}\right)_P$$

with the statement[25] that: "In the gas at very low pressure the fugacity is equal to the pressure. Hence f* does not change with the temperature at constant pressure, and the next to the last term disappears." The statement that: "at very low pressure . . . f* does not change with the temperature at constant pressure" is strictly only true when the pressure equals zero at which pressure

$$\left(\frac{\partial \ln f^*}{\partial T}\right)_P$$

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[25] Lewis and Randall: Op. cit., p. 200.

is not defined; at any pressure above zero the fugacity differs from the pressure by an amount calculable from the equation

$$\mathrm{RT} \ln \mathrm{f}(\mathrm{T},\mathrm{p}) = \mathrm{RT} \ln \mathrm{p} - \int_0^{\mathrm{p}} \alpha(\mathrm{T},\mathrm{p})d\mathrm{p}$$

and

$$\left(\frac{\partial \ln \mathrm{f}^*}{\partial \mathrm{T}}\right)_{\mathrm{P}}$$

does change slightly with the temperature at constant pressure.[26]

Second method of evaluation of $(\partial \ln \mathrm{f}/\partial \mathrm{T})_{\mathrm{P}}$. The value of $(\partial \ln \mathrm{f}/\partial \mathrm{T})_{\mathrm{P}}$ in terms of H, h, R, and T can be obtained directly from the equation of definition of f of this paper without the use of equation (XV), and this derivation is complete in itself. In the evaluation by this method the two gaps in the first method are filled at the same time; this method has the additional advantage that it is shorter than the first method. The proof, accomplished by means of Leibniz's rule, is as follows. Differentiating the equation of definition of f

$$\mathrm{RT} \ln \mathrm{f}(\mathrm{T},\mathrm{P}) = \mathrm{RT} \ln \mathrm{P} - \int_0^{\mathrm{P}} \alpha(\mathrm{T},\mathrm{P})d\mathrm{P},\ 0<\mathrm{T}<\infty,\ 0<\mathrm{P}\leqq\phi(\mathrm{T}),$$

with respect to T holding P fast, one obtains

$$\mathrm{R} \ln \mathrm{f}(\mathrm{T},\mathrm{P}) + \mathrm{RT}\left(\frac{\partial \ln \mathrm{f}(\mathrm{T},\mathrm{P})}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \mathrm{R} \ln \mathrm{P} - \left(\frac{\partial}{\partial \mathrm{T}}\int_0^{\mathrm{P}} \alpha(\mathrm{T},\mathrm{P})d\mathrm{P}\right)_{\mathrm{P}};$$

$$\mathrm{RT}\left(\frac{\partial \ln \mathrm{f}(\mathrm{T},\mathrm{P})}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \frac{1}{\mathrm{T}}\int_0^{\mathrm{P}} \alpha(\mathrm{T},\mathrm{P})d\mathrm{P} - \left(\frac{\partial}{\partial \mathrm{T}}\int_0^{\mathrm{P}} \alpha(\mathrm{T},\mathrm{P})d\mathrm{P}\right)_{\mathrm{P}},$$
$$0<\mathrm{T}<\infty,\ 0<\mathrm{P}\leqq\phi(\mathrm{T}).$$

The function, $\alpha(\mathrm{T},\mathrm{P})$ has already been defined on the boundary, $\mathrm{P} = 0$, $0<\mathrm{T}<\infty$, by the equation

$$\alpha(\mathrm{T},0) = \mathrm{K}(\mathrm{T}).$$

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[26] There is no objection of course on the part of the author of this paper to the use of approximate equations in many problems. Approximate equations are undoubtedly invaluable in many problems. However, Lewis rightly stresses the important role of the fugacity in "exact equations," and therefore a clear statement of the underlying physical hypotheses, and rigorous derivations are vital.

The fact that the experimental error increases and may ultimately exceed α as the pressure approaches zero as a limit does not justify neglect of the difference between the fugacity and the pressure at any pressure above zero in a rigorous development of the theory of thermodynamics, since the physical hypothesis (experimental fact) has been stated that

$$\lim_{\mathrm{P} \doteq 0} \alpha(\mathrm{T}',\mathrm{P}) = \mathrm{K}(\mathrm{T}'),$$

where K(T′) at a given temperature denotes a constant different from zero except at the Boyle temperature. To assume that at all pressures below a certain fixed pressure the fugacity is identical with the pressure would be to make a physical hypothesis in conflict with the physical hypothesis (experimental fact) just reviewed.

Two additional physical hypotheses will now be made. The first is that

$$\left(\frac{\partial\alpha}{\partial T}\right)_P\bigg|_{P=0} = \frac{dK}{dT}$$

exists on the boundary, $P = 0$, $0 < T < \infty$, and the second is that

$$\left(\frac{\partial\alpha}{\partial T}\right)_P$$

is continuous on the boundary, $P = 0$, $0 < T < \infty$. Lewis and Randall do not mention these two hypotheses, but it is necessary to make the assumption that $(\partial\alpha/\partial T)_P$ approaches a limit when the pressure approaches zero as a limit in the evaluation of

$$\left(\frac{\partial \ln f(T,P)}{\partial T}\right)_P$$

either by their method or by this method; it is not sufficient merely to assume that

$$\lim_{P \to 0} \alpha(T',P) = K(T'),$$

where $K(T')$ denotes at a given temperature a constant different from zero except at the Boyle temperature. A geometrical representation (Fig. 1) of $\alpha(T,P)$ makes clear the plausibility of the two physical hypotheses just stated. Applying Leibniz's rule to the partial derivative of the integral, one obtains

$$\left(\frac{\partial}{\partial T}\int_0^P \alpha\,(T,P)dP\right)_P = \int_0^P \left(\frac{\partial\alpha}{\partial T}\right)_P dP,\ 0 < T < \infty,\ 0 \leqq P \leqq \phi(T),$$

and it follows at the same time that the right hand integral is a continuous function of T and P in the domain, $0 < T < \infty$, $0 \leqq P \leqq \phi(T)$.[27] Hence

$$\left(\frac{\partial \ln f(T,P)}{\partial T}\right)_P = \frac{1}{RT^2}\int_0^P \alpha(T,P)dP - \frac{1}{RT^2}\int_0^P T\left(\frac{\partial\alpha}{\partial T}\right)_P dP,\ 0 < T < \infty,\ 0 < P \leqq \phi(T).$$

In the integral calculus the definite integral

$$\int_a^b F(x)dx$$

is first defined for a function, $F(x)$, that is defined and continuous in a closed interval, $a \leqq x \leqq b$. The definition of the definite integral is readily extended in the case of a function, $f(x)$, that is defined and continuous in the open interval, $a < x \leqq b$, and that is finite in this interval, that is,

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[27] W. F. Osgood: "Lehrbuch der Funktionentheorie," 5. Aufl., Bd. 1, S. 123; "Advanced Calculus," pp. 461, 462.

$$|f(x)| < G, \; a < x \leqq b,$$

where G denotes a positive constant.[28]

The function

$$\alpha(T,P) = \frac{RT}{P} - v, \; o < T < \infty, \; o < P \leqq \phi(T),$$

fulfills the latter conditions when T is assigned any value different from zero and then held fast, and the integral

$$\int_{o}^{P}\left(\frac{RT}{P} - v\right) dP, \; o < T < \infty, \; o < P \leqq \phi(T),$$

is therefore defined. The same is true of the function

$$T\left(\frac{\partial \alpha}{\partial T}\right)_P = \frac{RT}{P} - T\left(\frac{\partial v}{\partial T}\right)_P, \; o < T < \infty, \; o < P \leqq \phi(T),$$

and the integral

$$\int_{o}^{P}\left(\frac{RT}{P} - T\left(\frac{\partial v}{\partial T}\right)_P\right) dP, \; o < T < \infty, \; o < P \leqq \phi(T),$$

and hence it is also true of the function

$$-\left(v - T\left(\frac{\partial v}{\partial T}\right)_P\right) = \left(\frac{RT}{P} - v\right) - \left(\frac{RT}{P} - T\left(\frac{\partial v}{\partial T}\right)_P\right), \; o < T < \infty, \; o < P \leqq \phi(T),$$

and the integral

$$-\int_{o}^{P}\left(v - T\left(\frac{\partial v}{\partial T}\right)_P\right) dP, \; o < T < \infty, \; o < P \leqq \phi(T).$$

Therefore from the definitions laid down and the physical hypotheses made explicitly in this paper it follows that the integral

$$\int_{o}^{P}\left(v - T\left(\frac{\partial v}{\partial T}\right)_P\right) dP$$

is a function of T and P continuous in the domain, $o < T < \infty$, $o < P \leqq \phi(T)$, and finite in the domain, $o < T < \infty$, $o < P \leqq \phi(T)$. Since

$$\int_{o}^{P} \alpha(T,P) dP = \int_{o}^{P}\left(\frac{RT}{P} - v\right) dP, \; o < T < \infty, \; o < P \leqq \phi(T),$$

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[28] It is of course also possible to extend the definition of the definite integral still further for a function, f(x), that is defined and continuous at all points of the open interval, $a < x \leqq b$, but which does not remain finite in the interval, but this possible further extension is not involved here.

and

$$\int_0^P T\left(\frac{\partial\alpha}{\partial T}\right)_P dP = \int_0^P\left(\frac{RT}{P} - T\left(\frac{\partial v}{\partial T}\right)_P\right)dP, 0<T<\infty, 0<P\leqq\phi(T),$$

hence

$$\left(\frac{\partial \ln f(T,P)}{\partial T}\right)_P = \frac{1}{RT^2}\int_0^P\left(\frac{RT}{P} - v\right)dP - \frac{1}{RT^2}\int_0^P\left(\frac{RT}{P} - T\left(\frac{\partial v}{\partial T}\right)_P\right)dP$$

$$= -\frac{1}{RT^2}\int_0^P\left(v - T\left(\frac{\partial v}{\partial T}\right)_P\right)dP, 0<T<\infty, 0<P\leqq\phi(T).$$

From the first and second laws of thermodynamics and the definition of H it is readily proved that

$$\left(\frac{\partial H}{\partial P}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_P.$$

Hence

$$\int_P^{P'}\left(v - T\left(\frac{\partial v}{\partial T}\right)_P\right)dP = H(T,P') - H(T,P), 0<T<\infty, 0<P\leqq\phi(T),$$

where P′ denotes a constant greater than zero. Hence

$$\lim_{P \doteq 0}\int_P^{P'}\left(v - T'\left(\frac{\partial v}{\partial T}\right)_P\right)dP - H(T',P') = -\lim_{P \doteq 0} H(T',P)$$

where T′ denotes a constant greater than zero, and

$$\int_0^{P'}\left(v - T'\left(\frac{\partial v}{\partial T}\right)_P\right)dP - H(T',P') = -\lim_{P \doteq 0} H(T',P).$$

This result may be stated in words: At a given temperature Lewis's molal heat content (Gibbs's chi function for one mol) approaches a limit when the pressure approaches zero as a limit. Further, the limit that the molal heat content approaches is a function of the temperature only; this limit will be denoted by h(T). Therefore

$$-\int_0^{P'}\left(v - T'\left(\frac{\partial v}{\partial T}\right)_P\right)dP = h(T') - H(T',P').$$

In this equation T′ denotes any value of T greater than zero and P′ denotes any value of P greater than zero and the primes may now be dropped. Hence finally

$$\text{(XVI)} \qquad \left(\frac{\partial \ln f(T,P)}{\partial T}\right)_P = \frac{h(T) - H(T,P)}{RT^2}.$$

The evaluation of the fugacity of a gas the volume of which is given by the equation of Beattie and Bridgeman[29] will be carried out to illustrate the relations of the fugacity in a concrete case. The equation of Beattie and Bridgeman is easily integrated with respect to the volume at constant temperature, and since the conditions (I) and (II) presupposed in the definition of fugacity must hold if the equation of Beattie and Bridgeman is assumed, therefore it is easy to obtain the fugacity from this equation of state. The equation of Beattie and Bridgeman, which has been found by them to represent the pressure-volume-temperature relations of the following gaseous elements and compounds He, Ne, A, H_2, N_2, O_2, CO_2, CH_4, and $(C_2H_5)_2O$ accurately over a wide range of temperature and pressure, is

$$P = \frac{RT\,(1-\epsilon)}{v^2}\,[v + B] - \frac{A}{v^2},$$

where T denotes the absolute thermodynamic temperature; P, the pressure; v, the volume; $A = A_o(1 - a/v)$; $B = B_o(1 - b/v)$; $\epsilon = c/(T^3v)$; R denotes the gas content; A, B, a, b, and c denote constants that depend on the kind of substance under consideration. The basis of the equation in kinetic theory has been stated by Beattie and Bridgeman[30] as follows:

"The proposed equation rests upon the two main assumptions that the kinetic and cohesive pressures can be treated separately and that the law of force (the specific form of which does not enter into the treatment) shall be such that it will diminish rapidly with distance. Both of these assumptions are common to the treatment of a large number of kinetic theory problems."

"In the deduction of [the equation], general physical considerations have been presented rather than detailed computation founded on the assumption of certain laws for the distribution of velocities and for the forces acting between the molecules. The first reason for this choice is that the utility of an equation of state depends largely upon its ability to reproduce the measured pressure-volume-temperature data and to give accurate values for the thermodynamic derivatives, and hence in the evaluation of the specific form of functions used much consideration was given to the representation of the experimental measurements. In the second place, [the equation] differs from the Lorentz equation of state, which has been deduced in a rigorous manner from the general laws of kinetic theory, only in that the three second order constants a, b and c have been introduced."

The equation satisfies the general relations that are satisfied by real gases. Thus

$$\lim_{P \doteq 0} \frac{Pv}{T'} = R,$$

where T′ denotes any constant greater than zero, and

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[29] J. A. Beattie and O. C. Bridgeman: A new equation of state for fluids, Proc. Am. Acad., 63, 229 (1928); also J. Am. Chem. Soc., 50, 3133 (1928).

[30] Proc. Am. Acad., 63, 240 (1928).

$$\lim_{P \doteq 0} \alpha(T',P) = \lim_{P \doteq 0}\left(\frac{RT'}{P} - v\right) = \frac{c}{T'^3} - B_o + \frac{A_o}{RT'}.$$

The isotherms of $\alpha(T,P)$ for nitrogen calculated from the equation of Beattie and Bridgeman and based on their constants for this gas are represented graphically in Fig. 1. The deviations of the calculated values of $\alpha(T,P)$ from the experimental values of Holborn and Otto, Onnes and van Urk, Verschoyle, and Bartlett are small on the scale of this diagram in the range of the plotted curves: the calculated and the experimental values of $\alpha(T,P)$ along these isotherms are given in Table I.[31] The variation of $\alpha(T,P)$ with pressure at constant temperature has been discussed; a diagram showing the variation with temperature at constant pressure of the experimental values of $\alpha(T,P)$ for nitrogen has been published recently by W. Edwards Deming and Lola E. Shupe.[32] From the equation of Beattie and Bridgeman it follows that

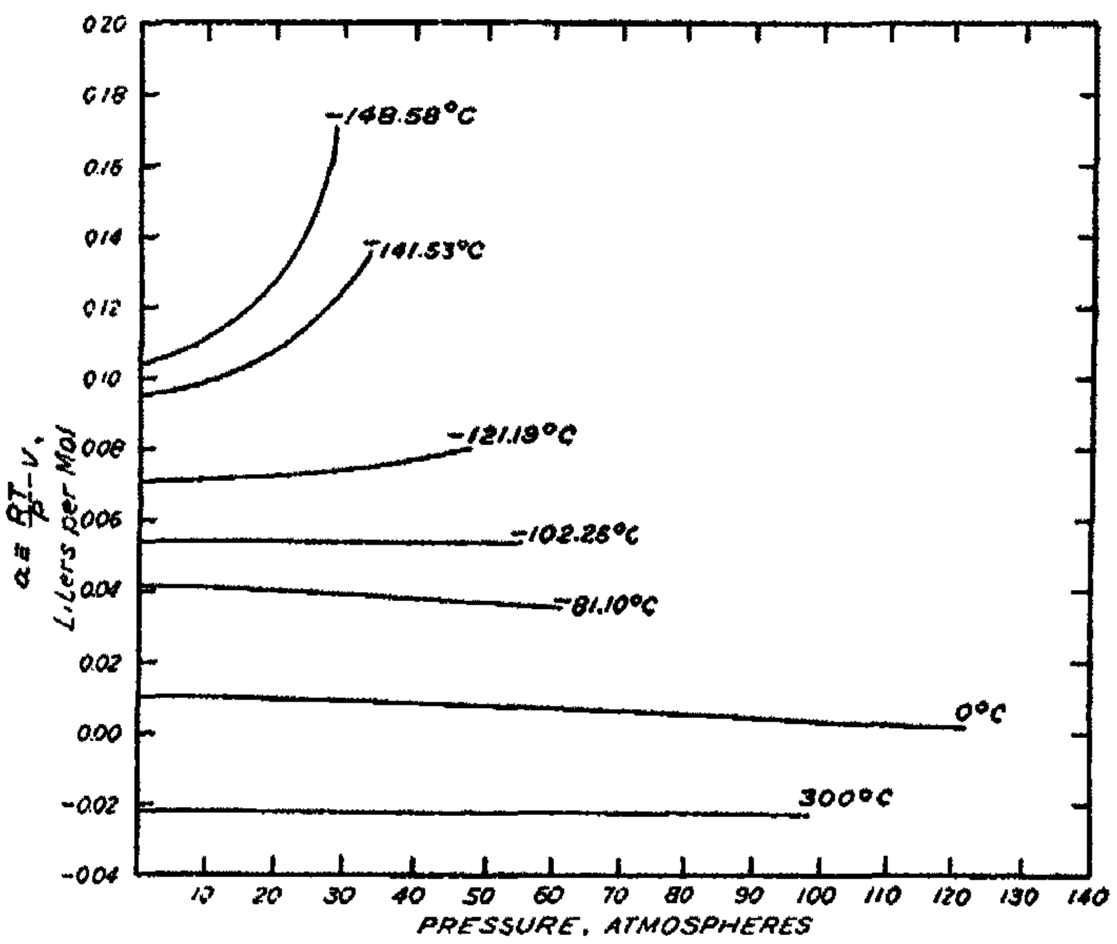

Fig. 1

Isotherms of the alpha function for nitrogen calculated from the Beattie-Bridgeman equation (constants of Beattie and Bridgeman). The differences between the calculated values of alpha and those determined experimentally by several investigators are small on the scale of this diagram in the range of the plotted curves (See Table I).

$$\left(\frac{\partial\alpha}{\partial P}\right)_T\Big|_{P=0} = \frac{1}{RT}\left[\frac{cB_o}{T^3} + bB_o - \frac{aA_o}{RT} + \left(B_o - \frac{A_o}{RT} - \frac{c}{T^3}\right)^2\right]$$

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[31] The calculated values of *the pressures at different volumes* along these isotherms are taken from the table of Beattie and Bridgeman, as are also the experimental values of Holborn and Otto, Onnes and van Urk, Verschoyle, and Bartlett: Proc. Am. Acad., 63, 282-284 (1928).

[32] Phys. Rev., (2) 37, 641 (1931).

TABLE I

The Pressure and Alpha Function of Nitrogen along Isotherms and Isometrics[a]

$$\left(\alpha \equiv \frac{RT}{P} - v\right)$$

Temp. °C.	Source	Volume, liters/mol	2.00	1.00	0.67⁻	0.50	0.40	0.33⁺	0.29⁻	0.25	0.22⁺	0.20	0.18⁺
		Density, mols/liter	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5
300	Calc.[b]	Pressure, atmospheres	23.78	48.10	73.01	98.54							
300	Calc.	α, liters/mol	−0.02	−0.02	−0.02	−0.02							
300	R[c]	Pressure, atmospheres	23.76	48.03	72.86	98.29							
300	R	α, liters/mol	−0.02	−0.02	−0.02	−0.02							
0	Calc.	Pressure, atmospheres	11.15	22.19	33.17	44.11	55.04	66.00	77.01	88.10	99.30	110.65	122.17
0	Calc.	α, liters/mol	+0.01	+0.01	+0.01	+0.01	+0.01	+0.01	+0.01	+0.00⁺	+0.00⁺	+0.00⁺	+0.00⁺
0	R	Pressure, atmospheres	11.15	22.22	33.22	44.18	55.13	66.10	77.11	88.18	99.33		
0	R	α, liters/mol	+0.01	+0.01	+0.01	+0.01	+0.01	+0.01	+0.00⁺	+0.00⁺	+0.00⁺		

[a] The values of the pressure in this table are taken from the table of Beattie and Bridgeman: Proc. Am. Acad., 63, 282-284 (1928).

[b] Calculated from the Beattie-Bridgeman equation.

[c] Observed pressures of Holborn and Otto smoothed to even values of the density by Beattie and Bridgeman but not smoothed for temperature, and values of alpha calculated therefrom by the author.

TABLE I (Continued)

The Pressure and Alpha Function of Nitrogen along Isotherms and Isometrics

$$\left(\alpha \equiv \frac{RT}{P} - v\right)$$

		Volume, liters/mol	2.00	1.00	0.67^-	0.50	0.40	0.33^+	0.29^-	0.25	0.22^+	0.20	0.18^+
Temp. °C.	Source	Density, mols/liter	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5
0	L[d]	Pressure, atmospheres	11.16	22.24	33.23	44.16	55.07						
0	L	α, liters/mol	+0.01	+0.01	+0.01	+0.01	+0.01						
0	V[e]	Pressure, atmospheres	11.15	22.20	33.19	44.14	55.08	66.03	77.02	88.08	99.24	110.54	122.01
0	V	α, liters/mol	+0.01	+0.01	+0.01	+0.01	+0.01	+0.01	+0.01	$+0.00^+$	$+0.00^+$	$+0.00^+$	$+0.00^+$
0	Br[f]	Pressure, atmospheres	11.16	22.23	33.22	44.16	55.09	66.04	77.02	88.07	99.23	110.57	122.13
0	Br	α, liters/mol	+0.01	+0.01	+0.01	+0.01	+0.01	+0.01	+0.01	$+0.00^+$	$+0.00^+$	$+0.00^+$	$+0.00^+$
−81.10	Calc.	Pressure, atmospheres	7.72	15.15	22.31	29.23	35.94	42.46	48.82	55.04	61.16		
−81.10	Calc.	α, liters/mol	+0.04	+0.04	+0.04	+0.04	+0.04	+0.04	+0.04	+0.04	+0.04		

[d] Observed pressures of Onnes and van Urk smoothed to even values of the density by Beattie and Bridgeman but not smoothed for temperature, and values of alpha calculated therefrom by the author.

[e] Observed pressures of Verschoyle smoothed to even values of the density by Beattie and Bridgeman but not smoothed for temperature, and values of alpha calculated therefrom by the author.

[f] Observed pressures of Bartlett smoothed to even values of the density by Beattie and Bridgeman but not smoothed for temperature, and values of alpha calculated therefrom by the author.

TABLE I (Continued)

The Pressure and Alpha Function of Nitrogen along Isotherms and Isometrics

$$\left(\alpha \equiv \frac{RT}{P} - v\right)$$

Temp. °C.	Source	Volume, liters/mol	2.00	1.00	0.67^-	0.50	0.40	0.33^+	0.29^-	0.25	0.22^+	0.20	0.18^+
		Density, mols/liter	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5
−81.10	L	Pressure, atmospheres	7.74	15.19	22.37	29.29	35.98	42.47	48.80	54.97	61.00		
−81.10	L	α, liters/mol	+0.04	+0.04	+0.04	+0.04	+0.04	+0.04	+0.04	+0.04	+0.04		
−102.25	Calc.	Pressure, atmospheres	6.83	13.30	19.45	25.30	30.87	36.19	41.29	46.18	50.91	55.48	
−102.25	Calc.	α, liters/mol	+0.05	+0.05	+0.05	+0.05	+0.05	+0.05	+0.05	+0.05	+0.05	+0.05	
−102.25	L	Pressure, atmospheres	6.83	13.31	19.47	25.33	30.91	36.22	41.29	46.16	50.85	55.38	
−102.25	L	α, liters/mol	+0.05	+0.05	+0.05	+0.05	+0.05	+0.05	+0.05	+0.05	+0.05	+0.05	
−121.19	Calc.	Pressure, atmospheres	6.02	11.64	16.87	21.73	26.27	30.48	34.41	38.07	41.49	44.69	47.70
−121.19	Calc.	α, liters/mol	+0.07	+0.07	+0.07	+0.07	+0.07	+0.08	+0.08	+0.08	+0.08	+0.08	+0.08
−121.19	L	Pressure, atmospheres	6.03	11.65	16.89	21.75	26.26	30.46	34.38	38.05	41.48	44.66	47.60
−121.19	L	α, liters/mol	+0.07	+0.07	+0.07	+0.07	+0.07	+0.08	+0.08	+0.08	+0.08	+0.08	+0.08

TABLE I (Continued)

The Pressure and Alpha Function of Nitrogen along Isotherms and Isometrics

$$\left(\alpha \equiv \frac{RT}{P} - v\right)$$

		Volume, liters/mol	2.00	1.00	0.67^-	0.50	0.40	0.33^+	0.29^-	0.25	0.22^+	0.20	0.18^+
Temp. °C.	Source	Density, mols/liter	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5
−141.53	Calc.	Pressure, atmospheres	5.15	9.83	14.05	17.83	21.21	24.19	26.79	29.05	30.98	32.60	33.94
−141.53	Calc.	α, liters/mol	+0.10	+0.10	+0.10	+0.11	+0.11	+0.11	+0.12	+0.12	+0.13	+0.13	+0.14
−141.53	L	Pressure, atmospheres	5.16	9.84	14.05	17.81	21.16	24.14	26.78	29.12	31.16	32.91	34.41
−141.53	L	α, liters/mol	+0.09	+0.10	+0.10	+0.11	+0.11	+0.11	+0.12	+0.12	+0.12	+0.13	+0.13
−148.58	Calc.	Pressure, atmospheres	4.85	9.20	13.06	16.46	19.41	21.94	24.07	25.81	27.19	28.22	28.93
−148.58	Calc.	α, liters/mol	+0.11	+0.11	+0.12	+0.12	+0.13	+0.13	+0.14	+0.15	+0.15	+0.16	+0.17
−148.58	L	Pressure, atmospheres	4.85	9.20	13.07	16.47	19.43	21.98	24.14	25.93	27.41	28.61	29.56
−148.58	L	α, liters/mol	+0.11	+0.11	+0.12	+0.12	+0.13	+0.13	+0.14	+0.14	+0.15	+0.16	+0.16

and that

$$\left(\frac{\partial \alpha}{\partial T}\right)_P\bigg|_{P=0} = -\frac{A_o}{RT^2} - \frac{3c}{T^4}.$$

Beattie and Bridgeman[33] write that their "equation of state extrapolates to low pressures with a high degree of accuracy" and it is therefore suitable for use in the calculation of fugacity. In order to make this calculation one integrates the equation

$$RT\left(\frac{\partial \ln f}{\partial P}\right)_T = v,$$

proved on page 2896, with respect to P, obtaining as a result

$$RT \ln \frac{f(T,P')}{f(T,P)} = \int_P^{P'} v dP, \; 0 < T < \infty, \; 0 < P \leqq \phi(T),$$

where P′ denotes a constant greater than zero. Now T and v may be made the independent variables instead of T and P, and v may be allowed to become infinite. Thus

$$\begin{aligned} RT' \ln f(T',v') = \lim_{v \doteq \infty}\Bigg[& RT' \ln v\, f(T',v) - \frac{2B_oRT'}{v} + \frac{2A_o}{v} + \frac{2cR}{T'^2v} + \frac{3bB_oRT'}{2v^2} \\ & - \frac{3aA_o}{2v^2} + \frac{3cB_oR}{2T'^2v^2} - \frac{4bB_ocR}{3T'^2v^3}\Bigg] - RT' \ln v' + \frac{2B_oRT'}{v'} \\ & - \frac{2A_o}{v'} - \frac{2cR}{T'^2v'} - \frac{3bB_oRT'}{2v'^2} + \frac{3aA_o}{2v'^2} - \frac{3cB_oR}{2T'^2v'^2} + \frac{4bB_ocR}{3T'^2v'^3}, \end{aligned}$$

where T′ denotes a constant greater than zero and v′ denotes a constant greater than or equal to Φ(T′), where $v = \Phi(T)$, $0 < T < \infty$, is the equation of the boundary of the stability field of the gas separating it from the stability fields of solid and liquid. It has already been proved that

$$\lim_{v \doteq \infty} \frac{f(T',v)}{P} = 1,$$

and thus application of the theorem that the limit of the product of two variables is equal to the product of the limits of the two variables leads to the result:

$$\lim_{v \doteq \infty}\left(\frac{f(T',v)}{P}\right)(Pv) = RT'.$$

Hence the fugacity calculated from the equation of Beattie and Bridgeman is obtained in the form

$$\ln f(T',v') = \ln \frac{RT'}{v'} + \frac{2B_o}{v'} - \frac{2A_o}{RT'v'} - \frac{2c}{T'^3v'} - \frac{3bB_o}{2v'^2} + \frac{3aA_o}{2RT'v'^2} - \frac{3cB_o}{2T'^3v'^2} + \frac{4bB_oc}{3T'^3v'^3}$$

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[33] J. Am. Chem. Soc., 50, 3157 (1928).

and in this equation the primes may now be dropped since T′ is any value of T greater than zero and v′ is any value of v greater than or equal to Φ(T′). The result may also be written in the virial form

$$\ln f(T,v) = \ln \frac{RT}{v} + \frac{2\beta}{RTv} + \frac{3\gamma}{2RTv^2} + \frac{4\delta}{3RTv^3},$$

where

$$\beta = RTB_o - A_o - \frac{Rc}{T^2},$$

$$\gamma = - RTB_ob + A_oa - \frac{RB_oc}{T^2},$$

$$\delta = \frac{RB_obc}{T^2}.$$

For gaseous nitrogen the constants have the following values according to Beattie and Bridgeman:[34]

A_o = 1.3445, atmospheres × liters² ÷ mols²;
B_o = 0.05046, liters ÷ mols;
a = 0.02617, liters ÷ mols;
b = −0.00691, liters ÷ mols;
c = 4.20 × 10⁴, degrees Kelvin³ × liters ÷ mols;

and thus

$$\ln f(T,v) = \ln \frac{RT}{v} + \frac{0.10092}{v} - \frac{2.6890}{RTv} - \frac{84000.}{T^3v} + \frac{0.001046}{2v^2}$$

$$+ \frac{0.10556}{2RTv^2} - \frac{6358.}{2T^3v^2} - \frac{58.578}{3T^3v^3},$$

where T is measured in degrees Kelvin; v, in liters per mol; and f, in atmospheres. The constants of Beattie and Bridgeman are based on experimental determinations extending from −148.58°C. to 400°C. and up to 133.91 atmospheres and the equation for the fugacity based on these constants can only be expected to hold very accurately within this range.

A table of the specific volumes and fugacities of nitrogen (as well as other thermodynamic properties) at different temperatures and pressures from −70°C. to 600°C. and up to 1200 atmospheres based on experimental measurements from −70°C. to 400°C. and up to 1000 atmospheres has been published recently by Deming and Miss Shupe.[35] The fugacities were computed from the smoothed values of α by Lewis and Randall's graphical method. This table illustrates very clearly the relations of the temperature, pressure, and fugacity. The values of the pressure and fugacity at 0°C. and 0.18182 liters per mol (6.490 cc. per gram) calculated from the equation with the constants of Beattie and Bridgeman are: pressure, 122.17 atmospheres; fugacity,

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[34] J. Am. Chem. Soc., 50, 3136 (1928).

[35] Phys. Rev. (2), 37, 638 (1931).

117.81 atmospheres; those interpolated[36] in the table of Deming and Miss Shupe are: pressure, 121.87 atmospheres; fugacity, 117.79 atmospheres. This is the highest pressure at this temperature at which the equations with the constants of Beattie and Bridgeman can be expected to yield very accurate values of the pressure and fugacity. It may be added that Deming and Miss Shupe[37] have also published a set of constants for the equation of Beattie and Bridgeman based on experimental measurements in the range, −70°C. to 400°C. and up to 1000 atmospheres. Their constants differ slightly from those of Beattie and Bridgeman, presumably due to the fact that they are based on measurements extending over a wider range of pressure. Deming and Miss Shupe state that: "The agreement between observed pressures and those calculated [from the equation of Beattie and Bridgeman with the constants of Deming and Miss Shupe] is remarkably good down to $v=3$ cc. per g. [0.084048 liters per mol] over the entire temperature range ... Thus the equation ... reproduces trends and pressures satisfactorily from −70°C. to 400°C. down to 3 cc. per g. Below 3 cc. per g. the calculated pressures are invariably too low, and the discrepancy becomes very large at low temperatures and low volumes."

Conclusion

The definition of fugacity adopted in this paper, namely,

$$\text{(X)}\quad RT\ln f(T,P) = RT\ln P - \int_0^P\left(\frac{RT}{P} - v\right)dP,\ 0<T<\infty,\ 0<P\leqq\phi(T),$$

$$f(T,0) = 0,\ 0<T<\infty,$$

or, in the equivalent form,

$$f(T,P) = Pe^{-\frac{1}{RT}\int_0^P \alpha(T,P)dP},\ 0<T<\infty,\ 0\leqq P\leqq\phi(T),$$

is based on the physical hypothesis (experimental fact) stated by Lewis and Randall that

$$\lim_{P\doteq 0}\left(\frac{RT'}{P} - v\right) = K(T'),$$

where $K(T')$ denotes at a given temperature a constant different from zero except at the Boyle temperature. This equation of definition is an equation that is used in the experimental determination of fugacity, and it has been shown to lead directly and rigorously to the equations that Lewis and Randall write as their definition of fugacity. This equation of definition of fugacity cannot, however, be proved from the definition of Lewis and Randall, although it is an equation that Lewis and Randall write for the fugacity, since their definition is satisfied by an infinite number of possible functions of the temperature and pressure different from the function defined by equation (X) as well as by the latter function.

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[36] The interpolated values were kindly supplied by Dr. Deming and Miss Shupe.

[37] J. Am. Chem. Soc., 52, 1388 (1930).

The definition of this paper also shows on inspection that the fugacity has the dimensions of pressure, and the character, stressed by Lewis and Randall,[38] of an "ideal vapor pressure."

Beattie and Bridgeman have presented an equation of state that they find represents the pressure-volume-temperature relations of many gases very accurately over a wide range of temperature and pressure. The alpha function of gaseous nitrogen calculated from the equation of Beattie and Bridgeman with their constants is represented graphically in Fig. 1. A comparison of the values of alpha calculated from the equation of state with those resulting from experimental measurements by several investigators is given in Table I. Beattie and Bridgeman write[39] that the "equation of state extrapolates to low pressures with a high degree of accuracy"; it is therefore suitable for use in the calculation of fugacity. This calculation has been carried out and the equation of the fugacity obtained. The fugacity equation of gaseous nitrogen is presented with numerical coefficients based on the constants of Beattie and Bridgeman.

Acknowledgment

The author is indebted to Dr. L. H. Adams of the Geophysical Laboratory for suggestions in the constructive part of this work; in particular, for calling attention to the applicability of the equation

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

in the evaluation of the partial derivative of the fugacity with respect to the temperature. The kindness of Prof. J. A. Beattie of the Massachusetts Institute of Technology in supplying valuable information concerning the Beattie-Bridgeman equation, and that of Dr. W. Edwards Deming and Miss Lola E. Shupe of the Bureau of Chemistry and Soils, U. S. Department of Agriculture, in supplying interpolated values in their table, and in allowing an examination of their informative unpublished isothermal curves of the alpha function for nitrogen at different temperatures and extending up to high pressures, is gratefully acknowledged.

Geophysical Laboratory,
Carnegie Institution of Washington,
June, 1931.

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[38] Op. cit., p. 191.

[39] J. Am. Chem. Soc., 50, 3157 (1928).

WATER RELATIONSHIPS IN COLLOIDS

I. Vapor Pressure Measurements on Elastic Gels*

BY DAVID R. BRIGGS

Van Bemmelen,[1] who in 1894 first studied the relationship existing between the amount of water present in a gel and the relative vapor pressure exhibited by that water, used silicic acid as his experimental gel and obtained his results by allowing samples of the gel to come to equilibrium over H_2SO_4-H_2O mixtures of varying relative vapor pressures. He found that the relationship was not a reversible one, but depended to a great extent upon the previous history of the gel, i.e., different values for the relative vapor pressure of the H_2O were obtained at the same H_2O content of the gel depending upon whether or not the gel had reached that particular H_2O content from a wetter or a dryer state.

Where van Bemmelen had used desiccators containing H_2SO_4-H_2O solutions of varying relative vapor pressures and had allowed the gels to reach equilibrium against these, a process requiring weeks, Zsigmondy[2] repeated and extended his work using a quicker method resulting from an evacuation of the desiccators, thus allowing the vapors to reach equilibrium unhampered in their motions by air. His results were very similar to those of the earlier work but he found in addition that, as the gel aged, the amount of H_2O which it would hold against a given relative vapor pressure was decreased and the value became more nearly independent of the history of the gel. He found that CuO and Fe_2O_3 gels acted similarly to SiO_2 gels in that the un-aged gel showed this lack of reversibility of the water content-R.V.P. relationship.

There is another group of gels, however, the members of which do not exhibit this phenomenon of irreversibility of the relative vapor pressure curves. To this group belong such gels as those of the proteins, carbohydrates, and other plant and animal colloids. These are known as elastic gels to distinguish them from the non-elastic gels such as those studied by van Bemmelen and Zsigmondy. Katz[3] applied the method of van Bemmelen to a study of the vapor pressure isotherm of a large number of these gels, and found that the water held by these gels at equilibrium against a given H_2SO_4 soln. of given relative vapor pressure was the same, independent of the amount of water with which the gel had previously been associated. He was not able to obtain very definite results when he used Zsigmondy's improved method. Katz made measurements upon a large number of these gels, finding them to follow

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* Contribution from the Otho S. A. Sprague Memorial Institute and the Department of Pathology, University of Chicago.

[1] J. M. Van Bemmelen: Z. anorg. Chem., 5, 466 (1894); 13, 233, (1897); 18, 14, 98 (1898); 30, 265 (1902).

[2] R. Zsigmondy: Z. anorg. Chem., 71, 356 (1911); Physik. Z., 14, 1098 (1913).

[3] J. R. Katz: Kolloidchem. Beihefte, 9, 1 (1917).

characteristic S-shaped curves, very similar to each other in form though varying markedly in the actual amounts of water held at a given relative vapor pressure by unit mass of dry gel.

This R.V.P.-H_2O content curve is a very important characteristic of a gel. Since the relative vapor pressure exhibited by the water over a solution or in the interstices of a colloid is a direct measure of its activity coefficient, these curves resolve themselves into H_2O content-H_2O activity coefficient curves. From such a curve it becomes possible to estimate the amount of water which a given colloid will retain in any system so long as we know the coefficient of activity of the H_2O against which it is in equilibrium, and provided the system is such that the colloid is unchanged in its chemical state. This curve serves thus as a measure of the water-binding capacity of a given colloid, and all methods for measuring the amount of water associated with the colloid should give points on the curve corresponding to the relative activities of water at which the measurements are made. The manner in which this curve applies to measurements of "bound water" will be described in a following section.

The method used by Katz for determining the water content of elastic gels at various relative vapor pressures, besides being very slow and time consuming, is open to the danger of having the gel attacked, especially at the higher relative humidities, by molds and other organisms. Such action would cause a change in the chemical nature of the material, thus destroying the validity of the results. A quicker method for finding the relative vapor pressures of such substances is therefore desirable.

When attempting to determine the activity* of water in a system, it is, of course, seldom possible to obtain the accuracy from vapor pressure measurements that can be gained from freezing point determinations, especially when the activity of the water in the system under consideration is not greatly different from that of pure water. With gels, however, the amount of water present thruout the course of the H_2O content-H_2O activity curve is of the order of the weight of the dry gel itself or, usually, less. Such gels are really merely moist powders upon which freezing points, though definitely obtainable, are subject to a large percentage of error. This is due to the fact that, in such a material, heat conductivity is very low, the total heat change upon freezing is small, the consistency of the material makes it impossible to mix it well during the cooling process, and the undercooling is usually large. The thermometer or thermocouple used in the determination therefore shows the thermal changes only with a low degree of approximation, and the calculated activity of the water is much less accurate than is to be obtained thru vapor pressure measurements.

The method used in the experiments herein described for determining the relative vapor pressures of the gels is one which had been used for determining vapor pressures of liquids by Smith and Menzies.[4] The instrument is called

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* Whenever the term "activity" of water is used in this paper, it is to be understood to signify the *relative activity* or *activity coefficient* of the water.

[4] A. Smith and A. W. C. Menzies: J. Am. Chem. Soc., 32, 1412 (1910).

an isotenoscope, and may be best described by reference to Fig. 1. The isotenoscope itself (A) consists of a bulb (X) in which the material, the vapor pressure of which is desired, is placed. This, when working with liquids, may be sealed on to the rest of the instrument, but, in the present case, where solids and semi-solids are to be used, it is made to connect with the remainder of the instrument by a well-ground joint which is always sealed with a good vacuum wax. In the U-tube (Y) of the isotenoscope is placed a small amount of liquid, this acting as a manometer to indicate when the pressure inside the bulb (X) is the same as that in the outside part of the system in which the mercury manometer (B) is placed. This liquid may be the same as that inside the bulb (X) if a liquid is being examined but otherwise must be some liquid of negligible vapor pressure (at the temperature at which determinations are to be made). In each arm of the U-tube are placed small chambers (Z) which serve to allow gases to pass thru the U-tube without blowing the liquid over into (X) or out into the other parts of the system.

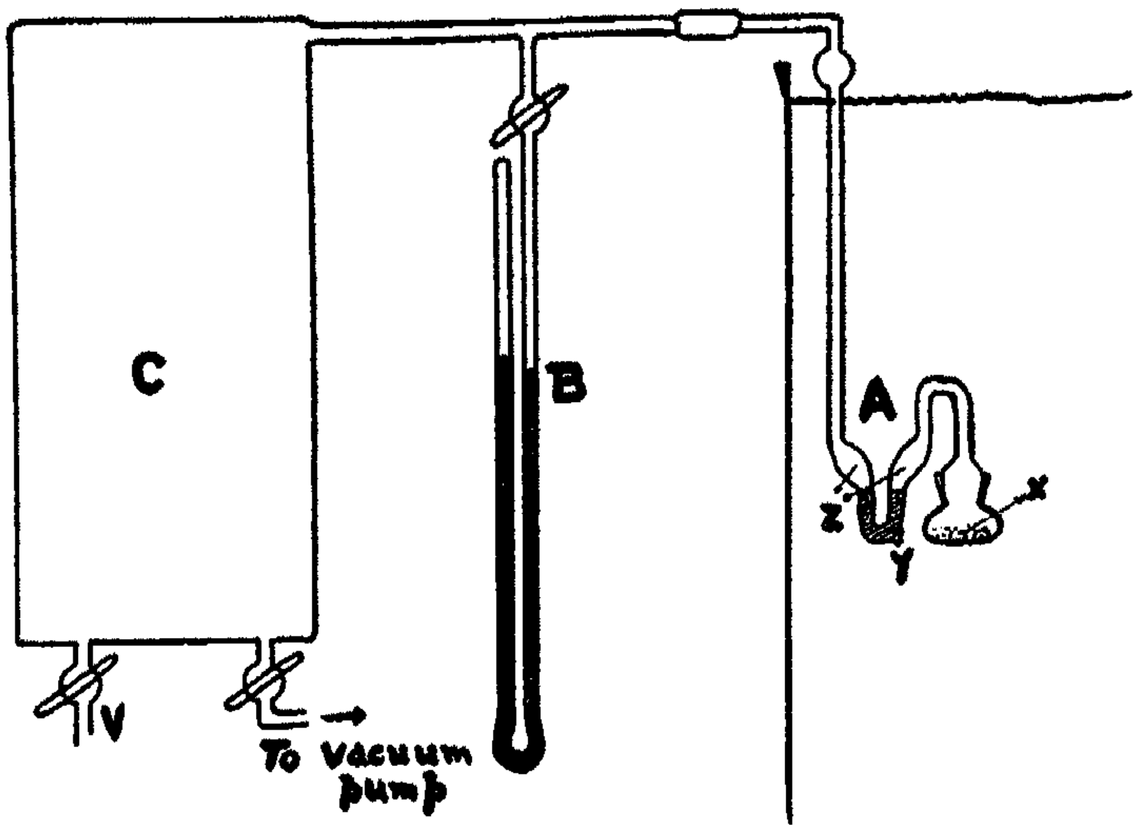

FIG. 1

To make a determination of the vapor pressure of water contained in a semi-dry gel, the isotenoscope containing the sample in the bulb (X) is placed in a water bath of known and accurately constant temperature and connected thru a rubber pressure tube with the outside system consisting of a mercury manometer (B), a large airtight chamber (C) and a vacuum pump. The system is then evacuated until the water vapor from the sample in (X) is passing over freely into the external system. The liquid used in (Y) is a clear petroleum oil of negligible vapor pressure. The construction of the isotenoscope is such that when the vapor begins to move freely (at low pressure) from the sample, any air in (X) will be quickly carried over and thru the U-tube. When this has occurred the pressure in the external system can be again increased by opening valve (V) in chamber (C) until the level of the oil in the U-tube manometer (Y) is at the same height in both arms, signifying the pressure to be the same in all parts of the system. The stop-cock in the manometer (B) can then be shut off and the pressure read at will. A cathetometer may be used to read the difference in the height of the mercury in the two legs of this manometer. The object in having chamber (C) in the system is to make it possible to vary the pressure in the external system gradually in order to be able to catch the liquid in (Y) at exactly the same height in both arms of the U-tube. When the vapor pressure of a liquid is being measured, there is required little time for the sample to come to equilibrium after exhausting the system, but when the sample consists of a semi-dry powder as much as an hour may be required for equilibrium to be regained. The actual amount of water removed from the sample in (X) is very small but it, of course, must all come from the surface region of the particles of powdered gel and time is required for equilibrium to be reestablished between the inside of the particle, the surface, and the vapor above it. For this reason it is well to have the gel ground to a fine powder before wetting.

In preparing the sample, the dried material is ground to pass a 60 mesh screen, is weighed into one gram lots and then, just before the determination is to be made, is mixed with the desired amount of water (approximately) from a micropipette. The mixing is carried out as quickly and thoroughly as possible on a glass plate with a spatula and removed quickly into the vessel (X) of the isotenoscope. After the vapor pressure has been determined, the sample is removed to a weighed bottle, weighed, desiccated and weighed again to determine the exact amount of water contained by the dry solid at the time its vapor pressure was obtained.

The results obtained by this method can be repeated using the same material (distilled water) to an accuracy of approximately 0.1 mm. mercury in vapor pressure. At 25°C, the temperature at which most of the readings were made in these experiments, where the vapor pressure of pure water is 23.517 mm. mercury this would amount to an error of 0.4% to 0.5%. With the moist powdered gels the accuracy was not so high, being of the order of about 1%.

In order to find out how well the H_2O content-H_2O activity curves obtained by this method agree with those determined by allowing the gel to come to equilibrium with H_2SO_4-H_2O mixtures in desiccators at constant temperature, the curves were determined on four substances by both methods. These substances were cellulose (filter paper), casein (nach Hammarsten), fibrin (crude), and agar (Merck). The accompanying graph, Fig. 2, illustrates how well the two methods agree. In that part of the experiment in which the gel was allowed to come to equilibrium with H_2O-H_2SO_4 mixtures, the relative vapor pressures of these mixtures were calculated from determinations of their specific gravities and data found in Landoldt-Börnstein's Tables. The weighed samples of dry colloid were placed over the mixture for a period of six weeks and kept at a constant temperature of 40°C. They were removed weekly, weighed, and mixed up to allow more uniform ab-

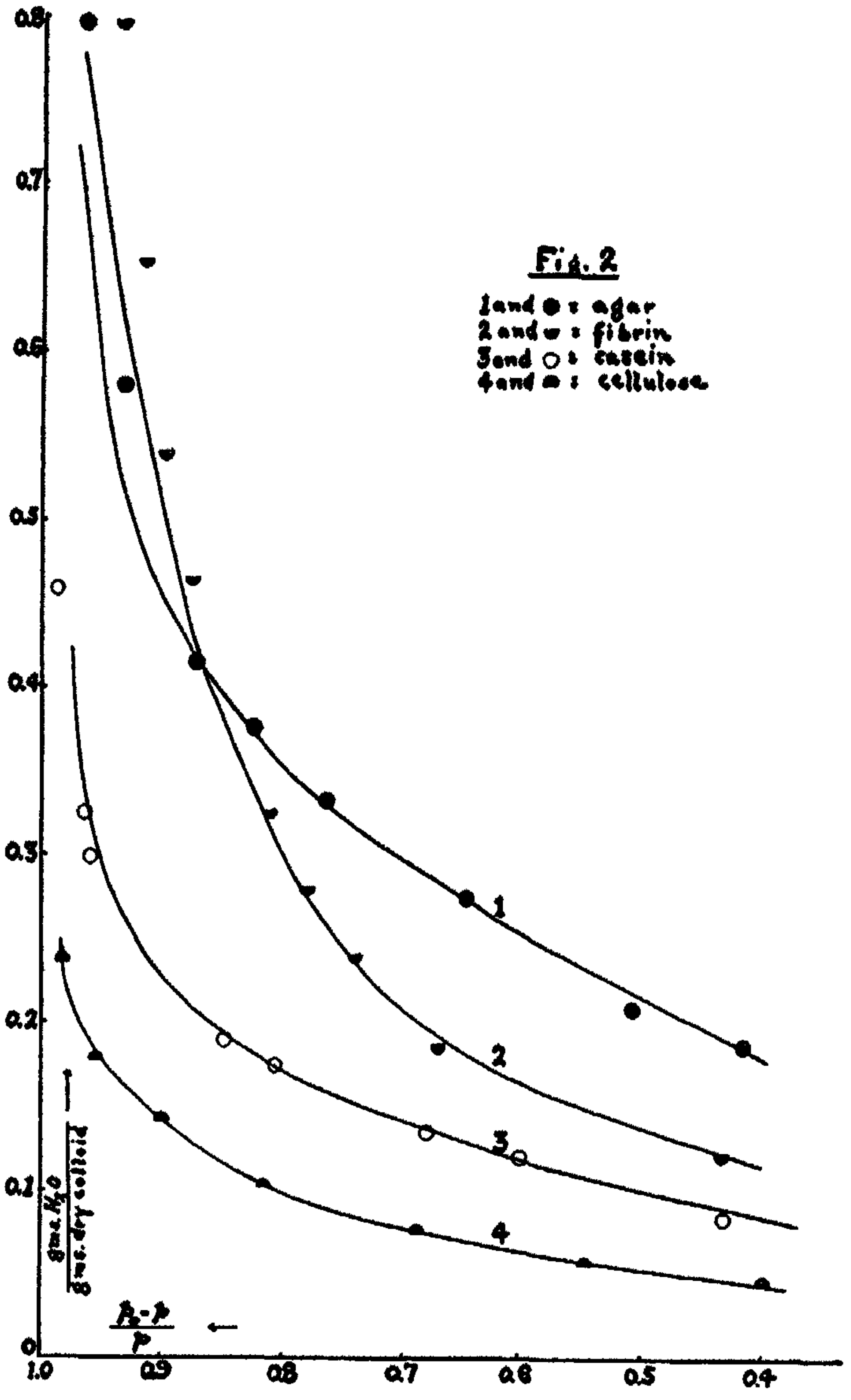

Fig. 2

sorption of water. The H_2O-H_2SO_4 solutions were renewed at the same time. Equilibrium had been reached at the lower relative vapor pressures at the end of three weeks and altho the change was very slow at the end of six weeks for the samples of higher relative vapor pressures it is doubtful if they had entirely reached equilibrium at that time. The only deviation between the two methods is to be seen at the higher relative vapor pressures, and, of the two methods, the isotenoscope method would seem to be the more accurate in this region of the curve; the curves obtained by this method appear more rational.

It is possible to use the isotenoscope method on gels down as far on the H_2O content-H_2O activity curve as an activity of 0.3 with considerable accuracy. For measurements at water contents of the gel so low as to give a relative vapor pressure of less than 0.3 the isotenoscope cannot be used with the degree of accuracy that may be attained from measurements made at equilibrium over H_2SO_4 solutions of low relative vapor pressures. When the relative vapor pressure or activity coefficient of the water in the gel reaches a value of .98 and above, the determinations usually can be more accurately attained from freezing point observations, but in this region of the curve the isotenoscope method of measurement is much more accurate than the method based on equilibrium being attained over H_2SO_4-H_2O mixtures.

It is to be remembered that with these "elastic" gels the equilibria observed between the gel and the water it contains are truly reversible and therefore subject to thermodynamic considerations. These have been most ably described by Katz.[3]

The activity of water may be taken as a measuring rod defining the physical status of the water present in a system. When the activity of water is varied it is an indication of a corresponding change in the free energy content of that water. There are, in general, two manners by which the free energy content of a solvent may be decreased, temperature remaining constant. The first is that which is characteristic of ideal dilute solutions in which the entire energy change during dilution consists in a kinetic energy exchange between the molecules of the added solvent and the molecules of the solvent already present in the solution. In this case, the energy lost by the added solvent is equal to that gained by the solution and there is no evolution or adsorption of heat accompanying the change in the activity of the solvent. The second manner in which the free energy content of the solvent may be decreased is that which is characteristic of concentrated solutions. Nernst[5] defines the ideal concentated solution as one in which all changes in the free energy content of the solvent are accompanied by an evolution or absorption of an equivalent amount of heat by the system. In this case the forces acting to change the activity of the solvent are gravitational in nature; the free energy lost by the added solvent is converted into potential energy capable of doing useful work, or in the absence of a mechanism designed to transform this potential energy into useful work, is evolved directly as heat.

Concerning that portion of the H_2O activity-H_2O content curve for any material in which the maximum work done or the total free energy change in the solvent, $-\Delta A$, as calculated from the equation—

$$-\Delta A = RT \ln p_1/p_2$$

(p_1 and p_2 being the vapor pressures of the H_2O in the two limiting points of such portion of curve) is equal to the change in total energy of the system, $-\Delta E$, Nernst has drawn certain important conclusions, viz.,

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[5] W. Nernst: Wied. Ann., 53, 57 (1894).

(1) The system is following the laws of ideal concentrated solns.

(a) $\partial E/\partial T = 0$, and there is no change in the heat of dilution (inhibition) with temperature.

(b) $\Delta A = \Delta E$, and a given change in A may under proper conditions be converted into work with a high degree of efficiency.

(2) The decrease in the activity of the water present is brought about completely by gravitational forces (forces of attraction) and not by the kinetic energy exchanges which attain a similar result in dilute solutions.

The free energy content of a mol of water will be the same at a given relative activity and temperature regardless of the manner in which the activity may have been modified. The great difference between these two type systems (ideal dilute soln. and ideal concentrated soln.) lies in the fate of the free energy lost by the water during the process by which its activity was modified. In the first instance, i.e., that of an ideal dilute solution, free energy lost by solvent used to dilute the solution is converted quantitatively into an increase in free energy of the solvent already present in the system. The amount of kinetic energy possessed by each solute molecule is equal to that which that molecule would possess if it were a gas at the same temperature and doesn't change with concentration. In the second case, that of an ideal concentrated solution, the activity of added water is decreased by coming under the influence of forces of attraction or gravitation, probably electrostatic in nature, existing in the environment of the surfaces of the foreign molecules, in such a manner that the molecules of H_2O have their kinetic energy decreased, likewise their free energy, to an extent proportional to the strength of the force acting to retain them in the environment of these surfaces.

The important point in this connection is, that while the relative vapor pressure or activity of the water in either of these two systems might be the same (and would be at equilibrium) the fate of the free energy lost by the water in coming to this activity is quite different in the two cases.

While no system will belong absolutely to either one of these types of solutions, the dilute solutions of crystalloids tend toward ideal dilute solutions while the concentrated solutions of such crystalloids as H_2SO_4 and of colloids in general tend toward exhibiting the properties of ideal concentrated solutions.

It is not possible by measurements of the relative activity of water in a given system to determine to what extent each of these two manners by which the activity of the water may be influenced, may be acting upon the water in that system. Freezing point determinations on solutions of colloids designed to find the molecular weight of those colloids, for example, must always be open to the criticism that an unknown fraction of the freezing point depression will be due to the reduction of the activity of the water by the imbibitional forces active at the surfaces of the colloid micellae. The relative importance of these two methods by which the activity of the water can be influenced, can only be found by a comparison of the total free energy change in the water, ΔA, with the total energy lost from the system, ΔE, during the process of dilution. When $\Delta E = 0$, the laws of dilute solutions are being obeyed and there is none of the influence upon the activity of the water due to the gravitational forces between components of the system. If $\Delta A = \Delta E$, the entire change in the activity of the water is due to these forces. Intermediate conditions would be observed when $\Delta A > \Delta E$ and $\Delta E > 0$. It is characteristic of ideal dilute solutions that the relative vapor pressure of the solvent for any given concentration of the solution does not change, with temperature, i.e.,

$$\frac{\ln (p_0 - p)/p}{T} = 0$$

That this is not true for those solutions in which there is an evolution or absorption of heat with dilution, has been demonstrated.* In this case the value $(p_0 - p)/p$ is found to diminish slightly with increased temperature. The greater the heat lost when a given amount of colloid is mixed with a given amount of water, the more markedly will the value $(p_0 - p)/p$ be found to vary with temperature.

Katz has shown that colloids follow the laws of concentrated solutions as their water content is varied from zero water content up to a water content corresponding to a relative vapor pressure of 0.20 to 0.30. Thru this region of the H_2O content-H_2O activity curve, $-\Delta E$ is equal to $-\Delta A$. As more H_2O is added, however, very little more heat is evolved, which may be taken to indicate that the loss of free energy by this added water is being converted into a gain in free energy of the water previously added or by the gain in kinetic energy of the colloid micellae, accompanied by a tendency for the micellae to pass into true solution.

Table I illustrates that the value of $(p_0 - p)/p$ does not vary appreciably for a colloid (fibrin) of a water content corresponding to an activity of 0.60, between temperatures of 45°C and 15°C. These data were obtained upon a single sample in the isotenoscope placed in a bath, the temperature of which could be varied to and held constant at any temperature within the range

TABLE I

Temp.	Vapor pressure H_2O	Observed	$(p_0 - p)/p$
44.9°C	71.10 mm	44.7 mm	.629
40.5	56.35	35.6	.632
36.4	45.16	28.6	.633
32.0	35.38	22.3	.631
28.8	29.40	18.3	.623
24.9	23.40	14.9	.637
20.6	18.03	11.2	.621
16.4	13.86	8.6	.620
14.4	12.19	7.6	.623

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* See Nernst: "Theoretical Chemistry," 123 (1923).

given. Similar results are given by other colloids and at activities varying from 0.4 to 1.0. At the lower activities results were not so definite, but even at activities as low as 0.25 there was to be observed no variation of the value $(p_0 - p)/p$ with temperature which could be definitely taken as greater than the error of the experiment. It is to be concluded therefore, that measurements observed on the activity of water in colloids at 25°C with the isotenoscope will not vary appreciably from the activity which the water in the same system would show at, say, 37°C or 0°C. Values so obtained should, therefore, be applicable to conditions at body temperature or to results obtained by the freezing point method, a comparison which is made later in the discussion of "bound water" measurements.

It is also to be concluded from these and from the data of Katz that water associated with a colloid in amounts up to that required to show an activity of 0.20 to 0.40 on the H_2O content-H_2O activity curve for that colloid, is bound to or associated with the colloid primarily in accordance with the laws of ideal concentrated solutions but that the additional water needed to bring the activity to any higher value on the curve is bound to or associated with the colloid mostly in the manner which is characteristic of dilute solutions. The amount of water bound by a colloid between activities 0 and 0.40 is always found to be smaller than that bound between activities 0.4 and 1.0, but that found in the former region of the curve is much more strongly bound than that in the latter.

While it is not possible, from activity measurements on a given system, to estimate how much of the water in that system may have been brought to that activity by each of the two possible manners just described, it is possible under certain circumstances to find out in what manner acid or alkali added to a protein may influence the water-binding capacity of that colloid. For instance, if an electrolyte-free, isoelectric protein were investigated, the H_2O activity-H_2O content curve would be that of the pure colloid. If then, to this isoelectric protein were added acid or alkali in an amount such that there resulted a protein salt containing no appreciable excess of acid or alkali, and a similar curve determined for this protein salt, the added water-binding capacity at any given activity of water should give some indication as to the mechanism by which these bound crystalloid ions might be influencing the water-binding capacity of the protein. Since the swelling capacity of a colloid and its water-binding capacity must be very closely related if not identical phenomena, light thrown on one should serve to elucidate the other.

A sample of casein was prepared by precipitation at its isoelectric point according to the method of Van Slyke and Baker.[6] It was found to be very nearly free from ash, containing only 0.11%. A 10 gm. sample of this casein was titrated (in 100 cc. H_2O) with NaOH until it showed approximate neutrality to indicators. After 30 minutes of continued stirring in order to allow equilibrium to be attained, the pH was determined electrometrically and found

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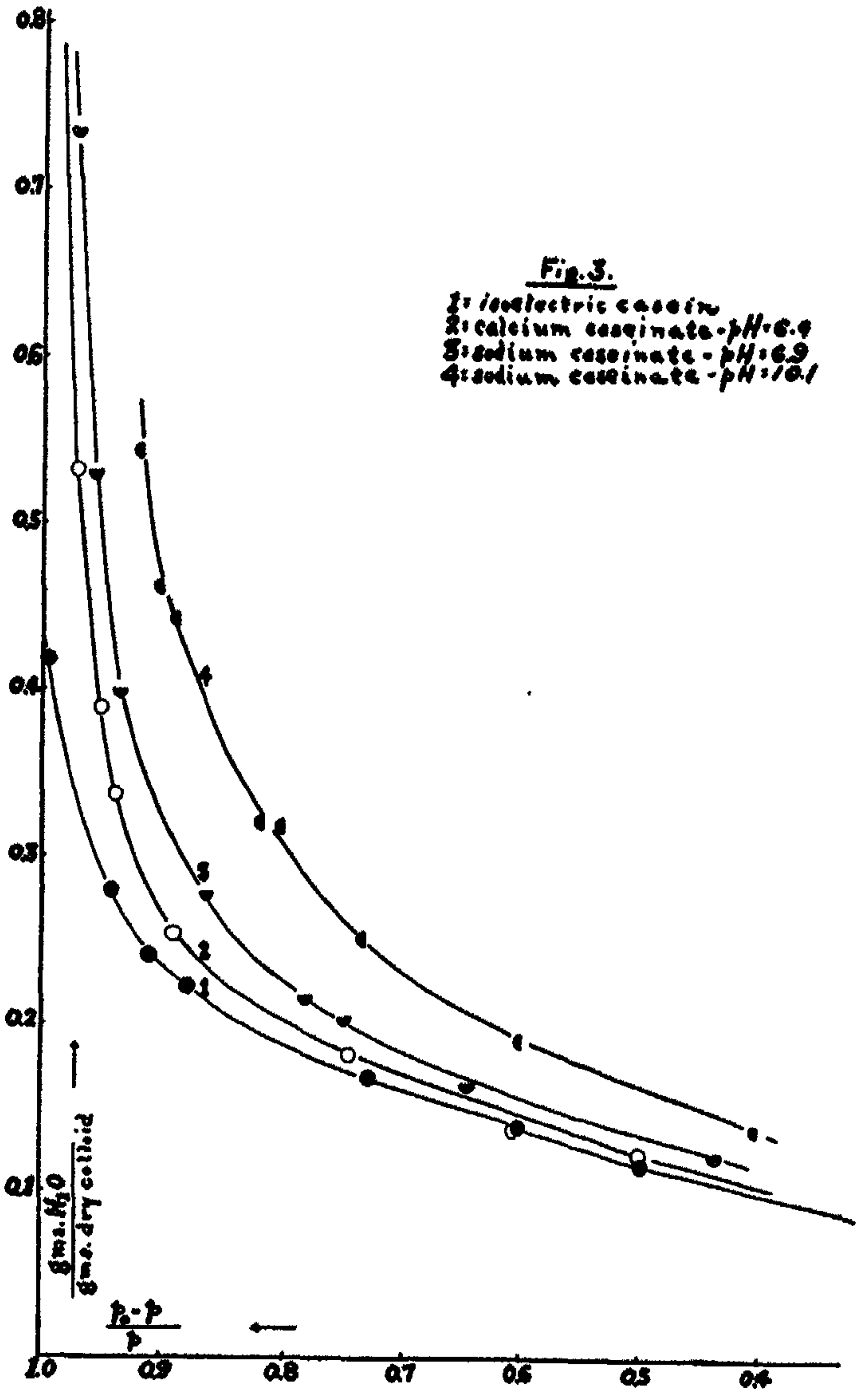
[6] D. D. Van Slyke and J. C. Baker: J. Biol. Chem., 35, 127 (1918).



to be 6.9. The amount of NaOH required was 46 cc. of .1205 N NaOH or 0.555×10^{-3} equivalents of alkali per 1 gm. of casein. To a second 10 gram sample of casein was added 1.11×10^{-3} equivalents of NaOH per gm. of casein, and to a third sample was added 0.555×10^{-3} equivalents of $Ca(OH)_2$ per gm. of casein. The second sample showed a final pH of 10.1 and that containing the $Ca(OH)_2$ was of pH 6.4.

These samples were carefully dried at 35°C under vacuum and then ground to pass a 40 mesh screen, after which the relative vapor pressure-water content curve was determined by the method already described. The results are shown in graphic form in Fig. 3 together with the curve for the original isoelectric casein which had also been dried under vacuum in order to remove any traces of alcohol or ether which might have remained in the casein after preparation and which would lead to erroneous results in the vapor-pressure apparatus.

The data for the casein and caseinates are given in Table II a,b,c, & d. The first two columns in each subtable give the observed relative vapor pressure and the observed water content (per gram of dry solid). The third column gives the value for the water content at the observed R.V.P. as calculated to equal the *sum* of the water held by the isoelectric casein at the same R.V.P. (obtained from the curve for isoelectric casein, by extrapolation, between observed points) and the water which would be present in a solution containing the same number of dissolved molecules as there are Na or Ca atoms present in the corresponding caseinate. This is the same as would be obtained if it were assumed that all of the alkali present had reacted to form alkali caseinate, that this resulting salt were completely ionized, and that the total water imbibed by the alkali caseinate were the sum of the waters held by the isoelectric casein and by the alkali ions, separately.

The grams of $H_2O(g)$ which would be present in a solution containing the same number of dissolved molecules as there are Na or Ca atoms present in a gram of caseinate can be calculated from the equation

$$g = \frac{\text{Mol fraction of alkali present in 1 gm. dry caseinate} \times 1000 \times 1.86}{\text{Freezing point of water in the caseinate}}$$

The freezing point (Δ) of the wetted caseinate can be obtained from its R.V.P. from the equation

$$\log \text{R.V.P.} = -.004211\Delta - .0000022\,\Delta^2$$

For example. For Na Caseinate (pH 6.9) containing $.555 \times 10^{-3}$ mols of Na in 1 gm. of dry caseinate, at a R.V.P. of .935 or $\Delta = 6.85°$, assuming all the Na ionized, the water held by these ions at this R.V.P. would be

$$g = \frac{.555 \times 10^{-3} \times 10^{3} \times 1.86}{6.85} = 1.51 \text{ gms.}$$

Casein (isoelectric) at the same R.V.P. binds 0.266 gms. $0.151 + 0.266 = .417$ gms. as shown in column 3, of Table II.

The curve for isoelectric casein is typical in form for colloids which are insoluble and which possess no, or practically no, ionizable groups. It approaches the water-content axis in a manner indicating that it would take up (imbibe) only about 50% of its own weight of water when immersed in pure water (of activity = 1.) or suspended in an atmosphere saturated with water vapor.

A survey of the curves in Fig. 3 and of the data in Table II indicates that for the Na salts, the *added* water-binding capacity of the casein is very nearly equal to that which would be gained if all the Na present were ionized and acting as dissolved integral particles. The data on the Ca caseinate indicates a much lower degree of ionization.

TABLE II

A = gm. H_2O per gm. dry solid.
B = gm. H_2O per gm. dry solid + H_2O of Na^+

(a)
Casein (isoelectric)

R.V.P.	A
.996	.417
.941	.279
.910	.241
.880	.222
.730	.168
.601	.139
.498	.116
.202	.081

(b)
Na-Caseinate (pH 6.9)

R.V.P.	A obs.	B	Obs/Calc
.974	.734	.727	1.011
.957	.530	.535	.991
.935	.399	.417	.957
.865	.277	.283	.979
.784	.216	.224	.964
.751	.204	.208	.980
.647	.164	.171	.959
.438	.124	(.132)	.939
.180	.060	(.072)	.833

(c)
Na Caseinate (pH – 10.1)

R.V.P.	A obs.	B	Obs/Calc
.919	.542	.493	1.100
.901	.462	.430	1.074
.888	.441	.398	1.108
.819	.320	.301	1.063
.803	.318	.287	1.108
.734	.251	.235	1.068
.600	.190	.179	1.062
.403	.138	.124	1.112

(d)
Ca Caseinate (pH 6.4)

R.V.P.	A obs.	B	Obs/Calc
.986	.807	.906	.891
.973	.530	.577	.919
.951	.388	.430	.902
.936	.337	.370	.911
.891	.253	.285	.887
.746	.181	.193	.938
.607	.137	.153	.895
.501	.122	.126	.967

The fourth column in the subtable of Table II indicates the fraction that the observed value bears to the calculated. For Na caseinate (pH 6.9) the average value is 0.957, for the Ca caseinate the average value is 0.913, and for the Na caseinate (pH 10.1) it is 1.087. In the latter case the effect of the few OH^- ions present and necessary to maintain a pH of 10.1 is omitted from the calculations. This would amount to about .0001 N in every case (an equilibrium condition—the OH^- conc. per unit of water changes little with the water content) and its part in binding water is negligible.

These values may be taken to indicate that for all the caseinates the salt is ionized and that the water binding capacities of these salts is the sum of the water binding capacities of the positive ions and of the negative micelle, this latter being the same as for the isoelectric micelle. In the case of the Na caseinate (pH 10.1) it is probable that some hydroylsis had taken place during the drying process, due to the high OH^- concentration, and that the small molecules resulting caused the water binding capacity of this caseinate to be unduly high in the method of determination herein used. In later experiments more care was observed in the drying process in order to reduce this hydrolysis to a minimum.

In order to check these results another sample of casein was prepared in a similar manner. In this case, however, the improvements upon the original method for the preparation of casein, as suggested by Van Slyke[7] were employed. The purified casein, as prepared by the original method, is redissolved before drying, at pH 6.8 by NaOH, supercentrifuged in this state to throw out any Ca caseinate or calcium phosphate, then reprecipitated with acetic acid at pH 4.7 and electrodialysed in this state before washing with hot 70% alcohol, alcohol and ether. There results an especially pure sample of casein, free of ash and free of a fraction soluble in hot 70% alcohol. It is not surprising that in this sample the water bound by the isoelectric casein at an activity 0.90 is found to be slightly less (.214 g as compared to .233 g. per gm. dry protein) than that obtained for the first sample used, which contained 0.11% ash.

Instead of attempting to determine the whole curve, in this series of expts. a number of points were found for each caseinate at as near the R.V.P. = 0.90 as possible. A larger series of caseinates was prepared. A Na-caseinate containing $.277 \times 10^{-3}$ gm. mols of Na per gm. of casein showed a pH of 6.5, that containing $.555 \times 10^{-3}$ gm. mols per gm. casein showed a pH of 6.9, that containing $.832 \times 10^{-3}$ gm. mols per gm. casein showed a pH of 8.5 and that containing 1.11×10^{-3} gm. mols, a pH of 10.1. Two Ca-caseinates were also prepared, one containing $.277 \times 10^{-3}$ gm. mols of Ca per gm. of casein showed a pH of 6.4 and one containing $.555 \times 10^{-3}$ gm. mols per gm. of casein showed a pH of 9.4. It is to be remembered that the pH values observed were those of the caseinates at equilibrium with the alkali in approximately 100 cc. of water, 10 gm. samples of dry isoelectric casein being used in the preparation of each caseinate. Since the concentration of OH^- ion was in no case greater than .0001 N (this in the case of the caseinate of pH 10.1), the amount present in the 100 cc. of H_2O would never be sufficiently great to shift the pH of the caseinate appreciably upon desiccation. The observed pH's then can be taken as very near to the actual pH's of the samples regardless of the H_2O content.

Table III gives the observed values of the water content of these caseinates at the corresponding R.V.P.'s in the immediate environment of the R.V.P. value of 0.90. The extrapolation value at R.V.P. = 0.90 is also given. Subtracting the amount of H_2O held by the isoelectric casein at R.V.P. = 0.90 from the amount held by the caseinate at the same R.V.P., a value for the water bound by the Na and Ca ions present is obtained. From the actual molar concentration of these atoms known to be present it is possible to cal-

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[7] D. D. Van Slyke: Chem. Age, 32, 163 (1924).

TABLE III

A = gm. H_2O per gm. dry solid

(a)		(b)		(c)	
Isoelectric Casein		Na-Caseinate (pH 6.5)		Na-Caseinate (pH 6.9)	
R.V.P.	A	R.V.P.	A	R.V.P.	A
.936	.246	.913	.274	.882	.293
.874	.199	.907	.265	.905	.312
.899	.209	.881	.245	.899	.301
.901	.213	.904	.262	.914	.317
.901	.218	.895	.261	.871	.281
Extr. .90	.214	Extr. .90	.261	Extr. .90	.304
		Observed due to Na^+	.047	Observed due to Na^+	.090
		Calc. due to Na^+ 100% Ionized	.048	Calc. due to Na^+ 100% Ionized	.095
		Obs/Calc	.980	Obs/Calc	.947

(d)		(e)		(f)		(g)	
Na-Caseinate (pH 8.5)		Na-Caseinate (pH 10.1)		Ca-Caseinate (pH 6.4)		Ca-Caseinate (pH 9.4)	
R.V.P.	A	R.V.P.	A	R.V.P.	A	R.V.P.	A
.899	.348	.912	.462	.885	.211	.910	.253
.887	.340	.896	.413	.893	.220	.910	.245
.913	.393	.898	.407	.926	.246	.879	.221
.881	.310	.881	.373	.910	.228	.917	.246
.912	.364	.914	.472	.917	.241	.889	.226
Extr. .90	.350	Extr. .90	.415	Extr. .90	.225	Extr. .90	.238
Obs. due to to Na^+	.136	Obs. Na^+	.201	Obs. Ca^{++}	.011	Obs. Ca^{++}	.024
Calc. due to Na^+	.143	Calc. Na^+	.101	Calc. Ca^{++}	.048	Calc. Ca^{++}	.095
Obs/ Calc	.951	Obs/ Calc	1.052	Obs/ Calc	.229	Obs/ Calc	.253

culate the amount of water which would be needed to form a solution of these ions which would show a R.V.P. = 0.90 provided these were 100% ionized. The ratio observed/calculated designates the degree of ionization of these cations of the corresponding caseinates provided, of course, the process of drying of the samples has not been accompanied by any hydrolysis. All possible care was taken to dry the caseinates at a low temperature and as quickly as possible in order to decrease the hydrolysis of the casein. These were dried in a vacuum oven at 22° C, the solution being spread in a thin layer over a large surface. Drying was complete in from three to four hours.

That no hydrolysis did occur during the preparation and drying of these samples was ascertained in the following manner. A membrane of gun cotton was prepared from an 8% soln. of gun cotton in acetic acid by dipping a clean alundum cup into the solution and allowing it to drain, while suction was applied to the inside of the cup, for a few minutes before the cup was entirely immersed in warm water. Such a membrane, after thorough washing, is ready for use and has been found to be permeable to all molecules under a molecular weight of 3000-4000. Such a membrane was used to wash the dissolved samples used in the above determinations. Five grams of the caseinate to be investigated for hydrolytic products were dissolved in 100 cc. water, the cup bearing the membrane was then immersed in the solution, and the solution reduced to a small volume by suction applied to the inside of the cup. More water was added to the soln. and the process repeated until about 300 cc. of liquid had been sucked thru the membrane. This fitrate was then concentrated to 10 cc. and biuret and Nessler tests made to determine the presence of protein decomposition products. These were entirely negative in all cases with the exception of the Na caseinate of pH 10.1 in which case a faint positive biuret was observed. This test proved beyond doubt that hydrolytic products played an entirely negligible part in increasing the water-binding capacity of the samples when they were changed from the isoelectric protein to the salts and that the entire effect was due to the cations existing in the caseinates.

Table IV consists of data derived from specific conductivity measurements on the above-mentioned caseinates at 25°C and at a water content such that there would be 10 cc. of water in 1 gram of dry caseinate. The concentration of the alkali would then be that indicated in the table. Specific conductivities were determined upon these alkalies in the absence of the protein. (The values of $Ca(OH)_2$ are extrapolated). The proteinate solns. showed a specific gravity of about 1.030 and therefore each caseinate soln., consisting of 10 cc. of water + 1 gram dry caseinate, occupied a volume of 10.67 cc. This value was employed in the calculation of the equivalent conductivity, Λ, for the caseinate, i.e.,

TABLE IV

Electrical conductivity data on Na and Ca Caseinates and corresponding alkali solutions

ormality of Alkali NaOH	$\kappa \times 10^3$ Alkali solution alone 25°C	$\kappa \times 10^3$ Alkali solution + 100 g. casein per 1000 cc. alkali 25°C	Λ_a for alkali alone 25°C	Λ_c for alkali + 100 gm. Casein per 1000 cc. alkali 25°C	Λ_c/Λ_a
.0277	6.26	1.079	226.0	41.5	18.36
.055	12.20	2.015	220.0	38.7	17.59
.0831	17.98	2.950	216.3	37.5	17.33
.1110	23.70	3.845	213.7	36.9	17.27
$Ca(OH)_2$					
.0555	11.22	0.498	202.2	9.57	4.73
.1110	22.44	0.974	202.2	9.35	4.62

$$\Lambda_a = \frac{\kappa_a . 1000}{N}$$

$$\Lambda_c = \frac{\kappa_c . 1067}{N}$$

The value Λ_e/Λ_0 shows the percentage conductivity of the caseinate when compared to that of the alkali before the casein was added. The percentage conductance by the cation in the NaOH and $Ca(OH)_2$ soln., as calculated from the mobilities at 18°C. of these cations and the OH^- ion, would be approximately 20% and 21% for the Na and Ca ions respectively. Comparing these and the values shown in the last column of Table IV it is seen that the Na caseinates, carrying about 18% the current carried by the corresponding hydroxide, are much more nearly completely ionized than are the Ca caseinates, which carry only about 4.7% the current carried by the hydroxide. This is the same conclusion as is to be drawn from the relative vapor pressure data in the preceding experiments. No quantitative relationship between these two groups of data is inferred, however.

It is especially important to note that, while at lower vapor pressures the part played by the colloid, i.e. the isoelectric protein, itself in binding water is of more importance than that played by the ions bound thereto, as the activity of the water present approaches the value, 1.0, the effect exerted by the colloid becomes insignificant as compared to that resulting from the ions which themselves are bound by salt valences to the colloid. With colloids in equilibrium with water, then, the degree of hydration of the colloid is determined largely, if not entirely, by the number of cations or anions which may be ionized from it, yet held to it by salt valences, and by the activity of the water against which it may be in equilibrium.

Summary

The isotenoscope method for measuring the vapor pressures of liquids is found to be a quick method applicable to the determination of the relative vapor pressure, or activity coefficient of water contained in colloids. The measurements thus obtained are accurate to about 1% when made at 25°C. and within the range of relative vapor pressures lying between 0.98 and 0.30 on the R.V.P.-water content curve. Above and below these values of relative vapor pressure, this method does not yield values which are as accurate as those which may be obtained from freezing point data and from data obtained by allowing equilibrium to be attained over H_2SO_4-H_2O mixtures, respectively.

The limitations of activity data, as a means of differentiating between, and of evaluating the individual forces which may be acting to reduce the activity of water in a given system, are discussed.

Vapor pressure data made upon isoelectric casein and upon various Na and Ca caseinates of varying cation content, are offered as evidence that the change in water-binding capacity (likewise swelling capacity) of a protein is the *sum* of the water-binding capacity of the isoelectric protein and the water binding capacity of the ionized atoms which are bound to the protein when the salts are formed. The Na-caseinates are found to be nearly 100% ionized as compared to the Ca caseinates which are about 20% ionized. Hence the antagonistic effects of these two cations in their influence upon the degree of hydration of colloids.

MIGRATION STUDIES WITH FERRIC OXIDE SOLS

I. Positive Sols

BY FRED HAZEL AND GILBERT H. AYRES

Introduction

It is well known that the hydrogen ion has a stabilizing effect on positive iron oxide sols. Flocculation values of electrolytes have been shown to be markedly greater for sols of high acidity than for sols of low acidity.[1,2,3] It is evident, however, that these values can be only an approximate measure of the stability. Thus, the flocculation measurements give qualitative information regarding the relative differences in stability between sols, but they do not indicate the differences quantitatively. The reason for this is made clear by recalling that the stability of suspensoid sols is due primarily to a potential difference in the double layer, the magnitude of which cannot be determined, in any sense, by flocculation methods. Measurements of velocity of migration in an electric field are a much more exact way of determining the stability because these data are a direct measure of the stabilizing potential.

Cataphoretic measurements made in a U-tube by observing the movement of the boundary between the suspension and the clear dispersing liquid under the influence of an applied potential[4] are open to serious objection. In this connection Mattson[5] has pointed out that the conductivity of the suspension is greater than that of the dispersing medium even if the latter consists of an ultrafiltrate of the sol. The potential gradient is therefore not uniform. The movement of the particles at the boundaries is proportional to the drop of potential at that point, and this is constantly changing due to ionic migration. Since the current must flow for a considerable time to produce a measurable displacement, the effects of heating, electrolysis and polarization may be considerable. Furthermore, the changes in the concentration of the different ions must affect the charge on the particle.

In an effort to overcome these experimental difficulties Cotton and Mouton,[6] Svedberg,[7] Ellis,[8] Powis[9] and Kruyt[10] have resorted to microscopic and ultramicroscopic methods for studying cataphoresis. The most accurate and elaborate ultramicroscopic method has been developed by Svedberg and

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[1] Ghosh and Dhar: J. Phys. Chem., **30**, 830 (1926).

[2] Freundlich and Lindau: Kolloid-Z., **44**, 198 (1928).

[3] Hazel and Sorum: J. Am. Chem. Soc., **53**, 49 (1931).

[4] Burton: Phil. Mag., (6) **11**, 434 (1906).

[5] Mattson: J. Phys. Chem., **32**, 1532 (1928).

[6] Cotton and Mouton: "Les ultramicroscopes et les objets ultramicroscopiques" (1916).

[7] Svedberg: Nova Acta Soc. Sc. Upsaliensis, (4) **2**, 149 (1907).

[8] Ellis: Z. physik. Chem., **78**, 321 (1911).

[9] Powis: Z. physik. Chem., **89**, 91 (1915).

[10] Kruyt: Kolloid-Z., **19**, 161 (1916).

Anderson.[11] A simpler but quite exact means of observing migration of colloidal particles is due to Mattson.[5] The technique of the latter investigator was employed in the present study.

Experimental

A diagrammatic reproduction of the cataphoresis cell* is shown in Fig. 1. It consists of a thick-walled tube 1.85 mm. inside diameter and 11.5 cm. long, terminating in two larger tubes, A and B, which contain cylindrical platinum electrodes placed close to the ends of the horizontal tube; electrical connections are made through mercury wells. At O the tube is ground down to within about 0.6 mm. of the inner wall, and the plane surface polished. At right angles to O, on the side the light is to enter, another plane surface is made. By means of an adjustable adapter the cell is clamped firmly to the microscope objective.

There exists at a glass-water interface an electrical double layer in which the glass is negatively charged and the water is positively charged. Upon applying a difference of potential across the ends of the capillary, electroendosmosis will take place with the result that the water is transferred to the cathode. However, since the cell is a closed system, as much water as flows along the walls in one direction must return through the center in the opposite direction. It follows that the liquid will be at rest somewhere in an annular layer between the axis and the walls. When colloidal particles are observed at different depths in the capillary, therefore, the electroendosmotic motion of the liquid is superimposed upon the electrophoretic motion of the particle; if the observed particle has no apparent velocity, it is obvious that the electroendosmotic motion of the liquid is equal and opposite to the motion of the particle. von Smoluchowski[12] has calculated with the aid of some theoretical deductions that the liquid will be at rest at a distance of 0.7 of the radius away from the axis of the tube. The calculation has been shown to agree with experiment.

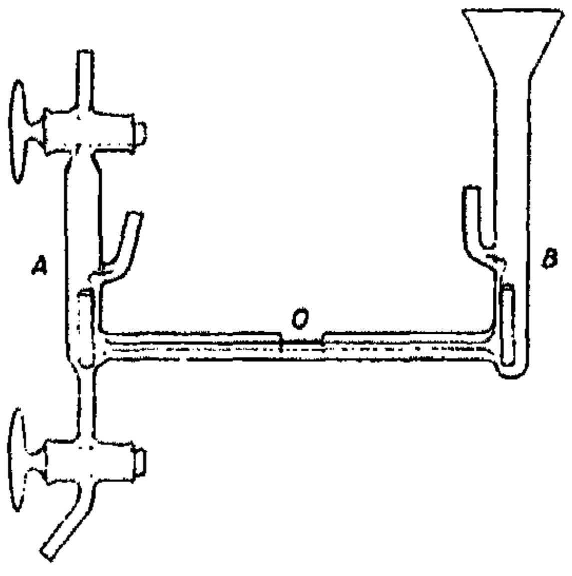

Fig. 1

It is necessary, therefore, to have the microscope focused on a layer of the liquid 0.7 of the radius away from the axis, in order to observe the true velocity of the particles. This adjustment was accomplished as follows: The diameter of the capillary and the thickness of the glass over the capillary were measured both by an objective micrometer and by a cathetometer:

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[11] Svedberg and Anderson: Kolloid-Z., **24**, 156 (1919).

* This cell was designed by Mattson and furnished by the Arthur H. Thomas Company.

[12] von Smoluchowski: Graetz, "Handbuch Elektr. Magn." **7**, 383 (1921).

Diameter of capillary	1.85 mm.
Glass over capillary	0.58 mm.

From these values and the free working distance of the microscope objective, 1.0 mm., it was calculated that in order to focus on a point at a distance of 0.7 of the radius away from the axis of the capillary, the lower rim of the lens mount must be adjusted 1.21 mm. above the ground face of the capillary. This adjustment was made by means of the cathetometer.

The optical set-up was a typical slit-ultramicroscope, the source of illumination being a 120 volt D.C. carbon arc. The objective used was a Zeiss D^*, having numerical aperture 0.75 and primary magnification 40; by the use of eyepiece 10 a magnification of 400 was obtained. The ocular was equipped with a cross-ruled scale each division of which covered a distance of 0.02 mm. on the objective micrometer.

To obtain velocity readings the terminals of the cell were connected to a direct current circuit of 90 volts, furnished by two 45-volt radio "B" batteries; the current could be reversed by means of a double-throw switch. The time required for a particle to traverse 10 scale divisions was determined by means of a tenth-second stop watch. Ten readings were taken in alternate directions for each sample and the mean selected as the most reliable value. (It is important to keep the stop-cocks well greased in order to prevent a leakage of the liquid while velocity readings are being taken, otherwise the readings in opposite directions will be at considerable variance due to a drift of the liquid.)

The velocity of migration, V, in μ/sec./v./cm., is given by the following expression:

$$V = \frac{S \times l}{t \times E}$$

where S is the distance, in μ, traversed by the particle in t seconds, E is the potential across electrode separated by l centimeters. Thus for a distance S = 200 μ, and a potential of 90 volts between electrodes 11.5 cm. apart:

$$V = \frac{200 \times 11.5}{t \times 90} = \frac{25.6}{t}\ \mu/\text{sec./v./cm.}$$

The determinations of pH were made by means of the glass electrode.[3]

Results

The data in the following tables are for sols of an iron content of 0.006 grams per liter. They were prepared by dilution from the same stock sample of colloid.

Table I shows the relation of the pH of the system to the migration velocity of the particles. Small amounts of HCl or KOH were added to adjust the pH of the system.

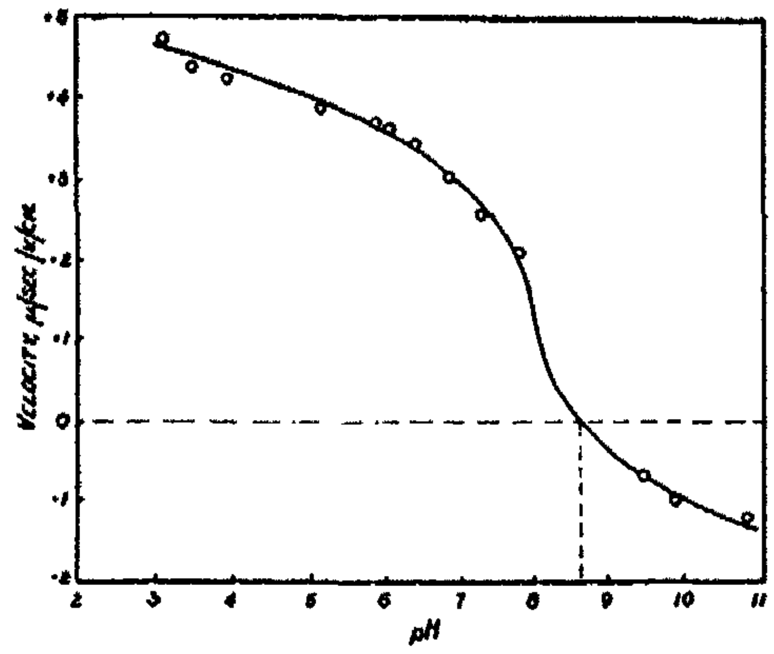

Fig. 2

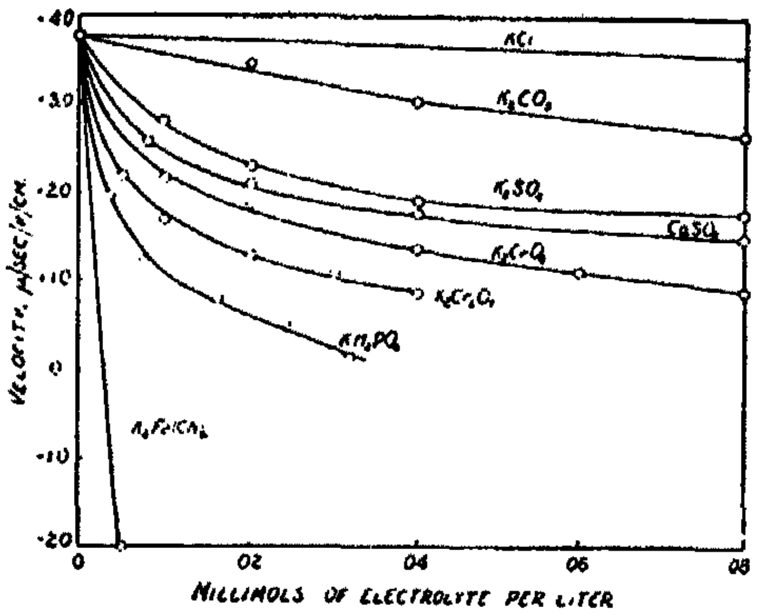

Fig. 3

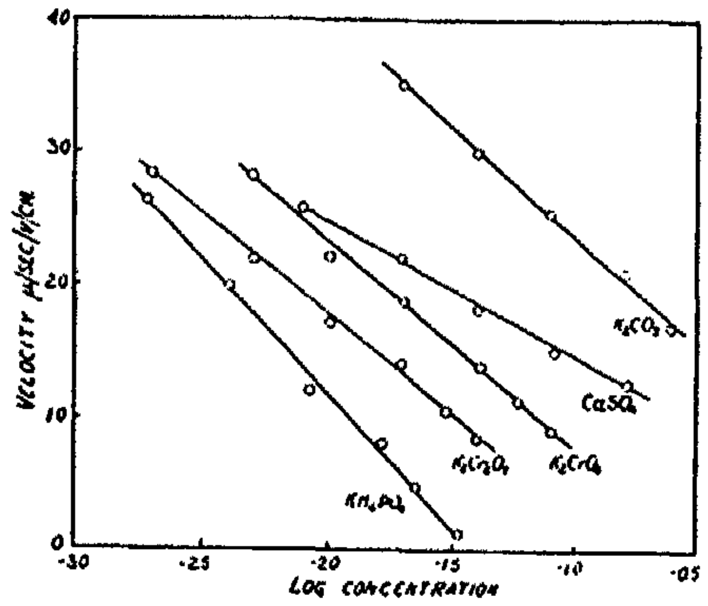

Fig. 4

TABLE I

Series VI B

Sol No.	pH	Time (sec.)	Velocity μ/sec./v./cm.
1	3.1	5.5	+4.7
2	3.4	6.0	+4.3
3	3.9	6.1	+4.2
4	5.1	6.7	+3.8
5	5.8	6.9	+3.7
6	6.0	7.0	+3.6
7	6.3	7.4	+3.4
8	6.7	8.4	+3.0
9	7.2	10.0	+2.5
10	7.7	12.2	+2.1
12	9.4*	40.3	−0.6
13	9.8*	24.0	−1.0
14	10.7*	21.1	−1.2

The asterisk * is used in this and all of the following tables to denote systems in which the addition of electrolyte caused precipitation of the colloid as evidenced by the development of a distinct turbidity within two hours.

Fig. 2 shows the velocities plotted against pH values.

In order to study the effect of addition of various electrolytes on the migration velocity of the colloidal particles, a sol was prepared containing 0.012 grams of iron per liter and having a pH of 5.7. The sol was then diluted to 0.006 grams of iron per liter with solutions of electrolytes of varying concentration. The results are given in Table II, where electrolyte concentrations are expressed in millimols per liter of total mixture.

Fig. 3 illustrates the data of Table II graphically. That the migration velocity is a logarithmic function of the concentration of electrolyte is shown in Fig. 4 where a plot of the velocity against log c gives a straight line.

Table III gives data for sols of Series I, pH 4.0; Series III, pH 6.4; Series IV, pH 7.3; Series II, pH 5.7 is also included for comparison. The behavior of the sols with a mono-, a bi-, a tri-, and a tetravalent ion is shown.

Figs. 5, 6, 7 and 8 show graphically the behavior of KCl, K_2CrO_4, KH_2PO_4 and $K_4Fe(CN)_6$, respectively, with the sols of different hydrogen ion concentration.

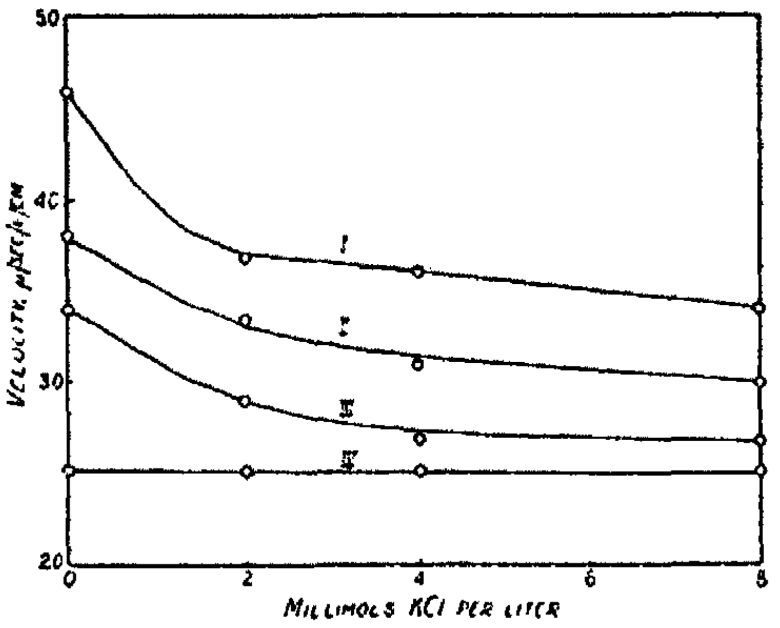

Fig. 5

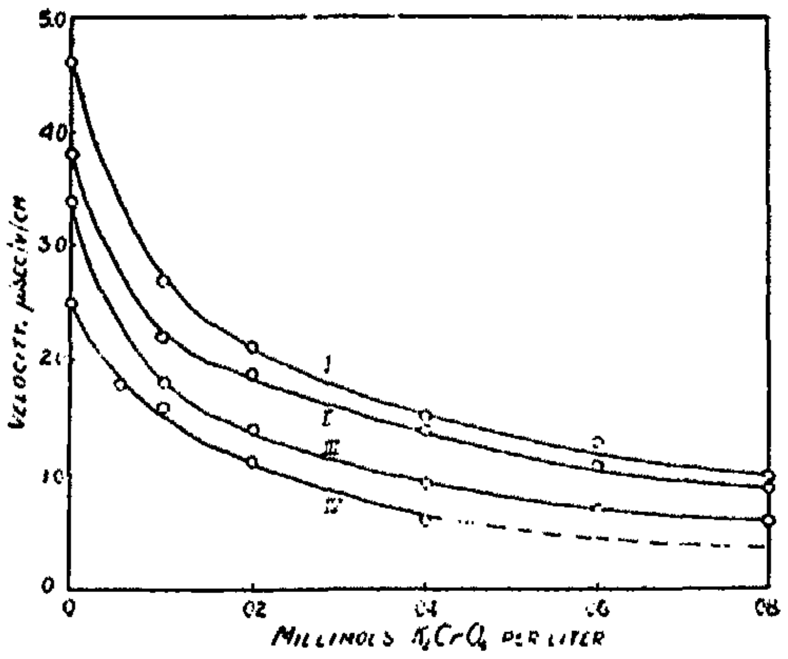

Fig. 6

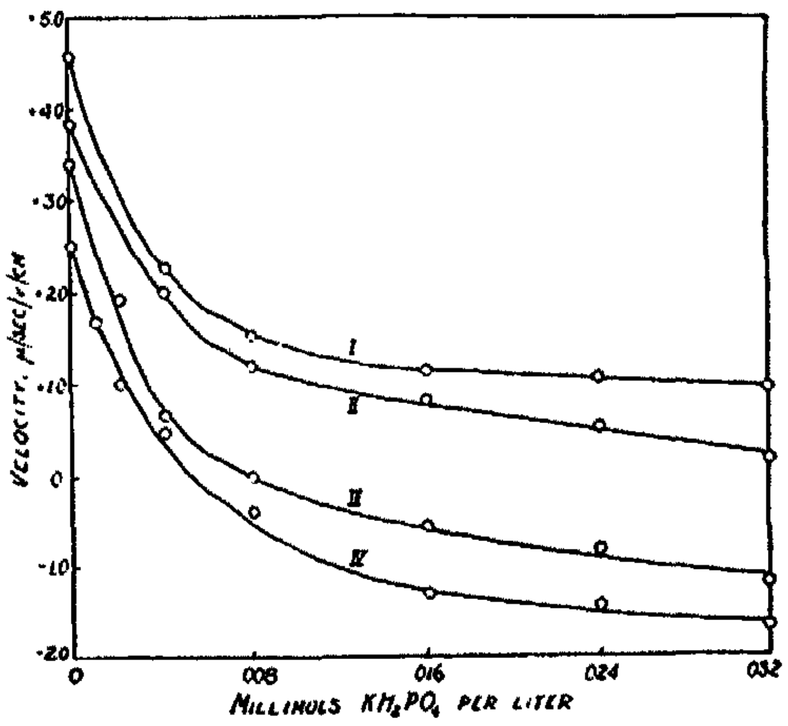

Fig. 7

TABLE II

Sol No.	Millimols electrolyte per liter	Time sec.	Velocity μ/sec./v./cm.
		KCl	
1	0	6.6	+3.8
2	2	7.7	+3.3
3	4	8.2	+3.1
4	8	8.5	+3.0
5	16	8.3	+3.1
6	24	8.4	+3.0
		K_2CO_3	
1	0	6.6	+3.8
2	0.02	7.2	+3.5
3	0.04	8.4	+3.0
4	0.08	9.7	+2.6
5	0.16	12.1	+2.1*
6	0.32	14.8	+1.7*
		K_2SO_4	
1	0	6.6	+3.8
2	0.01	7.9	+3.1
3	0.02	9.8	+2.6
4	0.04	11.6	+2.2
5	0.08	12.0	+2.1
6	0.12	12.6	+2.0*
7	0.16	13.7	+1.9*
		$CaSO_4$	
1	0	6.6	+3.8
2	0.008	9.7	+2.6
3	0.02	11.8	+2.2
4	0.04	14.0	+1.8
5	0.08	17.0	+1.5*
6	0.12	17.5	+1.5*
7	0.16	18.1	+1.4*
		K_2CrO_4	
1	0	6.6	+3.8
3	0.01	11.5	+2.2
4	0.02	13.6	+1.9
5	0.04	18.7	+1.4*
6	0.06	22.8	+1.1*
7	0.08	27.5	+0.9*

TABLE II (Continued)

Sol No.	Millimols Electrolyte per liter	Time sec.	Velocity μ/sec./v./cm.
	$K_2Cr_2O_7$		
1	0	6.6	+3.8
2	0.005	11.5	+2.2
3	0.01	15.5	+1.7*
4	0.02	19.2	+1.3*
5	0.03	22.5	+1.1*
6	0.04	32.0	+0.8*
	KH_2PO_4		
1	0	6.6	+3.8
4	0.004	12.7	+2.0
5	0.008	20.5	+1.2*
6	0.016	31.3	+0.8*
7	0.024	48.8	+0.5*
8	0.032	—	+0.1*
	$K_4Fe(CN)_6$ (pH of sol = 5.2)		
1	0	6.8	+3.7
2	0.00025	9.3	+2.7
3	0.0005	10.8	+2.3
4	0.0010	17.5	+1.5*
5	0.0015	46.0	+0.6*
6	0.002	28.3	−0.9*
7	0.003	12.4	−2.1*
8	0.005	7.5	−3.0
9	0.01	7.0	−3.7
10	0.02	6.2	−4.0
11	0.04	5.8	−4.3
12	0.08	6.2	−4.0
13	0.25	5.6	−4.5
14	1.0	5.1	−5.0
15	10.0	5.1	−5.0

TABLE III

Sol	No.	Millimols electrolyte per liter	Velocity, μ/sec./v./cm.			
			Series I pH = 4.0	Series II pH = 5.7	Series III pH = 6.4	Series IV pH = 7.3
A	1	0	+4.6	+3.8	+3.4	+2.5
KCl	2	2	+3.7	+3.3	+2.9	+2.5
	3	4	+3.6	+3.1	+2.7	+2.5
	4	8	+3.4	+3.0	+2.7	+2.5
	5	16	+3.2	+3.1	—	—
	6	24	—	+3.0	—	—
	7	32	+2.8	—	—	—
B	1	0	+4.6	+3.8	+3.4	+2.5
K_2CrO_4	2	0.005	—	—	—	+1.8
	3	0.01	+2.7	+2.2	+1.8*	+1.6*
	4	0.02	+2.1	+1.9	+1.4*	+1.1*
	5	0.04	+1.5*	+1.4*	+0.9*	+0.7*
	6	0.06	+1.3*	+1.1*	+0.7*	+slight*
	7	0.08	+0.9*	+0.9*	+0.6*	+slight*
C	1	0	+4.6	+3.8	+3.4	+2.5
KH_2PO_4	2	0.001	—	—	—	+1.7*
	3	0.002	—	—	+1.9*	+1.0*
	4	0.004	+2.3	+2.0	+0.6*	+0.5*
	5	0.008	+1.5*	+1.2*	±0.0*	−0.4*
	6	0.016	+1.1*	+0.8*	−0.6*	−1.3*
	7	0.024	+1.0*	+0.5*	−0.8*	−1.4*
	8	0.032	+0.9*	+0.1*	−1.3*	−1.7*
				pH = 5.2		
D	1	0	+4.6	+3.7	+3.4	+2.5
$K_4Fe(CN)_6$	2	0.00025	+4.3	+2.7	—	+1.5*
	3	0.0005	+3.8	+2.3	+0.5*	—
	4	0.0010	+2.5	+1.5*	−0.3*	±0.0*
	5	0.0015	+1.9*	+0.6*	—	—
	6	0.002	+1.6*	−0.9*	−1.4*	−2.8
	7	0.003	+0.3*	−2.1*	−2.4	—
	8	0.005	−1.7*	−3.0	−3.5	−4.3
	9	0.010	−3.0	−3.7	−4.6	−4.8
	10	0.020	−3.4	−4.0	−5.0	—

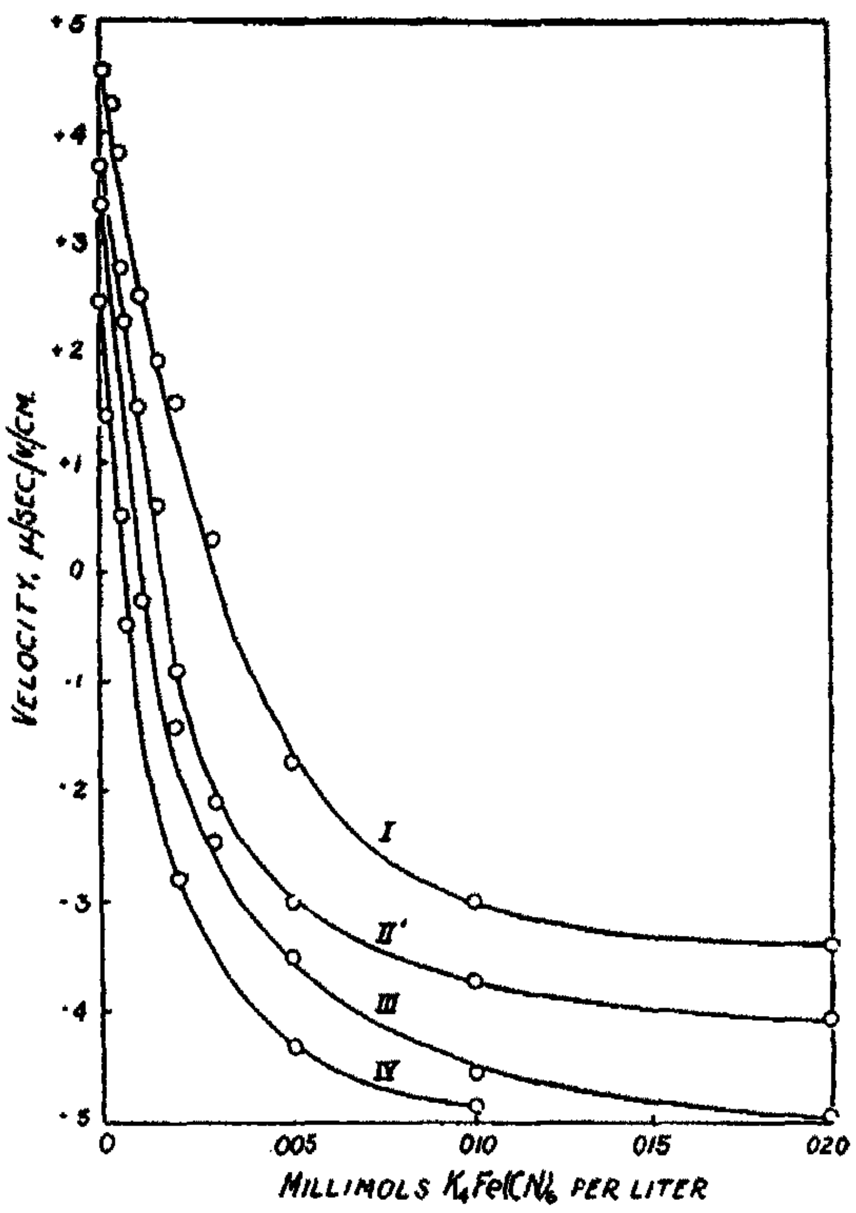

FIG. 8

Discussion

The velocity data incorporated in Tables I, II and III may be used to calculate the zeta potential of the particles. The value of zeta is supposed to represent the difference in potential which exists between the fixed and the movable part of the double layer. An example of the calculation is included at this point, using the formula of Helmholtz and Perrin:

$$\zeta = \frac{4\pi\eta v}{HD}$$

where ζ = the zeta potential in volts

v = velocity of the particles in cm. per second

H = potential gradient, in volts per cm.

D = dielectric constant of the medium

η = viscosity of the medium. (The absolute viscosity of water at the temperature of the experiment is usually taken. It may be obtained from tables.)

Substituting in the above formula for $v = 3.0$ μ/sec./v./cm. = 0.0003 cm./sec./v./cm., and assuming that $D = 80$, the dielectric constant of water, we have for a potential gradient of one volt per centimeter:

$$\zeta = \frac{4 \times 3.1416 \times 0.01 \times 0.0003 \times 300 \times 300}{1 \times 80}$$

$$\zeta = 0.042 \text{ volt.}$$

300 × 300 is put in the numerator to convert H and ζ into absolute units. This calculation shows that velocities may be converted to values of zeta by simply multiplying by the factor 0.014.

We have purposely avoided making calculations of the zeta potential because of their doubtful value. An excellent summary of the chaotic state that has resulted from these calculations is given by Mooney.[13] McBain[14] and Harkins[15] have also criticized this practice. The main difficulty seems to center around the fact that the dielectric constant of colloidal systems that contain electrolytes is not accurately known. Furthermore, the factor of 4 in the Helmholtz-Perrin formula was derived for a cylindrical particle. Debye and Hückel[16] have shown this factor to be 6 for a spherical particle. In addition, the viscosity factor introduces confusion. Some investigators base their calculations on the viscosity of the pure dispersing phase while others use the viscosity of the colloidal dispersion.

From the above considerations we conclude that the magnitude of the potential difference existing in the electrical double layer cannot be calculated to the satisfaction of all. Nevertheless, colloidal theory tells us that the stability of suspensoid sols is due to this potential difference, and the greater the latter, the more stable the sol. Inspection of the Helmholtz-Perrin formula shows that all of the factors on the right side of the equation are accessible to direct measurement; since η is constant at constant temperature, H is a constant amounting to one volt per centimeter, and D is assumed to be constant, we may combine the values of $4\pi\eta/HD$ into a single constant, and write:

$$\zeta = k\,v$$

which shows that the potential difference of the double layer is directly proportional to the migration velocity of the particles. It follows that measurements of migration give the best approximation concerning the stability of the particles.

An inspection of the curve shown in Fig. 2 shows that the isoelectric point falls at a pH of about 8.6; this is for a very pure sol obtained by dialyzing for a week at a temperature of 90°. Hydrochloric acid was used in making the sols in the acid range. The hydrogen ion is very strongly adsorbed, the

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[13] Mooney: J. Phys. Chem., 35, 329 (1931).

[14] McBain: J. Phys. Chem., 28, 706 (1924).

[15] Harkins: Colloid Symposium Monograph, 6, 17 (1928).

[16] Debye and Hückel: Physik. Z., 25, 49 (1924).

negative chloride ion playing a subordinate role. We might reason, *a priori*, that the farther the system is removed from the isoelectric point, on the acid side, the more stable the positive sol will be. The data of Table II shows that this is true for systems with a pH as low as 3.1. However, there is a limit to the charging effect of the hydrogen ion as shown by the shape of the curve in the low pH range; it would appear that the surface of the particles is becoming saturated with hydrogen ions. At high acidities, where saturation of the surface is reached, the discharging effect of the chloride ion would probably be noticed. It is difficult to realize this portion of the curve experimentally because of the pronounced solvent action of hydrochloric acid for ferric oxide.

The same line of reasoning can be applied to the negative part of the curve. Moderate concentrations of potassium hydroxide give a stable negative sol, due to the strong adsorption of hydroxyl ions. High concentrations of potassium hydroxide decrease the stability, causing flocculation; in this case it is, of course, the potassium ion which discharges the particles.

Table II and Fig. 3 show that the discharging action of the ferrocyanide ion is the most pronounced, whereas the chloride ion has the least effect; bivalent and trivalent ions occupy intermediate positions. Fig. 4 shows that the middle portions of the velocity-concentration curves are logarithmic in form. This type of relation is frequently encountered in colloid chemistry, especially in adsorption phenomena.

The results of this investigation have confirmed in a remarkable way the investigations of Powis[17] in showing that it is not necessary to deprive the particles *completely* of their charge in order to cause flocculation; a lowering of the potential to a certain "critical potential" is sufficient to cause coagulation. Powis found the critical potential for oil-water emulsions to be 30 millivolts. A charge of 30 millivolts would correspond to a migration velocity of 2.1 μ/sec./v./cm. In the tables presented earlier, all of the samples are indicated * in which the critical potential was reached, as evidenced by the fact that sufficient flocculation had taken place in order to produce a distinct turbidity within two hours. It will be noticed that the samples so designated vary in velocity from $+1.9$ to -2.1 μ/sec./v./cm. In order to have a stable sol, therefore, it is necessary to have sufficient electrolyte adsorbed to contribute a potential difference of over 30 millivolts.

Addition of alkali to a sol which is stabilized by hydrogen ions will first lower the potential to the critical value, when the sol begins to flocculate although the particles are still positively charged; larger quantities of alkali reduce the charge to zero and then produce a negatively charged particle which is, however, not a stable negative colloidal particle until enough alkali has been added to increase the charge to above the critical potential. Inspection of Fig. 2 shows that the lower part of the curve would cut the -2.0 velocity axis at a pH of approximately 12.5. Addition of sufficient alkali

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[17] Powis: Z. physik. Chem., 89, 186 (1915).

to give a system of this pH (or above) should therefore give a stable negative sol. This view was tested experimentally by flocculation methods and found to be qualitatively correct.

Similar considerations apply to the sols on addition of other electrolytes.

Figs. 5, 6, 7 and 8 clearly demonstrate the stabilizing effect of the hydrogen ion, a property which has been emphasized previously by one of the authors.[3] The curve for potassium chloride with a sol of pH 7.3 indicates that the chloride ion has no effect on the migration velocity of the particles. The chloride ions are unable to compete with the strongly adsorbable hydroxyl ions.

Summary

1. The migration velocity of positive ferric oxide sols has been studied by observation of the movement of single particles under the ultramicroscope.

2. The effects of hydrogen ion concentration and of addition of electrolytes on the migration velocity have been investigated.

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CATALYTIC ACTION OF AN ALUMINUM OXIDE CATALYST*

BY WILDER D. BANCROFT AND AVERY B. GEORGE

Introduction

There appear in the literature some differences of opinion in regard to the explanation for the action of oxide catalysts when prepared under different conditions. Adkins[1] has advanced a hypothesis in which he considers that the catalytic activity of alumina is conditioned by its molecular porosity or the distances between the aluminum atoms. This is determined in part by the size, shape and position of the radicals attached to the aluminum when the aluminum compound goes into the solid state. In terms of this hypothesis it is held that decarboxylation is favored by large pores in the aluminum, and that ethylene formation is favored by small pores. Large and small in this case refer to units of molecular dimensions. Adkins says that catalysts which are colloidal give small pores when water is driven off, as the water is adsorbed, so they are favorable to ethylene formation. True hydroxides give less ethylene, and the catalysts prepared from the ethoxides favor the carbon dioxide formation, and these give large pores. The data of Adkins giving the relative amounts of ethylene and carbon dioxide obtained are given in Table I.

TABLE I

	Catalyst	Wt. C_2H_4 gm.	Wt. CO_2 gm.	Ratio Wt. C_2H_4/Wt. CO_2
1.	Ethoxide on pumice	2.46	4.57	0.538
2.	Isopropoxide on pumice	1.95	4.50	0.433
3.	Methoxide on pumice	2.30	4.40	0.522
4.	Amalgam interaction with H_2O	5.95	3.10	1.92
5.	Ethoxide precipitated by H_2O	6.75	3.75	1.80
6.	Isobutoxide on pumice	2.10	4.30	0.488
7.	Propoxide on pumice	2.50	4.90	0.510
8.	Butoxide on pumice	2.90	4.60	0.630
9.	Ethoxide pills from powder	2.80	4.10	0.682
10.	Nitrate pills from powder by precipitation with NH_4OH	5.90	3.20	1.84
11.	Pills from precipitate by action of HCl on $NaAlO_2$	5.00	3.70	1.35

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* This work is done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] J. Am. Chem. Soc., 44, 385, 2175 (1922).

On the other hand Taylor[2] regards an oxide catalyst as composed, not of a single catalyst, but of two catalysts, metal ions and oxide ions. The nature of the changes induced in the adsorbed reactant is determined by the charge of the ion on which the reactant molecules is adsorbed. The extent of the two alternative changes will be determined by the relative extent of adsorption of reactant on the two ions, on the relative frequency of the two ions in the surface, and on their specific individual catalytic activities. These several factors, extent of adsorption, frequency of ions in the surface, and catalytic activity will be determined by the degree of saturation of the lattice ions (i.e. catalytic structure) and by the extent to which the ions are already covered by poisons (salts ammonia, water, etc.) In this explanation alkali poisons favor dehydrogenation or decarboxylation, while acid poisons favor the dehydration process.

With these two different views on the matter, it seemed that this would be a good field for investigation, in order to arrive at the correct explanation. The substance chosen to be decomposed was ethyl acetate, for this was used by Adkins in some of his work. Sabatier[3] classifies the decomposition of ethyl acetate at 400°C when using different catalysts, as follows.

$$2CH_3COOC_2H_5 \xrightarrow{Al_2O_3} (CH_3)CO + 2C_2H_4 + CO_2 + H_2O$$

$$2CH_3COOC_2H_5 \xrightarrow{TiO_2} 2CH_3COOH + 2C_2H_4$$

$$2CH_3COOCH_5 \xrightarrow{ThO_2} (CH_3)CO + CO_2 + C_2H_4 + C_2H_5OH$$

From the above reactions it can be seen that a determination of the relative amount of the gases, ethylene and carbon dioxide, would give a means of measuring the course of the reaction. This was exactly the procedure followed, and the result was expressed as the ratio, Weight C_2H_4/Weight CO_2, which is the relation of dehydration to decarboxylation.

Experimental Procedure

Preparation of Catalysts. The alumina catalysts used in this work were prepared by a number of different methods. Most of the catalysts were prepared by the procedures used by Adkins, in order that the two sets of results might be put on a comparative basis.

Catalyst No. 1. 200 grams of $Al(NO_3)_3.9H_2O$ were dissolved in about two liters of distilled water, and then concentrated ammonium hydroxide was added to the hot solution until the precipitation was complete. The precipitate was washed a few times by decantation, then filtered, washed, and dried in an electric oven at about 120°C. The dried alumina was broken up into small, fairly uniform pieces, which were used in the runs.

Catalyst No. 2. A solution of 10 grams of $Al(NO_3)_3.9H_2O$ in 50 cc. of water was made up, and 10 grams of washed pumice were soaked in this hot

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[2] Colloid Symposium Monograph, 4, 19 (1926).

[3] Sabatier: "La Catalyse en Chimie organique," 341 (1920).

solution for about five minutes. Then the solution was drawn off, and 50 cc. of concentrated ammonium hydroxide added to the pumice. This treatment caused the hydrated aluminum oxide to be precipitated on the pumice, after which the ammonium hydroxide was drawn off, and the supported catalyst washed with water a few times. The catalyst was dried in the electric furnace at 120°C, and then over a bunsen burner for a few minutes.

Catalyst No. 3. 30 grams of $Al(NO_3)_3.9H_2O$ were heated in an evaporating dish until the pure Al_2O_3 remained, thus driving off the water and the oxides of nitrogen. This solid was broken up into small pieces for use, as in the case of catalyst No. 1.

Catalyst No. 4. 10 grams of $Al(NO_3)_3.9H_2O$ were dissolved in a small volume of distilled water, and to this concentrated solution 12 grams of washed pumice were added. The mixture was heated on a water bath, until the pumice was fairly dry, and then further drying was obtained by placing the catalyst in the electric furnace at about 115°C. The catalyst was then heated until all of the nitric acid was driven off, after which it was ready for use.

Catalyst No. 5. Some aluminum ethoxide was put on a watch glass, and exposed to the air for a period of time. The ethoxide hydrolyzed with the formation of aluminum oxide, which was broken up into small pieces for use.

Catalyst No. 6. Four grams of aluminum ethoxide were melted and 3 grams of washed pumice was added to the melt. This was allowed to cool, and then moist air was passed over the catalyst for about five hours, after which it was exposed to the air for a long period of time before use.

Catalyst No. 7. Some of the dry washed pumice, which is a silicate of sodium, potassium and aluminum, was used as a catalyst.

Apparatus and Procedure. The apparatus consisted of a flask for vaporizing the liquid, this being connected to a reaction tube heated by an electric furnace, with a system for condensing the liquid products, and an eight-liter bottle, which served as a gasometer for collecting the gases evolved, at the other end. A saturated solution of sodium chloride was used as the confining liquid in the gasometer, as the gases evolved are only very slightly soluble in this solution. A thin layer of the catalyst was spread along the reaction tube for a length of 20 cm. The furnace was heated to a temperature of about 450°C, at which temperature all of the runs were made. The procedure followed was to put a measured amount of the ethyl acetate into the flask through the funnel at the top. At the end of a run the amount of liquid left was measured, then the amount of ethyl acetate actually used could be determined. The flask containing the ethyl acetate was immersed in an oil bath, and the rate at which the ethyl acetate vapors were allowed to pass over the catalyst was controlled by varying the temperature of the oil bath. The bath was kept at a temperature of 80°-90°C, in which range about 40 grams of ethyl acetate were vaporized per hour. The ethyl acetate vapors were passed through the catalyst tube, the liquid products being condensed, and the gaseous products collected in the gasometer on emergence from the heated tube. The weight of the liquid product, and the volume of gas were determined. Then a sample of the gas was taken from the gasometer, and analyzed for carbon dioxide and ethylene. The carbon dioxide was removed by absorbing the gas in a solution of sodium hydroxide, while the ethylene was determined by passing the gas into a pipette containing fuming sulphuric acid, thus obtaining the necessary data.

Experimental Results

The first runs were made using the catalysts prepared from the aluminum ethoxide, numbers 5 and 6 as given above, and the data obtained are given in Table II. The ratios obtained from Adkins' data are also given.

TABLE II

Catalyst	Ratio Wt. C_2H_4/Wt. CO_2	Adkins' Ratios
Unsupported No. 5	2.18	0.682
Supported No. 6	1.66	0.538

The percentage increase in the amount of ethylene formed from the unsupported catalyst over the supported one compares very well with that obtained by Adkins. However, the ethylene/carbon dioxide ratios obtained by Adkins are very much lower than the values found in this work. He prepared this catalyst by exposing the aluminum ethoxide to the air for a long time, so this was a case of slow hydrolysis. Since the ethoxide used by him should be the same as that employed in this work, the difference in values might be due to impurities in the air. The catalyst employed here was not exposed directly to the atmosphere of the laboratory. It seemed that ammonia would be the most likely present, so a catalyst was made from the ethoxide by hydrolyzing it in a solution of ammonia. After drying, this catalyst was used in a run, and the ethylene/carbon ratio obtained was 1.22. Now this value is much less than the 2.18 obtained above, and while it is not as low as Adkins' value, this shows that the presence of ammonia causes a low ethylene/carbon dioxide ratio. So this shows that the presence of ammonia, and probably other basic impurities in the air, will account for the low values obtained with the ethoxide catalysts.

Now we thought that if Adkins' explanation was right, it should be possible to take a catalyst which is predominately decarboxylating, thus having large pores, and change it over to a dehydrating catalyst with small pores, by heating to a high temperature thus causing the catalyst to sinter. An experiment was made along this line using some of catalyst No. 1, prepared by precipitation of the hydrated oxide from an aluminum nitrate solution with ammonium hydroxide. The first two runs were made without heating the catalyst above the temperature of the furnace. Then another portion of the catalyst was heated over a Meker burner for about a half hour, in order to cause the catalyst to be sintered. The data obtained are given in Table III.

TABLE III

Catalyst	Ratio Wt. C_2H_4/Wt. CO_2
Not sintered No. 1	2.14, 2.16
Sintered No. 1	2.44

These figures show that the sintered catalyst apparently does give a larger ratio of ethylene/carbon dioxide. The catalyst used was a predominantly dehydrating one, so perhaps this 14% increase in the ethylene/carbon ratio is not fair data on which to base a conclusion. Some of the catalyst prepared by hydrolyzing the ethoxide in an ammonia solution was sintered in the same way as was the No. 1 catalyst, and a run made. The ratio obtained was 1.39, the percentage increase of the ratio being practically the same as the 14% given above. This shows that the increase of the ethylene/carbon dioxide ratio, due to sintering, was practically the same starting with a catalyst of low or high ethylene/carbon dioxide ratio. As shown above, ammonia caused a marked decrease in the value of the ratio, so even at the high temperature of sintering there must be some of the ammonia present.

A further experiment was done along this line, for some of the catalyst prepared from the aluminum ethoxide was heated to a high temperature and sintered, then it was used in a run. In this case a value of 2.95 was obtained for the ratio, as compared to 2.18 for the unsintered catalyst. This increase in the amount of ethylene formed cannot be accounted for entirely by sintering, for part of the catalyst became dark colored on heating. As alumina would not become dark by this treatment, this change was probably due to some organic material present, as carbon, which became charred. This change apparently favors the formation of ethylene. So the values given in Table III above, and the data obtained by sintering the ethoxide catalyst hydrolyzed in the presence of ammonia illustrate better the change involved due to sintering, and this amounts to about a 14% increase of the ethylene/carbon dioxide ratio. However, the increase in the amount of ethylene obtained by sintering the catalyst was considerably less than the difference between the dehydrating and decarboxylating catalysts. So from this it seemed that the facts could not be explained in this way.

A miscellaneous experiment was made using some of the washed pumice as the catalyst. With this substance a ratio of 62.5 was obtained, which means that there was only very little carbon dioxide formed. This seemed very interesting, and as pumice is a complex silicate, it may be that substances of this type have possibilities in contact catalysis. The reason for making this experiment was to determine whether or not the support used had any effect on the reaction, and it apparently has.

In order to compare the activity of a supported catalyst prepared by precipitation with ammonium hydroxide, the procedure as given for catalyst No. 2 above was used. Many people have compared the activity of oxide catalysts prepared by precipitation with ammonium hydroxide, with supported catalysts prepared by heating a nitrate solution containing the support, as pumice. This is not a just comparison, for in this case the effect of the ammonia is neglected, while it may have a marked effect. The results obtained with catalyst No. 2 gave a rather high ratio, much higher than would be expected. It seems that this was due to the fact that this method of preparation did not give a uniform surface layer of the alumina. In fact portions of the pumice were not completely covered so the catalyst really consisted of some alumina on the surface and also some of the uncovered pumice. Now that pumice was found to be a good catalyst for the formation of ethylene this will account for the high ethylene ratio.

A comparison was now made of a supported catalyst on pumice and an unsupported one, both being prepared by heating $Al(NO_3)_3.9H_2O$, thus the catalyst obtained should be free from any adsorbed ions, which is not true in the case of the precipitation methods. Catalysts number 3 and 4 were used, and the data are given in Table IV.

TABLE IV

Catalyst	Ratio Wt. C_2H_4/Wt. CO_2
Unsupported No. 3	3.84
Supported No. 4	3.57

In this case the unsupported catalyst gives a little larger amount of ethylene than does the supported one, but the difference is very small.

While the experiments on the sintering of the catalysts did show an increase in the amount of ethylene formed, this could not be the major factor, for the difference was not great enough to account for the facts. Consequently the next approach was to study the effect of the adsorbed ions on the oxide surface. According to Taylor's theory the basic radicals are primarily decarboxylating, so if ammonium hydroxide was added to an oxide catalyst the adsorption of the ammonia should increase the amount of carbon dioxide formed. A catalyst was prepared according to the procedure given for catalyst No. 4 above. This catalyst was assumed to be practically pure, being free from adsorbed ions, and its ethylene/carbon dioxide ratio was 3.57 as shown in Table IV above. Now some of this catalyst was soaked in concentrated ammonium hydroxide for a few minutes, thus causing the ammonia to be adsorbed on the alumina. After washing and drying the catalyst it was used in a run, and an ethylene/carbon dioxide ratio of 2.80 was obtained. This shows that the presence of the ammonia increased the relative amount of carbon dioxide formed.

Some of catalyst No. 2 was treated in exactly the same way as was catalyst No. 4 above, and then some runs were made with it. In this case the formation of ethylene was favored, but this was due to the fact that on soaking the supported catalyst some of the alumina layer was removed from the pumice, thus leaving more exposed pumice, which favors the formation of ethylene. The catalysts prepared by heating $Al(NO_3)_3.9H_2O$, as No. 3 above, favor the formation of larger amounts of ethylene than do those prepared by the precipitation with ammonium hydroxide. This fits in very well with the general explanation, that the adsorbed ions have an effect, and that the basic radicals favor decarboxylation.

Another series of experiments was carried out in order to determine the effect of adsorbed ions on the oxide surfaces. A catalyst was prepared using the same procedure as that employed in making catalyst No. 4 above. This catalyst was then divided into three parts. One run was made using the pure aluminum oxide catalyst, then one of the other portions was soaked in a zinc nitrate solution, and the other in an aluminum sulphate solution. In the first case zinc was taken up by the surface, while in the second case sulphate was adsorbed, the other two ions being common to the initial state of the catalyst. The solutions used contained equivalent concentrations of the salts, and in the case of the one with zinc nitrate, the catalyst was heated until all the nitric acid was driven off. On making runs with these catalysts, the effect of the acid and the basic radicals could be determined. According to the theory, the zinc should favor decarboxylation, while the sulphate favors the dehydration, or the formation of ethylene. The data obtained are given in Table V.

TABLE V

Catalyst	Ratio Wt. C_2H_4/Wt. CO_2
Al_2O_3 pure	2.75
Al_2O_3 + Zinc	1.13
Al_2O_3 + Sulphate	12.5

From the data given in the above table, it has been shown that the presence of the zinc causes an increase in the amount of carbon dioxide formed, while the sulphate favors an increase in the amount of ethylene formed. These results are in harmony with the theory set forth by Taylor, and as the facts are explained much better with this than by the theory of molecular porosity, it seems that the theory set forth by Taylor is probably the correct one.

Conclusions

1. The increase in the relative amount of ethylene obtained by sintering an aluminum oxide catalyst is considerably less than the difference between the dehydrating and decarboxylating catalysts.

2. The use of washed pumice as a catalyst gives very large amounts of ethylene, with little carbon dioxide.

3. The catalysts prepared by heating $Al(NO_3)_3.9H_2O$, favor the formation of larger amounts of ethylene than do those prepared by the precipitation with ammonium hydroxide.

4. While there was a slight increase in the amount of ethylene obtained by sintering a catalyst, this was small as compared to the effect of adsorbed substances. So the results of this paper show that Taylor's theory, which states that the extent of the changes induced in the adsorbed reactant will be determined by the specific individual catalytic activities of the adsorbed ions or their reaction products, is probably the correct one.

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GUANIDINE AND NITROUS ACID. II*

BY WILDER D. BANCROFT AND S. LOUISA RIDGWAY

Although considerable work has been done on guanidine, its structure is far from being a settled question—as is shown by the different formulae adopted by various authors. A study of the reaction between guanidine and nitrous acid was undertaken in order that some interesting points in regard to the reaction itself might be cleared up, and that some light might be shed on the structure of guanidine through the speed of the reaction. Work on the decomposition products at various stages is being done by Mr. B. C. Belden[1] of this laboratory.

The reaction of nitrous acid and primary aliphatic amines has long been known to give the corresponding alcohol, nitrogen, and water. Conversely the evolution of nitrogen with nitrous acid has been used in the detection and estimation of primary aliphatic amines. This method was brought into prominence by Van Slyke's[2] scheme for the analysis of proteins and protein residues; and more especially by his very convenient apparatus. Van Slyke found experimentally how amino groups in natural amino acids, in which he was particularly interested, reacted. The large majority gave up their nitrogen quantitatively in five minutes, but he found some that reacted more slowly. He noticed that other compounds containing NH_2 groups reacted at different speeds.

His method has been extended by other workers to a large number of compounds. The time needed for complete evolution of nitrogen varies considerably even in simple compounds according to the position of the amino group. Dunn and Schmidt[3] showed this admirably for various amino acids having the amino group alpha, beta, gamma, delta, and epsilon to the carboxyl group. The reaction velocity becomes slower for each increase in the number of carbon atoms separating the two groups. Taylor,[4] in a recent series of papers has studied the reaction carefully in order to determine the order and the velocity in different cases. His method of carrying out the reaction was necessarily considerably different from that of Van Slyke. In the latter an unknown excess of nitrous acid is present in such high concentration as to be decidedly unstable, forming NO and HNO_3. Taylor found that pure nitrous acid of not greater than 0.2 N strength could be stabilized quite well if it were not shaken, no gas bubbled through it, and if it were not in contact with air. He used 0.05 N solutions, and determined the

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* This work is done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] J. Phys. Chem., **35**, 2684 (1931).

[2] J. Biol. Chem., **9**, 185 (1911); **12**, 275 (1912).

[3] J. Biol. Chem., **53**, 401 (1922).

[4] J. Chem. Soc., **1927**, 1923; **1928**, 1099, 1897; **1929**, 2052; **1930**, 2741.

amount of unchanged nitrogen compound rather than the volume of nitrogen evolved. He found that the velocities varied greatly according to the type of compound and the place of the amino group in it. Velocity varies according to the product, [compound $H^{\cdot}$] [NO_2^-] [HNO_2], and the reaction is of the third order. The compounds investigated were ammonia, methyl amine, n-propyl amine, diethyl amine, glycine ethyl ester, and some aliphatic amino acids. In these latter, velocity varies as [$NH_3^{\cdot}$ $RCOO^-$] [HNO_2]^2, but a complex is probably formed between $NH_3^{\cdot}$ $RCOO^-$ and HNO_2, making the first expression given perfectly general.

Other factors than the relation of the amino group to the compound have been found to influence the velocity of the reaction. Dunn and Schmidt found temperature to be important. Taylor found that salts and mineral acids have a depressing effect due to lowering of the nitrite ion concentration, while the ion of the compound, nitrite ion, or nitrous acid in excess have an accelerating one. Neither Dunn and Schmidt or Taylor have given any results on the action of nitrous acid on the NH_2 group of amides. From their *fundamentally different structure, they would be expected to act differently.* It has been found that mineral acid must be added before they react.

In the case of more complex compounds there is a great deal of confusing data and disagreement as to what they signify. It is either definitely or tacitly assumed by most authors that, if a compound reacts with pure nitrous acid to give off one or more atoms of nitrogen, the nitrogen evolved represents one or more $-NH_2$ groups present in the original compound. If acid must be added before nitrogen is evolved, it is assumed that the original compound did not contain an $-NH_2$ group, but that under the influence of the acid, it rearranged to form one. (Acetic acid is present in the Van Slyke apparatus, so in cases where there is a slow reaction which might be due to acetic acid, the reaction with *pure* nitrous acid must be carried on in another way.) This explanation is simple and plausible as long as we are dealing with compounds not having more than one nitrogen atom on a carbon, as for example acetamide. It may still be the best one for every case.

A review of the work done on guanidine in this connection brings up some interesting questions. Pellizzari[1] reported a small amount of cyanamide formed by the reaction of nitrous acid on guanidine (not in the Van Slyke apparatus); he also reported nitrosoguanidine as an intermediate compound. Hale and Vibrans[2] made a small number of runs on guanidine in a modified Van Slyke apparatus to use for comparison in other work. With glacial acetic acid and mixtures of glacial acetic and higher fatty acids nearly at the boiling temperature, two nitrogens of guanidine were liberated in 12-15 minutes. With hot 50% and 85% acetic acid, 5.4% and 9.6% respectively were evolved. Plimmer,[3] using the Van Slyke apparatus, found very little reaction in the presence of acetic acid, gradually increasing reaction up to 1/3 of the total nitrogen in the presence of increasing amounts of HCl up to 1.6 N

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[1] Gazz., **51 I**, 224 (1921).

[2] J. Am. Chem. Soc., **40**, 1059 (1918).

[3] J. Chem. Soc., **127**, 2651 (1925).

(approx.), liberation of about 2/3 of the nitrogen in the presence of 2 N acid, and nearly complete reaction with considerably more acid. All the runs lasted approximately 24 hours. The following figures are part of a table given in his article:

Expt. 1

With	Hrs.	Temp.	% N. evolved
2 cc. H_2O	25	13	10.0
2 cc. HCl	24	11	20.1
4 cc. HCl	23	11	31.6
5 cc. HCl	24	12	77.9
6 cc. HCl	24	10	80.1
7 cc. HCl	24	13	87.4
	Expt. 2		
2 cc. H_2O	24	10	3.5
2 cc. HCl	23.5	9	12.4
3 cc. HCl	23.5	10	14.7
4 cc. HCl	23.5	11	27.8
5 cc. HCl	25	11	71.8
6 cc. HCl	24	12	81.5
7 cc. HCl	23.5	14	88.4
8 cc. HCl	23	14	90.5

The extraordinary thing about Plimmer's data is that there is no figure between 31.6% nitrogen evolved and 71.8% nitrogen evolved. It looks as though the second nitrogen came off instantaneously when it came off at all, while the third nitrogen came off slowly and incompletely. This is so unlike anything that is known that the reaction has been studied with some care. As might have been expected, the results turned out to be another case of the misleading experiment. Plimmer was not misled because he apparently never noticed the remarkable features of his data. Plimmer's results are in disagreement with the statement of Krall[1] who says that guanidine reacts with only one of its nitrogen atoms even in the presence of excess mineral acid. He may have considered a concentration of less than 1.5 N as an excess reasonably enough. Hynd and MacFarlane[2] on the other hand agree with Plimmer. Because the investigations were going on independently at the same time, and Plimmer published first, they do not give full data. They disagree in that they get complete evolution of nitrogen with 6% and 12% sulphuric acid (approx. 1.2 and 2.4 N), while Plimmer never gets an entirely complete reaction even in the presence of the larger amount of acid. It may be that there is some specific difference between hydrochloric and sulphuric acids. In general our results confirm those of Plimmer.

Through all this work, various formulae have been assigned to guanidine to account for its behaviour, not only toward nitrous acid, but in its other

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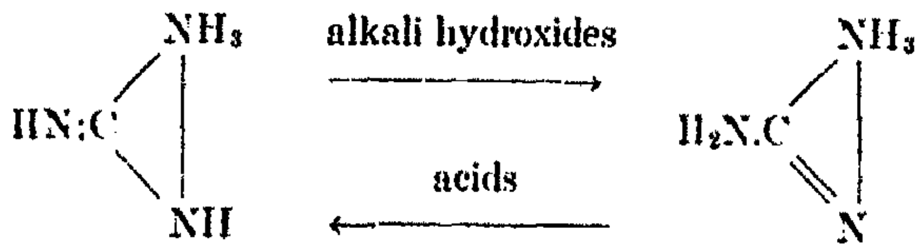
[1] J. Chem. Soc., 107, 1396 (1915).

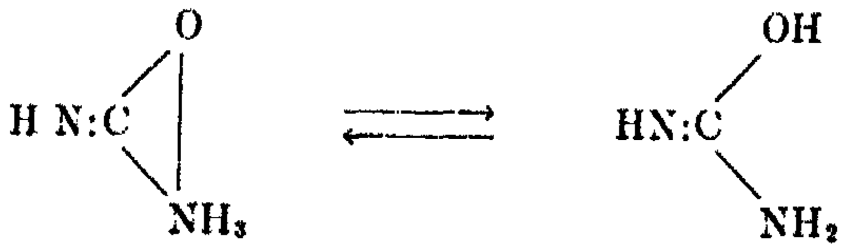
[2] Biochem. J., 20, 1264 (1926).

reactions, syntheses, and decompositions. $HN:C.(NH_2)_2$ has few supporters now as the formula for free guanidine. Krall[1] in order to explain his results postulates:

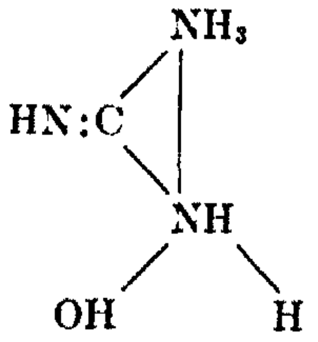


I II

Plimmer[2] adopts I which he considers changes to $HN:C(NH_2)_2$ in the presence of strong acid and accounts for the liberation of 2/3 of the nitrogen. This is analogous to the structures Werner[3] assumes for urea:



Hynd and MacFarlane[4] consider that since guanidine is a very strong monacid base, the formula should be



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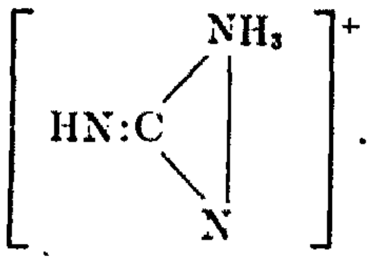
dissociating to give a guanidine ion



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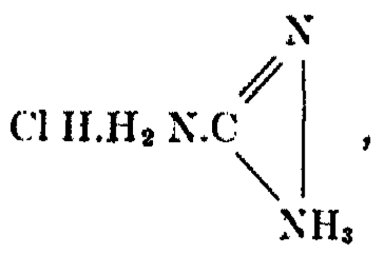
In the presence of strong acid, they consider that this then changes to



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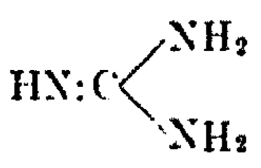
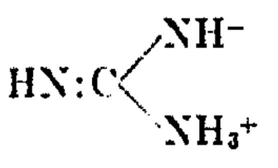
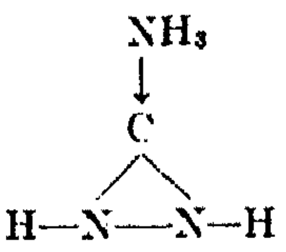
[1] J. Chem. Soc., 107, 1396 (1915).
[2] J. Chem. Soc., 127, 2651 (1925).
[3] "The Chemistry of Urea" (1923).
[4] Biochem. J., 20, 1264 (1926).

the free amino group reacts with nitrous acid, and urea is formed, immediately reacting with nitrous acid. All of these formulae have been discussed by Bancroft and Barnett.[1] They have criticized that of Hynd and MacFarlane on the basis that it is unnecessary and improbable to have two pentavalent nitrogens on the same carbon. In any case guanidine can only be a monacid base, for all the nitrogens are on the same carbon.

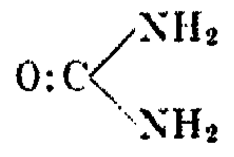
According to Sidgwick,[2] all of these ring formulae for guanidine and the corresponding ones for urea are impossible on the best modern theory of atomic linkage. From the covalency rule, nitrogen can have only four covalent linkages, three of which are normal and one coordinate. Its external shell can not contain more than eight electrons. It has five to start with and therefore can not take on more than three more. A nitrogen with three normal covalent linkages may join coordinately with a positive ion such as hydrogen and thus form a positive ion with four covalent linkages. This is capable of forming an ionic linkage with a negative ion such as chlorine. $NH_4^{\cdot}$ in NH_4Cl is an example of such a case. All so-called pentavalent nitrogens have one ionized link. He gives as the only possible formulae:

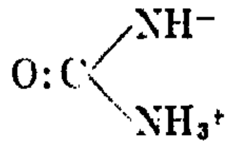


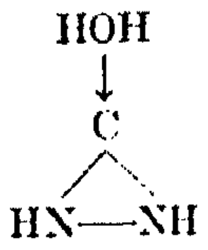




These last two would have electric forces in the molecule which would make the boiling point of guanidine higher than that of compounds, of the same class and approximately the same molecular weight, containing only normal covalent linkages. The second molecule represented is really that of an internal salt, which would have salt-like properties—solubility in water, insolubility in ether and benzene, and a relatively high boiling point. The last molecule represented would have properties intermediate between the first two. The corresponding forms for urea are:—







The same considerations apply to these as well. The physical properties of guanidine which are important for our purpose are compared with those of acetamide, a normal acid amide of the same molecular weight, propyl amine, and urea in the following table.

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[1] J. Phys. Chem., 34, 1217 (1930).

[2] Non-resident lecturer at Cornell for the second term 1930-31.

Name	M.W.	M.P.	B.P.	Solubility in	
				Water	Ether
N-propyl amine	59	—	49	soluble	soluble
Acetamide	59	82	222	97 gm/100	dif. sol.
Urea	60	132.6	dec.	79 gm/100	.0004 gm/100
Guanidine	59	dec. 160[1]	—		

As they stand, these properties do not conclusively favor any one formula for guanidine or urea.

We attempted to reproduce Plimmer's[2] work, for it seemed significant, if true, that each atom of nitrogen in guanidine should come off separately and at its own rate. Our results show very good agreement with his, and are much more detailed. We can not conclude on the face of this however that the nitrogens each have a separate rate. For each particular concentration of acid, whose effect on the rate of reaction of guanidine and nitrous acid we wished to study, we constructed a time-reaction curve. These were made by running the reaction under as nearly constant conditions as possible for different lengths of time.

The standard large-sized Van Slyke apparatus was used at room temperature —approximately 25°. 8.7 cc. glacial acetic acid and 34.8 cc. 30% sodium nitrite were introduced into the apparatus and shaken to form nitric oxide to wash out the air. When air was thoroughly washed out, 20 cc. of the mixture were left in the reacting chamber, 5 cc. of approximately 0.85% guanidine carbonate and 2-4 drops of caprylic alcohol (to prevent foaming) were introduced through the side burette. This was followed by the necessary amount of mineral acid, put in all at once rather than 1 cc. at a time as previous workers have done. The nitrogen evolved was measured in cc.'s and changed to milligrams by Van Slyke's table. Blanks were found for each set of conditions, and all results were corrected for these. If the reaction required a half hour or less, the shaking was as continuous as possible; if the time was longer, the shaking lasted through the first five and the last twenty minutes. For the runs with 5 cc. of acid, the shaking was for the last ten minutes only. The amount of shaking was found to be very important, as shaking decomposes nitrous acid very rapidly. The guanidine carbonate was from the Eastman Kodak Co. The nitrogen content, all of which was assumed to be from the guanidine radical, was determined by the Kjeldahl method. Cf. Taylor.[3] The experimental error in this work was large, especially over long periods of time. Stopcocks were kept well ground and greased, and all runs where there was any possibility of slow leaks were carefully discarded; but there remain differences due to slight temperature changes, differences in mixing or shaking, etc.

With 1.56 and 1.72 N HCl (4 cc. and 4 1/2 cc. respectively of concentrated or 11.3 N acid), the reaction was quite slow. No distinction could be made

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[1] Krall: J. Chem. Soc., 107, 1396 (1915).

[2] J. Chem. Soc., 127, 2651 (1925).

[3] J. Chem. Soc., 1927, 1923.

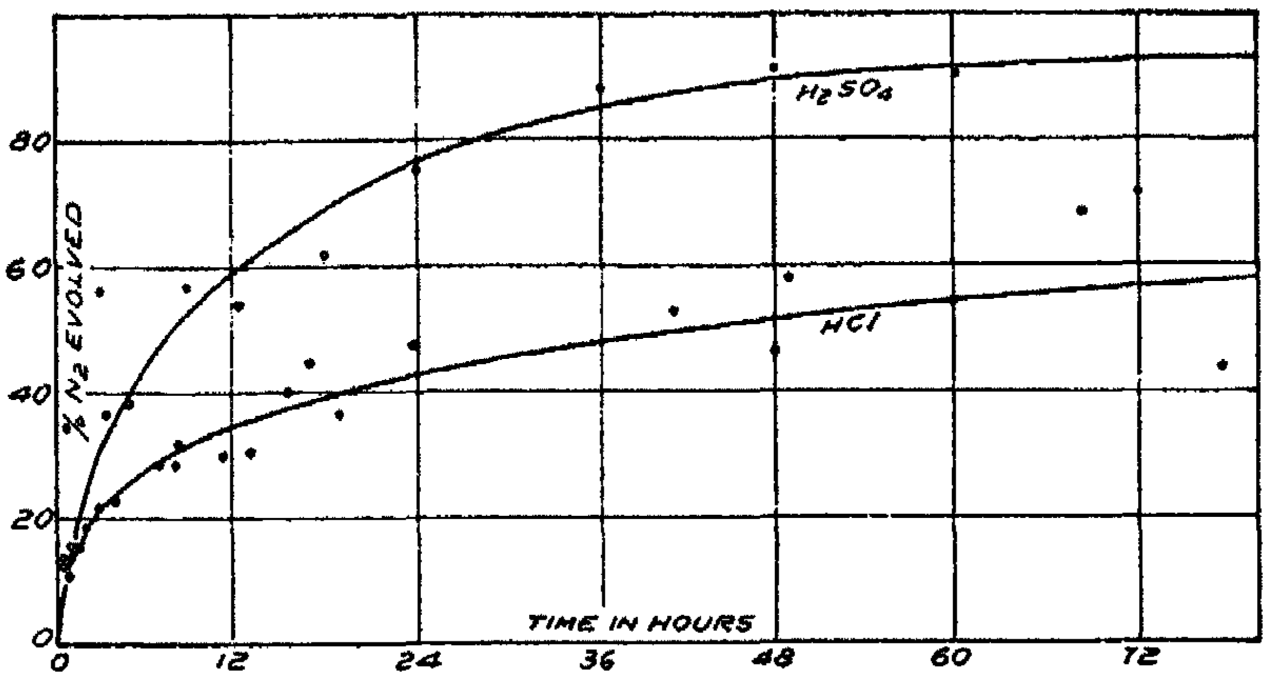

FIG. 1
Reaction of Guanidine and 4 cc of Acid

between the rates at which the first and second nitrogen atoms were liberated in the second case. In the first, after a relatively fast initial evolution of about 20% of the nitrogen, the curve flattened out. With 4 cc. of acid, the first third of the nitrogen was about gone at the end of 24 hours, the length of Plimmer's run. He used a slightly different-sized apparatus, so that the 4 cc. of acid he used gave a somewhat higher concentration; he made his runs at a lower temperature. The two differences are counterbalancing. He did not use 4 1/2 cc. of acid. With 5 cc. of HCl, 1.88 N, the whole reaction was very much faster, so that as Plimmer found, at the end of 24 hours, 2/3 or more of the nitrogen was liberated. As a matter of fact, we found that in the first hour, sixty percent of the total nitrogen was evolved, and then the reaction became slow. The experimentally obtained values for the three concentrations of HCl are given in Tables I-III, and in Figs. 1-4. These results show conclusively that the second nitrogen of guanidine does not come off quickly after the first nitrogen has been liberated relatively slowly

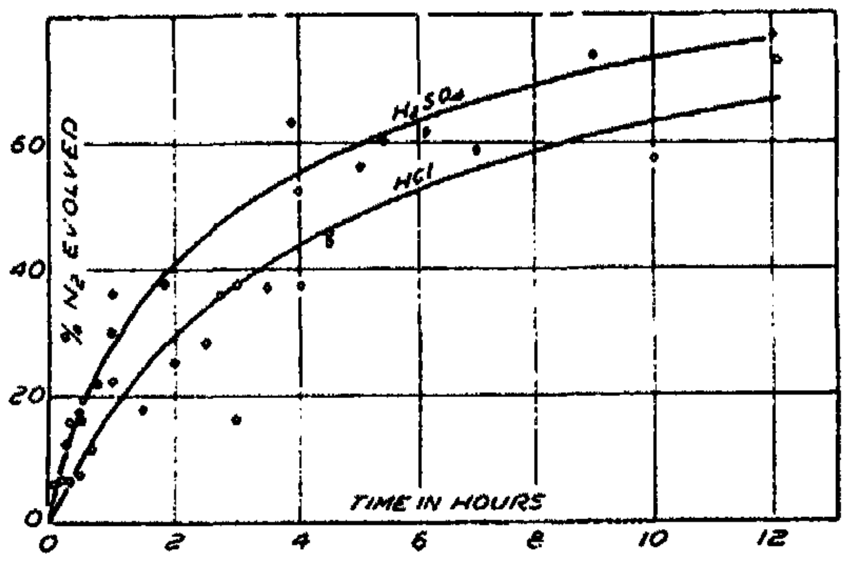

FIG. 2
Reaction of Guanidine and 4½ cc of acid.

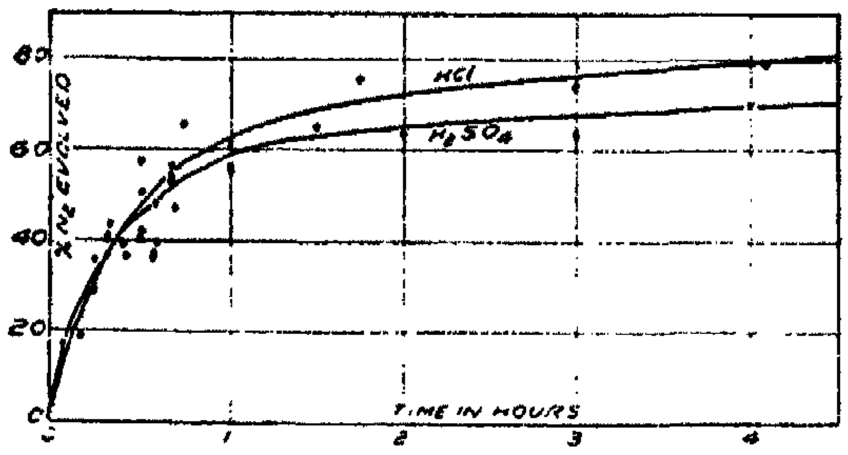

Fig. 3
Reaction of Guanidine and 5 cc of Acid.

and nearly completely, as Plimmer's results seem to indicate. We find instead quite normal time-reaction curves.

TABLE I
Reaction with 4 cc. HCl
Total nitrogen 18.14 mg.

Time	N evolved mg	% total N evolved	Time	N evolved mg	% total N evolved
3/4 hr	2.47	10.8	15 3/4	7.24	39.9
1 1/2	2.78	15.3	17	8.10	44.6
2	3.38	18.6	19	6.58	36.3
3	3.93	21.6	23 7/10	8.60	47.4
4	4.06	22.4	41 1/6	9.55	52.6
7	5.10	28.1	48	8.37	46.1
8 1/3	5.09	28.1	49	10.49	57.8
8 1/2	5.73	31.6	60	9.80	54.0
11 1/2	5.40	29.8	68 1/3	12.34	68.0
13 1/4	5.46	30.1	77 1/3	7.90	43.6

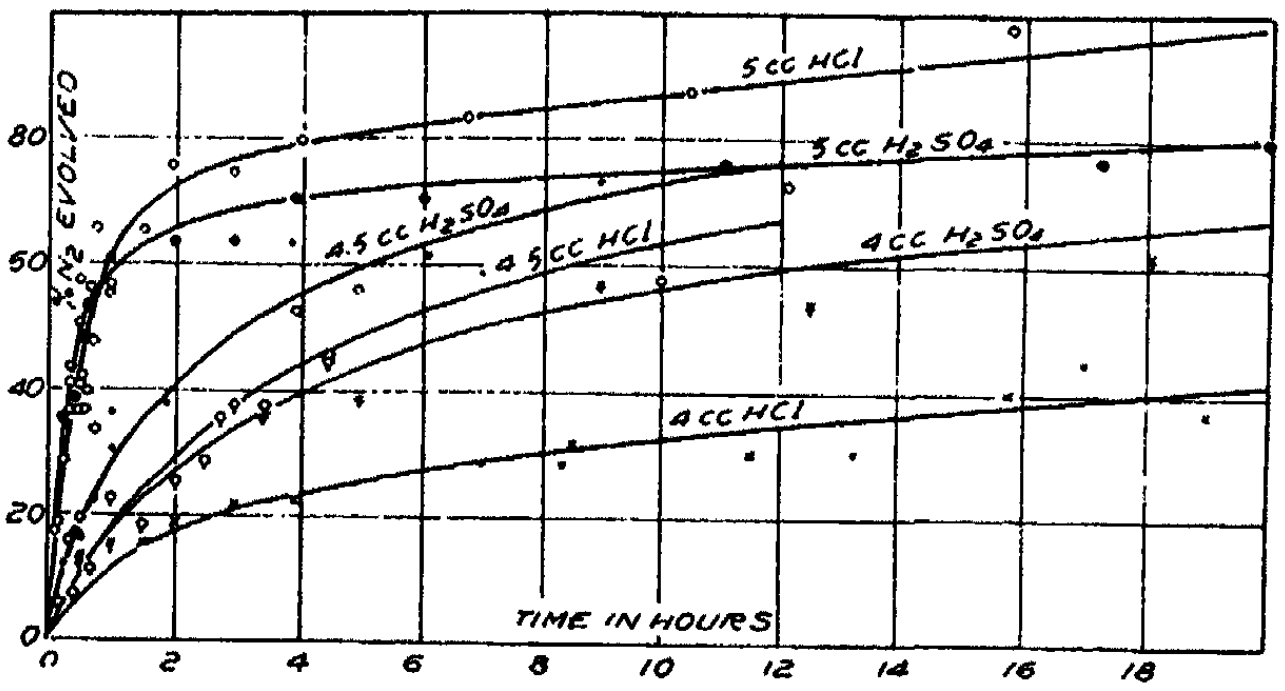

Fig. 4
Comparison of Reaction of Guanidine with 4, 4½ and 5 cc of Acid

TABLE II

Reaction with 4 1/2 cc. HCl
Total nitrogen 18.14 mg.

Time	N evolved mg	% total N evolved	Time	N evolved mg	% total N evolved
5 min	1.09	6.0	2 1/2	5.19	28.6
10	1.09	6.0	2 3/4	6.49	35.8
15	1.10	6.1	3	2.95	16.3
20	2.86	15.7	3	6.79	37.4
25	1.32	7.3	3 1/2	6.74	37.2
25	3.07	16.9	4	9.52	52.5
30	3.46	19.1	4 1/2	8.06	44.4
40	2.03	11.2	4 1/2	8.22	45.3
1 hr	4.01	22.6	5	10.16	56.0
1 1/2	3.27	18.0	10	10.51	58.0
2	4.58	25.3	12 1/10	13.19	72.7

TABLE III

Reaction with 5 cc. HCl
Total nitrogen 18.14 mg.

Time	N evolved mg	% total N evolved	Time	N evolved mg	% total N evolved
5 min	3.13	17.3	40 min	9.71	53.6
10	3.40	18.7	40	10.21	56.3
15	5.20	28.7	42	8.56	47.2
20	6.60	36.3	45	11.91	65.6
20	7.38	40.8	50	7.83	43.2
21	7.90	43.6	1 hr	9.99	55.1
25	6.59	36.4	1	10.15	56.5
30	7.31	40.3	1 1/2	11.80	65.0
30	7.61	41.9	1 11/12	13.76	75.8
30	9.23	50.9	3	13.43	74.0
30	10.40	57.3	4 1/12	14.39	79.3
35	6.58	36.2	6 3/4	15.21	83.3
35	6.60	36.4	10 1/2	15.81	87.1
36	7.20	39.7	15 3/4	17.70	97.6
40	9.63	53.1	19 5/6	19.27	106.2

Sulphuric acid was used also, to find out whether or not there is a specific effect due to the acid. As we have already noted, Plimmer never got complete evolution of nitrogen with HCl while Hynd and MacFarlane did with H_2SO_4. In order to make the results comparable with those for which HCl was used, concentrated H_2SO_4 was diluted with water until it was just equivalent to the concentrated HCl, volume for volume, and an equal volume of H_2SO_4 could be substituted for HCl. The normality of the two reaction mixtures with the different acids was then just the same. Using 5 cc. of acid, HCl accelerated the reaction more than H_2SO_4, while with the lower concentrations just the opposite was true. The experimental results are given in Tables IV-VI, and in Figs. 1-4. With H_2SO_4, as with HCl, all the evidence is against the rapid liberation of the second nitrogen after the slow liberation of the first.

TABLE IV

Reaction with 4 cc. H_2SO_4
Total nitrogen 18.14 mg.

Time	N evolved mg	% total N evolved
1/2 hr	2.23	12.3
1/2	2.43	13.5
1	2.78	15.3
2	3.42	18.9
2 1/20	10.17	56.0
3 1/2	6.57	36.2
5	7.07	38.1
9	10.31	56.8
12 1/2	9.77	53.8
18 1/12	11.22	61.9
24	13.61	75.0
36	15.98	88.1
48	16.57	91.3
60 1/4	16.35	90.1
72	12.98	71.6

TABLE V

Reaction with 4 1/2 cc. H_2SO_4
Total nitrogen 18.14 mg.

Time	N evolved mg	% total N evolved
1/4 hr	2.24	12.4
1/2	2.95	16.3
3/4	4.00	22.1
1	5.57	30.7
1	6.62	36.5
1 5/6	7.02	37.8
3 11/12	11.49	63.3
5 1/3	10.98	60.5
6 1/6	11.18	61.6
7	10.67	58.8
9	13.34	73.5
12	13.81	76.1

TABLE VI

Reaction with 5 cc. H_2SO_4
Total nitrogen 18.14 mg.

Time	N evolved mg	% total N evolved
15 min	6.46	35.6
25	7.23	38.9
35	8.72	48.1
1 hr	11.04	60.9
2	11.51	63.4
3	11.49	63.3
4	12.73	70.2
6 1/12	12.73	70.2
11 1/12	13.92	76.7
17 1/4	13.86	76.4
20	14.50	79.9

Strong acids greatly accelerate the reaction between guanidine and nitrous acid. On the other hand, guanidine is known to react very slowly with nitrous acid in the presence of cold acetic acid. It will be profitable to discuss the effects which may be common to all acids. In the Van Slyke apparatus, all acids may do two things. First they liberate nitrous acid from the sodium nitrite. The general reaction is:

$$NaNO_2 + HA \rightarrow NaA + HONO.$$

If the acid is weak, as acetic, we have

$$Na^{\cdot} + NO_2^- + HA \rightarrow Na^{\cdot} + A^- + HNO_2,$$

and considerable amounts of both nitrous and the added acid are present. If the acid is strong, as the mineral acids, we have

$$Na^{\cdot} + NO_2^- + H^{\cdot} + A^- \rightarrow Na^{\cdot} + A^- + HNO_2$$

and larger amounts of nitrous acid are formed. That this is actually the case is shown by the much deeper blue solution when mineral acid is added. Theoretically the larger the excess of nitrous acid the faster the reaction takes place, and this might explain why guanidine reacts slowly with acetic acid and quickly with hydrochloric and sulphuric acids. Practically, a very large excess acts almost the same as a different very large excess. This is well illustrated by the fact that the reaction in the Van Slyke apparatus (where there is a large excess of nitrous acid even in the absence of mineral acid) has been reported as practically monomolecular, while Taylor,[1] working more carefully and without a large excess, finds that the reaction is trimolecular. The difference in amount of nitrous acid liberated by weak and strong acids can not be sufficient to account for the difference in the reaction velocity in the presence of weak and strong acids and in the presence of different amounts of the same acid.

The second possible effect is that of the hydrogen ions. Since each acid has its own ionization constant, the hydrogen ion concentration should be different in each case and the speed of the reaction different. But if the hydrogen ion concentration were about the same in equivalent amounts of two acids, the difference might well be within the limits of experimental error. The effect of the hydrogen ion concentration is sufficient to account for the difference in reaction in the presence of strong and weak acids. That the hydrogen ion concentration must be taken into account was shown in another way. Even with an excess of nitrous acid comparable to that in the Van Slyke apparatus in the presence of mineral acid, formed by dissolving nitrogen trioxide in water, the reaction velocity was greatly cut down in a low acid concentration. It would seem that the hydrogen ions acted in some way on guanidine (and other compounds which do not react with pure nitrous acid) to change it into a form attacked by the nitrous acid.

There must further be some effect due to the acid itself. Sulphuric acid is less highly ionized than hydrochloric acid, but at two of the concentrations tried, it was the more effective in promoting the reaction. Besides the dif-

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[1] J. Chem. Soc., **1928**, 1099, 1897; **1929**, 2052.

ference in reaction rates in the presence of different quantities of the same acid, cf Fig. 5, are far too great to be explained in any way on the basis of change in hydrogen ion concentration alone. The work of Hale and Vibrans,[1] to which reference has already been made, gives us another illustration of a change in reaction velocity with different amounts of acid for which explanation on the basis of hydrogen ion concentration is impossible. For the same time and conditions, they get approximately 2/3 of the nitrogen evolved with glacial acetic and 1/10 with 85%.

The facts of the reaction of guanidine and nitrous acid may be summarized to date in this way. With pure nitrous acid, guanidine does not react. With acid as a catalyst, it reacts slowly until a certain concentration of acid (which is specific for the acid) is reached; it then reacts fairly fast to give off the first two atoms of nitrogen. The third atom of nitrogen comes off more slowly than the first two. At present we can give no fuller explanation of the bearing of these facts on the decomposition of guanidine than is given in the following discussion.

B. C. Belden[2] of this laboratory has made experiments to ascertain the products formed by guanidine in its decomposition. This must be done largely outside the Van Slyke apparatus for there the concentration of inorganic salts is so high as to interfere with the tests for the small amounts of nitrogenous material present. Our first hypothesis was that urea is formed. The equation for the reaction of an amino group with nitrous acid as it is usually written gives urea from guanidine, the two substances are known to be closely related, Hynd and MacFarlane[3] favor that view, and we obtained qualitative tests for urea in the guanidine reaction mixture after reaction in several cases. These reactions, taken in part from Werner,[4] may be considered to represent this reaction:

$$CN_2H_3NH_2 + HONO \rightarrow CON_2H_4 + N_2 + H_2O$$
$$CON_2H_4 + HONO \rightarrow HNCO + N_2 + 2\,H_2O$$
$$HNCO + HONO \rightarrow N_2 + H_2O + CO_2 \text{ and } HNCO + H_2O + HA$$
$$\rightarrow CO_2 + NH_4A \qquad NH_4A + HONO \rightarrow N_2 + HA + 2\,H_2O.$$

But urea obviously cannot be formed, for in the Van Slyke apparatus it would be acted on immediately in the presence of the strong mineral acid and the reaction would proceed to an end at once. Actually the last forty percent of the nitrogen is very slow to come off. The next suggestion was that cyanamide is formed, possibly through nitroso guanidine as an intermediate, as Pellizzari[5] reported in his experiments. These equations would represent the reaction: $CN_3H_5 + HONO \rightarrow CN_3H_4{\cdot}NO + H_2O$

$$CN_3H_4{\cdot}NO \rightarrow CNNH_2 + N_2 + H_2O$$
$$CNNH_2 + HONO \rightarrow HNCO + N_2 + H_2O,$$

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[1] J. Am. Chem. Soc., 40, 1059 (1918).

[2] J. Phys. Chem., 35, 2684 (1931).

[3] Biochem. J., 20, 1264 (1926).

[4] "The Chemistry of Urea" (1923).

[5] Gazz., 51 I, 224 (1921).

and the HNCO reacts as before. By experiments with pure nitrous acid, guanidine carbonate, and sulphuric acid, all in aqueous solution, Belden[1] showed the formation of 80% of the theoretical amount of cyanamide, assuming that the reaction was stopped before any of it decomposed. In experiments which Werner[2] did with cyanamide and nitrous acid (in much more concentrated solution and under different conditions from those in the Van Slyke apparatus) he found that forty percent of the nitrogen of cyanamide reacted rapidly and that the last sixty percent reacted slowly, due, he assumed, to the fact that forty percent of the cyanamide is in the $CN \cdot NH_2$ form at the beginning and that the $HN{:}C{:}NH$ form only changes slowly to the first as it is used up. This last agrees very well with our data, better than assuming that the first nitrogen or fifty percent of the cyanamide nitrogen comes off rapidly. However, pure cyanamide put into the Van Slyke apparatus under the conditions, as nearly as possible, in which it would be formed there from guanidine, reacted slowly (with 5 cc. of HCl). Some of it should have reacted rapidly i.e. the part corresponding to the first forty percent of the nitrogen of cyanamide or approximately the second thirty percent of guanidine.

Summary

1. The more important factors affecting the speed of the reaction, $RCH_2NH_2 + HONO$, are discussed.

2. Evolution of nitrogen by the action of nitrous acid is generally considered to mean that the compound originally contained, or rearranged to contain, an $-NH_2$ group. This may not be true if more than one nitrogen is attached to a carbon.

3. The work on nitrous acid and guanidine to date is summarized.

4. The various formulae given to guanidine are discussed. No conclusions are drawn.

5. Experimental results on the reaction of guanidine and nitrous acid in the presence of hydrochloric and sulphuric acids of 1.5 to 1.9 normality are given. This work agrees generally with previous work, especially that of Plimmer. It is more detailed for the acids and the concentrations of those acids which it covers.

6. Guanidine and pure nitrous acid do not react. In the presence of acid up to a certain concentration, they react slowly. In the presence of acid above that concentration, they react quickly to liberate two atoms of nitrogen. The third atom of nitrogen is evolved more slowly.

7. Of the possible effects of acid in promoting the reaction between guanidine and nitrous acid—greater concentration of nitrous acid, hydrogen ion concentration, and a specific effect due to the acid itself—the last two are most active.

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[1] J. Phys. Chem., 35, 2684 (1931).

[2] "The Chemistry of Urea" (1923).

8. Some preliminary experiments on the decomposition products of guanidine by nitrous acid are discussed.

This paper has raised several important questions which it has left unanswered. It was written to summarize the work so far because of the intrinsic interest and importance of the subject, and in an effort to formulate the issues clearly. These may be considered to be: (1) the structure of guanidine; (2) the probable rearrangement in the presence of acid by which it is made open to attack by nitrous acid; (3) the specific effects of different acids; (4) the nature of the decomposition products of the reaction between guanidine and nitrous acid in the intermediate and final stages, and the consequent explanation of the time-reaction curve.

Cornell University.

THE CHEMILUMINESCENCE OF SOLID SODIUM

BY ROBERT M. BOWIE

As long ago as the time of Davy, it was known that freshly cut surfaces of sodium or potassium in open air, when viewed in the dark, give off a faint light. G. Rebaul in 1910 correctly stated that this effect was due to the formation of the hydroxide upon reacting with the moisture in the air. In this article, eighteen reactions are described which were used to determine the nature of the reaction which produces the luminescence. It was found that the liberation of hydrogen always accompanied the production of light, but its production did not always accompany the liberation of hydrogen. In no reaction in which a halide was formed, was luminescence produced. The luminescence seemed to be associated with the breaking of a hydrogen-oxygen bond (or bond to some element resembling oxygen, as sulfur) of a vaporous, polar molecule. The spectrum of this chemiluminescence consisted of a narrow band with a maximum at about 510 mμ.

Sodium metal when freshly cut and viewed in the dark, gives off a faint greenish light. This fact was probably noticed first by Davy as indicated by G. Rebaul[1] in his article. Linneman[2] also noted the fact in 1858, correctly stating its color, and gave an idea as to its intensity. He found that at about 60° or 70°, sodium produced a light as bright as phosphorus.

G. Rebaul[3] in 1910 worked with a sodium-potassium alloy. He showed quite conclusively that, although the phenomenon always accompanied the rupturing of the surface, it could not be ascribed to triboluminescence, since with dry air, the rupturing of the surface went on but no light was produced. From this he concluded correctly that it was the formation of the hydroxide from the moisture in the air which produced the light.

Spectrographically, it has been found that the chemiluminescence consists of a narrow band with a maximum at about 5100 A°. It was the purpose of this investigation to determine the nature of the reaction which accompanied or produced the luminescence.

The Investigation

In order to conduct these experiments, it was necessary to have a means of producing a new surface of metal in a controlled atmosphere. In order to do this, the metal was placed in a small pressure gun having a cylinder five inches long with a bore 5/8 inches in diameter. The piston was forced down by a threaded rod turned by a handle. The metal was forced through a No.

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[1] G. Rebaul: Compt. rend., **168**, 1195 (1910).

[2] E. Linneman: J. prakt. Chem., **75**, 128 (1858).

[3] G. Rebaul: Compt. rend., **168**, 1195 (1910).

60 wire gauge hole in the end of the "gun" into a pyrex glass tube having two side arms. The controlled atmosphere was admitted through one and drawn out through the other.

In operation, the gas was first passed through the necessary drying or humidification trains and then into the tube for a period of half an hour in order to sweep out all other gases. About an inch or two of sodium wire was then exuded and the rate of reaction noted and compared roughly with the rate of reaction with moist air. The values obtained appear in column 3 in Table I. The light was then turned out and, after a sufficient time had elapsed, another few inches of fresh wire were exuded. At the same time, a piece of metal outside of the tube in the moist air of the dark room, was placed back of the tube so that it was viewed through the tube. In this way, the light emitted by the metal wire in the controlled atmosphere was compared roughly with that produced by moist air. Values thus obtained appear in column 4 of Table I. The reacting substances are given in column 1.

Table I

Table of Comparative Reactivity and Luminescence of Various Reaction Mixtures upon Solid Sodium

Substance Reacting		Admixed Gas	Relative Reactivity Moist air = 1	Luminescence Relative to Moist air = 1
O_2			0.2	0
O_2	+	H_2O	1	1
H_2			0	0
H_2	+	H_2O	1	1
CO_2			0	0
CO_2	+	H_2O	1.5	1.2
HO_2			1	1
Cl_2			0.9	0
Br_2			0.8	0
I_2			0	0
HCl			1.5	0
C_2H_5OH			0.6	0
CH_3OH			0.6	0
H_2S			0.4	0.2
H_2S	+	H_2O	2 or 3	1.5
HNO_3		Dry air	1.2	0.1
C_2H_5COOH		Dry air	0.8	0.1
C_2H_5COOH		Dry H_2	0.8	0.1
SO_2			0	0
SO_2	+	H_2O	0.9	0
NH_3			0.6	0

Oxygen, after passing through an H_2SO_4 train and two $CaCl_2$ tubes, produced a grayish coat upon the metal wire at a moderate rate. However, no light accompanied the reaction. When the gas was passed through a humidification train before entering the tube the reaction which took place resembled that with moist air, in that the white coating formed at the same rate and the light given off was of the same color and intensity.

Hydrogen, when dried in the same way as the oxygen, did not react with the sodium nor was there any light produced but when humidified, a whitish coat was formed on the wire of sodium in the same way as with moist air. The light given off was of the same color and intensity as that obtained with moist air.

The reaction with dried CO_2 was the same as with dried hydrogen. Moist CO_2, although reacting at about the same rate as moist air produced a dryer looking white coat upon the metal which appeared to be more loosely attached. It consisted chiefly of Na_2CO_3. The light given off was slightly more intense than with moist air, but the color was the same.

The three cases mentioned above indicate that water vapor was necessary to produce the effect. Water vapor alone should, therefore, produce the effect. To test this, water which had been previously boiled, was kept at about 70°C in a flask which was connected to one side arm of the tube while an aspirator was connected to the other. After evacuating for a period of about an hour, sodium was exuded into water vapor. The reaction resembled that of moist air, both as to rapidity and luminescence.

Reactions with the halogens, chlorine, bromine, and iodine, were tried. The chlorine, made by the reaction of H_2SO_4 on NaCl and MnO_2 was passed over solid $KMnO_4$ and then dried. The bromine was merely volatilized by reduction of pressure and passed directly into the observation tube. The vapor pressure of iodine was so low at 20°C that it did not react. With both chlorine and bromine the reaction proceeded slightly less rapidly than with moist air, producing a white coat upon the wire. In neither case was light produced.

HCl produced by dehydration of concentrated HCl solution with H_2SO_4 reacted very rapidly with the sodium wire, turning it completely to NaCl. However, no light was produced.

Inasmuch as all the above experiments pointed to the fact that water vapor was necessary for the production of light, other substances resembling water in some of their chemical properties, were tried. Vapors of ethyl and methyl alcohols reacted slowly with the metal to form very wet looking coats, but produced no light.

H_2S was tried because of its marked resemblance to H_2O in chemical properties. The gas produced by the reaction of H_2O upon Al_2S_3 was dried by passing over more Al_2S_3 and thence over $CaCl_2$. It produced a very faint light upon only the fresh surface although the fairly slow reaction continued for some time after. The color of the light was the characteristic greenish blue. Moist H_2S reacted very rapidly with the metal, at times producing heat enough to melt the wire which then formed in little balls. In the dark, these balls appeared as bright bluish specks which quickly disappeared. Finally one of these balls took fire and burned with the characteristic yellow flame of sodium, consuming all the metal in the tube.

In the case of nitric acid, the concentrated material was mixed with twice its volume of H_2SO_4 and placed in a flask on a hot plate. Previously dried air was passed over the surface of the acid and into the observation tube. With the acid at a temperature of 40°C a slight glow was produced which increased in intensity as the temperature was raised to 85°C. Inasmuch as there were two acids in the flask, there is a possibility that H_2SO_4 may have caused the luminescence. If this had been the case, then a sulfate would have been formed. Therefore, the coated wire was placed in distilled water, allowed to react, acidified with HCl, boiled to remove CO_2, and treated with a $BaCl_2$ solution. The absence of a white precipitate indicated that no H_2SO_4 had entered into the reaction.

The glacial acetic acid was also placed in a flask on a hot plate. Previously dried air was passed over its surface and thence through a $CaCl_2$ tube into the observation tube. At a temperature of 105°C, a very faint glow appeared, which evidently continued at a lower temperature, but diminished in intensity.

Strange to say, SO_2 produced no reaction when dry and no light when dampened or dry, although the reaction of the dampened gas appeared to be rapid enough.

Inasmuch as all the substances listed so far have had either a neutral or an acid reaction, an alkaline substance was tried. NH_3 was dried by passing over solid KOH and was then allowed to enter the observation tube. Although sodamid was formed quite rapidly, no light was produced.

In the above experiments, it was found that the liberation of hydrogen always accompanied the luminescence, but that its liberation was not always accompanied by light. Light never accompanied the formation of a halide. Furthermore, the data indicated that the luminescence was associated with the breaking of a hydrogen-oxygen bond (or a bond to some element resembling oxygen, as sulfur) of a vaporous, polar molecule.

The author is deeply indebted to the Physics Department of Iowa State College for the loan of the apparatus and for the materials used in this investigation. He also wishes to thank Dr. J. W. Woodrow, under whose guidance this work was carried to completion.

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THE INFLUENCE OF STRONG ELECTROLYTES UPON THE CATALYTIC INVERSION OF SUCROSE BY HYDROCHLORIC ACID AT 30°

BY WILLIS W. FLOYD

Introductory

The usual stoichiometric equation for the inversion of sucrose indicates that the hydrolysis is a bimolecular reaction between sucrose and water, thus,

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6.$$

Studies of the colligative properties of aqueous sucrose solutions[1] however, show that the sucrose exists as a hydrate in solution. The most probable mechanism, therefore, is that the dissolved sucrose first forms a hydrate with the water, and that it is this hydrate which is catalytically hydrolyzed by the hydrogen ion. The equation for the hydration of the sucrose may be written,

$$C_{12}H_{22}O_{11} + xH_2O \rightarrow C_{12}H_{22}O_{11}\cdot xH_2O, \qquad (1)$$

where x is a variable number, usually of the order of 6 ±2. The sucrose hydrate may then combine with the hydrogen ion to form an intermediate complex which rapidly decomposes to produce the products of the inversion, according to the equation,

$$C_{12}H_{22}O_{11}\cdot xH_2O + H^+ \rightarrow C_{12}H_{22}O_{11}\cdot xH_2O\cdot H^+ \rightarrow 2C_6H_{12}O_6 + (x-1)H_2O + H^+. \qquad (2)$$

Or, the sucrose hydrate may be hydrolyzed by the hydrogen ion directly into the reaction products, as represented by the equation,

$$C_{12}H_{22}O_{11}\cdot xH_2O + H^+ \rightarrow 2C_6H_{12}O_6 + (x-1)H_2O + H^+. \qquad (2')$$

Since the inversion velocity is increased by increasing the proportion either of the sucrose or of the hydrogen ion, but is not increased by increasing the proportion of the water, it follows that either reaction (2) or reaction (2′), rather than reaction (1), must be the measured reaction. That is, the hydration of the sucrose is immeasurably rapid in comparison with the catalytic decomposition of the sucrose hydrate into glucose and fructose. If this is true, the inversion of sucrose proceeds essentially as a unimolecular reaction.

There has been much disagreement among the investigators[2] as to the unimolecularity of the inversion process. The results obtained by the in-

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[1] Bousfield: Trans. Faraday Soc., 13, 141 (1917); Frazer and Myrick: J. Am. Chem. Soc., 38, 1907 (1916); Scatchard: 43, 2406 (1921).

[2] a. Armstrong and Caldwell: Proc. Roy. Soc., 74, 195 (1904); Caldwell: 78A, 272 (1906); Colin and Chaudun: J. Chim. phys., 24, 507 (1927).

b. Meyer: Z. physik. Chem., 62, 59 (1908); Worley: Proc. Roy. Soc., 87A, 555 (1912); Fales and Morrell: J. Am. Chem. Soc., 44, 2071 (1922).

c. Hudson: J. Am. Chem. Soc., 30, 1160 (1908); Rosanoff, Clark, and Sibley: 33, 1911 (1911); Jones and Lewis: J. Chem. Soc., 117, 1120 (1920).

genious method of Pennycuick[3] show that there is a slight but steady increase in the unimolecular velocity constant as the inversion proceeds. This increase, however, is of the same order of magnitude as the common experimental error and so is usually overshadowed by the latter. Hence, for practical purposes the velocity coefficients determined by the ordinary polarimetric method may be considered constant throughout the entire course of the inversion.

It has long been known that certain neutral salts increase the rate of inversion of sucrose by acids. Considerable experimental work has been done on this neutral salt effect, and an extensive, widely varied theoretical literature has been produced in the attempt to explain it. Several of these better known theories are summarized in a recent article by Bowe.[4]

Of particular interest in connection with modern theories of reaction kinetics in general are the efforts on the part of some to correlate the velocity of sucrose inversion with the thermodynamic concept of the activities of the reactants. As defined by Lewis,[5] the activity of a constituent of a system is the true measure of its thermodynamic concentration. Hence, the velocity of a given reaction is proportional to the product of the activities of the reactants, each raised to a power equal to the coefficient of the reactant in the equation which represents the given reaction.

W. C. M. Lewis and his associates[6] have used the hydrogen electrode to determine the activity of the hydrogen ion in acid solutions containing sucrose. The electromotive force measurements of Taylor and Bomford[7] show that the activity of the hydrogen ion in such solutions increases during the inversion process. Scatchard[8] has shown that the hydrogen electrode does not give reliable values of the hydrogen ion activity in sucrose solutions. The hydrogen gas hydrogenates the sucrose, producing an inconstant hydrogen pressure, and the sucrose produces an unknown change in the liquid junction potential of the cell.

Brönsted[9] represents the inversion of sucrose by acids as occurring in two steps. The first step consists of the formation of an intermediate complex from a sucrose molecule and a hydrogen ion,

$$C_{12}H_{22}O_{11} + H^+ \rightarrow C_{12}H_{22}O_{11}\cdot H^+. \qquad (3)$$

This is followed by the hydrolysis of the intermediate complex to form glucose and fructose, with the re-liberation of the hydrogen ion,

$$C_{12}H_{22}O_{11}\cdot H^+ + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6 + H^+. \qquad (4)$$

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[3] Pennycuick: J. Am. Chem. Soc., **48**, 6 (1926).

[4] Bowe: J. Phys. Chem. **31**, 291 (1927).

[5] Lewis: Proc. Am. Acad., **37**, 49 (1901); J. Am. Chem. Soc., **35**, 16 (1913); **45**, 16 (1923). Cf. also Lewis and Randall: **43**, 1112 (1921).

[6] Jones and Lewis: J. Chem. Soc., **117**, 1120 (1920); Moran and Lewis: **121**, 1613 (1922); Corran and Lewis: J. Am. Chem. Soc., **44**, 1673 (1922).

[7] Taylor and Bomford: J. Chem. Soc., **125**, 2016 (1924).

[8] Scatchard: J. Am. Chem. Soc., **48**, 2026 (1926).

[9] Brönsted: Z. physik. Chem., **102**, 169 (1922).

He assumes that reaction (4) is exceedingly rapid as compared with reaction (3). Accordingly, he represents the velocity of inversion of sucrose by the expression,

$$v = kc_s c_h \frac{f_s f_h}{f_x} = k \frac{a_s a_h}{f_x}. \tag{5}$$

Here c, f, and a indicate the concentrations, the activity coefficients, and the activities of the components, respectively. The subscripts (s), (h), and (x) refer respectively to the sucrose, the hydrogen ion, and the intermediate fugitive complex.

The present investigation was undertaken with the view of studying the influence of strong electrolytes upon the rate of inversion of sucrose by acids. From the results obtained we have hoped to gain further information concerning the inversion process and to test the applicability of the modern theories of solution. To this end we have employed four typical salts of different valence types. To emphasize the specific influence of the salts upon the velocity of inversion we have arbitrarily chosen to employ constant concentrations of sucrose and of acid, and to vary only the concentration of the salt.

Materials and Apparatus

Sucrose. The sucrose used in this research was the purest crystalline rock candy available. It was first pulverized and preserved in a desiccator over anhydrous calcium chloride. Duplicate determinations showed an ash content of less than 0.001 percent.

Hydrochloric Acid. Constant boiling hydrochloric acid[10] was taken as the source of the standard acid. From this a 0.5 N acid was prepared by dilution.

Salts. The salts used in preparing the ionic solvents were of the "Analyzed" quality. They were further purified by at least two crystallizations from pure distilled water. After heating to constant weight, the solutions of sodium chloride and potassium sulphate were made up by direct weighing. The barium chloride was allowed to stand over anhydrous calcium chloride until analysis showed it to be the pure dihydrate, $BaCl_2 . 2H_2O$. It was weighed directly as such. A concentrated "mother" solution of magnesium sulphate was prepared and then standardized on a weight molal basis by precipitation as barium sulphate. The various concentrations of this salt were made by the proper dilution of the mother solution.

Apparatus. The polarimeter was a high precision, triplefield Schmidt and Haensch instrument, readable by two verniers to 0.01°. The 40 cm. inversion tubes were encased in metal jackets through which water was circulated under pressure from a constant-temperature water-bath. This bath was electrically heated and electrically controlled to within ± 0.02° of a temperature such that the water passing through the inversion tube was exactly 25° ± 0.02, or 30° ± 0.02, depending on the temperature chosen. The temperature of the water bath was read on a standard thermometer, graduated in

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[10] Foulk and Hollingsworth: J. Am. Chem. Soc., 45, 1220 (1923).

0.1° and readable to ± 0.01°. A short stem thermometer graduated in 0.2° was immersed in the inversion solution. An intense sodium light was used for illumination.

All flasks, burettes, and pipettes were accurately calibrated by weight at 25° and at 30°. Each polarimetric reading recorded is the mean of at least two independent readings, and each is accurate to ± 0.01°.

Experimental Procedure

For each experiment exactly 1.7109 grams of sucrose (air weight) and the desired quantity of salt, weighed to one-tenth of a milligram, were transferred to a 50 cc. calibrated flask. The sucrose and salt were then dissolved in a minimum amount of distilled water, exactly 10 cc. of the 0.5 N hydrochloric acid were added, and the whole was made up to volume at the temperature of the experiment. The solution was thoroughly shaken, quickly weighed to the nearest centigram, and then transferred as quickly as possible to the inversion tube. Care was taken to have the temperature of the component solutions at the temperature of the bath before mixing. The instant of adding the acid to the sucrose solution was taken as zero time.

Polarimetric readings were taken at definite time intervals. From six to ten readings were taken in the early period of the inversion and an equal number near completion. Each reading recorded is the mean of two or more readings taken about 30 seconds apart. For every solution duplicate series of measurements were made. When these did not agree other series were made until satisfactory agreement was obtained.

Calculation of the Coefficients

To calculate the values of the inversion constants we have made use of an algebraic modification of a method first used by Guggenheim.[11] His relation is,

$$kt_i + 2.3026 \log (v_i' - v_i) = A.$$

On transposing this reduces to,

$$2.3026 \log (v_i' - v_i) = -kt_i + A.$$

Here v_i is the ith reading of the series taken in the early period of the inversion, v_i' is the ith reading of the series taken near completion, and A is a constant. The reading v_i is taken at time t_i measured from the instant of starting the inversion; v_i' is taken at time $t_i + \tau$ measured from the instant of starting the inversion. The constant time interval τ is at least twice the half period of the inversion. Since in sucrose inversion the polarimetric reading decreases with the time, $v_i > v_i'$, hence the signs of v_i and v_i' must be interchanged in the relation derived by Guggenheim to give a usable expression. The relation then obtained is

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[11] Guggenheim: Phil. Mag., (7) **2**, 538 (1926).

$$2.3026 \log (v_i - v_i') = -kt_i + A. \qquad (6)$$

The mean value of the velocity coefficient k is found by use of this relation without determination of the initial and final inversion readings.

An example will serve to illustrate the method employed. For the solution 0.1 molar with respect to sucrose, 0.1 molar with respect to hydrochloric acid, and 2 molar with respect to sodium chloride at 25° the following data were obtained:

t_i	v_i	$t_i + 960$	v_i'
$t_1 = 60$ min.	$v_1 = 7.92°$	$t_1 + 960 = 1020$ min.	$v^{1\prime} = -1.05$
$t_2 = 120$	$v_2 = 6.81$	$t_2 + 960 = 1080$	$v_2' = -1.26$
$t_3 = 180$	$v_3 = 5.83$	$t_3 + 960 = 1140$	$v^{3\prime} = -1.44$
$t_4 = 240$	$v_4 = 4.94$	$t_4 + 960 = 1200$	$v_4' = -1.60$
$t_5 = 300$	$v_5 = 4.14$	$t_5 + 960 = 1260$	$v_5' = -1.75$
$t_6 = 360$	$v_6 = 3.41$	$t_6 + 960 = 1320$	$v_6' = -1.90$
$t_7 = 420$	$v_7 = 2.73$	$t_7 + 960 = 1280$	$v_7' = -2.03$
$t_8 = 450$	$v_8 = 2.44$	$t_8 + 960 = 1410$	$v_8' = -2.08$

Substituting these values in the relations,

$$2.3026 \log (v_1 - v_1') = -kt_1 + A,$$
$$2.3026 \log (v_2 - v_2') = -kt_2 + A,$$
$$2.3026 \log (v_3 - v_3') = -kt_3 + A, \text{ etc.,}$$

we obtain the following equations:

$$2.3026 \log 8.97 = -\ 60k + A, \qquad \text{(i)}$$
$$2.3026 \log 8.07 = -120k + A, \qquad \text{(ii)}$$
$$2.3026 \log 7.27 = -180k + A, \qquad \text{(iii)}$$
$$2.3026 \log 6.54 = -240k + A, \qquad \text{(iv)}$$
$$2.3026 \log 5.89 = -300k + A, \qquad \text{(v)}$$
$$2.3026 \log 5.31 = -360k + A, \qquad \text{(vi)}$$
$$2.3026 \log 4{,}76 = -420k + A, \qquad \text{(vii)}$$
$$2.3026 \log 4.53 = -450k + A. \qquad \text{(viii)}$$

The velocity coefficient, k, may be evaluated by eliminating the constant A from any two of these equations. In order to weight each reading equally we eliminate A from equations (i) and (iii), (i) and (v), (i) and (vii), (iii) and (v), (iii) and (vii), (v) and (vii), (ii) and (iv), (ii) and (vi), (ii) and (viii), (iv) and (vi), (iv) and (viii), and (vi) and (viii), respectively. Thus, we obtain twelve independent values of k. The mean of these twelve values is the value taken for k for this determination. The subtractions are indicated below:

(i) – (iii) gives, $120k = 2.3026 (\log 8.97 - \log 7.27)$;
$k = 0.0017511$.

Similarly,

(i) – (v) gives, $k = 0.0017525$,
(i) – (vii) gives, $k = 0.0017601$,
(iii) – (v) gives, $k = 0.0017540$,
(iii) – (vii) gives, $k = 0.0017646$,
(v) – (vii) gives, $k = 0.0017752$,
(ii) – (iv) gives, $k = 0.0017518$,
(ii) – (vi) gives, $k = 0.0017440$,
(ii) – (viii) gives, $k = 0.0017498$,
(iv) – (vi) gives, $k = 0.0017363$,
(iv) – (viii) gives, $k = 0.0017486$,
(vi) – (viii) gives, $k = 0.0017650$.

Average: $k = 0.0017544$.

All of the values found for the velocity coefficient, k, are average values obtained in this manner.

Experimental Results

The experimental results of this investigation are given in Tables I-V. Table I shows the velocity coefficients of inversion of sucrose found at 25° for the ionic solvents listed. Tables II to V list the velocity coefficients of inversion of sucrose in aqueous solutions, respectively, of sodium chloride, barium chloride, potassium sulphate, and magnesium sulphate at 30°. Here m is the molality, N the normality, and μ the total ionic strength as defined by Lewis and Randall.[12]

TABLE I

The Velocity Constants of Inversion of Sucrose in 0.1 Molar Hydrochloric Acid Solutions at 25°

Solvent	$k.10^5$ (1)	 (2)	 Mean
Salt-free acid	79.65	79.05	79.35
1 N NaCl	115.94	115.10	115.52
2 N NaCl	175.89	175.44	175.67
0.9853 N $BaCl_2$	107.78	108.50	108.14
1.9705 N $BaCl_2$	150.88	150.97	150.93
1 N $MgSO_4$	28.63	29.20	28.91
2 N $MgSO_4$	25.72	26.17	25.94

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[12] Lewis and Randall: "Thermodynamics," 6th Impr., 373 (1923).

TABLE II

The Velocity Constants of Inversion of Sucrose in 0.1 Molar Hydrochloric Acid Solutions containing Sodium Chloride at 30°

HCl	NaCl	NaCl			k.10⁵	
m	N	m	μ	(1)	(2)	Mean
0.1026	0	0	0.1026	163.40	163.03	163.215
0.1028	0.1	0.1028	0.2056	168.06	169.62	168.840
0.1048	1	1.0480	1.1528	237.60	236.24	236.920
0.1060	2	2.1386	2.2455	349.35	347.20	348.275
0.1095	3	3.2852	3.3947	523.31	523.69	523.500
0.1123	4	4.4924	4.6047	808.61	795.48	802.045
0.1156	5	5.7790	5.8946	1144.65	1151.98	1148.315

TABLE III

The Velocity Constants of Inversion of Sucrose in 0.1 Molar Hydrochloric Acid Solutions containing Barium Chloride at 30°

HCl	$BaCl_2$	$BaCl_2$			k.10⁵	
m	N	m	μ	(1)	(2)	Mean
0.1026	0	0	0.1026	163.40	163.03	163.215
0.1033	0.4926	0.2544	0.8665	191.09	189.09	190.090
0.1041	0.9853	0.5127	1.6422	225.60	225.09	225.345
0.1049	1.4779	0.7752	2.4305	267.10	265.57	266.335
0.1058	1.9705	1.0413	3.2330	309.98	309.04	309.510
0.1068	2.4632	1.3178	4.0524	367.12	368.38	367.750
0.1081	2.9558	1.5974	4.9003	435.41	437.62	436.515

TABLE IV

The Velocity Constants of Inversion of Sucrose in 0.1 Molar Hydrochloric Acid Solutions containing Potassium Sulphate at 30°

HCl	K_2SO_4	K_2SO_4			k.10⁵	
m	N	m	μ	(1)	(2)	Mean
0.1026	0	0	0.1026	163.40	163.03	163.215
0.1028	0.1	0.0514	0.2570	110.970	109.860	110.415
0.1032	0.3	0.1548	0.5676	62.962	62.271	62.617
0.1037	0.5	0.2592	0.8814	48.900	47.521	48.211
0.1042	0.7	0.3646	1.1980	40.390	38.896	39.643
0.1048	0.9	0.4717	1.5199	35.683	36.175	35.929

TABLE V

The Velocity Constants of Inversion of Sucrose in 0.1 Molar Hydrochloric Acid Solutions containing Magnesium Sulphate at 30°

HCl	$MgSO_4$	$MgSO_4$			$k.10^5$	
m	N	m	μ	(1)	(2)	Mean
0.1026	0	0	0.1026	163.40	163.03	163.215
0.1027	0.1	0.0514	0.3083	115.570	115.380	115.475
0.1028	0.3	0.1542	0.7196	79.322	79.329	79.326
0.1029	0.5	0.2571	1.1313	66.849	67.574	67.212
0.1031	1.0	0.5155	2.1651	57.657	56.023	56.840
0.1033	1.5	0.7746	3.2017	52.211	51.957	52.084
0.1036	2.0	1.0358	4.2468	50.565	51.007	50.786
0.1040	2.5	1.2999	5.3036	50.358	50.612	50.485
0.1046	3.2	1.6736	6.7990	52.418	51.709	52.064
0.1055	4.0	2.1088	8.5407	54.853	55.097	54.975

Discussion of the Experimental Results

The data recorded in Tables II to V are shown graphically in Fig. 1. Here the velocity coefficients of inversion at 30° are plotted against the total ionic strength of the solution. Since the molal concentration of the hydrochloric acid remains very nearly constant, the ionic strength is essentially a measure of the concentration of the added salt.

It is to be noted that the chlorides increase the velocity of inversion at a rate which increases rapidly with the salt concentration. In solutions of equal ionic strength the uniunivalent chloride has a greater accelerating effect than biunivalent chloride. This same order holds if equivalent normal concentrations are employed. The reverse order holds, however, if molar or molal concentrations are employed. These differences indicate that the cation of the salt is not entirely without effect upon the inversion velocity.

Harned and Hawkins[13] have studied the acid hydrolysis of certain esters in solutions containing alkali chlorides and nitrates. They find that the velocity coefficient of hydrolysis increases with the salt concentration, passes through a maximum, and then decreases with further increase in the salt concentration. We find in the present work no indication of such a maximum value either for sodium chloride or for barium chloride. On the contrary, the rate of hydrolysis increases at a rate which increases more and more rapidly with increasing ionic strength. Especially is this true for the sodium chloride solutions.

The sulphates markedly decrease the inversion velocity. Potassium sulphate has a greater retarding effect than the bibivalent magnesium sulphate, regardless of the basis of concentration taken. The values of the velocity

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[13] Harned and Hawkins: J. Am. Chem. Soc., 50, 85 (1928).

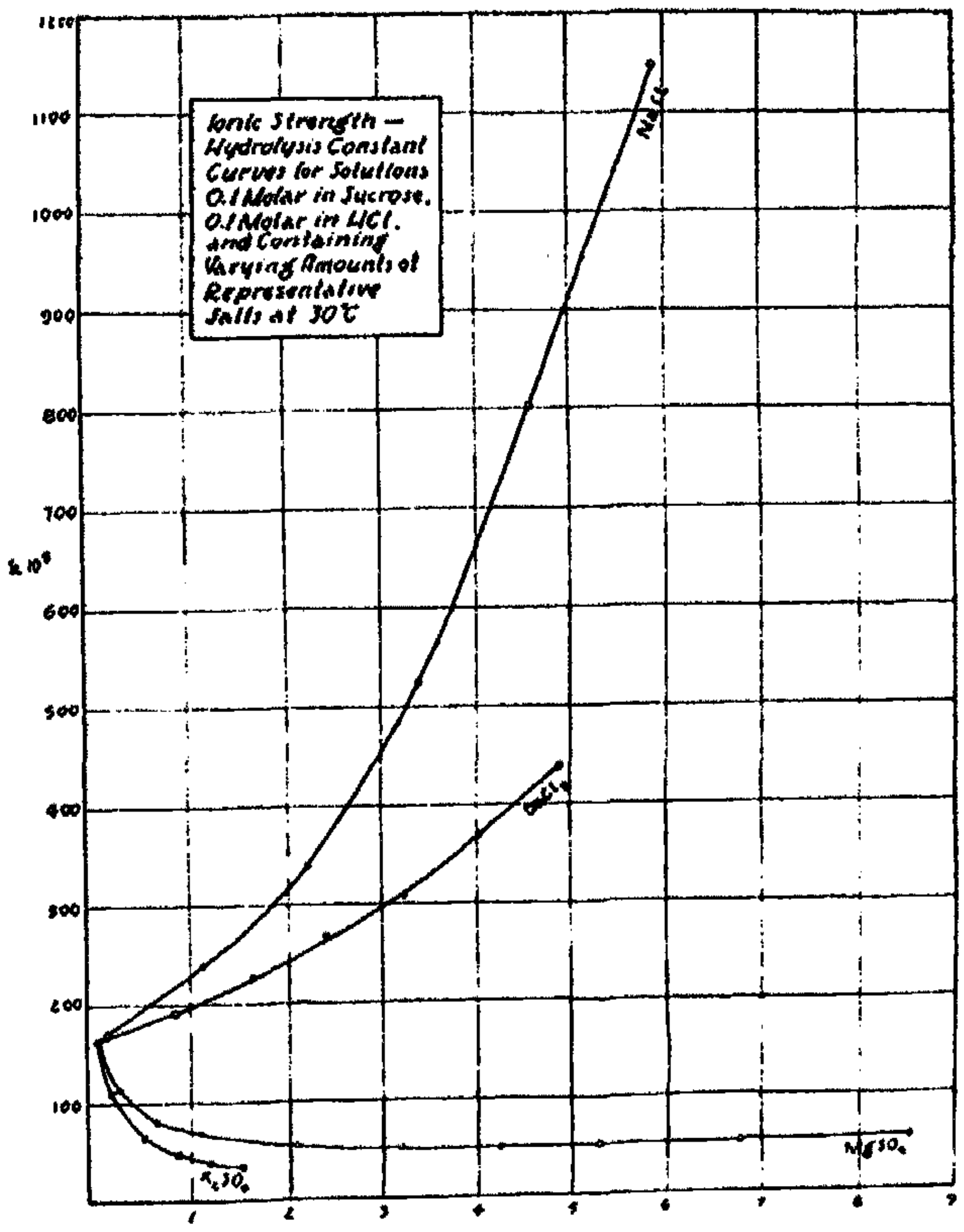

FIG. 1

coefficient for the magnesium sulphate solutions pass through a slight minimum at an ionic strength of about 4.5. Those for the potassium sulphate solutions decrease still more rapidly with increase in μ, to practical saturation. Here, as in the case of the chlorides, the cation evidently exerts some influence.

The Neutral Salt Effects

The data showing the influence of the neutral salts upon the rate of the inversion are collected in Tables VI to IX. Here M signifies the molar, N the equivalent concentration of the salt, k the inversion coefficient in the salt solution, and k_0 the coefficient in salt-free acid. The salt effect is given as the percentage increase or decrease in k_0.

The salt effects, measured as percentage change in k_0, are plotted against the equivalent concentrations of the added salts. These are shown in Fig. 2. The two chlorides produce positive, the two sulphates produce negative salt effects on the inversion of sucrose. The effects are very pronounced, especially

TABLE VI

The Effect of Sodium Chloride on the Velocity of Inversion of Sucrose by Hydrochloric Acid at 30°

NaCl M	NaCl N	$\frac{k}{k_0}$	$100(\frac{k}{k_0} - 1)$	$r = \frac{1}{M}\log\frac{k}{k_0}$
0	0	1	0	— —
0.1	0.1	1.0345	3.45%	0.1473
1.0	1.0	1.4516	45.16	0.1619
2.0	2.0	2.1338	113.38	0.1646
3.0	3.0	3.2074	220.74	0.1687
4.0	4.0	4.9140	391.40	0.1729
5.0	5.0	7.0356	603.56	0.1695

TABLE VII

The Effect of Barium Chloride on the Velocity of Inversion of Sucrose by Hydrochloric Acid at 30°

$BaCl_2$ M	$BaCl_2$ N	$\frac{k}{k_0}$	$100(\frac{k}{k_0} - 1)$	$r = \frac{1}{M}\log\frac{k}{k_0}$
0	0	1	0	— —
0.2463	0.4926	1.1647	16.47%	0.2689
0.4927	0.9853	1.3807	38.07	0.2844
0.7390	1.4779	1.6318	63.18	0.2878
0.9853	1.9705	1.8963	89.63	0.2821
1.2316	2.4632	2.2532	125.32	0.2865
1.4779	2.9558	2.6745	167.45	0.2891

TABLE VIII

The Effect of Potassium Sulphate on the Velocity of Inversion of Sucrose by Hydrochloric Acid at 30°

K_2SO_4 M	K_2SO_4 N	$\frac{k}{k_0}$	$100(\frac{k}{k_0} - 1)$	$r = \frac{1}{M}\log\frac{k}{k_0}$
0	0	1	0	— —
0.05	0.1	0.6765	−32.35%	−3.3946
0.15	0.3	0.3836	−61.64	−2.7741
0.25	0.5	0.2954	−70.46	−2.1184
0.35	0.7	0.2429	−75.71	−1.7559
0.45	0.9	0.2201	−77.99	−1.4608

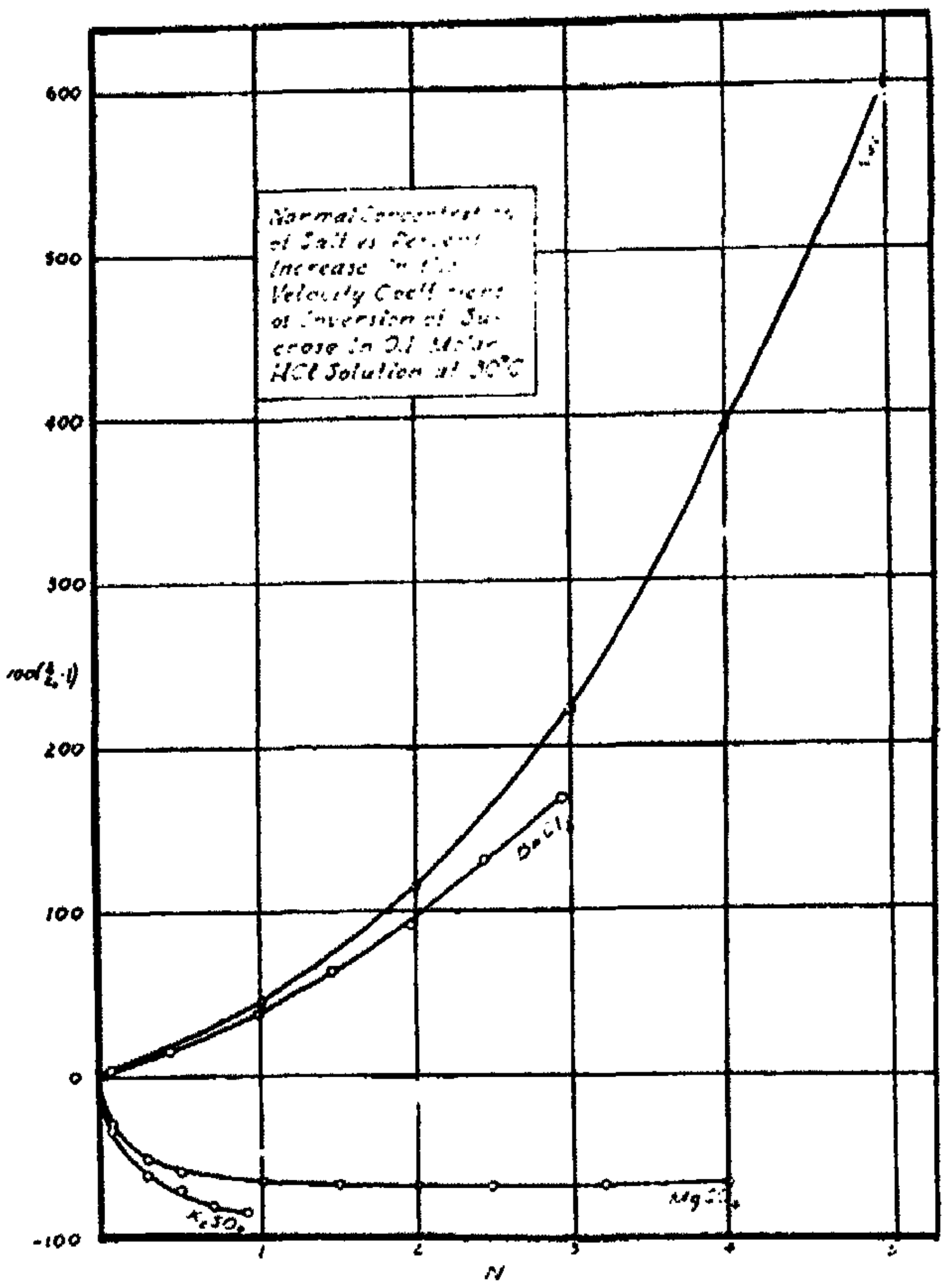

Fig. 2

Table IX

The Effect of Magnesium Sulphate on the Velocity of Inversion of Sucrose by Hydrochloric Acid at 30°

$MgSO_4$ M	$MgSO_4$ N	$\frac{k}{k_0}$	$100(\frac{k}{k_0} - 1)$	$r = \frac{1}{M} \log \frac{k}{k_0}$
0	0	1	0	— —
0.05	0.1	0.7075	−29.25%	−3.0054
0.15	0.3	0.4860	−51.40	−2.0891
0.25	0.5	0.4118	−58.82	−1.5412
0.50	1.0	0.3483	−65.17	−0.9161
0.75	1.5	0.3191	−68.09	−0.6614
1.00	2.0	0.3112	−68.88	−0.5070
1.25	2.5	0.3093	−69.07	−0.4077
1.60	3.2	0.3190	−68.10	−0.3101
2.00	4.0	0.3368	−66.32	−0.2363

those of sodium chloride and of potassium sulphate. The inversion coefficient for the 2 normal sodium chloride solution, for example, is more than double that for the salt-free solution, and for the 5 normal solution the increase is over 600% of the constant for the salt-free acid. The negative effect of potassium sulphate is even more striking. The addition of this salt in an amount sufficient to make a 0.2 normal salt solution decreases k_0 by 50% of its value, and the inversion coefficient for the 0.7 normal solution is only one-fourth that for the solution containing no salt.

Schmid and Olsen[14] have proposed the empirical relation,

$$k = k_0 \times 10^{rM},$$

as describing generally the influence of neutral salts on the velocity of hydrolytic reactions. Here k is the velocity coefficient measured for the salt solution, k_0 is the coefficient in the absence of the salt, r a constant specific for each salt, and M the molar concentration of the salt. A test of the applicability of this relation to sucrose inversion may be made by writing the equation in the logarithmic form,

$$r = \frac{1}{M} \log \frac{k}{k_0},$$

and then determining the actual constancy of r by substitution of the measured values of M, k, and k_0. The values of r thus determined are given in column 5 of Tables VI to IX. Judging by the constancy of r, we see that the Schmid-Olsen equation describes reasonably well the positive salt effects produced in the inversion of sucrose by the chlorides in concentrations above 0.5 molar. This conclusion agrees with the results obtained by Kautz and Robinson[15] in their study of the influence of the alkali and alkaline earth chlorides on the rate of hydrolysis of sucrose by hydrochloric acid. The equation of Schmid and Olsen is totally inapplicable, however, in describing the negative salt effects produced by the sulphates. When the salt effects are negative, the values of r, of course, are also negative, and are not constant for any range of salt concentration.

Brönsted and his co-workers[16] distinguish between two types of neutral salt effects. The one, the primary salt effect, is produced when the added salt changes the activity coefficients of any of the reactants of the system as given by equation (5); the other, the secondary salt effect, consists of a change in the actual concentrations of any or all of the reactants, due to the addition of the salt.

Brönsted[17] characterizes the primary salt effect in hydrogen ion catalysis as being at all dilutions an exponential function of the salt concentration. This postulate may be deduced, in the case of sucrose inversion, by evaluat-

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[14] Schmid and Olsen: Z. physik. Chem., 124, 97 (1926).

[15] Kautz and Robinson: J. Am. Chem. Soc., 50, 1022 (1928).

[16] Brönsted: Z. physik. Chem., 102, 169 (1922); 115, 337, (1925); Brönsted and Pedersen: 108, 185 (1924); Brönsted and Teeter: J. Phys. Chem., 28, 579 (1924); Brönsted and King: J. Am. Chem. Soc., 47, 2523 (1925).

[17] Brönsted: Trans. Faraday Soc., 24, 630 (1928).

ing the "kinetic activity factor," $\frac{f_s f_h}{f_x}$ of equation (5), from the expression,[15]

$$-\ln f = +0.5z^2\sqrt{\mu} - B\mu. \tag{7}$$

Here f is the activity coefficient and z the valence of the molecule, while μ is the ionic strength and B a characteristic constant of the solution. Substitution in equation (5) of the value of f obtained from equation (7) gives,

$$v = kc_s c_h e^{\mu(B_s + B_h - B_x)}, \tag{8}$$

where B_s, B_h, and B_x are constants of the solution due to the influence of the sucrose, the hydrogen ion, and the critical complex, respectively. Obviously, equation (8) requires that the primary salt effect in sucrose inversion, as measured by the velocity of the reaction, shall vary exponentially with the salt concentration.

Furthermore, since for very small values of μ we may write,

$$e^{\mu(B_s + B_h - B_x)} = 1 + \mu(B_s + B_h - B_x),$$

equation (8) becomes, for dilute solutions,

$$v = kc_s c_h \left[1 + \mu(B_s + B_h - B_x)\right]. \tag{8'}$$

Equation (8′) is the basis of Brönsted's hypothesis that for dilute solutions the primary salt effect in hydrogen ion catalysis is a linear function of the salt concentration.

The salt effects observed in this investigation may be described in terms of Brönsted's concepts, outlined above. Specifically, the chlorides produce positive primary salt effects in the catalytic inversion of sucrose by hydrogen ion. Up to chloride ion concentrations of about 0.4 N, these effects vary linearly with the salt concentration, as expected from equation (8′). To test the applicability of equation (8) throughout the entire concentration range, we plot the logarithm of the velocity coefficient against the ionic strength, as shown in Fig. 3. Using the method of least squares we obtain the equation of the most probable straight line for the several points. The test of the exponentiality of the salt effect is the agreement between the experimental points and the points on this line. For the sodium chloride solutions the equation obtained by least squares is,

$$\log_{10} (k.10^5) = 0.1488\mu + 2.2029. \tag{9}$$

This equation may be written in the exponential form,

$$k = 160.10^{-5}.e^{0.3426\mu}.$$

The equation obtained similarly for the barium chloride solutions is,

$$\log_{10} (k.10^5) = 0.0891\mu + 2.2044. \tag{10}$$

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[15] The sign of the B-term must be negative in the equation given by Brönsted in order to obtain equation (8)

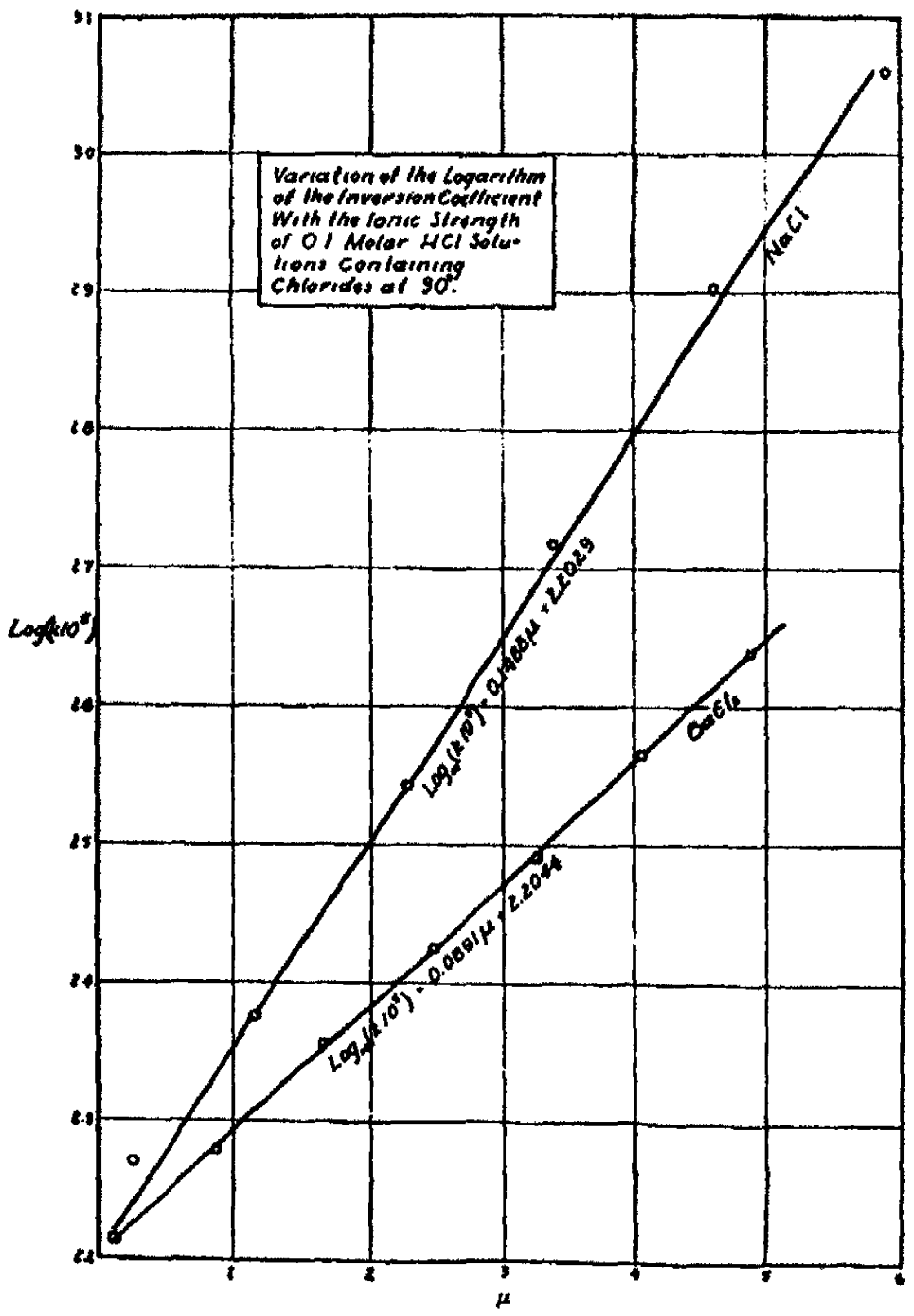

FIG. 3

Or, in the exponential form,

$$k = 160.10^{-6}.\, e^{0.2052\mu}.$$

The agreement is reasonably close but not exact in the case of the sodium chloride solutions, and is quite good for the barium chloride solutions. We conclude, therefore, that for fixed proportions of acid and of sucrose, the primary salt effect in sucrose inversion is an exponential function of the ionic strength of the solution.

The negative salt effects produced by the sulphates are predominantly secondary. The sulphate ion probably combines with the hydrogen ion to form the incompletely dissociated hydrosulphate ion, thus decreasing the actual concentration of the hydrogen ion in the solution. This explanation is in harmony with that proposed by Harned and Hawkins[13] for similar decreases in the hydrolytic activity of the hydrogen ion in ester hydrolysis in sulphate solutions. It also agrees with Randall and Failey's[19] explanation of the anomalous decreases caused by sulphates in the activity coefficients of acids of intermediate strength. No doubt the sulphates, as the chlorides, produce positive primary salt effects in the inversion of sucrose, but these are overshadowed by the much greater negative secondary effects.

At equal ionic strengths, we see that the positive and the negative effects of barium chloride and of magnesium sulphate, respectively, are slightly less than the effects of the respective sodium and potassium salts. This suggests that the specific effects of the cations are not to be readily interpreted on the basis of interionic attraction alone. The extent of hydration of the cation evidently plays an important part. If the relative hydration had no influence, then since the sodium salt produces a greater positive primary salt effect than the barium salt, we should similarly expect the potassium salt to produce a greater positive primary effect than the magnesium salt at equal ionic strengths. Thus the total *negative* effect observed for potassium sulphate should be *less* than that for magnesium sulphate. On the contrary potassium sulphate produces a *greater* negative effect than magnesium sulphate. Apparently, the sodium ion is more highly hydrated per equivalent of electric charge than is the barium ion in solutions of equal ionic strength. The magnesium ion, on the other hand, is much more highly hydrated than the potassium ion. It appears, therefore, that the more highly hydrated the ions of the salt, the larger are the positive primary salt effects in hydrogen ion catalysis.

The Temperature Coefficients of the Inversion and the Heats of Activation of the Sucrose

The temperature coefficients of the velocity, k_{30}/k_{25}, are shown in the fourth column of Table X. Employing the Arrhenius formula in the form,

$$2.3026 \log \frac{k_2}{k_1} = \frac{Q}{R}\left(\frac{T_2-T_1}{T_2T_1}\right),$$

we have calculated the heats of activation of the sucrose. Here R is the gas constant, taken in cals. per degree, T is the absolute temperature, and Q is the heat of activation. The values of Q are found in the last column of Table X.

From Table X it is seen that the temperature coefficient of the velocity and the calculated heat of activation of the sucrose are unaffected by chlorides but are decreased by sulphates. This is in conformity with the results of Rice and Lemkin.[20] They find that the temperature coefficient of the acid catalysis of the acetone-iodine reaction is unchanged by the alkali and alkaline earth salts of the strong monobasic acids, but is decreased by sulphates.

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[19] Randall and Failey: J. Am. Chem. Soc., 49, 2678 (1927).

[20] Rice and Lemkin: J. Am. Chem. Soc., 45, 1896 (1923).

TABLE X

The Temperature Coefficients and Heats of Activation of Sucrose in Hydrochloric Acid Solutions with and without Neutral Salts

Solvent	$K_{25}.10^5$	$k_{30}.10^5$	$\frac{k_{30}}{k_{25}}$	Q
Salt free acid	79.35	163.22	2.0570	25,917 cals./mol.
1 N NaCl	115.52	236.92	2.0509	25,811
2 N NaCl	175.67	348.28	1.9939	24,798
0.9853 N $BaCl_2$	108.14	225.35	2.0839	26,385
1.9705 N $BaCl_2$	150.93	309.51	2.0507	25,807
1 N $MgSO_4$	28.91	56.84	1.9662	24,294
2 N $MgSO_4$	25.94	50.79	1.9576	24,137

Mean value of k_{30}/k_{25} for solutions containing chlorides = 2.0449.
Mean value of k_{30}/k_{25} for solutions containing magnesium sulphate = 1.9619.
Mean value of Q for solutions containing chlorides = 25,702 cals./mol.
Mean value of Q for solutions containing magnesium sulphate = 24,215 cals./mol.

The classical value obtained by Arrhenius for the temperature coefficient of the inversion of sucrose between 25° and 35°,

$$k_{35}/k_{25} = 4.13,$$

is slightly greater than double the values of the ratio, k_{30}/k_{25}, here obtained. This is consistent with the increase of the temperature coefficient of sucrose inversion with temperature. The values of the heat of activation found for the salt-free solutions and for the solutions containing the chlorides closely approximate the classical value of 26,000 cals. per mol. obtained by Arrhenius for the heat of inversion.

Summary

1. The velocity coefficients of the inversion of sucrose by 0.1 molar hydrochloric acid have been determined for solutions of sodium chloride, barium chloride, potassium sulphate, and magnesium sulphate, respectively, in varying concentrations at 30°.

2. The chlorides increase the velocity of the inversion at a rate which increases with the concentration of the salt. They produce positive primary salt effects which in the dilute range are linear, and in the entire range exponential, functions of the salt concentration.

3. The sulphates markedly decrease the inversion velocity, producing negative secondary salt effects.

4. Apparently, the more highly hydrated the ions of the added salt, the larger are the positive primary salt effects in the hydrogen ion catalysis of sucrose inversion.

5. The equation of Schmid and Olsen, $k = k_0 \times 10^{rM}$, does not describe the negative salt effects produced by the sulphates in sucrose inversion. For concentrations of the salt above 0.5 molar, this relation describes reasonably accurately the positive effects of the chlorides.

6. The temperature coefficients of the inversion, k_{30}/k_{25}, have been determined for hydrochloric acid solutions containing sodium chloride, barium chloride, and magnesium sulphate, respectively. The temperature coefficient for the solutions containing the chlorides is the same as that for the salt-free acid. That for the magnesium sulphate solution is lower.

7. From the temperature coefficients the heats of activation of the sucrose have been calculated.

THE EFFECT OF MERCURIC IODIDE AND AMMONIUM CHLORIDE ON GLASS*

BY CLARA E. MILLER

Introduction

In 1928 J. Rinse[1] measured the vapor pressure of mercuric iodide over a long temperature range (130°-347°C.) by a static method, using a glass-spring indicator. He obtained a continuous vapor pressure-temperature curve instead of one showing a sharp break between the saturation curve and the Boyle-Gay-Lussac curve for gases; in other words, at temperatures in the vicinity of the saturation point, the vapor pressure of the iodide was considerably lower than was expected. This was the same phenomenon noticed by McHaffie and Lenher[2] in the case of water vapor and of toluene vapor, and they explained it by the adsorption of the vapors on glass which took place to an increased extent in the neighborhood of the dew-point.

In all of these cases it would be necessary to assume that the adsorbed layer was several hundred molecules thick in order to account for the observed lowering of the vapor pressure but this assumption does not seem correct since it is improbable that the unsaturated forces at the surface of the glass extend to such a distance. However, several years ago Frazer, Patrick and Smith[3] demonstrated the difference between a freshly fused glass surface and one chemically corroded. They showed that there was no more than a unimolecular layer of toluene adsorbed on a glass surface which was molecularly plane, whereas the adsorption was great and the vapor pressure followed a curve similar to those obtained by McHaffie and Lenher when the glass had been treated with chromic acid cleaning solution. The chromic acid-sulfuric acid mixture so etched and corroded the glass by removing alkali from it that capillary condensation took place. Water vapor itself also has this effect.

Altho Rinse[4] found that etching by water vapor could not account for the shape of the curves he obtained, the possibility remains that in his experiments the mercuric iodide itself attacked the glass. With this point in mind, he made an effort to determine whether there was any chemical action between glass and mercuric iodide by placing a known weight of the latter in a glass tube, heating it to 600°C., recovering the iodide by subliming it into the tip of the tube, and reweighing it. He found that the same weight of the iodide could be recovered as was originally placed in the tube and concluded that no

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* Contribution from the Chemistry Laboratory of the Johns Hopkins University.

* From a dissertation submitted to the Board of University Studies of the Johns Hopkins University in partial fulfillment of the requirements for the Doctor of Philosophy degree.

[1] Smits and Rinse: Rec. Trav. chim., 47, 35 (1928).

[2] McHaffie and Lenher: J. Chem. Soc., 127, 1559 (1925); 1926, 1785; 1927, 272.

[3] Frazer, Patrick and Smith: J. Phys. Chem., 31, 897 (1927).

[4] Rinse: J. Chem. Soc., 1928, 1442.

chemical action had taken place. Nevertheless, sufficient reaction might have occurred to roughen the surface of the glass without causing any change in mass as far as could be determined by weighing to tenths of a milligram. The method used by Frazer, Patrick and Smith[1] and later by Latham[2] to demonstrate the action of cleaning solution on glass was therefore used again to show the effect of mercuric iodide and also of ammonium chloride on a glass surface.

Experimental

The experimental procedure was essentially the same as that first used by McHaffie and Lenher[3] and it is described by them as well as by Frazer, Patrick and Smith[4] and Latham.[5] A definite volume of dry air-free toluene was enclosed in a pyrex bulb which had been fused and blown thru phosphorus pentoxide to prevent access of moisture and which therefore had a molecularly plane surface. The bulb was closed off from the rest of an evacuated system by means of a mercury U-tube which also served as a manometer to measure the vapor pressure of the toluene. Both the bulb and the U-tube were in a thermostat capable of being maintained at any temperature between 50°C. and 25°C., and the pressure of the toluene was observed at different temperatures within this range.

The toluene vapor was then pumped out of the bulb, air dried with phosphorus pentoxide was admitted, and the bulb was removed from the apparatus. A small amount of mercuric iodide[6] having been introduced into it, the bulb was then sealed into an evacuating system, evacuated, sealed off and heated at 450°C. in an electric furnace for twelve hours. After this, the bulb was opened to the atmosphere and quickly put into place again to be evacuated. This time it was surrounded by an oil-bath heated to 150°C. and the mercuric iodide was thus removed from it by distillation. After the iodide had apparently all distilled away, the pumps were allowed to run for a period of about ten hours so as to remove completely all traces of the iodide vapor before dried air was again admitted to the apparatus. The bulb was then replaced in its original position in the thermostat, evacuated, toluene vapor introduced and another series of vapor pressure measurements carried out. All glass blowing was done thru phosphorus pentoxide and every precaution was taken for keeping water vapor away from the surface of the bulb.

The same procedure was carried out using another bulb and ammonium chloride[7] instead of mercuric iodide.

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[1] loc. cit.

[2] Latham: J. Am. Chem. Soc., 50, 2987 (1928).

[3] McHaffie and Lenher: loc. cit.

[4] Frazer, Patrick and Smith: loc. cit.

[5] Latham: loc. cit.

[6] The mercuric iodide used here was prepared by precipitation, purified by sublimation, and dried in a desiccator over phosphorus pentoxide.

[7] The ammonium chloride was prepared by subliming Baker's C. P. ammonium chloride three times. To dry it, the pure salt was placed in one end of a tube, the other end of which contained phosphorus pentoxide; the chloride was warmed several times daily for nine days. These special precautions were taken to dry the compound thoroughly in order to prevent its decomposition into ammonia and hydrogen chloride at a relatively low temperature.

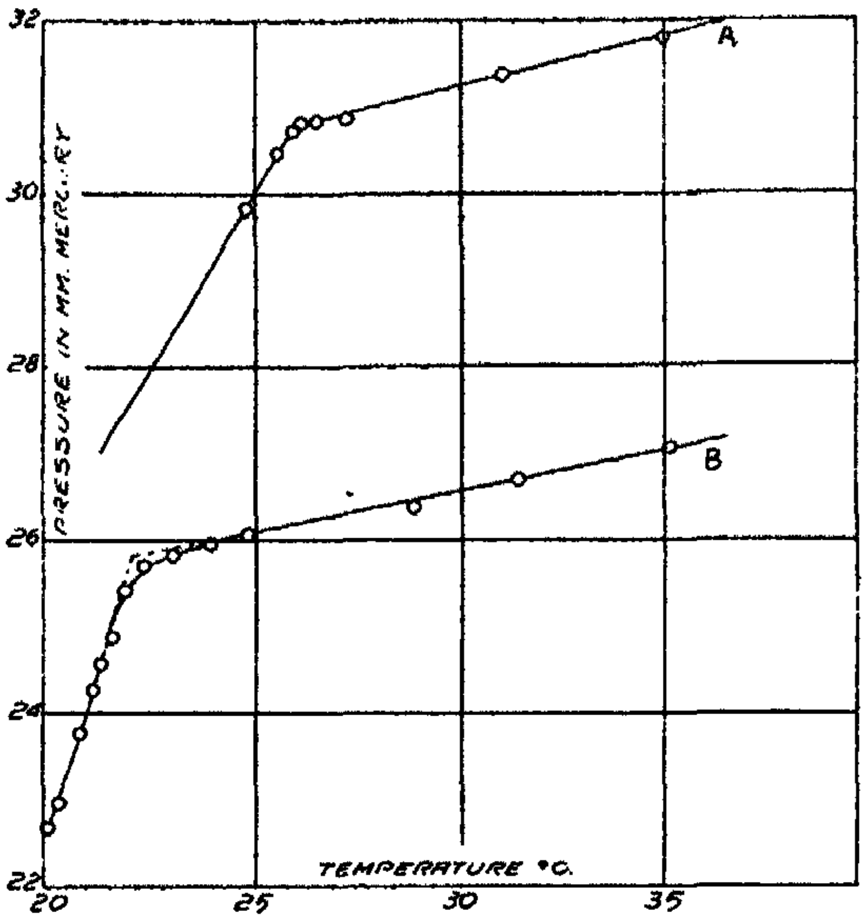
32
30
28
26
24
22
20
25
30
35
PRESSURE IN MM. MERCURY
TEMPERRATURE °C.
A
B

Fig. 1

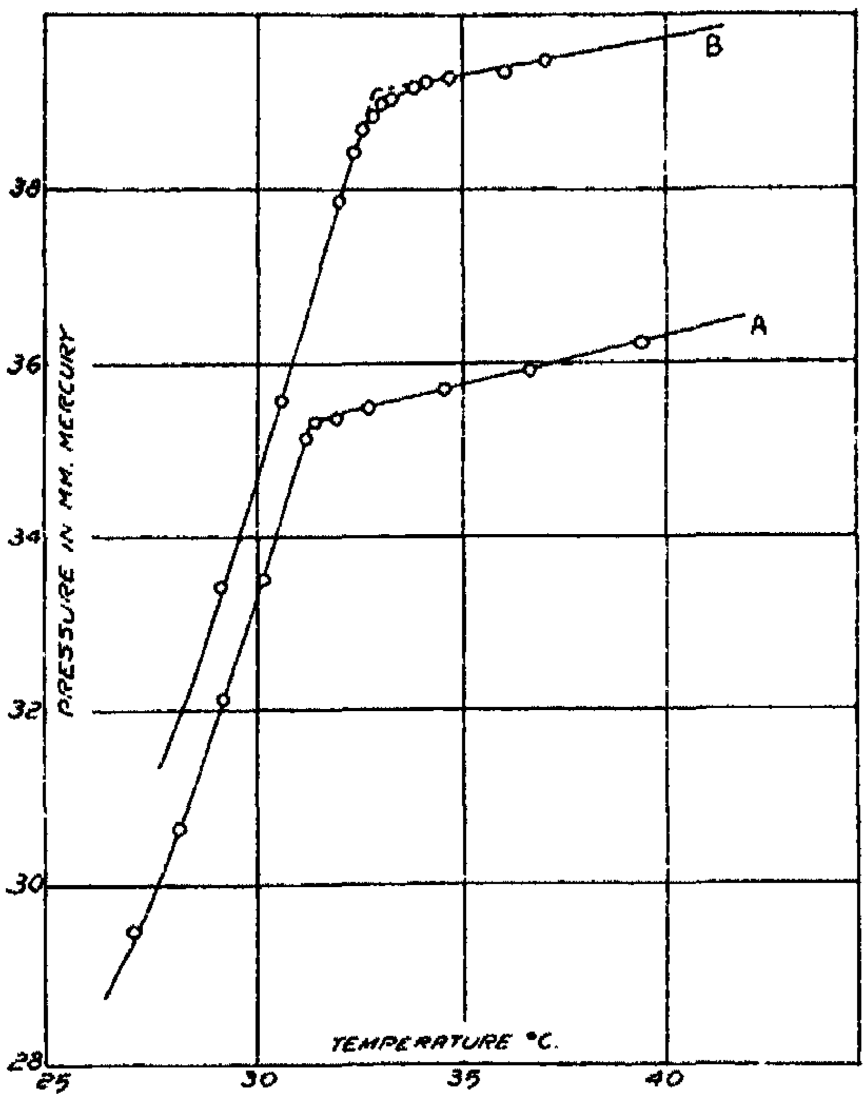
38
36
34
32
30
28
25
30
35
40
PRESSURE IN MM. MERCURY
TEMPERATURE °C.
A
B

Fig. 2

The first series of measurements of the vapor pressure of toluene, obtained with a fused glass bulb, is given in Table I and the pressure is plotted against the temperature in Curve A of Fig. 1. The sharp break between the liquid and gas curves shows that no adsorption had taken place; in other words, in this case the surface of the bulb was molecularly plane. On the other hand, Table II and Curve B (Fig. 1) show that, after the glass had been heated in contact with mercuric iodide vapor, its surface had been attacked and roughened to such an extent as to cause considerable adsorption; the curve is markedly rounded off in the neighborhood of the dew-point.

Ammonium chloride was also found to have a decided effect on glass. Tables III and IV give the results obtained for the vapor pressure of toluene in a pyrex bulb before and after it was heated with ammonium chloride. The graphs of these results are shown in curves A and B of Fig. 2. In the

TABLE I

Temp. °C	Pressure mm.	Temp. °C	Pressure mm.	Temp. °C	Pressure mm.
40.04	37.82	32.22	36.82	30.93	36.73
36.00	37.41	31.50	36.83	30.56	36.41
33.58	37.04	31.10	36.83	29.74	35.84

TABLE II

Temp. °C	Pressure mm.	Temp. °C	Pressure mm.	Temp. °C	Pressure mm.
40.16	33.08	27.37	31.70	26.14	30.29
36.37	32.70	27.35	31.72	25.85	29.78
33.86	32.36	27.08	31.56	25.08	28.67
29.87	32.08	26.89	31.40	25.33	28.95
28.97	31.97	26.63	30.89	24.86	28.28
28.07	31.84	26.38	30.59		

TABLE III

Temp. °C	Pressure mm.	Temp. °C	Pressure mm.	Temp. °C	Pressure mm.
20.98	22.0	25.20	27.49	27.70	29.50
22.10	23.43	26.20	29.14	29.57	29.71
23.14	24.63	26.95	29.35	31.60	29.93
24.20	26.12	26.43	29.33	34.48	30.24

TABLE IV

Temp. °C	Pressure mm.	Temp. °C	Pressure mm.	Temp. °C	Pressure mm.
24.14	27.41	27.83	32.84	29.02	33.25
25.60	29.56	28.03	33.0	29.7	33.26
27.59	32.69	28.25	33.05	31.00	33.34
27.36	32.41	28.80	33.17	32.0	33.50
27.03	31.86				

case of ammonium chloride etching of the glass could be readily detected by the eye. In fact, in one bulb treated, where the temperature of the furnace was allowed to rise to 500°C. for a period of several hours, the effect was so great that it could be photographed.

In addition to the increased adsorptive power of glass produced by heating mercuric iodide in it, a further effect of this compound on glass must be noted. In the experiment with mercuric iodide, it was observed that a black residue remained in the bulb and black streaks were seen on the sides. This was not accidental. Several other pyrex tubes heated with mercuric iodide showed the same effect and some ground pyrex glass turned quite black when heated in contact with pure mercuric iodide. Some ground soft glass heated in the same way showed no change in color. The mercuric iodide was removed from the latter and the glass was boiled with water. The solution obtained in this way gave a positive test for iodide ion showing that the mercuric iodide had reacted with the soft glass. However, no test for iodide ion was given by a solution similarly obtained from ground pyrex glass, nor could the identity of the black substance be determined, altho its formation gave visible evidence that a reaction took place between the mercuric iodide and the pyrex.

Discussion

It has long been known that glass is by no means an inert substance but that it is attacked by many reagents, especially such highly polar ones as water and hydrogen chloride. A consideration of the chemical constitution of glass helps to explain this action.

Such studies on glass as have been made[1] show not only that it contains silicates as definite compounds but that it may be considered as a sponge of silica threads soaked in silicates and the products of their ionic dissociation. The silica apparently acts as a sort of solvent medium and it probably enters into combination with the silicates, producing solvation of the ions and salt molecules. Altho this reduces the ion mobilities to a great extent, Warburg[2] and Le Blanc and Kirschbaum[3] have been able to measure the ionization of glass, and the latter found that soft glass is ionized to the extent of eighty percent at 250°C. The conduction is due to the transference of the sodium ion alone, the other constituents of glass being part of a rigid system. This conclusion was verified by Kraus and Darby.[4] It is the presence of sodium ions dispersed thru the viscous mass of silica, silicates, and borosilicates, that enables one to account in some measure for the corrosive action mentioned.

The hydrolysis of glass is perhaps the most marked of these reactions especially at elevated temperatures. New vessels made of even the most resistant glasses, Jena and Pyrex, lose several milligrams in weight when

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[1] W. E. S. Turner: "The Constitution of Glass" (1927).

[2] E. Warburg: Ann. Physik, 21, 622 (1884).

[3] Le Blanc and Kirschbaum: Z. physik. Chem., 72, 468 (1910).

[4] Kraus and Darby: J. Am. Chem. Soc., 44, 278 (1922).

water is boiled in them for several hours[1] and those made of less resistant glasses are visibly etched and corroded. Sodium hydroxide is always found in the solution so made and it is quite likely that the reaction between the water and the glass is an ionic one since the temperature coefficient of water is very high and the proportion of sodium ions present in the glass also increases with the temperature. The electronegative hydroxyl ion from the water evidently reacts with the electropositive sodium ion in the glass. This conclusion is strengthened by the fact that the action of water is greatly diminished when the surface of the glass has been attacked sufficiently for it to become coated with a layer of silica.[2]

Hydrochloric acid also has a very special action on glass which has been studied by Foerster[3] who found that the attack of concentrated solutions especially at high temperatures was very great. It may also be recalled in this connection that in one of the methods devised by Jannasch[4] to decompose refractory silicates, the silicate is heated with hydrogen chloride under pressure between 200°C. and 250°C. Hydrogen chloride also contains a highly electronegative ion which tends to combine with sodium, and sodium chloride as well as silica were found in the residues obtained upon evaporation of a solution of 24.24% hydrochloric acid which had been boiled for several hours in a glass flask.[5]

Probably no glass has ever been made which is completely resistant to such chemical action. Pyrex glass has the most favorable composition for resistance to water and acid but even it is appreciably attacked by water and hydrochloric acid.[6] Jena glass shows a behavior similar to that of pyrex.

Mercuric iodide may easily be placed in the category of highly polar compounds for, altho at ordinary temperatures it is but slightly ionized, it contains an electronegative halogen element. Rinse[7] found that dissociation of the iodide took place at 450°C. and it seems a reasonable assumption that at this elevated temperature when the forces between the mercury and iodine were weakened, the iodine would enter into combination with the sodium ion in the glass. This assumption is justified by the experiment described in this paper in which a soluble iodide was found to have been formed when mercuric iodide was heated with soft glass. Even pyrex was attacked sufficiently for a marked change in its adsorptive power to be observed.

Furthermore, later results obtained by Rinse[8] showed that he could obtain vapor pressure-temperature curves for mercuric iodide in which there were sharp breaks at the dew-point provided he did not first heat his apparatus to a high temperature. After he had once heated it above 500°C., he obtained

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[1] Cauwood, English and Turner: J. Soc. Glass Technology, 1, 153 (1917); Cauwood and Turner: 2, 219 (1918).

[2] Mylius and Groschuff: Z. physik. Chem., 55, 101 (1907).

[3] Foerster: Z. anal. Chem., 33, 299 (1894).

[4] Jannasch: Ber., 24, 273 (1891).

[5] Dimbleby, Cauwood and Turner: J. Soc. Glass Technology, 10, 304 (1926).

[6] International Critical Tables, 2.

[7] Smits and Rinse: Rec. Trav. chim., 47, 35 (1929).

Rinse: J. Chem. Soc., 1928, 1442.

continuous curves in every determination. It is very likely that the high temperature brought about some decomposition of the iodide and consequently a reaction between it and the glass took place.

The special action of mercuric iodide on pyrex producing the black compound is difficult to explain since the information obtained about it is very meager. Perhaps the fact that pyrex glass contains arsenic may be responsible for this action since Jena glass contains no arsenic and Rinse made no mention of having noticed similar behavior in experiments with the latter kind of glass.

That ammonium chloride should attack glass is also to be expected. Clarke and Steiger[1] demonstrated that dry ammonium chloride could be used to decompose the most refractory silicates, iron silicates resisting the action of strong hydrochloric acid being readily decomposed by the ammonium salt. In other cases, those of the zeolites, sodium was found to be quantitatively replaced by the ammonium radical. Ammonium chloride has also been proven a valuable reagent for testing the durability of glass. Its action may depend on its tendency to decompose into hydrogen chloride and ammonia; at the high temperature used in the experiment described here, even the dry salt tends to decompose to some extent.

Other continuous vapor pressure curves may be explained by similar action upon the glass surface. Measurements made by Rinse[2] indicated that iodine gave continuous curves while the curves for mercury showed sharp breaks at the dew-point. Here again it appears that the presence of an electronegative substance is necessary for attack upon glass.

It seems, then, rather improbable that any polar substance could be heated in glass without reacting to some extent with it. The surface of the glass after such action, no matter what pains had been taken beforehand to make it molecularly plane, would be so roughened that its extent could not be determined and calculation of the thickness of an adsorbed layer would be impossible. It may be said, therefore, that glass is not a suitable substance upon which quantitative studies of the extent of adsorption at high temperatures can be made unless the compound adsorbed can be proved to have no chemical action upon the glass.

In conclusion, the author wishes to acknowledge her gratitude to Dr. J. C. W. Frazer, who suggested this work and under whose guidance it was carried out.

Summary

1. Measurements of the vapor pressure of toluene in a fused pyrex bulb and in the same bulb after heating it with mercuric iodide show extensive adsorption in the latter case. This effect is attributed to the fact that mercuric iodide attacked the surface of the glass, leaving it coated with a layer

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[1] Clarke and Steiger: Am. J. Sci., (4) 8, 245 (1899); (4) 9, 117 (1900); (4) 13, 33 (1902).

[2] Rinse: J. Chem. Soc., 1928, 1442.

of silica. The extent of the surface was then indeterminably great and no calculations of the thickness of the adsorbed layer could be made with accuracy.

2. Mercuric iodide reacts with soft glass at a high temperature to produce a soluble iodide and with pyrex to form a black compound whose identity has not been determined.

3. Adsorption measurements also show that ammonium chloride has a great effect in roughening the surface of glass.

4. The corrosive action of mercuric iodide and of ammonium chloride has been compared with that of other chemical reagents, especially hydrogen chloride. This action has been attributed to the existence of free sodium ions in the glass and has been shown to render glass an unsuitable substance for use in adsorption vessels where the adsorption of polar compounds at high temperatures is to be studied.

Baltimore, Md.

HYDROCARBONS AS DISPERSION MEDIA: A REVIEW*

BY BASIL C. SOYENKOFF

Methods of Preparation

In a previous communication,[1] evidence was brought to show that peptization and colloid stability can occur in the absence of ions. It still remained to find whether such behavior was exceptional or usual in the case of non-polar liquids as dispersion media.

Chemical literature contains numerous references to colloid systems in benzene and other hydrocarbons. For the purposes of a preliminary discussion, we shall classify these organosols according to the methods employed in preparing them, since the latter at least indicate the chemical composition of the dispersed phase,—a point on which other data often are lacking.

Among the dispersion methods, electrical dispersion was resorted to by Svedberg[2] to obtain sodium and potassium sols in ligroin, pentane and liquid methane. In spite of the painstaking precautions taken to insure the purity of the solvent and prevent its decomposition by the oscillatory discharge, the resulting sols were unstable.

Hall[50] prepared dispersions of aluminium (and apparently also of silver, copper, lead and iron) by means of a 1000 v. a.c. arc in "high grade transformer oil." In some cases, the dispersed phase settled out rapidly (f. inst. copper in 24 hours).

Haurowitz[3] prepared the benzinosols of nickel, iron, aluminium, lead, tin, zinc, copper, manganese and brass. High frequency discharge was produced among small particles of metallic foil suspended in benzine, optimum results being obtained with 0.5-1.5 amp. at 180 v. Since no special effort was made to prevent the decomposition of the dispersion medium, Haurowitz's sols probably contained some colloid carbon. The sols remained stable for months provided rubber had been previously added. Colophony, cholesterol and lecithin had no protective action.

Berl, Barth and Winnacker,[4] using high-frequency alternating potentials of about 25000 v., obtained hexane dispersions of magnesium, zinc, lead, tin, copper and iron, which remained stable only in the presence of dissolved rubber. The most concentrated lead sol contained 1.32% Pb and 0.75% rubber, the amount of Pb in stable dispersion being in general proportional to that of the added rubber. Its protective action was therefore considered as possibly due to the formation of addition compounds.

Among the colloid systems prepared by mechanical dispersion we have emulsions in which an aqueous solution of soap, gelatin etc., constitutes the dispersed phase surrounded by a hydrocarbon (benzene, paraffin oil) as the continuous phase.

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* Contribution from the Department of Chemistry, N. Y. U. College of Dentistry.

Thermal dispersion has been used in several instances. Thus von Weimarn[5] stratified glycerine under xylene and heated the lower layer; glycerine vapor condensed to an emulsion in xylene. Pochettino[51] heated selenium above its melting point in contact with an "inert" solvent (paraffin, naphthalene etc.) which was solid at room temperature. The mixture assumed a red coloration due to the diffusion of selenium vapor through the hydrocarbon. Solid colloidal systems were obtained on cooling, which yielded coarse and rather unstable sols on treatment with benzene, carbon bisulfide etc. Adding selenium to boiling aniline produced colloid dispersions which settled out in 24 hours (in a few minutes when placed in direct sunlight). Very dilute dispersions in glycerine resulted in a similar manner.

The method described by Semenoff, Schnalnikoff and collaborators deserves a special mention here. The two components (the metal and the frozen dispersion medium) are simultaneously vaporized in the vacuum of a diffusion pump, and the mixed vapor allowed to condense on the outer surface of a glass tube filled with liquid air. Solid mixtures result in which the dispersed phase is present in a state of very fine subdivision (not more than 27 atoms in a particle according to X-ray evidence). Using a similar method, v. Bogdandy, Boehm and Polanyi[6] obtained an Ag-naphthalene mixture containing 1.2% of the metal and yielding, when treated with xylene, a red suspension which existed only for a short time. Roginsky and Schalnikoff[7] prepared the organosols of sodium, potassium, rubidium, caesium, cadmium and mercury. Benzene, hexane, toluene, and xylene (in a few cases also ethyl ether and ethyl alcohol) served as the dispersion media; they were carefully purified by vacuum distillation. The stability of the sols varied from a few minutes to two hours at room temperature.

A further study of these sols was made by Tomaschewsky.[8] The solid mixtures containing sodium were ruby red immediately on melting; the transmitted light was not polarized. Before the room temperature was reached, however, a condensation of the particles occurred; the sols became polydisperse and violet colored in reflected light, the violet component being polarized. Colloid Na in ether remained stable for at least a month, in xylene for 12-20 hours, in benzene and hexane was difficult to prepare. The organosols of the other alkali metals were dark blue in color; K in ether was stable after two month's time, K in xylene lasted for about ten days, and Rb and Cs in ether for less than half an hour.

Many molecularly complex substances yield colloid dispersions in hydrocarbons merely on the addition of the solvent and, sometimes, heating. Rubber, gums, synthetic products like polystyrenes, phospholipins[9] etc., belong in this class. Lyophilic organosols have been comprehensively discussed by Whitby[10] and by Staudinger.[11]

Some of the substances soluble in benzene can act as peptizing agents. Thus Evers[12] obtained a black benzenosol of platinum by hydrogenating rubber under pressure in the presence of Pt powder.

Loewe[9] notes that methylene blue, insoluble in chloroform, can be dispersed in a chloroform sol of kephalin, and the amounts of the dissolved dye are in agreement with those calculated from the adsorption isotherm.

Amberger[13] triturated a concentrated solution of silver nitrate in water with lanolin and allowed the mixture to stand for a few hours; aqueous NaOH was then added in small portions. The resulting brown paste was soluble in chloroform, ethyl ether, petrolic ether, etc. The addition of ethyl alcohol produced a precipitate, containing as much as 74% Ag, which redispersed in the organic liquids mentioned above. Gold sols were similarly obtained by reducing gold chloride with hydrazine hydrate; they were purple in chloroform, blue in ethyl ether, petrolic ether, paraffin etc. The peptizing action of lanolin was traced to its non-saponifiable fraction.

Other instances of lipins acting as protective colloids are given by Dean:[14] "a chloroform solution of lecithin is able to take up or dissolve such substances as cobra venom, trypsin, rennet, and even oxide of iron."

Fatty acids (propionic to stearic) facilitate the dispersion of soaps in hydrocarbons;[15] in the case of nickel stearate peptized by stearic acid, it has been shown that the resulting dispersions are colloid.[1] More complex colloid systems can result in this way, as for instance the gold and silver organosols, prepared by von Weimarn[16] as follows. A mixture of aqueous gold chloride and sodium oleate is treated with ammonium nitrate, whereupon a dark colored precipitate rises to the surface. This coagulum yields ruby or purplish-red sols on shaking with organic solvents.

According to Haller, "adsorption compounds" of fatty acids and certain dyes form colloid dispersions in xylene.[16]

The condensation methods of colloid synthesis seem to have found more extensive application than the dispersion methods outlined above. The reaction AB + CD = AC + BD (BD being insoluble, and the other three compounds soluble), frequently resorted to in the preparation of hydrosols, has also proved useful with hydrocarbons as the dispersion media.

A sodium chloride sol, for instance, was prepared by Paal[17] by refluxing sodium malonic ester with chloracetic ester in benzene or toluene. The addition of petrolic ether precipitates the dispersed phase which contains 60-70% NaCl. The precipitate, if immediately transferred into pure benzene, will redisperse. A trace of moisture will cause the sol to coagulate. Paal concluded that the colloid was an "adsorption compound" of sodium chloride and an undetermined organic complex.

Na-ethyl-malonic ester, ω-chloracetophenone, chloroacetone, Na acetone dicarboxylic ester and acetyl chloride were used in subsequent preparations. Sodium bromide sol obtained with the corresponding bromine compounds was less stable, did not redisperse on precipitation and passed readily into jelly.

Von Weimarn[18] prepared colloid halides, sulfates and nitrates of the alkali and alkaline earth metals in mixtures of butyl and propyl alcohols with benzene, xylene etc., from the corresponding thiocyanates. Colloid chloride of copper was obtained[19] by mixing dilute benzene solutions of cupric oleate and hydrogen chloride, an excess of the oleate being necessary for the stability of the sol.

The benzenosols of nickel, cobalt, iron and chromium chlorides resulted similarly from the oleates of these metals.[20] In the case of nickel and iron, the sols were formed over the concentration range of 0.00001-0.001 normal. By varying the moisture content of benzene and the relative proportions of the reagents, suspensoid and emulsoid systems were produced of varying color and composition. Thus pink, blue, yellow and green varieties of the cobalt chloride sol were prepared.

The color changes exhibited by the above-mentioned benzenosols were further discussed by von Weimarn and coworkers,[21] as well as the protective action of rubber on suspensoids in benzene.[22] A copper chloride sol, which coagulated after 5 minutes in pure benzene, was kept for 40 days in 0.1 per cent rubber solution without any signs of settling out. The greater transparence and deeper color of the stabilized sols was also noted.

Kharichkov[23] used both the oleates and naphthenates of sodium, potassium, iron etc., in the preparation of dispersions of the corresponding chlorides in hydrocarbons. A copper sulfate sol was obtained on treatment of a benzene solution of copper naphthenate with sulphur trioxide.

A dispersion of arsenious sulfide, stable for at least six months, results when hydrogen sulfide is passed through a solution of arsenic triiodide in transformer oil.[50] Dispersions of other insoluble compounds (mercuric sulfide, barium sulfate, prussian blue) in the same medium were obtained in "an analogous manner."

Wo. Ostwald[24] obtained colloid nickel by boiling nickel carbonyl in benzene: the dispersed phase settled out on standing.

Hatschek and Thorne[25] used pale crêpe and colophony to stabilize Ostwald's nickel sols in benzene and toluene. Greenish sols only were obtained in the latter which sharply turned black on addition of benzene. The green suspension was found to contain basic nickel carbonate.[26] Since nickel carbonyl does not ionize, and its dissociation in the vapor phase begins at 200°, the possibility of a reaction between the carbonyl and benzene catalyzed by nickel was suggested.

On passing sulfur dioxide and hydrogen sulfide through benzene until the formation of precipitate, a dark yellow sol results[27] which can be concentrated by evaporation and dialyzed against benzene. The sols remain stable for at least four months; pyridine, resorcinol, hydrogen chloride, benzoic and formic acids etc., have no effect, while potassium hydroxide produces a white emulsion. The colloid particles pass through most of the dialyzing membranes, beef bladder and cellulose acetate being the only suitable ones. Most of the colloid remains in dispersed form after freezing.

The decomposition of an organic solvent by electric discharge yields colloid carbon besides other products. Tarczynski[28] arced benzene, carbon tetrachloride, chloroform etc. (at 8-10 amp. d.c.) between carbon or platinum electrodes. The resulting sols were brown in transmitted, olive green in reflected light; they were stable for at least two years.

Lastly, we have various procedures which involve a replacement of solvent; the starting point being either a true solution or colloid dispersion in a liquid miscible with some hydrocarbon.

For instance, on pouring an alcoholic (or acetone) solution of glucose into benzene a colloid suspension of the sugar resulted which varied in color from greenish blue to violet with opalescence in complementary colors.[29] Colloid glucose could be preserved for a month, sucrose for a week, while lactose gelated in about ten minutes. Sols of sodium chloride and copper chloride in aromatic hydrocarbons were similarly prepared.[30]

On shaking the crystalline hydrate of gold chloride with xylene, von Weimarn and Yanek[31] observed that some of it passed into solution; the liquid became pink colored when boiled, due to the formation of metallic gold. A number of other hydrated salts (magnesium, calcium, strontium, barium, zinc, cobalt and copper chlorides) dispersed in boiling xylene.[32] When a xylene sol of rubber was used as the dispersion medium, which was diluted quickly with more xylene after boiling to prevent the separation of an aqueous layer on cooling, there resulted stable suspensions of the corresponding salts which could be dried over phosphorus pentoxide.[33]

Neuberg[34] obtained colloidally dispersed carbonates by passing carbon dixode through the solutions of magnesium, calcium and barium oxides in methyl alcohol. The alcosols were miscible with benzene, chloroform etc.

Graham[35] displaced the water in a hydrogel of silica with alcohol. He further states that "the alcogel may be made a starting point in the formation of a great variety of other substitution jellies. . . . Compounds of ether, benzole and bisulphide of carbon have thus been produced."

Benzenogel of calcium germanate can be obtained in a similar manner.[36] Such structures differ from rubber jellies, being rigid and brittle, and perhaps are more properly classed with gelatinous precipitates rather than true gels.

Evidence of Colloidality

Some of the above authors made an effort to determine the degree of subdivision of the dispersed phase. Others apparently assumed a dispersion to be colloid because the dispersed substance was ordinarily insoluble in the medium; or, if soluble, separated in a gelatinous rather than crystalline form on cooling.

A sol should appear optically heterogeneous unless the colloid particles imbibe the solvent to a great extent. The ultramicroscopic observations recorded in literature are compiled below. The writer also ventures to add some of his own (made with the aid of a cardioid condenser and 15-25 amp. carbon arc as the light source).

Dispersed phase	Ultramicr. appearance	Reference
Lead protected with rubber	Numerous yellow particles	4
Rubber (smoked sheets)	Few ultramicrons	ibid.
Rubber (crêpe)	" "	3
Nickel protected with rubber	Numerous ultramicrons	ibid.
Selenium	Circular particles	51
"Adsorption compound" of fuchsine and stearin	Ultramicrons	16
"Ads. compd." of Nile blue and stearin	Tyndall cone only	ibid.
Lecithin, kephalin and mixts. of cerebrosides	Ultramicrons	37
Chlorides of heavy metals	Numerous particles	23
Nickel protected with rubber	Particles	25
Higher polymers of styrene and isoprene	Tyndall cone, sometimes a few ultra-microns	1
Gold (prepared according to Amberger)	Numerous bright particles	cf. p. 3002
Silver (from silver oxide and oleic acid)	Tyndall cone, no ultramicrons	p. 3003
Carbon (according to Tarczynski)	Tyndall cone, no ultramicrons	p. 3003
Iron sulfide	Numerous particles which vary widely in size	p. 300
Arsenic	Very pale (barely visible) particles	p. 3003
Copper chloride	Tyndall cone, no particles	p. 3003

The colloid solutions examined by the writer were both filtered through 602 (extra hard) Schleicher and Schüll paper and centrifuged for one hour. The latter treatment proved the more effective one in removing coarse particles.

Tarczynski's carbon sol, which is strongly opalescent (red brown in transmitted and olive green in reflected light) no longer contained ultramicroscopically visible particles after centrifuging. It is possible that, because of the dispersed phase being uncharged (cf. p. 3006) and due to the lower viscosity of hydrocarbons compared to water, the larger particles settle out more rapidly in those sols than in hydrosols.

Some of the ultramicroscopic observations tabulated above were made on lyophilic sols (rubber, lipins, Staudinger's molecular colloids); when aplied to such sols, however, optical methods yield doubtful information which must be supplemented by other evidence.

Since subsequent discussion will be limited to non-lyophilic (or nonswelling) colloids, the methods particularly applicable to lyophilic sols will be only briefly treated of here.

The coefficient of free diffusion offers perhaps the most reliable means of distinguishing between true and colloidal solutions. Northrop's method has been employed in approximate measurements.[1]

Staudinger[39] believes cryoscopic measurements to be reliable under certain conditions when the diffusiometric method is not likely to yield the correct values of molecular weight.

On the other hand, a freezing point determination is valid only when the solute remains dispersed in the liquid portion of the solvent which is in equilibrium with the solvent crystals. Moreover, the degree of dispersion should not change on cooling to the freezing point.

Since the cryoscopic method involves the use of concentrated solutions when applied to substances of high molecular weight, the solute may precipitate before the freezing point is reached. Sometimes (f. inst. nickel stearate) a suspension of finely divided jelly is formed which is quite fluid and exhibits only a trace of opalescence, although the suspended phase can be separated by filtration through ordinary paper.

Ebullioscopic determinations have been resorted to by Walden[40] to show that tetraisoamylammonium iodide is highly polymerized in chloroform and benzene solution.

Barger's vapor pressure method was used by Loewe.[9] Osmotic pressure, dialysis and ultrafiltration experiments require membranes of known and reproducible permeability. A beginning in this direction has been made by Bechhold[41] and by McBain and Kistler.[42]

Using Bechhold's precipitation membranes, Kroepelin and Brumshagen determined the osmotic pressure of rubber benzenosols.[43] Mark and Meyer[44] used porcelain filters in similar measurements.

Special methods based on viscosity measurements have been described by Staudinger.[39]

Evidence of Electric Charge

Several authors have observed the electrophoresis of benzenosols.

Hatschek and Thorne[25] (cf. p. 2996) made a detailed study of the behavior of their nickel sols in an electric field. A potential drop of about 10v./cm. caused no noticeable shift in the sol boundary after 8 hours. When 200-400 v./cm. were applied the sol deposited on both the electrodes in nearly equal amounts. The weight of the deposit was roughly proportional to the voltage drop and not to square of the same (as might be expected for particles originally uncharged). Ultramicroscopic observations showed that the particles often continued in the same direction upon the reversal of the poles, or, on the contrary, described curved paths and proceeded towards the opposite pole while the field remained constant. The particles which happened to be midway between the electrodes when the voltage was applied were not affected by the field.

Rubber, which was used as the protective colloid, did not migrate to either pole under similar experimental conditions. The specific resistance of a nickel sol in toluene equaled 0.96×10^{12} ohms, while that of the dispersion medium (toluene sol of rubber plus a little benzene) was 1.37×10^{12} ohms. No deposit was produced by 200 v. a.c. in 1.5 hours.

The green-colored nickel carbonate sols[16] migrated only to the anode. When precautions were taken to exclude oxidation, nickel sols were prepared which similarly contained only negative particles.

All of the above sols contained between 1-8 g. nickel per liter. More dilute sols (0.1-0.2 g. per liter) did not migrate to either pole when subjected to 400 v./cm.

Hatschek and Thorne are inclined to think that their sols contain charged particles, and that the magnitude and sign of the charge changes during the preparation.

Humphry and Jane[45] observed the effect of an electric field (200 v./cm.) on benzenosols which were caused to flow downward, in a thin stream, between charged plates immersed in benzene. They resorted to the optical method of striae in order to render colorless sols visible in benzene. Amberger's silver sols (cf. p. 2995) were deflected towards the anode,[46] Hatschek and Thorne's nickel sols both ways. Rubber sols[45] also migrated to both the poles; after careful drying, however, no deflection was observed. Büchner and Royen[47] investigated Humphry and Jane's method further. In every case which they observed (hydrosols and salt solutions in water) a spreading of the stream took place rather than unilateral deflection. Any solution or colloid of greater conductivity than the liquid, through which it was caused to flow, tended to spread between the electrodes. No spreading occurred when the conductivities were nearly equal. This might be expected because, at the boundary between two solutions of different conductivity, electric forces change in a manner equivalent to the effect of a surface electric charge.

Much higher field intensities (several kilovolts per cm.) were used by other investigators. Pochettino[51] connected platinum electrodes immersed in a selenium sol to the poles of a "small electrostatic machine of Wimshurst." A compact, strongly adherent deposit of selenium formed rapidly on the anode. The sols studied were obtained by dissolving the dispersions of selenium in solids (fluorene, retene, thymol, diphenylamine and triphenylamine) in carbon bisulfide and in benzene. Dispersions in phenanthrene, when dissolved in benzene, deposited on the anode; when dissolved in carbon bisulfide, on the cathode.

Von Weimarn's organosols of gold and silver[16] migrated to the anode in the field of an electrostatic machine. It is not stated, however, whether hydrocarbons or other organic solvents served as the dispersion media in those experiments.

Hall[50] subjected suspensions of metals and their salts (cf. pp. 2993, 2996) in transformer oil to 10-200 kv. for 1-3 hours, in order to determine whether the Cottrell method of precipitation was applicable to liquid media. A platinum plate and needle served as the electrodes. (The distance between the electrodes was given as 1 cm. in the calculations at the end of the article). The polarity was reversed in a number of the experiments, and high voltage a.c. was also used. There was no movement to either electrode, and the rate of sedimentation was not influenced by the electrical treatment.

Evers[12] (cf. p. 2994) subjected the platinum sol prepared by him to 40 kv./cm.; the whole of the dispersed phase deposited in half an hour. More material separated on the anode than on the cathode.

Few data are available regarding the electrical conductivity of colloid dispersions in hydrocarbons. The measurements made by Hatschek and Thorne have been referred to above.

The conductivity of nickel stearate benzenosols does not exceed that of benzene of ordinary purity (ca. 10^{-13} mhos.)[1]

Tomaschewsky[8] found the resistance of a potassium sol in xylene to approximate 10^{12} ohms.

Additional Electrophoresis Experiments

While studying the behavior of nickel stearate in benzene, the writer subjected a 1% dispersion of the soap to 20 kv./cm. for 6 hours. No change in color and no deposit resulted (an unpublished observation). The rectified output of a high-voltage transformer served as the source of potential.

Amberger's silver sol (cf. p. 2995) was next investigated. It did not move to either electrode in the field of an electrostatic machine (ca. 15 kv/cm.), the time of observation again being 6 hours. Partial coagulation occurred; some of the coarse particles formed settled out between the electrodes, others remained in temporary suspension. The filtrate was colored like the original sol diluted with two volumes of the solvent.

The above experiments led the writer recently to undertake further work in order to find out whether charged benzenosols were the rule, or, rather, an exception. Colloid systems were chosen in which the dispersed phase was, as far as it was known, insoluble in the dispersion medium; i.e. systems analogous to hydrophobic sols in water in which the electric charge would more likely be the main stability factor.

Experimental conditions further restricted the choice of sols to those which were colored and did not decompose when in contact with air.

With the aid of a battery (720 v.) and the line voltage (240 v. d.c.) in series, potential drops of up to 5000 v./cm. were easily realized by varying the distance between the electrodes.

The only source of higher voltage available at that time was an induction coil. A rectifying device was therefore built (Fig. 1), which consisted of two disks mounted on the same motor shaft. One of the disks, while rotating, closed the primary contacts (P) and allowed them to open again.

The second disk, covered with copper, carried a spring which, in a certain position, made contact with the ball K; another spring, connected to the high voltage end of the secondary, pressed against the disk.

The condenser C_2 discharged, about once a second, through the spark gap Sp which consisted of two brass balls, 2 cm. each in diameter and 1.2 cm. apart.

The sparking potential under the above conditions equals 38 kv. when one of the balls is grounded.[12] The distance between the electrodes of the cell was 6-7 mm., and hence the potential drop of the order of 60 kv./cm.

The design of the electrophoresis cells is illustrated on Fig. 2. The electrodes are finely polished and plated with platinum

The cells used in high voltage experiments (60 kv./cm.) were made of thick capillary tubing. The p.d. was applied for an hour, at the end of which time any change in color of the sol was noted, and the electrodes were examined for deposit with the aid of a microscope.

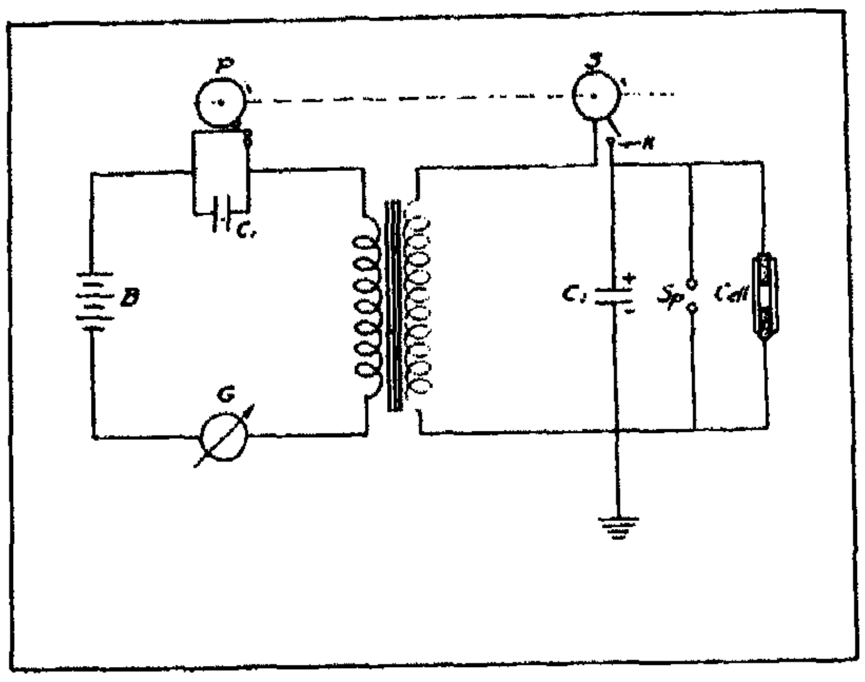

FIG. 1

B = 6 v.; C_1 = 4μf. (this value is rather critical); G is an ammeter (30 amp. scale); C_2 = ca. 150 μμf.

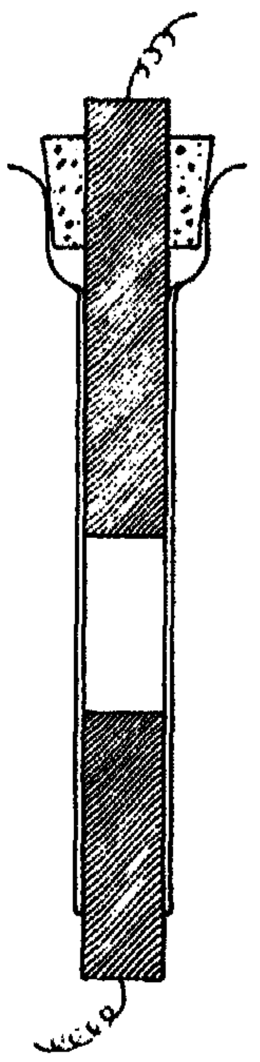

FIG. 2

Since the field strength was of such a magnitude as to drive to the electrodes all charged colloid particles within a fraction of one hour, the above observations were deemed sufficient.

In another set of experiments, where 5 kv./cm. were used, the inner diameter of the cell was 3 mm. The time of observation was six hours or longer

The preparation and properties of the sols used in the electrophoresis experiments are given below. (The non-volatile matter content was determined by evaporating a sample of the sol at room temperature in vacuo. Ultramicroscopic observations are given on p. 2998).

1. *Amberger's gold sol in xylene.* This sol was prepared according to the original directions[13] and reprecipitated with 4 vols. of ethyl alcohol, the precipitate dried in vacuo and dissolved in xylene. There was considerable sediment on centrifuging. Analysis of the supernatant sol showed the presence of 14.1 g. non-volatile matter and 2.44 g. gold per l. The sol is dark brown, almost opaque, and strongly opalescent, the reflected light being purple. There was no further sediment after two months.

2. *Colloidal silver in toluene* (from silver oxide and oleic acid). Silver oxide (0.1 g.) was heated on a water bath with 100 cc. of 5% oleic acid in toluene for 4 hours. On cooling to − 10°, a gelatinous precipitate of the silver soap separated. The sol, filtered and centrifuged, appeared red brown in transmitted and purple in reflected light. The silver content was 0.22 g./l.

3. *Colloid arsenic in xylene.* The arsenic sol was prepared by refluxing a dilute solution (1% or less) of arsenic trichloride over sodium; it was concentrated by distilling off $AsCl_3$ and xylene. The remainder appeared greenish gray and exhibited a faint Tyndall cone. No sediment separated in 3 years' time.

Colloid tin was also prepared by passing carbon monoxide through a solution of stannic chloride; it required an excess of the chloride for stability, reacted rapidly with moisture in the air and was therefore unsuitable for the electrophoresis experiments.

4. *Colloid nickel in toluene.*[26] The following mixture was refluxed for 1 hour: 20 cc. toluene, 20 cc. 1% nickel carbonyl and 10cc. of centrifuged 1% crêpe sol in toluene.* Metallic Ni precipitated; the filtrate was an opalescent black sol which showed no sediment on centrifuging. The sol contained 0.394 g. Ni per l.

5. *Tarczynski's carbon sol in xylene.*[28] Xylene (30cc.) was arced between carbon electrodes at 9 amp. d.c. or 15 min. The resulting suspension was turbid and polydisperse. It was quite clear when centrifuged, brown red in transmitted and olive green in reflected light. Non-volatile matter content was 1 g./l. When five cc. of the sol in a collodion bag were dialyzed against continuously renewed solvent for 2 days, the dispersed phase (about 1 mg.) precipitated as a purple powder.

6. *Pochettino's selenium sol in paraffin oil.*[51] Red (amorhpous) selenium was precipitated by passing SO_2 through an aqueous solution of selenium oxychloride, filtered and dried. It was ground to a fine powder, and a small amount (about 10 mg.) suspended in 10 cc. paraffin oil (nujol). The suspension was stirred for 3 hours and finally filtered. The filtrate was colorless, and the possible amount of dissolved selenium did not exceed 1 mg.

Next, 50 mg. selenium were added to 30 cc. paraffin oil at 180°, and the temperature raised to 200° in 5 minutes. A red coloration developed. The dispersion was rapidly cooled (by immersing the container in running water) and centrifuged. The portion which had not dispersed, together with the small amount of sediment, weighed 29 mg. The sol thus contained about 0.7 g./l. of selenium, although a small amount might have been lost to the atmosphere. It was markedly opalescent and orange red in color. There was no sediment after a month. Also, the sol is not sensitive towards direct sunlight.

7. *Colloid copper chloride in toluene* (according to von Weimarn). To 62 mg. copper oleate dissolved in 15 cc. toluene were added 5cc. of 1% crepe

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* Samples of crêpe and smoked sheets were obtained through the courtesy of the U. S. Rubber Company.

sol and 5 cc. 0.1 N HCl. A turbid orange suspension resulted which was evaporated to 5 cc. volume and centrifuged, yielding an orange green sol of 0.2 g./l. copper content.

Sols of similar appearance and properties are made by adding an ether solution of cupric bromide to toluene. The dispersion referred to above is the most concentrated one which could be obtained.

8. *Hatschek and Thorne's nickel carbonate sol in toluene.*[26] To 30 cc. toluene were added 10cc. of 1% rubber (smoked sheets) sol and 10 cc. of 1% nickel carbonyl in toluene. The temperature was raised to 100° in 3 hours and allowed to rise further to boiling point overnight. The filtered sol was pale green; its nickel content was 0.4 g./l.

9. *Iron sulfide sol in toluene.* To 10 cc. of 0.1% solution of ferric stearate in toluene were added 7 cc. of 1% rubber (smoked sheets) sol in toluene followed, drop by drop, by toluene saturated with H_2S until the color deepened to black (3 cc. altogether). The sol was strongly opalescent; it passed unchanged through hardened filter paper, and there was no sediment on centrifuging. The iron content was 0.43 g./l. The color changes to light brown in 4-5 days, unless the sol is preserved in a sealed vessel. Freshly prepared sols only were used in the electrophoresis experiments.

* * *

A particular effort was made to obtain dispersions which, according to previous investigators, migrate in an electric field. Thus Hatschek and Thorne's nickel sol was prepared and studied, as well as Pochettino's selenium-sols. The concentrated nickel carbonate sols, migrating to the anode, could not be readily prepared; for the addition of nickel carbonyl could be continued only up to a certain point, beyond which metallic nickel was formed.

Von Weimarn's colloid gold[16] in benzene usually precipitated within a few hours after its preparation, and in no case lasted longer than 4 days. The silver sols were more stable, but could more readily be prepared by the method outlined above (sol No. 2).

Evers's platinum sols[12] could not be obtained at atmospheric pressure, and the writer lacked facilities for high-pressure work.

Amberger's gold sol (sol No. 1) was prepared; the effect of high electric potentials on the silver sol has already been referred to (p. 0000).

The only sol affected by potential drops of 5 kv./cm. and lower was Hatschek and Thorne's colloid Ni. Indeed, 1000v./cm. were already sufficient to drive the dispersed phase to the electrodes within 10 minutes' time.

A number of sols, which showed no change when subjected to 5 kv./cm. for 6 hours and longer, underwent complete or partial coagulation at 60 kv./cm. Colloid iron sulfide precipitated instantly and completely. Sediment appeared in Amberger's gold and Tarczynski's carbon sols after a few minutes.

In the case of the carbon sols, centrifuging removed both the coarser particles and the tendency to precipitate in the electric field.

Colloid arsenic (sol No. 3), selenium (sol No. 6), copper chloride (sol No. 7) were not visibly changed after 1 hour at 60 kv./cm. These sols exhibited a distinct Tyndall cone even when viewed with the aid of a relatively weak source of illumination (f. inst. a flashlight). Selenium sol was the only one which contained bright particles visible particles; a very powerful illumination source (25 amp. arc) revealed the presence of numerous ultramicrons, just on the boundary of visibility, in the arsenic sol.

Unstable dispersions of selenium, similar to those described by Pochettino,[51] were prepared by fusing selenium under phenanthrene and dissolving the solidified mixture in benzene or carbon bisulfide. No deposit could be noticed on the electrodes when such dispersions were subjected to 3 kv./cm. for one hour, but at 30 kv./cm. it required less than a minute for the anode to acquire a red coating of selenium.

Reversing the connections from the induction coil, so that the grounded electrode became the anode, caused selenium to leave the high potential electrode (now the cathode) and to deposit on the new anode. The deposit of Se was thus transferred back and forth a number of times by reversing the polarity.

Selenium deposited on the anode from both the benzene and carbon bisulfide dispersions. In this respect the writer's observations differ from those of Pochettino, who states that the electrophoresis proceeds towards the cathode in phenanthrene-carbon bisulfide as the dispersion medium.

No deposit resulted when a solution of amorphous selenium in carbon bisulfide was subjected to the same p.d. for one hour.

Discussion of the Electrical Properties

The experimental evidence regarding electrophoresis in hydrocarbons as dispersion media is summarized below.

Dispersed phase	Evidence of electrophoresis	Reference
Gold	None after 6 hrs. at 5 kv./cm.; 60 kv./cm. cause partial pptn.	Sol No. 1
Platinum	Deposits (chiefly on the anode) at 40 kv./cm.	[12]
Silver (Amberger's).	Migrates to the anode.	[46]
	Undergoes partial pptn. at 15kv./cm. but does not move to either electrode.	p. 3001
Silver (from Ag oleate).	None after 20 hrs. at 5 kv./cm.	Sol No. 2
Silver (by electric dispersion)	None after 2 hrs. at ca. 200 kv./(cm?)	[50]
Lead.	None after 1 hrs. at ca. 200 kv./(cm?)	[50]
Copper.	None after 100 min. at ca. 200 kv./(cm?)	[50]
Nickel.	None after 10v./cm. for 8 hrs.; 90 v./cm. and higher cause the sol to deposit either on both the electrodes or only on the anode.	[25]
	Mobility ca. 2×10^{-3} cm./sec. (p.d. = 960 v., electrodes 1cm. apart).	Sol No. 4
Iron.	None after 2 hrs. at ca. 200 kv./(cm?)	[50]
Aluminium.	None after 3 hrs. at ca. 200 kv./(cm?)	[50]

Dispersed phase	Evidence of electrophoresis	Reference
Arsenic.	None after 60 kv./cm. for 1 hr.	Sol No. 3
Potassium	Electr. resist. approximates 10^{12} ohms.	[8]
Carbon (?).	None at 5 kv./cm. for 22 hrs.; none at 60 kv./cm. for 1 hr.	Sol No. 5
Selenium (in benzene).	Moves to the anode in the field of an electrostatic machine.	[51]
	Deposits rapidly on the anode at 30 kv./cm., no change for 1 hr. at 3 kv./cm.	p. 0000
Selenium (in paraffin oil).	None at 5 kv./cm. for 26 hrs.; none at 60 kv./cm. for 1 hr.	Sol No. 6
Nickel carbonate.	Deposits on the anode from concentrated sols; does not migrate in dilute sols (p.d. about 100-400 v./cm.).	[26]
	5 kv./cm. for 20 hrs. has no effect on a dilute sol.	Sol No. 8
Copper chloride.	5 kv./cm. for 20 hrs. has no effect.	Sol No. 7
Arsenious sulfide.	None after ca. 200 kv./(cm?) for 3 hrs.	[50]
Mercuric sulfide.	None after 2 hrs. at ca. 200 kv./(cm?)	[50]
Ferrous sulfide.	None after 16 hrs. at 5 kv./cm., instant pptn. at 60 kv./cm.	Sol No. 9
Barium sulfate.	None after 2 hrs. at ca. 200 kv./(cm.?).	[50]
Prussian blue.	None after 1 hrs. at ca. 200 kv./(cm?)	[50]

It is thus seen that potential drops of less than 5 kv./cm. have no noticeable effect on colloid dispersions in hydrocarbons, with the exception of Hatschek and Thorne's nickel sols.

When we recall that the particles in hydrosols exhibit nearly the same cataphoretic mobility (ca. 10^{-4} cm./sec. at 1 v./cm.); and furthermore that similarily charged particles should move faster in hydrocarbons due to the lower dielectric constant,—it follows that the majority of colloid dispersions in hydrocarbons either are uncharged or carry only a small fraction (less than 10^{-4}) of the charge possessed by the particles in water.

An electric field of great intensity (corresponding to several kv./cm.) exerts ponderomotor effects on particles suspended in a hydrocarbon which are not necessarily electrophoretic. The nature and magnitude of these phenomena depends on the size and shape of the particles, viscosity of the medium, distance between the electrodes and their shape, etc.

Thus if a suspension of dust particles in toluene is observed through the microscope, some of them will be seen to proceed towards one of the electrodes as soon as 5 kv./cm. is applied and to remain attached there. Oblong particles will form chains which orient themselves perpendicularly to the electrodes and eventually form a continuous path between them; while some of the smaller and nearly round particles begin to oscillate rapidly between the electrodes without actually touching the latter. Also, the free ends of the filaments adhering to the electrodes exhibit an undulatory movement.

Particles of higher dielectric constant than the medium would be expected to coalesce when subjected to a sufficiently strong electric field. Conductors (metallic particles) suspended in a liquid insulator can be considered to have an infinitely large dielectric constant.

Alternating potentials are equally effective in this case, and have been successfully used in the precipitation of water-in-oil emulsions: the water droplets "arrange themselves . . like the iron filings between the poles of the magnet, dance about and jiggle themselves into larger drops."[52]

At potential drops of the order of 60 kv./cm. particles which are too small to be resolved under the microscope come within the range of the forces which cause coalescence, as evidenced in the precipitation of Amberger's gold and silver sols, iron sulfide sol, etc. At the same time, sols which contain smaller particles (colloid arsenic and carbon) are not visibly changed.

It is rather difficult to explain, in view of the above, why high electric potentials, both d.c. and a.c., should have no effect on coarse dispersions of metals and their salts in transformer oil,[50] unless we assume, perhaps, that the viscosity of the medium was sufficiently high to prevent rapid coagulation.

Another manner in which the influence of an electric field manifests itself is to cause any suspended body of higher conductivity or dielectric constant than the medium to move towards the region of highest field intensity; for instance, to the anode if the negative pole is grounded.

Furthermore, ions are formed in increasing numbers as the voltage across the electrodes approaches the sparking potential; there is a rapid rise in conductance. Particles which were originally uncharged may then assume a charge, the phenomenon being similar to the electrification of smoke particles in the Cottrell precipitation process.

The precipitation of a sol on the electrodes (or between them) when subjected to several kv./cm. does not prove therefore that the dispersed phase is charged, although the behavior of some sols (Pochettino's colloid selenium) will not allow of a different interpretation.

The conclusion follows that stable sols can result (and do result in the majority of cases) in the absence of an electric charge, if we choose a nonpolar solvent as the dispersion medium.

The determination of electrophoretic velocity in benzenosols which are charged presents difficulties; colloid particles are often driven to the walls of the vessel[53] or deposited on the glass in the neighborhood of the electrodes (in case of the nickel sol).

That fraction of the electrical conductivity of a sol which represents the transport of electricity by the colloid particles should be more capable of measurement when a hydrocarbon serves as the dispersion medium instead of water. However, the calculation of migration velocities from conductivity data requires that we know the thickness of the Helmholtz double layer,[48]—a quantity which cannot be independently determined.

Stability Factors. All of the dispersions studied by the writer showed no sediment after 3 months, and some of them have been preserved unchanged for over three years (colloid arsenic, carbon, Amberger's gold and silver). Since the viscosity of the dispersion media (benzene, toluene and xylene) is less than half that of water, the above colloid systems compare favorably with hydrosols as regards their stability.

The electric charge cannot therefore be an important stability factor in the case of benzenosols.

The obvious reason for this is that the dispersion medium itself does not ionize and, although a number of substances yield ions when dissolved in benzene, the degree of ionization is extremely small except in concentrated solutions. The orientation of solvent molecules, contributing to the stability of charged particles, is absent in "dipole free" liquids like benzene, hexane and carbon tetrachloride.[54]

Only those colloid systems, in which at least part of the dispersed phase is insoluble in the medium, and which possess the optical properties of lyophobic sols, form the subject of this discussion.

In the absence of an electric charge, one is reduced to the assumption that the colloid particle derives its stability from a surrounding layer of some substance or substances soluble in the dispersion medium.

In numerous instances the behavior of benzenosols bears out this supposition. Thus, aside from a variety of sols in which rubber serves as the protective colloid and Amberger's sols in which lanolin is similarly used, we note that copper chloride sols require an excess of copper oleate for their stability,[19] colloid tin requires stannic chloride (p. 3003) while colloid carbon precipitates when the diffusible components are removed by dialysis.

Perhaps the most fundamental criterion whereby we distinguish between lyophobic and non-lyophobic (lyophilic and protected) sols is that of reversibility. Hydrophobic sols are metastable systems which precipitate irreversibly on evaporation and freezing.

Benzenosols (colloid carbon, silver, glucose etc.) on evaporation leave a residue which yields a sol of similar properties as soon as the solvent is added; rubber protected sols redissolve more slowly, possibly because the swelling and dispersion of rubber in benzene requires time. All of the sols show no change whatever on freezing.

The results of the writer's own experiments, together with observations of similar nature made by previous investigators, are given below.

Dispersed phase	Evidence of reversibility	Reference
Potassium.	Redisperses on evaporation.	[8]
Silver (lanolin).	Redissolves on pptn. and drying.	[13]
Gold (lanolin).	Redissolves on pptn. and drying.	[13]
	Unchanged by freezing in liquid air; redissolves instantly on evaporation.	Sol No. 1
Silver.	Redissolves instantly on evaporation.	Sol No. 2
Nickel (rubber).	Redisperses after precipitation with alcohol.	[25]
	Freezing in liquid air produces no change.	Sol No. 4
Arsenic.	Freezing in liquid air produces no change.	Sol No. 3

Dispersed phase	Evidence of reversibility	Reference
Carbon(?)	Unchanged on evaporation and freezing in liquid air.	Sol No. 5
Sulfur.	Slight ppt. after repeated freezing.	[27]
Selenium	Unchanged on freezing in liquid air.	Sol No. 6
Nickel carbonate (rubber)	Unchanged on freezing in liquid air.	Sol No. 8
Copper chloride (rubber)	Unchanged on freezing in liquid air.	Sol No. 7
Iron sulfide (rubber)	Unchanged on freezing in liquid air.	Sol No. 9
Sodium chloride.	Redisperses after being precipitated with petrolic ether.	[17]

This difference in behavior from the hydrophobic sols, where the electric charge is an important and probably dominant stability factor, is significant. The above benzenosols can most logically be classed with protected sols, except that the *protecting substance is not always colloid.*

Summary

The literature relative to the preparation of benzenosols and their behavior in the electric field is reviewed, as well as some additional experiments. Electrical factors of stability are shown to be unimportant in hydrocarbons as dispersion media.

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THE TEMPERATURE OF MAXIMUM REFRACTIVITY OF SOME AQUEOUS SOLUTIONS

BY NORA GREGG-WILSON AND ROBERT WRIGHT

The phenomenon of the maximum density of water at 4°C is generally explained on the assumption that ice molecules are produced in solution at a temperature somewhat above the freezing point. Since ice is less dense than water its presence will counteract the increasing density of water due to the lowering of the temperature. At 4°C the two effects will balance each other, and between 4°C and 0°C the rapid formation of ice molecules will more than overcome the normal contraction, thus causing an expansion to take place between 4°C and the freezing point.

The existence of the point of maximum density is thus seen to be due to the fact that the change of density on freezing is in the opposite direction to the normal change which accompanies fall of temperature in the liquid state. With most physical properties the change on freezing and the change with fall of temperature in the liquid are in the same direction. For example, water increases in viscosity and in surface tension with fall of temperature, and the viscosity and surface tension of ice are greater than that of water.

Now the mean refractive index of ice (1.31) is less than that of water (1.33), and the refractive index of water increases with fall of temperature. We may therefore expect to find a temperature of maximum refractivity (t.m.r.) corresponding to the temperature of maximum density (t.m.d.). But as the change of refractive index of water on freezing is only about 1.5% compared with a change of 8.5% in density, we should expect a greater concentration of ice molecules, i.e. a lower temperature, to be necessary at the t.m.r. than at the t.m.d.

Jamin[1] by means of his interferometer, found the t.m.r. of water to be very close to the freezing point. Pulfrich[2] using the instrument designed by himself, and employing the natural cold of a winter night, found the t.m.r. of water to be between −1°C and −2°C. These would seem to be the only recorded observations of the phenomenon.

It has long been known that the presence of a solute lowers the t.m.d. of water, the lowering being in general proportional to the concentration of the dissolved substance. An attempt has now been made to determine if a similar effect is to be found in the case of the t.m.r.

Experimental. Both the Pulfrich refractometer and the Jamin interferometer are difficult instruments to control at temperatures lower than that of the room. It was therefore decided to employ a Zeiss dipping refractometer which is slightly more sensitive than the Pulfrich instrument and was found to be readily workable at temperatures near the freezing point of water.

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The liquid to be investigated was placed in a weighing bottle and attached to the prism of the instrument by means of a rubber connexion, the instrument was then placed in the cooling bath and kept at a definite temperature for quarter of an hour, after which a reading was taken. No difficulty was found in holding the bath at a steady temperature by the addition of ice or if necessary of a small amount of common salt. The temperature of the bath was then lowered, and after equilibrium had again been reached, a second reading was taken, and so on. At temperatures near zero the field of view became obscured on account of the condensation of moisture on the back of the prism inside the instrument. This film of moisture made accurate readings impossible, but it was effectively prevented by the simple expedient of placing a granule of calcium chloride—wrapped in tin foil—on the upper surface of the prism before attaching the latter to the instrument. The presence of the granule decreases slightly the intensity of the light passing into the instrument, but does not interfere otherwise with the field of view.

It was hoped that it would have been possible to obtain readings on both sides of the t.m.r., and to observe decreasing refractive index with decreasing temperature. This was only found possible in the case of water itself. With all solutions the t.m.r. was considerably below the freezing point, and freezing took place before a decrease in refractive index could be observed. It was therefore decided to obtain the t.m.r. by means of an indirect graphic method.

The temperature coefficient of refractive index of an aqueous solution decreases with fall of temperature, till at the t.m.r. its value is equal to zero. The value of the coefficient was therefore determined at a series of temperatures, plotted against the temperature, and the curve exterpolated to find the temperature at which the coefficient was of zero value. This temperature is obviously the t.m.r.

In practice it was found most expedient to obtain readings of the refractive index at about 4° intervals of temperature, and hence calculate the temperature coefficient for the average temperature of each interval, carrying the series of readings to as low a temperature as possible.

Unfortunately the exterpolated value of the t.m.r. is by no means definite. There is moreover an additional error caused by the slight change of refractive index of the prism with fall of temperature. This change in the prism is however, according to the manufacturers of the instrument, of very small value, and may probably be safely neglected in comparison with the much greater error due to exterpolation.

As an example of the method we may consider a set of results obtained with water:—

T	R	dT	dR	dR/dT	T′
16°	15.45				
14°	15.85	2	.4	.200	15.0
11°	16.35	3	.5	.165	12.5
7°	16.85	4	.5	.125	9.0
3°	17.15	4	.3	.075	5.0

The first two columns give the temperatures and instrument readings, the temperature differences and instrument reading differences are given in the third and fourth columns, and the temperature coefficients and the corresponding average temperatures are in the last two columns. If the temperature coefficient dR/dT is plotted against the average temperature we get an approximately straight line, which on exterpolation to zero value for the coefficient indicates that the t.m.r. lies between 0° and −1°C, Fig. 1.

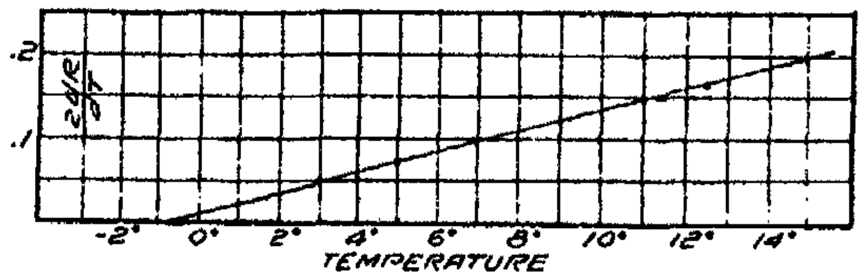

Fig. 1

Results. The t.m.r. for water has been found by a series of measurements to be in the neighbourhood of −0.5°C. As already stated this was the only case in which it was found possible to cool the liquid below the t.m.r., and find a decrease of refractive index with decrease of temperature. The values obtained at the different temperatures were as follows:—

T.	10°	6°	2°	−2°	−3°	−4°	−5°
R.I.	1.33370	1.33389	1.33424	1.33424	1.33416	1.33397	1.33385

Table I

Temperatures of Maximum Refractivities of Aqueous Solutions
(The figures indicate degrees below zero)

		Chloride	Bromide	Iodide	Nitrate
H	N/2	4.2	2.8	3.5	6.5
		4.2	3.0	3.9	7.4
	N/4	2.1	2.1	3.0	3.5
		2.1	2.0	3.0	3.4
Li	N/2	4.3	3.7	5.5	6.9
		3.8	3.8	5.3	6.8
	N/4	2.3	2.9	3.8	3.5
		2.5	2.3	3.5	2.5
Na	N/2	7.5	6.0	6.3	11.2
		9.8	7.0	6.8	10.9
	N/4	3.5	4.0	4.3	7.0
		3.6	3.9	4.2	6.6
K	N/2	6.5	7.8	8.3	10.0
		7.5	8.1	8.5	9.8
	N/4	3.5	3.5	4.5	6.2
		3.0	4.2	4.2	5.4

TABLE I (Continued)

		Chloride	Bromide	Iodide	Nitrate
NH$_4$	N/2	4.9	4.9	5.5	7.6
		5.9	4.3	5.8	8.1
	N/4	3.7	2.5	3.0	5.1
		3.0	3.0	2.8	5.3
		Sulphate	Formate	Acetate	Propionate
H	N/2	6.0	4.3	4.0	4.7
		6.4	4.6	4.5	4.8
	N/4	3.4	2.2	2.5	2.9
		3.4	1.7	2.6	2.7
Na	N/2	12.6	6.4	7.8	8.6
		12.0	6.0	8.0	8.4
	N/4	5.0	4.0	3.5	3.7
		5.4	4.4	3.3	4.2

The values of the t.m.r. for a number of solutions of N/2 and N/4 strengths are given in Table I, and the lowerings of the t.m.r. caused by the presence of some solutes in N/4 solution are compared with the corresponding lowerings of the t.m.d. in Table II. The figures for the t.m.d. lowerings are taken from a former paper by one of us.[1]

TABLE II

Lowering of T.M.R. N/4 Solutions

	Cl	Br	I	NO$_3$
H	1.6	1.6	2.5	3.0
Li	1.9	2.1	3.1	2.5
Na	3.1	3.5	3.8	6.3
K	2.7	3.3	3.8	5.3
NH$_4$	2.8	2.2	2.4	4.7

Lowering of T.M.D. N/4 Solutions

	Cl	Br	I	NO$_3$
H	1.3	1.8	2.2	3.1
Li	1.4	1.9	2.3	3.1
Na	3.1	3.7	4.0	5.0
K	2.8	3.2	3.7	4.5
NH$_4$	1.8	2.3	2.7	3.6

It will be seen that for any given solute the lowerings of the t.m.r. increase with concentration, but it is not certain that the two are directly proportional to each other. In comparing the density with the refractivity effects it must be remembered that the former are capable of much more accurate determination.

Physical Chemistry Department,
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March 31, 1931.

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[1] J. Chem. Soc., **115**, 119 (1919).

GELATIN IN WATER-ALCOHOL MIXTURES*

BY HELLMUT SIEBOURG

Jacques Loeb[1] in one of the last chapters of his book "Proteins and the Theory of Colloidal Behavior" has pointed out the peculiar phenomena of stability of gelatin in mixtures of water and alcohol. Following his line the purpose of this paper was to investigate the behavior of a standard gelatin solution after addition of water-alcohol mixtures containing increasing amounts of alcohol. Unfortunately alcoholic or partly alcoholic media exclude most of the methods used in colloid-chemistry and limit the investigation to processes which are not based upon the observation of ionic phenomena.

Experimental

Preparation of the mixtures.—Several standard solutions containing 1% gelatin, calculated on the moisture-free basis (105°), were prepared. The gelatin used was

"De-ashed Eastman Purified Gelatin" (Lot No. 50)

Moisture when packed	9.0 %
Ash on moisture-free basis	.03%
pH on 1% solution	4.8

Following the directions of S. E. Sheppard and R. C. Houck[2] the gelatin was put as small strips into a volumetric flask. The amount of water added for soaking was equal to five times the weight of the gelatin. The time of soaking however was extended to 24 hours (at 25°) as recommended by R. Wintgen and H. Loewenthal[3] in order to obtain results which could be duplicated. Solution was made by means of about 50 cc. water of 52°. This temperature was kept for 30 minutes. After 15 minutes, which in all cases was sufficient for complete solution, either HCl or NaOH was added in order to alter the hydrogen ion-concentration, except for the standard solution representing the isoelectric point (see below). Then the volumetric flask was nearly filled; final adjustment was performed later at the prescribed temperature. These 1% standard solutions were kept for an additional 48 hours at 25°, except that during the nights the temperature went down to about 20°. According to Sheppard and Houck[2] one can expect rapid changes of viscosity to have stopped, particularly in these relatively dilute solutions. Some of them showed gelatinization (thixotropical effect), and therefore it was necessary to liquefy them again by heating to 52° in the water bath.

Then the final mixtures could be prepared by dilution. The water was always added first, then the alcohol with vigorous shaking. The water

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* Contribution from the Chemical Laboratory of Washington University. This work has been made possible by a stipend from the "Germanistic Society of St. Louis."

used was conductivity-water with a relative conductivity of 2.2×10^{-6} reciprocal ohms. The alcohol was dried by several distillations from CaO, its conductivity being less than 3×10^{-7} reciprocal ohms. This degree of purity was sufficient for the precision of the measurements. The water was protected against CO_2 and the alcohol against moisture from the air; both were stored in closed bottles with connected burettes. In order to vary the composition of the final mixtures, 45 cc. water, or 40 cc. water plus 5 cc. alcohol, or 35 cc. water plus 10 cc. alcohol etc. were added to 5 cc. standard solution; the resulting mixtures contained 0%, or 10%, or 20% etc. alcohol. Thus it was possible to obtain in steps of 10% all mixtures with from 0% up to 90% alcohol. The hydrogen ion-concentrations were determined in the purely aqueous dilutions. This pH number was considered as significant for the whole series, because the behavior of the series was doubtlessly dependent upon the state of the gelatin in its pure aqueous solution. The dilute isoelectric gelatin had a pH 4.7. The gelatin content in all mixtures was only 0.1%. This seemed to be advisable in order to obtain sols comparable throughout the entire field covered in this investigation, even if the alcohol amounted to 90%.

There was some difficulty in preparing mixtures with more than 70% alcohol when starting with the isoelectric standard solution. It was found that these mixtures were obtained satisfactorily by adding the alcohol to the warmed aqueous part which was heated again to 52° in the water bath. Parallel trials with mixtures, where this treatment was unnecessary, showed that it had no appreciable influence upon the observed phenomena. While all the mixtures were almost water-clear, the last members of the series were milky and showed a light orange shade in transmitted light. In the case of the isoelectric gelatin this phenomenon took place with an alcohol content of 50-60%. The very strongly acid or basic gelatin mixtures were clear throughout the series.

Viscosity measurements.—The viscosity of all the mixtures was determined. The instrument used was an Ostwald-viscosimeter, which always

TABLE I

Viscosity in Millipoises:

pH =	1.2	4.1	4.7	7.5	10.4	12.8
0%	9.91	9.71	9.60	9.63	9.23	9.09
10%	12.10	13.23	12.78	12.88	12.35	12.23
20%	16.04	17.61	16.79	17.11	16.36	16.23
30%	19.91	21.92	20.64	21.38	20.27	20.21
40%	22.59	24.79	23.39	24.19	22.97	22.86
50%	23.54	25.64	24.41	25.10	23.98	23.92
60%	23.12	24.68	23.60	23.76	23.16	23.46
70%	21.45	22.42	21.60	21.57	21.22	21.82
80%	18.76	18.61	18.62	18.44	18.41	19.15
90%	15.78	15.15	15.14	15.14	15.15	16.23
Alcohol						

contained exactly 5 cc. of liquid. All measurements, time of outflow, as well as density in the pycnometer, were carried out at 25°. The results are to be seen in Table I and Fig. 1, in which the viscosity is given in millipoises for the various pH numbers. Each horizontal line represents the mixtures of the same alcohol content at different hydrogen ion-concentrations. Disregarding the shifts of the curves up and then down again with increasing alcohol content, which is due to the viscosity-curve of the pure water-alcohol mixtures, we always observe the same type of curves in the mixtures containing from 0 to 60% alcohol: namely between two maxima, in the neighbourhood of the isoelectric point, one minimum at this point and two other

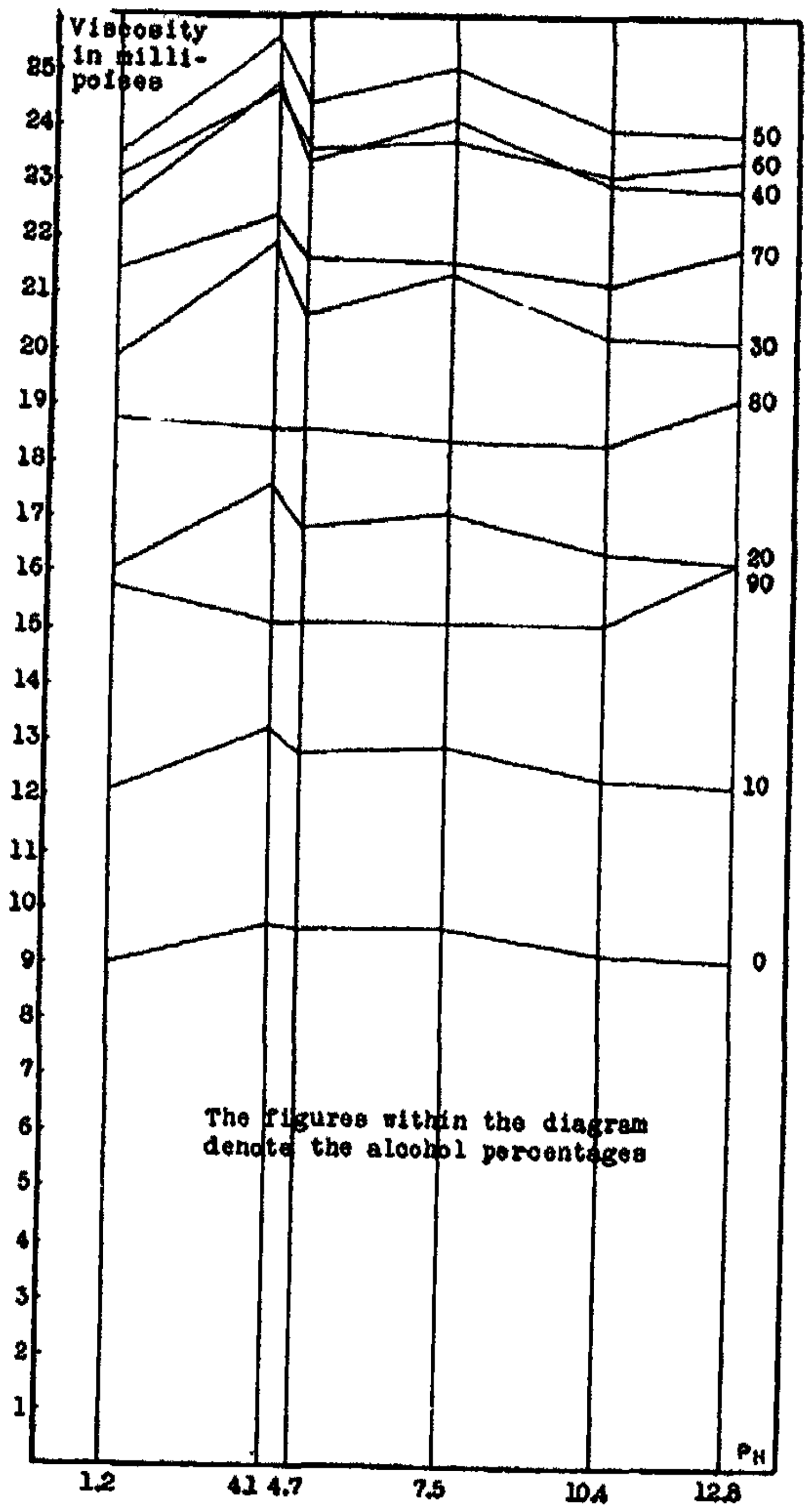

FIG. 1

minima in the strongly acid or basic regions. It is the same kind of curve previously recorded by other investigators as R. H. Bogue[3] and S. E. Sheppard and R. C. Houck.[4] The curves given here however were obtained with much more dilute gelatin solutions, and give not a quantitative but only a qualitative picture of the phenomena. Following the curves in the higher alcoholic mixtures it is found that they then deviate from the type of curve described above, taking on more and more a "U" shape which has a large minimum at and around the isoelectric point and two ascendent branches on both sides.

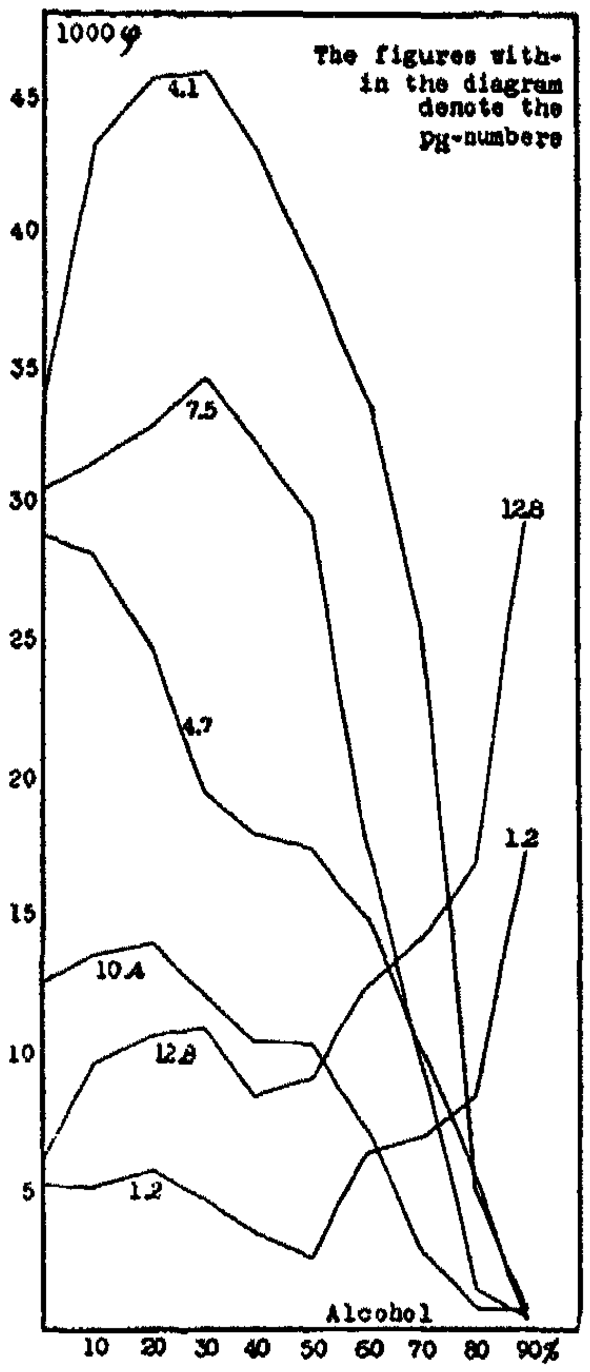

FIG. 2

Calculation of the volume of the dispersed phase. — There have been many discussions about the applicability of Einstein's equation[5] for the dependence of the viscosity upon the relative volume of the solute and the viscosity of the pure solvent. Mainly the troubles seem to have been caused by the elasticity of the various presumptions. However, working in such dilute solutions the application of this relation was not so doubtful. It may be noted that the calculation according to Arrhenius' logarithmic equation (6) gives exactly the same relative results. Einstein's formula, after solving it for the unknown relative volume φ of the dispersed phase, reads:

$$\varphi = \frac{\eta_s}{2{,}5 \times \eta_0} - 0.4.$$

While η_s is the viscosity of the system, η_0 has to be the viscosity of the pure solvent, i.e. in the cases concerned the viscosity of the corresponding water-alcohol mixtures which were prepared and measured separately. Table II gives the results of the calculation. Fig. 2 shows the value 1000 φ (the volume of the gelatin micelles in cubic centimeters per one-liter solution) plotted against the alcohol percentage of the mixture. Each curve thus represents the change of the volume of definite gelatin through increasing alcohol content in the solvent. Most interesting is the fact that in the case of isoelectric gelatin the volume seems to be nearly a linear function of the amount of alcohol, while in all other cases higher-order curves result. However we observe two distinctly different types, the one showing a minimum in a 90% alcohol mixture, the other one a maximum, the latter type appearing in the strongly acid or basic gelatin series. In these extreme cases there seems to be also a discontinuity when 40 or 50% alcoholic mixture is reached, while the other types of curves show their maximum at about the same place or a little earlier. Fig. 3 gives the same 1000 φ-values plotted against the Soerensen number pH, showing somewhat the same picture as Fig. 1 although more distinctly. Again the curves join the points of equal percentages of alcohol. Between 0 and 60% alcohol content the characteristics may vary a little but only quantitatively. Minima are at the isoelectric points, both ends of the curves run still lower, in between are maxima, incidently higher in the acid neighbourhood of the isoelectric point. Then beginning with 70% alcohol content

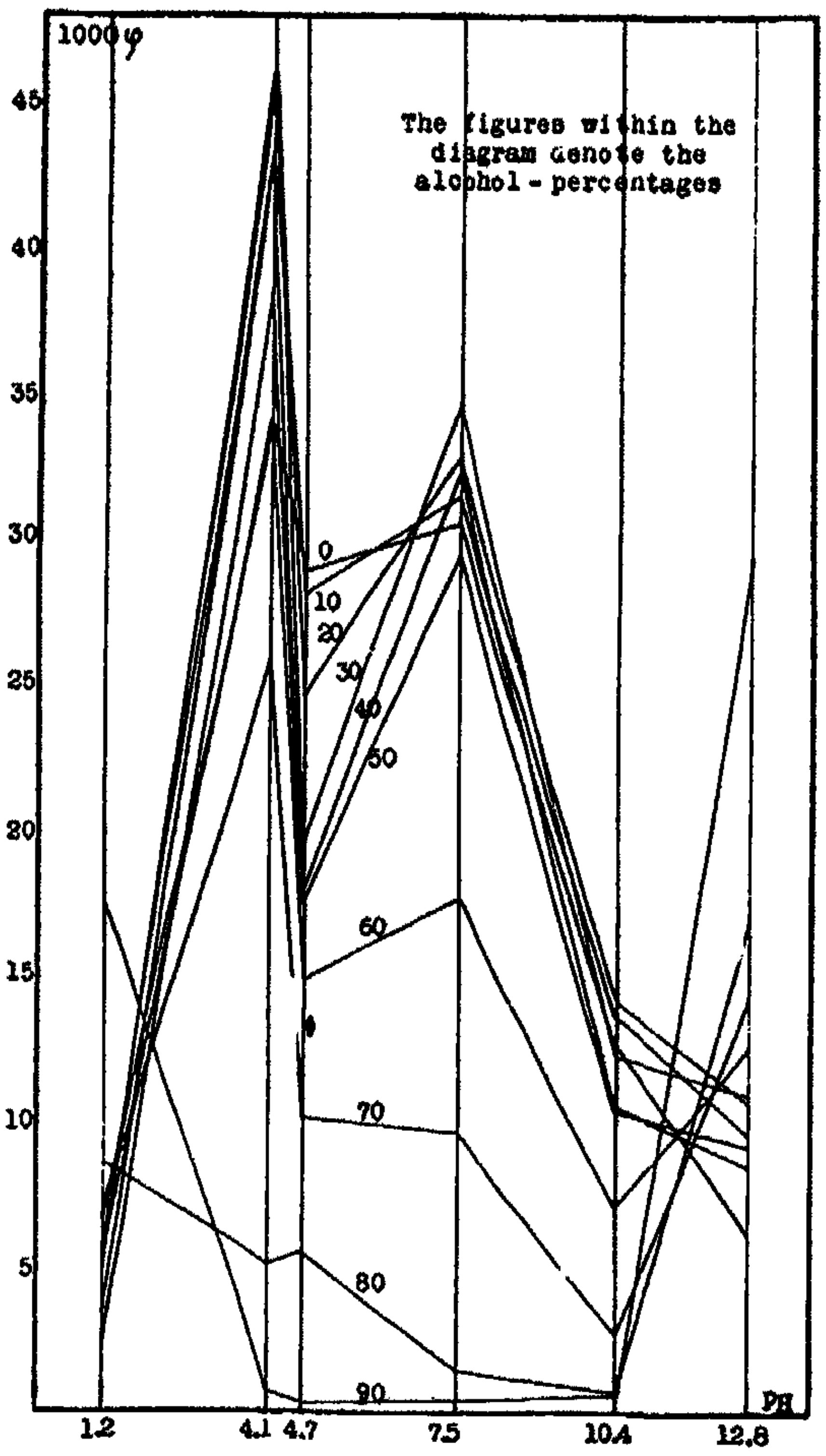

FIG. 3

TABLE II

1000 φ-values for the relative volume:

pH =	1.2	4.1	4.7	7.5	10.4	12.8
0%	5.3	34.1	28.9	30.5	12.6	6.2
10%	5.2	43.1	28.2	31.5	13.6	9.6
20%	5.8	45.6	24.7	32.8	14.0	10.7
30%	4.8	45.8	19.7	34.7	12.2	10.9
40%	3.6	42.9	18.0	32.3	10.4	8.4
50%	2.7	38.7	17.6	29.4	10.3	9.1
60%	6.4	33.8	14.8	17.7	7.1	12.4
70%	7.0	25.7	10.1	9.6	2.8	14.2
80%	8.4	5.1	5.5	1.5	0.8	16.9
90%	17.3	0.8	0.3	0.4	0.7	29.3
Alcohol						

the inversion easily can be observed, shifting the curve down and changing it to the before-mentioned "U"-shape. There results finally a large minimum flanked by two ascendent branches.

Discussion

The numerical values for the volume of the gelatin in the mixtures seem to be reasonable, due probably to the rather high dilution of the solutions used, so that Einstein's formula is applicable.

The curves given in the Figs. 2 and 3 may also be compared with the curves obtained for the swelling of gelatin by other investigators. They are so to speak the continuation in a far more dilute field, whether one considers the change of the volume as a taking up and loss of solvent by the micelles or as a change in the degree of hydration. It can be stated that the results given in this paper agree with the curves given for swelling effects by Jacques Loeb.[7]

The most important effect of the increasing replacement of solvent-water by solvent-alcohol is doubtlessly the shift of the dielectric constant. The lowering of the solubility can be neglected on account of the very high dilutions. However the behavior of the mixtures up to 60% alcohol makes it probable that the influence of the dielectric constant is not yet important or that it is covered by some other effect, since the change occurs more or less gradually. But later on the shape of the curves becomes turned completely. It is possible that the large minimum in Fig. 3 corresponds to the minimized effect of the electrolytes due to the lowering of the dissociation constant along with the lowering of the dielectric constant, and that only in the case of the originally strongly acid or basic gelatins there are, even at a very low degree of dissociation, ions enough to furnish the preformed gelatin-micelles with the necessary charges. The same numerous electrolyte ions of the strongly acid or basic gelatins may cause in the more aqueous mixtures a higher dispersion of the particles by breaking up the larger ones, thus decreasing the amount of bound solvent and the relative volume of the dispersed phase.

Our thanks are due to Dr. H. Lee Ward for his suggestions and interest throughout the progress of this work.

Summary

By means of viscosity measurements the behavior of standard gelatin solutions, diluted with water-alcohol mixtures, was observed and the relative volume of the dispersed phase was calculated. When starting with isoelectric gelatin the volume seems to be a linear function of the composition of the solvent, when starting with strongly acid or basic gelatin the volume shows its maximum in the highly alcoholic mixtures, in contrast to all other series. The results obtained may be compared also with curves of the swelling phenomena of gelatin.

References

[1] Jacques Loeb: "Proteins and the Theory of Colloidal Behavior," 2nd ed., (1924).
[2] S. E. Sheppard and R. C. Houck: J. Phys. Chem., **34**, 273 (1930).
[3] R. Wintgen und H. Loewenthal: Kolloid-Z., **34**, 291 (1924).
[4] R. H. Bogue: J. Am. Chem. Soc., **44**, 1343 (1922).
[5] Albert Einstein: Ann. Physik, (4) **19**, 289 (1906); **34**, 591 (1911).
[6] S. Arrhenius: Medd. K. Vetenskapsakad. Nobelinst., **3**, (21) (1917).
[7] Ref. 1, p. 120 ff.

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THE ADSORPTION OF WATER AND ETHYL ACETATE VAPORS BY SILICA GELS

BY ALBERT L. ELDER AND O. L. BRANDES

Recently, numerous experiments on the adsorption of various substances by silica gels have been reported. A comparative study of the relative efficiencies of Holmes' chalky silica gel and of Patrick's commercial gel, for adsorbing water from an air stream containing the vapor at various partial pressures, has not been reported.

The object of this investigation was to study the adsorbing powers of these two gels under similar conditions. In some of the experiments, an air stream containing water vapor at saturation values ranging from 25-100 per cent was used as the material to be adsorbed. In later experiments, ethyl acetate was substituted for water in order that comparisons between organic polar compounds and water could be made.

Preparation of the Gels

The Holmes' chalky gel used in this work was prepared according to the directions given by Holmes.[1] 0.8650 liters of sodium silicate of density 1.375 were diluted up to 17.3 liters with tap water. 1.16 liters of 2 N. ferric chloride were added slowly to the water-glass solution. The contents of the vessel were stirred during the addition of the ferric chloride and for a few minutes after the last of the ferric chloride had been added. The precipitate which formed slowly was allowed to stand for 50 hours and then filtered on fine cheese cloth. Five days later, the gel was cut into large lumps and placed on a drying rack. When a moisture content of 54.2 per cent had been attained, the gel was placed in a glass-stoppered bottle and allowed to "sweat" or synerize. During this process a better gel structure resulted.

One week later, the iron-gel was treated with steam for one hour. The iron-oxide was then removed with 9 N. sulfuric acid at a temperature of 80°C. Following the removal of the soluble salts by thorough washing with distilled water, the gel was air-dried and bottled. As needed, samples of the chalky silica gel were removed, reduced to the required size, activated, and used in the adsorption measurements.

The Patrick gel used was the ordinary commercial silica gel.

Apparatus and Experimental Procedure

The apparatus used was essentially that employed by Holmes and Elder[2] in their recent work on silica gels. Briefly, it consisted of two carefully calibrated flowmeters, a drying train, a train of saturators, a vapor mixing tube

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[1] "Laboratory Manual of Colloid Chemistry," 193 (1928).

[2] J. Phys. Chem., 35, 82-92 (1931).

and a gel adsorption tube. The saturators, mixing tube, and the adsorption tube were placed in a constant-temperature air-bath.

Adsorption measurements were made by placing a weighed sample of the activated gel of size 10-20 mesh in the adsorption tube and permitting a stream of air containing water or ethyl acetate vapor at a known partial pressure to pass over the gel. At intervals, the gel tube was removed from the thermostat, reweighed, and the gain in weight recorded as the per cent saturation of the gel under the conditions as specified by this experimental procedure. This process was continued until no more vapor was adsorbed by the gel.

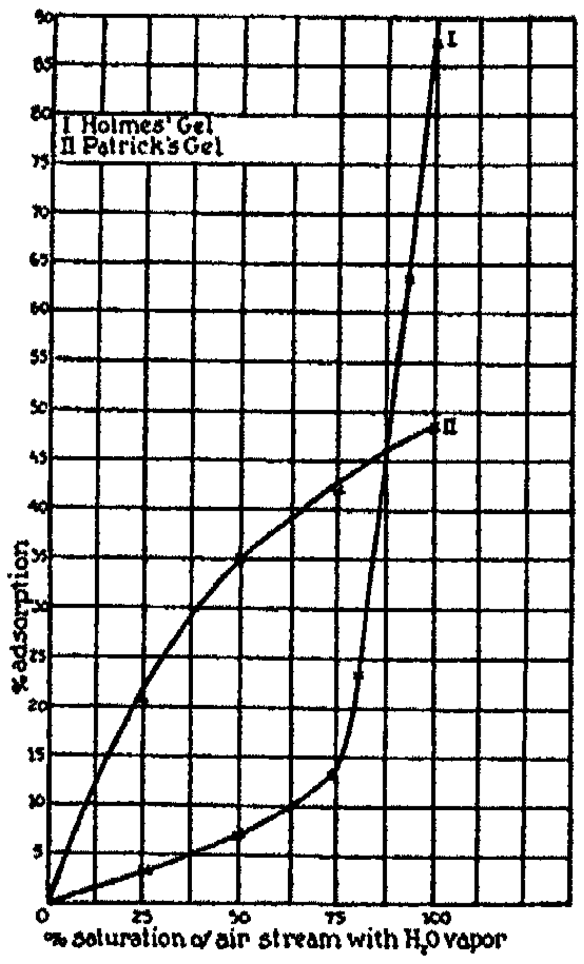

FIG. 1
Adsorption of water by silica gels under different partial pressures.

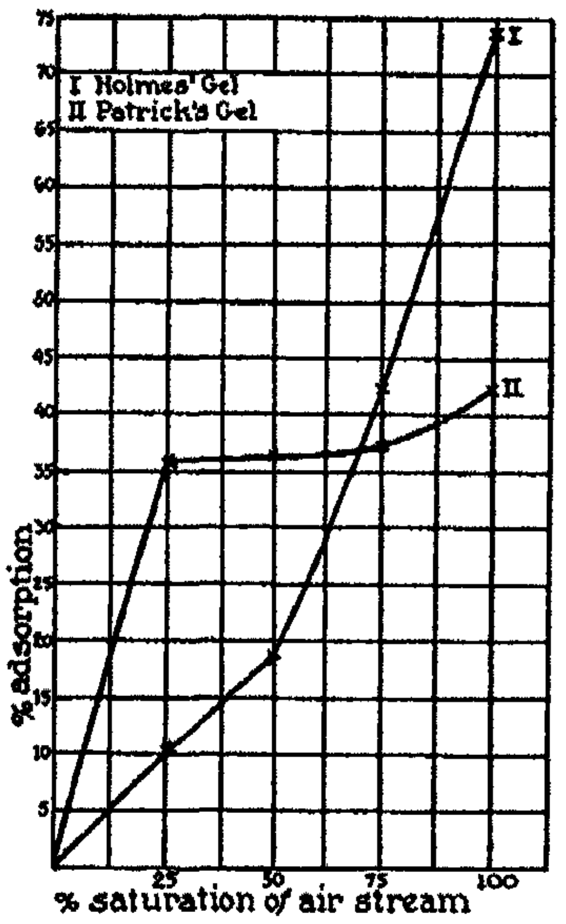

FIG. 2
Adsorption of ethyl acetate by silica gels under different partial pressures.

Activation of the gel was accomplished in all cases by placing the gel in a fused quartz tube surrounded by an electric furnace heated to 200°C. A stream of dry air was passed over the gel in the quartz tube at a rate of 300 cc per minute for two hours.

Any desired per cent saturation of air stream with either water or ethyl acetate could be obtained by mixing together known amounts of saturated and dry air. The rate of flow of air and water vapor through the apparatus was 300 cc per minute. The air and ethyl acetate mixtures were passed through at 100 cc per minute. All determinations were made at 30°C.

Results

The results of the experiments showing the adsorption of water vapor from an air stream are shown in Fig. 1. The saturation values of the air stream for these experiments were 100, 90, 80, 75, 50 and 25 per cent. A similar series of experiments are shown in Fig. 2 for the adsorption of ethyl acetate from an air stream at the saturation values of 100, 75, 50 and 25 per cent. The per cent saturation of the air stream with water or ethyl acetate has been plotted in Figs. 1 and 2 against the per cent adsorption by the gels of water and ethyl acetate at the known partial pressures. By per cent adsorption is meant the ratio of the grams of adsorbed material per gram of gel.

Summary

The data plotted in Figs. 1 and 2 show that at relatively low partial pressures Patrick's gel is more efficient than Holmes' chalky gel for adsorbing either water or ethyl acetate from an air stream. At higher partial pressures Holmes' chalky gel has the larger adsorption capacity of the two gels for adsorbing either water or ethyl acetate.

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THE CATALYTIC HYDROGENATION OF CARBON SUBOXIDE[1]

BY KENNETH A. KOBE[2] AND L. H. REYERSON

Of the known oxides of carbon, carbon monoxide and carbon dioxide have both been hydrogenated under a variety of conditions using different catalysts. The character of the catalysts used and the conditions of hydrogenation have been the determining factors in the type of products formed. The investigation here reported concerns itself with the hydrogenation of a third oxide of carbon commonly called carbon suboxide.[3] This oxide of carbon, C_3O_2, offered interesting possibilities in as much as we are dealing with a highly unsaturated molecule as well as a supposedly reactive one. If the commonly accepted structure of carbon suboxide, $O=C=C=C=O$, is correct we have four double bonds which can be reduced. A study of the catalytic hydrogenation of this molecule might give important information concerning the directive influence of a catalyst in the reduction of parts of the molecule. For example the carbon to carbon double bond may be reduced most easily or the carbonyl group may be attacked first. In any event the reduction of carbon suboxide should give rise to different products than are obtained by the reduction of carbon monoxide and carbon dioxide which have only a single carbon atom in the molecule. The following investigation reports the results obtained in the catalytic reduction of carbon suboxide.

Experimental

The method chosen for the preparation of the carbon suboxide was that of Ott and Schmidt[4] since this method has many advantages over the original method of Diels and Wolf.[5] Diacetyl tartaric anhydride, a substance easily prepared from tartaric acid and acetic anhydride, was used as the substance from which the suboxide was prepared. The apparatus was fairly simple and gave a good yield of carbon suboxide which was readily separated from the other products of the reaction.

The yield of carbon suboxide (41%) obtained by Ott and Schmidt was rather low. Diels, Beckmann and Tonnies[6] reported that they had secured a yield of 55-60% by modifying the apparatus of Ott and Schmidt, but gave

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[1] The material here presented formed a part of a thesis submitted to the graduate faculty of the University of Minnesota by Kenneth A. Kobe in partial fulfillment of the requirements for the degree of Doctor of Philosophy, July 1930.

[2] DuPont Fellow in Chemistry, 1928-1929.

[3] Reyerson and Kobe: Chem. Rev., 7, 479 (1930).

[4] Ott and Schmidt: Ber., 55, 2126 (1922).

[5] Diels and Wolf: Ber., 39, 689 (1906).

[6] Diels, Beckmann and Tonnies: Ann., 439, 76 (1924).

no data for their runs so that it is impossible to know whether or not these runs were consistent. Since the apparatus of Ott and Schmidt is rather delicate, it was decided to modify the construction. It was believed that better results would be obtained if the wires of the heating element were wound horizontally on a support member with practically no space between them and the glass walls of the containing vessel. Furthermore the flask holding the diacetyl tartaric anhydride should be attached to the tube containing the heating element so that the former could be easily disconnected for cleaning and recharging.

A two-liter balloon flask, A, (Fig. 1), was used to hold the diacetyltartaric anhydride. The support member of the heating element was made of five asbestos rings, M, which were separated from one another by glass rods, N. The rings had notches in them and 3 meters of platinum wire (.51 mm. diameter) were strung across the rings in such a manner that the direction changed on each ring, thus giving a criss-cross effect. Finally the rings were covered with an insulating cement. The tube B was made from 2-3/4" Pyrex tubing constricted at the bottom and sealed onto the neck of a two-liter balloon flask. After the neck and lead-in tubes, O, were sealed on, the heating element was slipped into the tube, and the lead-in wires, P, were pulled through the tubes. The top was then drawn down and a small tube sealed on. The top of B was extended above the heating element for some distance so that if necessary the top could be cut off, the tubes, O, cut off and the heating element removed for repairs. The flask A and tube B had the glass joints ground smooth and these were separated by a ring of rubber steam packing, F, which was coated with a thick rubber solution when put in place. The flasks A and B were then tightly clamped together (clamps not shown) by aluminum rings which could be drawn together by screw clamps. A series of three traps, C,D,E, and a manometer, J, were sealed onto the generator. The system was

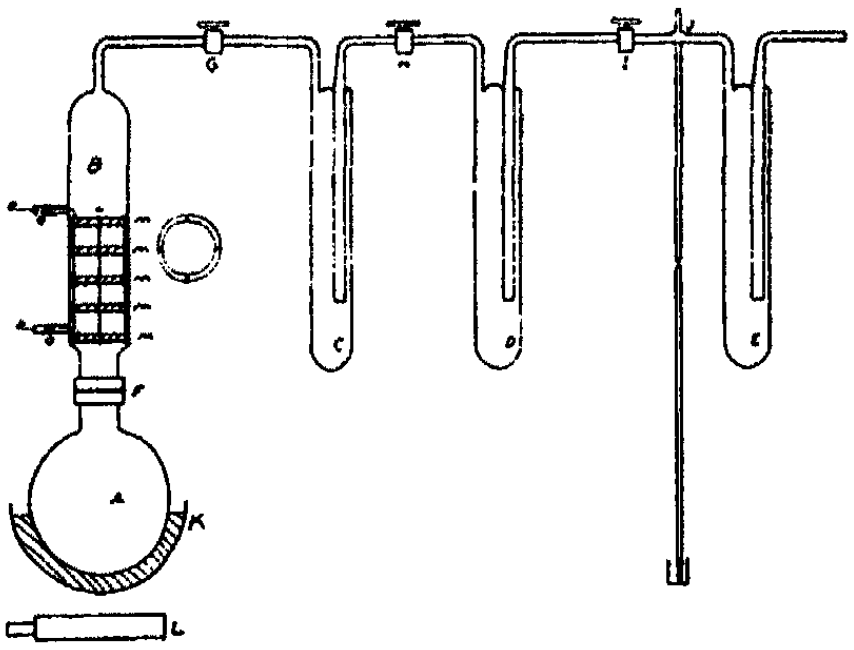

Fig. 1

evacuated to a pressure of about a millimeter of mercury and this was maintained in the apparatus during a run by continuously operating a pump. The pump was exhausted outside of the room since carbon monoxide is a product of the reaction. The flask A was heated by a melted salt mixture, K, consisting of 10 parts KNO_3 and 8.5 parts $NaNO_3$. This mixture has a melting point of 135°. The heat was supplied by a flat burner, L.

In all runs 200 grams of diacetyl tartaric anhydride[7] were placed in the flask A and the system evacuated. The temperature of the bath K was raised to 180° at the beginning of the run and increased to 220° toward the end. A current of 7.2 to 7.7 amperes through the filament heated it to a dull reddish yellow. A new filament was never found as effective as one that had been used. The vapors of diacetyl tartaric anhydride were drawn through the heated filament where decomposition into carbon suboxide, acetic acid, carbon monoxide, and carbon dioxide took place. The products of the reaction with the exception of carbon monoxide were frozen out in trap C which was cooled in liquid air. The pressure drop caused by the carbon monoxide passing thru the line gives an estimate of the decomposition taking place. At the conclusion of a run the acetic acid was separated from the carbon suboxide and dioxide by placing an alcohol bath at −35° about tube C for 30 to 40 minutes and condensing the suboxide and dioxide in trap D cooled in liquid air. Trap D was then surrounded by an alcohol bath at −110 to −115° and the carbon dioxide pumped off for about an hour. Some carbon suboxide was lost during the process but the amount was not great. The carbon suboxide was then distilled into a container immersed in liquid air. The data for the runs using this apparatus are given in Table I.

Table I

Yields of Carbon Suboxide

Run	Time of Run	Current amps.	Residue grams	C_3O_2 grams	Yield %
11	8 hrs., 45 min.,	7.2	79	32	50.8
12	8 hrs.	7.7	15	42	66.6
13	9 hrs., 10 min.	7.6	36	40	63.5
14	8 hrs., 25 min.	7.2	34	43	68.2
15	11 hrs., 30 min.	7.2	80	39.5	62.7
16	8 hrs.	7.2	37	45	71.4
17	9 hrs.	7.3	30	39	61.9
18	9 hrs., 30 min.	7.2	25	46	73.0

After the run was completed and the apparatus cut apart the tarry deposit on the heating element was burned off by passing a current through the wires and blowing a slow stream of air or oxygen through the tube B. In this way the possibility of a short circuit in the heating element during subsequent experiments was avoided.

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[7] Wohl and Oesterlein: Ber., 34, 1144 (1901).

Hydrogenation

In the actual hydrogenation a flow method was employed. The carbon suboxide was first distilled into tube A (Fig. 2) and this was immersed in an alcohol bath maintained at −50°C. Electrolytic hydrogen, which had been freed from oxygen and water vapor, was bubbled through the carbon suboxide and the mixed gases passed through 15 cc. of catalyst in tube D. The vapor pressure of carbon suboxide at −50° is 45 mm. The hydrogen-carbon suboxide ratio was therefore of the order of 15 to 1, to 16 to 1 depending upon the barometric pressure since the pressure of the mixed gases was maintained at very nearly that of the surrounding atmosphere. After passing the catalyst the gases were led through the trap F which was maintained at −60°.

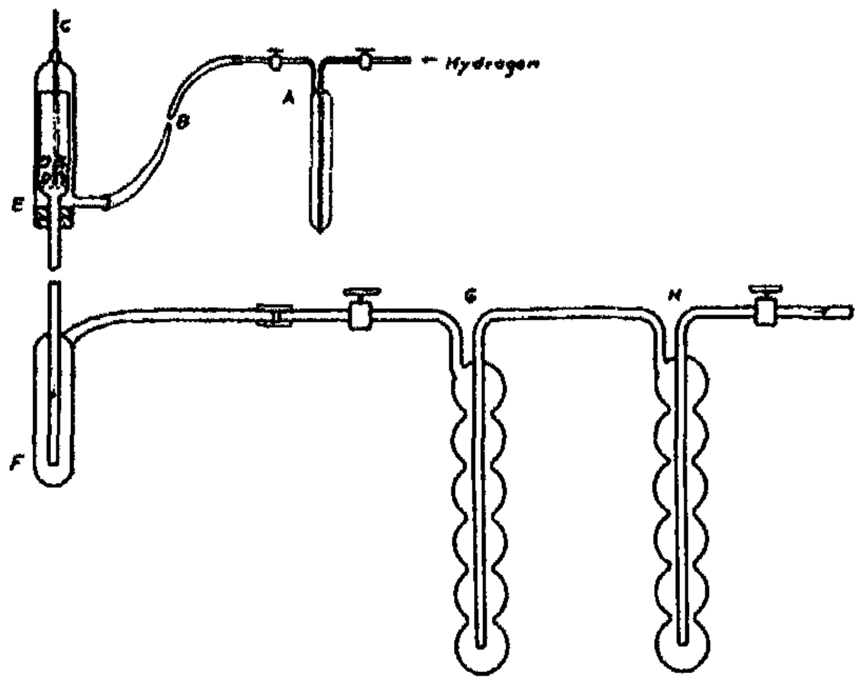

Fig. 2

Products of the reaction, not condensed in F, were frozen out in traps G and H which were cooled by liquid air. Excess hydrogen together with any carbon monoxide formed during the reaction passed the traps cooled in liquid air and was allowed to escape. The temperature of the catalyst was maintained by an electric heating coil which was wound about tube E. The thermometer, C, was used to follow the temperature of the catalyst during a run. With a catalyst present there was always a marked rise in the temperature of the catalyst (sometimes as much as 50°) when the gas mixture first came in contact with the granules of active material. The heating current was then adjusted so that the temperature fell to the starting value, and this was maintained to the end of the run. In run IV at 300° the catalyst was badly fouled and carbonaceous material was deposited on the sides of tube D. When the catalyst was removed and boiled in dilute nitric acid a red colloidal suspension was formed. This indicated considerable polymerization of the suboxide on the catalyst surfaces. The catalyst used and the quantity of reaction products are summarized in Table II.

Table II

Run	Temp.	Catalyst	Grams of C_3O_2 used	Grams of liquid produced	Liters of gas N.T.P.
II	200°	Nickel-silica gel used in Run I	39	8	—
III	200°	Fresh nickel-silica gel	39	5	4.0
IV	300°	Catalyst from run III, heated and reduced	30	4	3.15
V	200°	Palladized-silica gel	35	5	2.0
VI	250°	Catalyst from run V heated and reduced at 300°	32	5	2.8
VII	200°	Nickel-silica gel	42	4.5	4.05
X	200°	No catalyst	13	1 drop	1.31
XI	200°	20 cc. 8-14 mesh pyrex	12	1 drop	1.18

The Character of the Reaction Products

In considering the reaction products we shall designate as liquid-products whatever was condensed in trap F and as gaseous products those substances which were frozen out in traps G and H. The analysis and identification of the gaseous products will be taken up first. At the conclusion of a run bulbs G and H were shut off from bulb F and connected by a tube to a ten liter bottle filled with water in such a manner that gases could displace it. The liquid air was removed from around the bulbs and they were allowed to warm up to room temperature. The frozen products of reaction vaporized and displaced water from the bottle. A very small amount of liquid, about one half cc. usually remained unevaporated. This gave a color test with Schiff's reagent, but no phenyl hydrazone could be formed. The quantities were so small that no further tests were run on this liquid. The gas confined over water was allowed to stand for a day so that any carbon suboxide would react and dissolve in the water.

The gas from run III was analysed in a Hempel gas absorption pipette system but the accuracy was not sufficiently high. All succeeding analyses were made in the gas analysis apparatus developed by the U.S. Steel Corporation.[3] These results showed the gas to be a mixture of an unsaturated hydrocarbon, a saturated hydrocarbon, carbon monoxide, carbon dioxide, hydrogen, oxygen, and nitrogen. Since no special precautions were taken to keep traces of air out of the large bottle or the connecting tubing and the ratio of nitrogen to oxygen was found to be almost that of air, it was concluded that the nitrogen and oxygen came from such sources. A typical gas analysis is given in Table III. This was made on the gas mixture obtained in run VII.

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[3] "Methods of Chemists of the U. S. Steel Corporation for sampling and analysis of gases." Carnegie Steel Corporation (1927).

TABLE III

		I		II	Average
Carbon dioxide		44.5		44.5	44.5
Unsaturated hydrocarbon		29.7		29.5	29.6
Oxygen		.6		.6	.6
Carbon monoxide		2.0		2.2	2.1
Hydrogen	17.5	18.2	18.2	19.1	18.2
Saturated hydrocarbons as C_3H_8	2.1	2.1	2.2	2.2	2.2
Nitrogen					2.8

The principal hydrocarbon product was the unsaturated one so that its identification was next undertaken It was first identified by gas analysis methods and later established by the formation of a derivative. A complete analysis of the gas was first made. A sample of the original mixture was then taken and the carbon dioxide removed. Small portions of this residue were then mixed with oxygen and exploded. The decrease in volume and the amount of carbon dioxide formed was measured. The decrease in volume and the carbon dioxide which should result from the combustion of all the gases except the unsaturated was calculated from the complete gas analysis. By subtraction, the changes produced by the unsaturated hydrocarbon were obtained. The data for the analysis of the products of run V are given in Table IV and the results of the analysis of the products of run VI are given in Table V. The columns headed by the letters A, B, C, or D record the analytical results obtained on using separate samples of gas taken from the same source. The values are given in cubic centimeters of gas.

TABLE IV

Volume of gas taken	100.0		
Volume after CO_2 removed	87.6		
	A	B	C
Vol. used for combustion	12.0	15.2	15.6
Oxygen added to	93.6	93.3	93.4
Vol. after explosion	79.0	74.7	74.0
Volume after CO_2 absorption	72.6	66.3	65.3
Contraction	14.6	18.6	19.4
CO_2	6.4	8.4	8.7

Calculated amounts from complete analysis

	A	B	C
Unsaturates	1.98	2.51	2.57
CO	.04	.05	.05
C_3H_8	.19	.24	.25
H_2	6.03	7.63	7.82
Air	3.75	4.75	4.88
	11.99	15.18	15.57

TABLE IV (Continued)

Contractions calculated from above

	A	B	C
Due to C_3H_8	.57	.72	.75
Due to CO	.02	.02	.02
Due to H_2	9.04	11.46	11.73
	9.63	12.20	12.50
Contraction found	14.6	18.6	19.4
Difference due to unsaturated	5.0	6.4	6.9

Carbon dioxide calculated from above

Due to C_3H_8	.57	.72	.75	
Due to CO	.04	.05	.05	
	.61	.77	.80	
CO_2 found	6.4	8.4	8.7	
Difference due to unsaturated	5.8	7.6	8.1	
Unsaturated	1.98	2.51	2.57	
CO_2	5.8	7.6	8.1	
Contraction	5.0	6.4	6.9	*Av.*
CO_2/unsaturated	2.93	3.02	3.15	3.03
Contraction/unsaturated	2.52	2.54	2.68	2.58

TABLE V

	A	B	C	D	
Unsaturated	1.76	2.23	2.48	1.85	*Av.*
CO_2	5.37	6.60	7.27	5.37	
Contraction	4.38	5.68	6.22	4.34	
CO_2/unsaturated	3.05	2.96	2.93	2.90	2.96
Contraction/unsat.	2.49	2.54	2.51	2.35	2.47

CO_2/contraction = 2.96/2.47 = 1.197

If the unsaturated hydrocarbon were propylene the combustion reaction

$$2C_3H_6 + 9O_2 \ldots\ldots 6CO_2 + 6H_2O$$

would give the following theoretical rations: $\frac{\text{6 volumes of } CO_2}{\text{2 volumes of } C_3H_6} = 3$, $\frac{\text{5 volumes contraction}}{\text{2 volumes } C_3H_6} = 2.5$, $\frac{\text{6 volumes of } CO_2}{\text{5 volumes contraction}} = 1.20$. It is evident from the results that the unsaturated hydrocarbon gives values which check the theoretical values for propylene almost exactly. It is very doubtful that any of the hydrocarbon was cyclopropane which is the other hydrocarbon having the formula C_3H_6. In the first place the unsaturated hydrocarbon was readily absorbed in bromine water.[9] In the second place cyclopropane readily isomerizes to propylene in the presence of catalysts at the operating temperatures used in these researches.[10]

The gaseous products from Run VII were transferred to a bottle over bromine water and bromine was slowly added from a separatory funnel until a bromine color remained. The excess of bromine was removed by sodium sulfite and the solution extracted twice with ether which was then dried over calcium chloride. The ether was distilled off and the main fraction collected at 137° to 144°. The refractive index (Abbe), density and Carius halogen were determined on this fraction. In Table VI these results are compared with the known constants of propylene dibromide and 1,3 dibrompropane.

TABLE VI

	b.pt.	N_D^{20}	d_{20}	% Br
Values found	137-144	1.511(26°)	1.893(26°)	76.6
$CH_3CHBrCH_2Br$	140	1.520	1.933	79.2
$CH_2BrCH_2CH_2Br$	167	1.523	1.979	79.2

These results establish the fact that propylene was the unsaturated product of the hydrogenation. Since propylene was proved to be the unsaturated product in the hydrogenation of carbon suboxide it was assumed that the small trace of saturated hydrocarbon found was propane.

A summary of the analysis of the gaseous products for the various runs calculated on an air-free and hydrogen-free basis is given in Table VII. The air and hydrogen are not reaction products so are left out of the summary.

TABLE VII

Run	III	V	VI	VII	X	XI
CO_2	49.7	43.0	64.9	56.7	91.0	88.6
C_3H_6	44.4	51.0	33.7	39.8	4.2	6.1
CO		1.1	0.0	2.7	1.6	1.5
C_3H^8	5.9	4.9	1.4	2.8	3.2	3.8
Total volume of gas	1820	568	1320	3180	218	132
% yield of C_3H_6	6.3	2.5	4.2	9.2	.2	.2

Nature of the Liquid Products

The product collected in trap F consisted of a liquid with an odor resembling pyroligneous acid. In addition there was always a red semi-solid material suspended in the liquid. The amount of this red material varied with the catalyst used. When the nickel catalyst was used a relatively large amount of the red material was found in trap F. In fact there was often enough present to make the mixture almost semi-solid. On the other hand the palladium catalysts gave almost no solid substance. The products collected in trap F during runs I to VI were united for purposes of investigation

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[9] Freund: J. prakt. Chem., (2) 26, 370 (1882).

[10] Tanatar: Z. physik. Chem., 41, 735 (1902).

since the individual amounts were too small for accurate analysis. The entire amount was distilled in a micro-distillation apparatus.[11] Nine ml. of liquid having a boiling point of 116° at 738 mm. pressure was obtained. This was refractionated into three portions of 2.0 ml., 4.5 ml., and 2.5 ml. The middle fraction was used to determine the composition of this liquid. Combustions were made using the semi-micro combustion apparatus of Lauer and Dobrovolny.[12]

By combustion .0165 g. of the liquid gave .0239g. of CO_2 and .0107g. of H_2O. By calculation the percentage of carbon comes out to be 39.6 and the percentage of hydrogen, 7.20. In a second determination .013g. of the liquid gave .0198g. of CO_2 and .0089g. of H_2O. From this the percentage of carbon turns out to be 39.7 and the percentage of hydrogen, 7.27.

The empirical formula CH_2O best fits these results as the following comparison will show:

	Calculated	Found
percentage C	39.97	39.7
percentage H	6.72	7.2
percentage O	53.31	53.1

The molecular weight of the substance was determined by its depression of the freezing point of benzene. .1677 g. of liquid in 17.51 g. of C_6H_6 depressed the freezing point .436° which gives 115.2 as the calculated molecular weight. .1942g. of the material in 17.51 g. C_6H_6 depressed the freezing point .513° or by calculation a molecular weight of 113.7. The average molecular weight was therefore determined as 114.5. Thus the compound contains nearly four units of CH_2O in its composition. Acetic acid has the same percentage composition and is known to exist largely as a dimer in benzene. The liquid gave acid reactions toward indicators and had an odor of acetic acid. The aniline derivative of the material was therefore made and identified as acetanilide by a mixed melting point determination with a pure sample thus confirming that the liquid was chiefly acetic acid. By titration with a standardized NaOH solution fraction one was found to contain 85.6 percent of acid, fraction two. 94.8 percent acid, and fraction three 96.8 percent acid. No attempt was made to identify the traces of other substances from these three fractions. Fraction one became light brown in color after long standing, while fraction three remained colorless. All fractions contained a trace of material insoluble in water because a faint white cloudiness appeared upon dilution with water. The residue from the distillations behaved like other samples of polymerized carbon suboxide, so nothing further was done with it.

The liquid product from run VII was distilled and the distillate diluted with water. This was then titrated with standard NaOH. Calculation showed the amount of acetic acid to be 1.49 g. or a yield of 46.6 percent provided a mole of acetic acid was formed for every mole of propylene.

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[11] Cooper and Fasce: Ind. Eng. Chem., 20, 420 (1928).

[12] Lauer and Dobrovolny: Mikrochem. Pregl Festschr., 243 (1929).

Catalyst Poisoning

The first attempts to hydrogenate carbon suboxide in this investigation were carried out in an all-glass closed system. The gases were circulated through the catalyst by a glass magnetic pump and the drop in pressure followed as the gases reacted. It was hoped that these experiments would give some indication of the mechanism of reaction. In a preliminary experiment, using a circulating mixture of gases containing two volumes of hydrogen to one of carbon suboxide, there was observed a very slight decrease in pressure very soon after the magnetic pump was started. A palladized silica gel catalyst was used in this experiment and it was operated at room temperature. A sample of this same catalyst was found to be effective in hydrogenating ethylene under the same conditions. The palladium catalyst used in this closed system hydrogenation of carbon suboxide was found to be no longer effective in ethylene hydrogenation. Furthermore the catalyst could not be reactivated by customary methods of activation. A copperized gel used in an attempted hydrogenation of C_3O_2 at ordinary temperatures changed from a black to a brick red color. Carbon suboxide evidently poisoned the catalysts when operating under these conditions.

Attempted Reduction in Solution

Many unsaturated substances may be reduced in solution by hydrogen in the presence of a platinum oxide catalyst.[13] Fifteen grams of carbon suboxide was dissolved in anhydrous ether, and .23 g. of platinum oxide catalyst added. This mixture was shaken for four and one half hours in an atmosphere of hydrogen under pressure. The ether and carbon suboxide were allowed to evaporate at room temperature. No evidence of reduction products could be detected but there remained a small amount of red solid which acted like polymerized carbon suboxide. The water produced by the reduction of the platinum oxide catalyst undoubtedly reacted with the carbon suboxide to form malonic acid. This aided or catalysed the formation of the polymer.[6] A similar experiment in which 39 g. of liquid carbon suboxide with .25 g. of platinum oxide catalyst was shaken for an hour in hydrogen showed no pressure change after the initial pressure drop due to the reduction of the oxide catalyst. It was therefore concluded that reduction in the liquid state and in solution was not possible under the conditions used in these experiments.

The Mechanism of Reaction

The formation of propylene is a rather unexpected reaction product since a complete reduction of carbon suboxide should give propane. The other products formed in the reaction are readily accounted for by secondary reactions due to the water formed when the oxygen atoms are eliminated from the suboxide. The following equations represent the principal reactions occurring in this hydrogenation:

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[13] Voohees and Adams: J. Am. Chem. Soc., 44, 1397 (1922); Carother and Adams: 45, 1071 (1923).

[6] Diels, Beckmann and Tonnies: loc. cit.

$$C_3O_2 + 5H_2 \rightarrow C_3H_6 + 2H_2O \qquad (1)$$

$$C_3O_2 + 2H_2O \rightarrow CH_2(COOH) \qquad (2)$$

$$CH_2(COOH)_2 \rightarrow CH_3COOH + CO_2 \qquad (3a)$$

$$CH_2(COOH)_2 + n\ C_3O_2 \rightarrow \text{polymer} \qquad (3b)$$

When the propylene is formed, two molecules of water are produced (equation 1) which then react with another molecule of carbon suboxide to form malonic acid (equation 2). The malonic acid may then decompose to form acetic acid and carbon dioxide (equation 3a) since this reaction is known to take place at temperatures much below those maintained in the catalyst chamber.[14] This explains the presence of the acetic acid and also the relatively large amounts of carbon dioxide in the gaseous products of the reaction. A simultaneous reaction occurs in the formation of a polymer (equation 3b) which is caused by the presence of malonic acid (or possibly the water itself)[6] These reactions (3a and 3b) are influenced greatly by the character of the catalyst, since the nickel catalyst gave the most polymer while the palladium catalyst acted to produce very little polymer and more acetic acid.

In all of the simple reactions of carbon suboxide both ends of the molecule behave similarly, as in the case of the addition of water, a carboxyl group forms at each end of the molecule. In this hydrogenation the carbonyl group at the ends were attacked and the oxygen eliminated in the form of water. The hydrogenation of the unsaturated carbon-carbon linkages then continued producing propylene as the principal product. Nickel and palladium catalysts are known to be effective in the removal of the oxygen from carbon dioxide and carbon monoxide and in these cases a saturated hydrocarbon results. Since carbon suboxide was shown to be a very active poison for the hydrogenation of ethylene it should also poison the catalyst for the hydrogenation of propylene which explains the relatively small amount of saturated hydrocarbon formed. The very small conversion obtained when using an empty catalyst chamber or one filled with crushed pyrex indicates that the reaction is a catalytic one.

Summary

1. Carbon suboxide has been catalytically hydrogenated by passing a mixture of the suboxide and hydrogen over nickel or palladium coated silica gels.

2. Propylene was found to be the principal reduction product.

3. Secondary reactions account for the formation of acetic acid, carbon dioxide, and the polymer.

4. Carbon suboxide is a catalyst poison for hydrogen-ethylene reaction.

5. An improved apparatus for the preparation of carbon suboxide gives consistently higher yields than previously reported.

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[14] Lindner: Monatsheft, 28, 1041 (1907).

[6] Diels, Beckmann and Tonnies: loc. cit.

THE COLLOID CHEMISTRY OF THE NERVOUS SYSTEMS. II*

BY WILDER D. BANCROFT AND J. E. RUTZLER, JR.**

The etiology of many of the diseases of the nervous systems from the point of view of the mechanism involved is not thoroughly understood; for that reason classification has been hindered, and in many cases is based purely on symptomatology. Still more obscure is the mechanism of the action of drugs in relieving the symptoms of many of the disorders of the nervous systems; often all that is known is that a given drug will relieve the disorder. Of course such things as dosage and toxicity are well established. For that reason the classification of drugs into groups according to what they do inside the body when used in therapeutic doses is sometimes lacking. When one does not know what a drug actually does, it can only be classified by the symptoms of relief to which it may give rise. Quite obviously one would get into difficulties if he classified sodium bromide as a hypnotic because it helps put people to sleep. It is a peptizing agent, whereas the true hypnotics are agglomerating agents. Often a drug does not find its way into a group because clinically its biological side reactions prevent its use. For instance, iodism would probably intervene before one could find out that sodium iodide helps a certain type of catatonic excitement. Claude Bernard's theory of anesthesia enables us to classify anesthetics and narcotics under one head as agglomerating agents for the protein colloids of the nervous systems. As a consequence of the development of that theory in these laboratories[1] it is now quite clear that the alkali salts of hydrochloric, hydrobromic, and hydriodic acids, along with thiocyanic acid, and the organic compound ephedrine can be grouped under the heading of drugs that act largely by virtue of being peptizing agents.

The objects of this paper are three in number: first to show that such a classification as that above can in fact be realized; secondly to present new data on the action of sodium thiocyanate; and lastly to show that ephedrine can and does in some cases act as a peptizing agent in certain ills of the animal organism. By way of simplification, only the effects of these compounds that are obviously directly connected with the peptization of the protein colloids of the nervous systems will be considered. Then we will be able to see to what extent the main action of the compounds dealt with can be accounted for in the simplest manner. The German for thiocyanate is rhodanate. So, in this and future papers of this series sodium thiocyanate will be referred to as sodium rhodanate, and thiocyanic acid as rhodanic acid. The reason for

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* This work is done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

** Eli Lilly Fellow.

[1] Bancroft and Richter: J. Phys. Chem., 35, 215; Bancroft and Rutzler: 1185 (1931).

adopting this nomenclature is that outside of the chemistry profession one often finds that sodium thiocyanate is confused with either sodium cyanide, or with sodium thiosulphate.

The part that the lyotropic series plays in this study can not be too strongly emphasized for it looms large as a co-ordinating factor.[1] For egg globulin the series of anions is apparently rhodanate > iodide > bromide > chlorate > nitrate > chloride > acetate > sulphate > tartrate > citrate. In alkaline solution the rhodanate ion peptizes globulin the most, and the citrate ion the least. This series apparently holds for proteins in general, with the exception of gelatin where the water equilibrium is the important thing; even in this case the series is substantially the same as that for globulin. The accompanying series for the cations appears to be thorium > aluminum > hydrogen > barium > strontium > calcium > potassium > sodium > lithium. In this case the thorium ion precipitates negatively charged albumin the most, and the lithium ion the least. However, the really important thing is that the rhodanate, iodide, bromide, and chloride ions are good peptizing ions, while the sulphate, citrate, and tartrate ions are the poorest in that respect; they may even tend to agglomerate an albumin or globulin sol.

Since adsorption is specific, all substrates do not show the same order of adsorption for the different ions; so one might expect that in biological systems the lyotropic series as given for globulin will not hold rigidly. One gains the impression, however, that the three ions that are the best peptizing agents assume their place at the head of the lyotropic series for the protein colloids, the reversible agglomeration of which results in the malfunction of the nervous systems. That does not preclude in any way a situation in which these ions shift around among themselves.

1. Agglomeration-Peptization Phenomena

Upon going even superficially through the literature, or reading a good book on pharmacology or therapeutics, it becomes evident at once that qualitatively many of the actions of the chloride, bromide, iodide, and rhodanate ions are the same. Quantitatively there are great differences between the actions of these ions due to the varying degree to which they are adsorbed on the different protein substrates. Consider, for instance, the data[2] collated in Table I.

TABLE I

Compound	Average Dose Weight	Molecular Weight	Average Dose/Molecular Weight = Molecular Dose
$NaCl$	2.3 gms.	58.5	0.039 gm.
$NaBr$	2.3 gms.	102.9	0.0223 gm.
NaI	1.15 gms.	149.9	0.0076 gm.
$NaCNS$	0.14 gm.	81.1	0.0017 gm.

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[1] For more complete discussions of lyotropic series see Bancroft: "Applied Colloid Chemistry," 287-293 (1926); Gortner: "Outlines of Biochemistry," 201, 205 (1925); Bechhold: "Colloids in Biology and Medicine," 151-153 (1919).

[2] "Merck's Index" (1930).

The average dose varies almost in the order that these salts are found in the lyotropic series, but from this point of view the important thing for the moment is the number of gram molecules of the given salt that are administered to secure the desired effect. The "molecular dose" gives us these data. When arranged in descending order, as in the table, we have: chloride > bromide > iodide > rhodanate, the sodium ion being common to all of them. The meaning of this in all probability is to be found in the precepts of colloid chemistry. Quite obviously it takes less sodium rhodanate than it does iodide, and so on, to accomplish the desired result. Since the rhodanate ion is generally more strongly adsorbed by proteins than are the other ions, simply reversing the series, thus arranging the ions in the order of the degree to which they are adsorbed from most to least, gives us the well known lyotropic series: CNS > I > Br > Cl. The chlorate and nitrate ions may precede the chloride ion in the series but their side effects eliminate them from this consideration. That all of this is merely philosophical speculation seems highly improbable in view of the fact that all of these compounds are used to combat disturbances of the nervous systems arising from a degradation in the degree of dispersion of the protein colloids, as will become apparent. While the sodium ion is common to all of the compounds listed in Table I, and will, as the colloid chemist knows, exert practically a constant effect, sight must not be lost of the fact that as the tartrate and citrate end of the lyotropic series is approached the coagulating effect of the positive sodium ion on a negatively charged protein sol becomes more pronounced.

Although there are several ways of fixing the average doses of the compounds in Table I from Merck's Index, the general result represented there is characteristic of each of them. So, for certain disturbances of the nervous systems which involve a decrease in the degree of dispersion of the protein colloids, sodium rhodanate is the most efficacious compound of the four, and the others fall into line as indicated. This should emphasize the important part that the lyotropic series plays in living biological systems.

Gurdjian[1] investigated an interesting case of reversible agglomeration in the brain. The exposed floor of the fourth ventricle, the respiratory center, was heated to 75°; this resulted in the arrest of respiration. When the temperature came back to normal the respiration recommenced. It was found that strong salt solutions increased the respiratory rhythm. It is well known that many proteins are coagulated by heat. According to Mathews,[2] "the nervous tissues of frogs contain a globulin which coagulates at a very low temperature, 35°, and in the brains of mammals a globulin is present, Halliburton says, which is coagulated at about 42°. It is possible that the coagulation of this protein may be important in the pathology of heat stroke." Whether or not the temperatures of coagulation as stated are correct makes little difference, since in the experiment cited above the temperature was 75°.

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[1] Am. J. Physiol., 82, 261 (1927).

[2] "Physiological Chemistry," 582 (1915).

It seems natural that a solution of sodium chloride should help to repeptize the heat-agglomerated proteins of the floor of the brain.

In a previous discussion[1] the postulation was made that the agglomeration of the protein colloids of the respiratory center results in a lowering of the rate of respiration. This idea had its birth by reason of the fact that both morphine and "amytal" lower the rate of respiration under certain conditions, while sodium rhodanate increases the rate. The work of Gurdjian seems to substantiate this view. Further data along the same line are given in this paper.

Mercuric chloride is a good coagulating agent for protein sols; its action in the body is in all probability qualitatively the same. Carder and Coffindaffer reasoned[2] that the chloride ion should replace the mercuric ion if both were adsorbed by the proteins in the body. Thereupon they gave a fatal dose of mercuric chloride to 38 dogs; fifteen of the dogs received no treatment and, as a result, they died in from one to six days. The rest of the dogs were given injections of 0.8% sodium chloride solution daily until they either recovered or died. One month was the time limit allowed. Nineteen of the 23 dogs that were treated lived. Thus we have another case of the replacement of one substance by another, the mercuric ion by the chloride ion, with the resulting peptization of the agglomerated protein colloids.

Comparatively weakly adsorbed though it must be, sodium chloride has been shown to have an antagonistic effect toward strychnine.[3] When sodium chloride was injected subcutaneously into animals following a poisonous dose of strychnine, and at the same point at which the strychnine was introduced, the animal did not die. Thus, even a weakly adsorbed anion apparently antagonizes strychnine.

We have seen[4] that sodium rhodanate protects rabbits from a weak anaphylactic shock. On the basis of its position in the lyotropic series, one would expect that regardless of what the theory may be, sodium chloride ought to have anti-anaphylactic properties, though they should be quite a bit less pronounced. Langer[5] found this to be the case. He sensitized guinea pigs with sheep serum; this was followed by numerous two to four cc. doses of a 10% solution of sodium chloride, administered per os. When, 15 days after the sensitizing dose of sheep serum, the animals were again injected with the antigen they suffered an anaphylactic reaction. The reaction was definitely less severe than that experienced by animals that were not protected by the sodium chloride. Entirely analogous is the action of sodium chloride in preventing shock from proteotoxin.[6] The isolated uterus failed to react to proteotoxin after bathing it in a hypertonic solution of the salt. This experiment was then performed *in vivo*. It was found that, when a concentrated

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[1] Bancroft and Rutzler: J. Phys. Chem., **35**, 1185 (1931).

[2] J. Am. Med. Assoc., **81**, 448 (1923).

[3] Campo: Physiol. Abs., **12**, 308.

[4] Bancroft and Rutzler: J. Phys. Chem., **35**, 1185 (1931).

[5] Münch. med. Wochenschr., **59**, 2554 (1913).

[6] Zinsser, Lieb, and Dwyer: Proc. Soc. Exp. Biol. Med., **12**, 204 (1915).

solution of sodium chloride was injected, protection against the action of proteotoxin was established. In these cases sodium chloride quite definitely appears to prevent reversible agglomeration of the protein colloids of the sympathetic nervous system. Sodium chloride undoubtedly would reverse the action of proteotoxin were it used quickly and heroically enough after the first appearance of the symptoms of shock.

2. The Bromide Ion

The reversible agglomeration theory of the cause of certain disorders of the nervous systems, and the action of certain compounds in peptizing the agglomerated protein sols existing in the body during those disorders, demands that the bromide ion be a more powerful peptizing agent than the chloride ion is. It should be a more efficient peptizing agent into the bargain. Given in large enough doses[1] and frequently enough, potassium bromide brings about the symptoms of bromism. These symptoms are: muscular weakness, general mental and bodily sluggishness, loss of memory, often marked sleepiness, depression of spirits deepening into complete apathy, lowering of temperature, and finally an universal depression of function. "It seems to be proved that the bromide affects the whole nervous system, but in the lower animals the portions most susceptible are those tissues of the spinal cord whose function it is to receive the impulse from without, and the peripheral ends of the afferent or sensitive nerves. . . . It is chiefly valuable as a means of quieting non-inflammatory excitement of the reflex centers of the cord, of the peripheral afferent nerves, of the genital function, and of the cerebrum. It is especially valuable in *epilepsy*. . . . In *tetanus* and *strychnine poisoning*, if given with sufficient boldness, it is an excellent remedy." In reflex vomiting of certain types, and in delirium tremens potassium bromide may often be used to advantage.

It has been pointed out that for those cases with which we are concerned, it is much better to use the sodium salt of a given acid than the potassium salt, due to the toxicity of the potassium ion.[2] The following experiments illustrate the fact rather strikingly. A 2500-gram rabbit was given an intravenous injection of five cc. of a 20% solution of sodium rhodanate. During a period of 15 minutes nothing untoward happened to the animal, and further experimentation was carried out upon it. An intravenous injection of a 20% solution of potassium chloride into a rabbit weighing 2200 grams resulted in death with violent convulsions before more than three cc. of the solution could be administered. In each case the time required for the injection was about 40 seconds. This experiment leaves little doubt as to the comparative toxicity of the sodium and potassium ions. When one is not using large enough doses of a salt so that the potassium ion can demonstrate its toxic action, the fact that the potassium ion is nevertheless toxic and often working against the other ion is apt to be overlooked. So, the results upon

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[1] "United States Dispensatory," 988 (1907).

[2] Bancroft and Rutzler: J. Phys. Chem., 35, 1185 (1931).

which the report in the United States Dispensatory on the action of potassium bromide is based would very likely be more striking were they obtained by using sodium bromide. Even the sodium ion is somewhat toxic, for sea-water fish are killed by isotonic solutions of sodium chloride, but are able to live in distilled water.[1]

If the mechanism of the therapeutic action of the bromide ion upon the central nervous system is the peptization of reversibly agglomerated protein colloids, then it follows that the compound or the ion must find its way into these colloids. A man died 26 days after the ingestion of ten grams of sodium bromide. Analysis[2] for the bromide ion revealed the following amounts: liver, 0.037 gram; brain, 0.019 gram; kidneys, 0.037 gram; blood, 0.045 gram. Another person died after having taken 100 grams of sodium bromide in less than two days. In this case analysis revealed[3] that the greatest amounts of bromide were in the cerebral cortex, the lungs, and the kidneys, in which organs it varied from 0.3 to 0.5%. The gray matter of the cerebrum contained twice as much bromide as the white matter, the basal ganglions, or the cerebellum. This shows that the bromide ion can get into the brain, where it will peptize the protein colloids; so we are not postulating that this halide ion is acting upon a substrate that is inaccessible to it.

Wile[4] reports that the bromide ion displaces the chloride ion in the body, for the ingestion of bromides leads to the rapid elimination of chlorides and a consequent deficiency of the latter ion. This is exactly what one would expect, upon taking into account the fact that the bromide ion is more strongly adsorbed by protein sols than the chloride ion. Bernouilli[5] understood such a situation as this, for he maintains that the theory of chloride poverty is insufficient to explain the action of alkali bromides. Salts of hydrobromic acid cause a change in the colloidal material of the central nervous system; the bromide ions which take the place of the chloride ions alter the state of aggregation of the cell colloids, probably in the direction of greater swelling, and thus produce a functional change in the nerve cells, according to Bernouilli. Making good use of his knowledge, he injected sulphates and nitrates, with beneficial results, to relieve animals of bromide poisoning.[6] Such an action is exactly what one would expect from the relative positions in the lyotropic series of the three ions concerned.

There are many interesting uses for the bromides of sodium and potassium,[7] i.e., epilepsy, nervous insomnia, delirium tremens, tetanus, iodoform poisoning, strychnine poisoning, morphinism, hysteria, cerebral depressant, nerve sedative, etc. Bancroft and Richter[8] have discussed the action of bromides

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[1] McGuigan: "A Textbook of Pharmacology and Therapeutics," 83 (1928).

[2] Autentrieth: Münch. med. Wochenschr., 65, 33 (1918); Physiol. Abs., 3, 269 (1918).

[3] Vilén: J. Am. Med. Assoc., 87, 2136.

[4] J. Am. Med. Assoc., 89, 340 (1927).

[5] Archiv exp. Path. Pharm., 73, 355 (1914).

[6] Bechhold: "Colloids in Biology and Medicine," 381 (1919).

[7] "Merck's Index," 408, 469 (1930); Hatcher and Eggleston: "Useful Drugs" (1926); MacLeod: Brit. Med. J., 1897, 76; 1899, April 15; 1900, Jan. 20.

[8] J. Phys. Chem., 35, 1611, 1619 (1931).

in iodoform poisoning and epilepsy, indicating that an agglomerated condition of the brain and nerve colloids obtains in these two conditions; sodium bromide then acts to repeptize the affected colloids. In this connection it is interesting to note that Schiff[1] produced epileptic convulsions in dogs by passing an alternating current through the eyes. He then treated the animals, with daily doses of potassium bromide; it required larger amounts of electrical energy to produce the convulsions in the pretreated animals. This result would be easy to predict with the reversible agglomeration theory as a background.

The case of nervous insomnia requires attention because it brings up the question of the apparently paradoxical action of sodium bromide in hastening anesthesia in some cases. Nervous insomnia in all probability involves the condition of stimulation associated with a very slight agglomeration of the protein colloids of certain of the sensory nerves. The administration of sodium bromide would then quiet the patient by virtue of its peptizing action on those colloids; we have already seen that sodium bromide affects the peripheral nerves. Since sleep, in all probability, is intimately concerned with the agglomeration of certain protein colloids in the brain,[2] sodium bromide can not act directly in producing this condition. Sodium bromide, then, aids the onset of sleep by its quieting effect upon slightly stimulated sensory nerves. By the same mechanism it would tend to hurry the unconsciousness produced by an anesthetic, which certainly appears to be due to protein agglomeration. That anesthetics and sodium bromide do not act the same way in inducing sleep or anesthesia is also indicated, indirectly, by the data of Uchida.[3] He showed that narcosis induced by means of ether, chloroform, and morphine decreased the glycogen in the brain 53, 43, and 38% respectively; whereas continued treatment with sodium bromide produced only a slight variation in the amount of glycogen in the brain. Were sodium bromide acting in the same direction as the anesthetics it should produce more of a change in the brain glycogen. The idea[4] that the role of glucose in the body is to maintain the normal state of dispersion of the colloids may be of significance in this connection.

Delirium tremens generally comes on as a result of the continued and excessive use of alcohol, which is known to be an agglomerating agent. That sodium bromide, a peptizing agent, should be of use in the treatment of this condition seems quite obvious. Tetanus has been shown to be associated with coagulation[5] which makes clear the reason why sodium bromide is of use. Strychnine poisoning and morphinism were likewise considered to be attended by reversible agglomeration. Dutton[6] says that if the case of tetanus should require energetic treatment, sodium or potassium bromide may be injected

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[1] Z. ges. exptl. Med., 28, 127 (1922); Chem. Abs., 17, 416 (1923).

[2] Bancroft and Richter: Proc. Nat. Acad. Sci., 17, 295 (1931).

[3] Biochem. Z., 167, 9 (1926).

[4] Nechkovitch: Archiv intern. Physiol., 28, 285 (1927).

[5] Bancroft and Rutzler: J. Phys. Chem., 35, 1185 (1931).

[6] "Intravenous Therapy," 501 (1926).

intravenously. Campo,[1] and Danielewsky and Perichanjanz[2] realize that the bromide ion is antagonistic to strychnine; while Kremers[3] belies the statement that strychnine sulphate and potassium bromide in water solution are incompatible because of the precipitation of strychnine bromide.

The susceptibility of pigeons to convulsions induced by picrotoxin has been materially reduced[4] by feeding small quantities of sodium bromide over long periods of time. Here again we are dealing in all probability with the phenomenon of reversible agglomeration.

Dutton[5] lists the symptoms of hypertension of the brain as being: headache, a feeling of fullness in the head, vertigo, disturbances of the special senses, blunted intellect, the sense of painful thought, irritable temper, inability to concentrate the mind, and hallucinations. Unconsciousness may result from sudden attacks. Active hypertension may result from increased cardiac action, mental excitement, acute alcoholism, sunstroke, surcharge of irritants or toxins in the blood, etc. When the symptoms are brought about by acute alcoholism, sunstroke, or toxins, they are doubtless associated with the agglomeration of certain protein colloids. So, we find that Dutton states that bromides may be administered. Dr. Norman S. Moore of Ithaca has kindly given us[6] two useful bits of information concerning hypertension. The first is that in hypertension there may be traumatic effects in the brain; secondly, in a series of cases in which he has employed sodium rhodanate for the treatment of hypertension, the symptoms were relieved, but the blood pressure was not materially lowered. Mechanical agglomeration of protein sols is a recognized phenomenon,[7] and in some cases it may result from traumatism. The effect of sodium rhodanate in Dr. Moore's cases appears to the authors to be due to the peptization of certain traumatically agglomerated colloids of the brain. This gives us a further reason why bromides should be helpful in hypertension of the brain. Of course, sodium rhodanate should be quite a bit more effective, for it is a much better peptizing agent.

Dutton[8] says that intravenous injections of five to ten cc. of five or ten percent sodium bromide solution in physiological salt solution have been reported to relieve eczema of a nervous origin. Here again reversible agglomeration probably plays an important part, almost certainly in the nervous condition, and perhaps in the eczema itself. A later paper in this series will clear up this latter condition to some extent.

Yanushke and Masslov[9] performing acute experiments, showed that the calcium ion has no effect in relieving the action of convulsive poisons such as

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[1] Physiol. Abs., 12, 308.

[2] Archiv exptl. Path. Pharm., 105, 319 (1925).

[3] J. Am. Pharm. Assoc., 16, 840 (1927).

[4] Meyer-Nobel: Archiv. exptl. Path. Pharm., 130, 365 (1928).

[5] "Intravenous Therapy," 262 (1926).

[6] Private communication.

[7] Heilbrunn: "Colloid Chemistry of Protoplasm"; Marinesco: Kolloid-Z., 11, 207 (1912); III^e Congrès internationale de Neurologie et de Psychiatrie, Gand, 20-26 (1913).

[8] "Intravenous Therapy," 289 (1926).

[9] Z. exptl. Med., 4, 149 (1915); Chem. Abs., 9, 658 (1915).

cocaine, strychnine, and physostigmine. Considering that, at one time or another, cocaine and strychnine have been classed among those things that act by virtue of the reversible agglomeration of protein colloids, one would naturally predict that the calcium ion, which is an agglomerating agent for many protein sols, would not antagonize these compounds. They found, however, that the bromide ion has an antagonistic effect toward cocaine, strychnine, and physostigmine; this is, of course, exactly what one would expect.

In a recent paper the authors[1] called attention to the fact that sodium rhodanate stimulates the respiratory center of animals that are under the influence of "amytal" and morphine. Macht and Hooker[2] add the next three members of the lyotropic series, omitting the chlorate ion, when they conclude that the iodide, bromide, and nitrate ions all exert a stimulating effect on the respiratory center. They point out that this is of interest from the point of view of therapeutics, for the iodides and bromides are employed extensively in pathological respiratory conditions.

The asphyxial form of sunstroke probably should be classified as an indirect narcotic. Sodium or potassium bromide may be used[3] to relieve the delirium which may accompany this form of sunstroke. On page 182, Dutton says that one of the remedies for cerebral toxemia as a late-appearing result of arsenical (arsenicals are agglomerating agents) administration is sodium bromide. On page 221 we find: "Sleeplessness and delirium (in chronic alcoholism) are combatted by sodium bromide (30 grains) alone, or in combination with paraldehyde, 2 to 4 drams. Opiates in any form should be avoided." From our point of view the action of the paraldehyde is opposite to that of sodium bromide. It is most significant that Dutton says that opiates in any form should be avoided, for were they used it would amount to adding the agglomeration action of the opiate to that of the one that originally caused the disorder.

It is interesting to note that the symptoms of acute bromide poisoning,[4] mild collapse, impaired speech, stupor, and paralytic phenomena, bear a certain resemblance to catatonic stupor, which has been classed[5] as insanity due to the over-peptization of certain of the protein colloids of the brain.

Needless to state, these data on the action of the bromide ion in combatting a variety of nervous disorders class it as a drug which acts largely by peptizing reversibly agglomerated colloids.

3. The Iodide Ion

Asthma, arteriosclerosis, aneurisms, dyspnea, lead poisoning, and neuralgia are a few of the conditions that the alkali iodides may relieve.[6] McGuigan

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[1] Bancroft and Rutzler: J. Phys. Chem., 35, 1185 (1931).

[2] J. Pharmacol., 11, 63 (1918).

[3] Dutton: "Intravenous Therapy," 477 (1926).

[4] Sollmann: "A Manuel of Pharmacology," 689 (1917).

[5] Bancroft and Richter: Proc. Nat. Acad. Sci., 17, 294 (1931).

[6] "Merck's Index," 414 (1930); McGuigan: "A Textbook of Pharmacology and Therapeutics," 92 (1928).

says: "No benefit is to be expected from the iodides in degenerative conditions of the central nervous system such as locomotor ataxia except possibly in the earlier stages of the disorder. It may stop the progress of the disease, but it cannot repair the damage done to the nervous tissue." According to this author the alkali iodides are perhaps the standard remedy in the treatment of asthma, which is often a protein disturbance. Loewy[1] and Geyer[2] obtained very good results in treating asthma by the intravenous administration of sodium iodide. This falls in line with the fact that sodium rhodanate, a better peptizing agent, prevents mild anaphylactic shock.

Kehoe[3] has made some interesting observations concerning the use of iodides and rhodanates in heavy metal poisoning. He says that the rhodanates and iodides are more effective than the corresponding chlorides in reversing the coagulation of gelatin which is caused by heavy metal salts. Also, as one would expect, the rhodanate ion and the iodide can entirely prevent the coagulation by heavy metals. Kehoe says that the administration of alkalies and iodides or rhodanates may be of clinical value in lead and mercury poisoning, their action being to peptize certain of the body proteins that have become agglomerated as a result of the action of the heavy metal ions. He thus takes a significant step in the right direction. There seems to be some feeling that the alkali iodides react with the lead or mercury present in the body in cases of poisoning by these metals. That is not good chemistry and there is the statement in the literature of pharmacology that there is no evidence that iodides can react chemically with lead compounds as they are found in the tissues.[4]

Neuritis, which is an inflammatory condition of a nerve, has been combatted[5] successfully by using two to eight grams of sodium iodide, administered by intravenous injection. In this connection the junior author had an interesting experience. For three days previous to taking several one-gram doses of sodium rhodanate there was a slight neuritis in the right arm at the elbow. After taking two grams of sodium rhodanate in two days the neuritis disappeared and did not return. One can not be sure that the sodium rhodanate was responsible for the disappearance of the neuritis because there was no control experiment.

The symptoms of cerebrospinal meningitis, when the meninges of the brain are involved, are: delirium, stupor, semi-consciousness, etc. Sometimes the disease yields to treatment with potassium iodide and urea hydrochloride.[6] This seems to fall into line with the reversible agglomeration theory.

Campo[7] noted that sodium iodide, if injected soon enough, will prevent animals from death from strychnine poisoning. Also very important, but

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[1] Am. J. Clin. Med., 28, 305 (1921).

[2] Am. J. Clin. Med., 27, 316 (1920).

[3] J. Lab. Clin. Med., 5, 443 (1920).

[4] Seremin: Archiv exptl. Path. Pharm., 99, 96 (1923).

[5] Stark: Neb. State Med. J., Norfolk, 9, 1 (1924).

[6] Dutton: "Intravenous Therapy," 275 (1926).

[7] Physiol. Abs., 12, 308.

quite to be expected, is the observation[1] that sodium iodide has an antagonistic action to that of morphine.

Certain allergic phenomena fall nicely into line,[2] for the intradermal reaction to tuberculin on guinea pigs disappeared when the animals were given daily injections of one cc. of a 5% solution of potassium iodide. Unfortunately the antagonism was not lasting, for, a week after the injections were stopped, the allergic reaction reappeared and was as strong as it was in the beginning. Jumping from the skin to the heart, perfusion experiments on frogs[3] showed that the heart functions better with iodide and rhodanate mixtures than in Ringer's solution. Then, going to the other end of the lyotropic series, Handovsky showed that with mixtures of sulphates the heart acts very sluggishly, or not at all. The sulphates would tend to act as agglomerating agents, of course.

The lyotropic series plays a rôle in the contractions of surviving arterial strips,[4] for the rhodanate, iodide, and nitrate ions cause contraction, while the acetate, citrate, and tartrate ions cause extension.

The importance of avoiding the use of the potassium ion, when desirous of utilizing the peptizing action of a given anion, is shown admirably by the work of Macht.[5] Using Locke's solution, modified to contain iodides, and working on isolated organs, it was found that the potassium ion relaxed blood vessels and caused pronounced depression of the heart, while the sodium ion stimulated both slightly. The iodide ion was found to be a powerful stimulant for isolated organs; but in intact animals the stimulating effect of this ion was greatly inhibited by what Macht believed to be chemical combination between it and the blood proteins. What he was really dealing with is adsorption. Sodium iodide did not have a depressing effect, because both the sodium ion and the iodide ion are vasoconstrictors and cardiac stimulants. Potassium iodide exhibited the depressing effect of the potassium ion to a marked degree.

There is quite a bit of evidence that the iodide ion within the body is likely to become situated in disturbed areas. McGuigan[6] says: "After ingestion iodides may be found in any of the tissues but are more abundant in necrotic tissue such as tuberculous, syphilitic, and necrotic areas." Potassium iodide makes its way into the cerebrospinal fluid of a normal man[7] shortly after intravenous injection; further, it seems possible that neuro-syphilitic tissue takes up greater quantites of the iodide ion than normal nervous tissue. Carcinoma metastases contained measurable quantities of potassium iodide[8] five and one-half hours after a subcutaneous injection. The interesting thing

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[1] Githens and Meltzer: Proc. Soc. Exp. Biol. Med., **10**, 128 (1914).

[2] Duprez: Compt. rend soc. biol., **89**, 421 (1923).

[3] Handovsky: Archiv exptl. Path. Pharm., **97**, 171 (1923).

[4] Ellinger: Archiv ges. Physiol. (Pflüger's), **211**, 548 (1926).

[5] Bull. Johns Hopkins Hosp., **25**, 278 (1914).

[6] "A Textbook of Pharmacology and Therapeutics," 92 (1928).

[7] Achard and Ribot: Compt. rend. soc. biol., **66**, 916 (1910); Osborne: J. Am. Med. Assoc., **79**, 615 (1922).

[8] von den Velden: Chem. Abs., **7**, 139 (1913).

here is that the organs in which these metastases lay contained no potassium iodide. When dogs are treated[1] with potassium iodide the rate of autolysis of the organs, after death, was greater than in the case of normal dogs. The peptizing action of the iodide ion will account in a large measure for this difference.

The specific effect of the iodide ion upon the thyroid gland probably accounts for its lack of usefulness in combatting conditions where long-continued administration is indicated. The result is that the clinician loses a good peptizing agent. Enough work has been done with the alkali iodides to show that it acts in a manner similar to the corresponding bromides and rhodanates, as it should because of the place that it occupies in the lyotropic series.

4. The Rhodanate Ion

In discussing the rhodanates Sollmann[2] says: "These produce actions resembling the iodides; but their use has not become popular. They are not dissociated into cyanides, and are relatively non-toxic. Their normal occurrence in the saliva is interesting, but without practical significance.

"NaSCN influences the aggregation of colloids in the same way as the iodide ion, being even somewhat more solvent [a better peptizing agent]. This analogy suggested a therapeutic trial. In the limited number of cases in which it has been tested it was found to affect neuroses, arteriosclerosis, and syphilis in a manner analogous to the iodides, being even somewhat stronger. It also hastened the elimination of metals—perhaps by rendering the metal-protein compounds more soluble [in the light of modern colloid chemistry this means that the adsorbed metal ions are displaced to a greater or lesser extent by the strongly adsorbed rhodanate ion with the resultant increase in the degree of dispersion of the affected protein]. It resembles the iodides further in producing coryza, acne, and other symptoms of iodism. Nerking, 1913, reports many disagreeable effects especially in gastric hyperacidity [under which conditions the rhodanate ion probably becomes, in the stomach and upper parts of the alimentary tract, as good a coagulating agent as it is a peptizing agent in a more alkaline solution]. A conspicuous difference from iodides lies in the fact that it does not act on the thyroid gland.

"The earlier authors (Claude Bernard, etc.) considered the rhodanates as relatively non-toxic; and, as mentioned, they have been used therapeutically in gram doses. F. Franz confirms that no cyanide is split off in the animal organism. Intravenously, very large doses, 0.08 gm. per kilogram, produce no toxic symptoms. Even 0.36 gm. per kg. intravenously, produces practically no effect on the circulation or respiration or bile and urine flow. Lodholz described toxic effects from KSCN, which must have been due either to the potassium or to impurities."

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[1] Stookey: Proc. Soc. Exp. Biol. Med., 5, 119 (1908).

[2] "A Manual of Pharmacology," 706 (1917).

As a matter of medical and pharmacological record sodium and potassium rhodanate may be used in the following conditions:[1] arteriosclerosis, urinary gravel, lancinating pains in the tabes, stubborn migraine, sympathetic neuroses, to reduce blood pressure in chronic nephritis and in aortic insufficiency, spasmodic cough, catarrh, dyspnea, and mania. It is evident, especially in the light of the previous papers on the subjects from these laboratories which have been cited several times, that many of these conditions are associated with reversibly agglomerated proteins of the nervous systems. That being the case, and barring other complications we now know that it is perfectly natural that sodium rhodanate should be used, particularly in stubborn migraine, sympathetic neuroses, spasmodic cough, dyspnea, and mania.

Apart from the toxic psychoses mentioned by Borg[2] the rhodanate has a specific toxic action[3] that is not related to the cyanide ion, causing death in convulsions in from four to seven days when administered per os to rabbits in doses from 0.1 to 0.2 gm. per kilogram twice a day. There is a gradual anemia, albuminuria, and urobilinuria before death; following death no histological changes were found. These data need cause no alarm, for on the basis of a man weighing 150 pounds this dose, on the average, would be equivalent to 80 to 140 grams of sodium rhodanate during four or seven days, which is quite a lot of medicine no matter what its chemical composition. Takacs[4] reports that the intravenous injection of sodium rhodanate increases the leucocyte count, increases gastric secretion and gastric motility, slows the heart rate, and lowers the blood pressure.

It is common knowledge that the saliva and the urine contain small amounts of rhodanate ions: under normal conditions the stomach contains a minute amount of rhodanic acid.[5] A consideration of the rôle played by the rhodanate ion in regulating the particle size of the protein colloids in the living organism, particularly the human body, is indeed an inviting thesis; for instance, in pellagra the rhodanate content of the saliva and the urine is diminished,[6] returning to a higher level after the ravages of the disease have passed.

Aliphatic rhodanates have characteristic pharmacological effects[7] consisting of convulsions, fall in body temperature, and respiratory stimulation, all of which are due to their central action. When a double bond is present in the aliphatic part, the compounds are inactive presumably because they are readily decomposed in the body; they still act as local irritants, however. Aniline rhodanates are hematoxic. It was found that in general these salts are not analogous pharmacologically to the corresponding halogen derivatives.

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[1] "Merck's Index," 420, 486 (1930).

[2] Minnesota Medicine, 13, 281 (1930).

[3] Taubmann and Heilborn: Archiv exptl. Path. Pharm., 152, 250 (1930).

[4] Z. ges. exptl. Med., 50, 432 (1926).

[5] Nencki: Ber., 28, 1318 (1895).

[6] Sullivan and Dawson: J. Biol. Chem., 45, 473 (1920-21).

[7] Taubmann: Archiv exptl. Path. Pharm., 150, 257 (1930).

Evidently the organic rhodanates therefore are not to play an important rôle in treatments based on this theory of reversible agglomeration; although they are probably more soluble in the lipoids and thus theoretically would penetrate the cell walls more easily.

Small doses of potassium rhodanate administered orally in aqueous solution do not produce any effect[1] for they are absorbed and eliminated quickly. Dogs of ordinary weight can take four or five grams with no effect. If the path of the potassium rhodanate is through the digestive tract it acts as a purgative. Rabuteau also noticed that the subcutaneous injection of potassium rhodanate causes violent pain. The rhodanate ion is not entirely responsible for the pain, for it is produced by all other salts of potassium; sodium rhodanate is a great deal less painful than potassium rhodanate when introduced subcutaneously.

Johnson and Wormall[2] report that small amounts of potassium rhodanate, even such amounts as are in the saliva, have a distinct accelerating influence upon the amylolytic hydrolysis of starch. When the substrate is glycogen or dextrin, the effect of potassium rhodanate was less marked. The hydrolysis of starch caused by plant diastases is accelerated by potassium rhodanate. This work seems to indicate that the rhodanate ion has a definite physiological function. It was found in this laboratory[3] that sodium rhodanate in small amounts is capable of inactivating pepsin *in vitro* as shown by its loss of the power to digest egg albumin. This perhaps accounts in part for the gastric disturbances that sodium rhodanate sometimes brings about.

Early in the game it was thought to be advisable to determine the effect of the oral administration of 1.1 grams of sodium rhodanate, which is about four times the prescribed[4] single dose. Dr. Webb York[5] kindly conducted the experiment upon the junior author. Two hours after a heavy luncheon, when the gastric acidity should be relatively high, blood pressure, pulse, and respiration were determined. Then, a water solution of 1.1 grams of sodium rhodanate was taken orally. Every 20 minutes thereafter, for one hour, measurements of blood pressure, pulse, and respiration were made. The results are given in Table II. The data show that the sodium rhodanate exerted no great effect, the slightly high systolic blood pressure, and rapid pulse were due to a bit of apprehension on the part of the patient, for at that time we

TABLE II

Constant	Blank	20 minutes after NaCNS	40 minutes after NaCNS	60 minutes after NaCNS
Pulse Rate	84	78	78	78
Blood Pressure	140/75	138/75	137/62	130/75
Respiration Rate	12	16	14	14

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[1] Rabuteau: "Éléments de Toxicologie," 543 (1887).

[2] Proc. Leeds Phil. Lit. Soc., Sci. Sect., 1, part VII, 318 (1928).

[3] Unpublished work of George Bancroft.

[4] "Merck's Index," 486 (1930).

[5] Assistant Professor of Hygiene, Cornell University.

were not so fully informed about the action of sodium rhodanate as we are now. The fall in blood pressure during the experiment therefore can not be attributed to the action of the sodium rhodanate; it apparently sustained the pulse rate, however, and had a slight accelerating effect on the respiration. It is unnatural for the patient to have a feeling of hunger in the middle of the afternoon, yet 40 minutes after the sodium rhodanate was taken, a ravenous appetite developed. At no time was there even the slightest feeling of nausea; no gastric discomfort of any kind was noticed. Table III shows qualitatively how the rhodanate ion was eliminated. The test used was the red color produced by adding ferric chloride to the acidified sample. This shows that the sodium rhodanate was practically entirely eliminated in six days.

TABLE III

Time elapsed in hours	1½	3	6	9	18	21	25	29	44	69	93	117	144
Reaction of Saliva	1+	2+	2+	2+	1+	1+	2+			2+		0	
Reaction of Urine	1+	2+	3+	4+	5+	5+		5+	6+	5+	4+	3+	2+

These data suggested that it would be well to check up on the effect of sodium rhodanate on renal function. The phenolsulphonephthalein test[1] was used.[2] A subcutaneous injection of one cc. of a solution (6 mg./cc.) of the dye was made in the deltoid region of the left arm, one hour ten minutes after a breakfast consisting of a fried egg sandwich and a cup of coffee. Five minutes previous to the injection, the subject drank one glass of water. The urine was collected hourly for three consecutive hours, the volume recorded, and the amount of dye determined colorimetrically. Ten hours later the subject was given, by mouth, 1.5 grams of sodium rhodanate in water solution. The effect upon the pulse and respiration are shown in Table IV. Here again, we observe an increase in the rate of respiration, presumably due to peptization in the respiratory center. The sodium rhodanate lowered the pulse rate. After the sodium rhodanate was administered, the patient purposely did not micturate until the next morning, about eight hours later.

TABLE IV

Time in minutes	0	5	25	40
Pulse Rate		67	56	62
Respiration Rate	12		17	16

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[1] Hawk and Bergeim: "Practical Physiological Chemistry," 675 (1926).

[2] The authors wish to take this opportunity to thank Barton F. Hauenstein, M.D., Tompkins County Pathologist, who performed this test, for his help during the progress of the research that we have been carrying out in this field. We also thank B. C. B. for allowing us to have this and other tests performed upon him.

There was no feeling of gastric discomfort. The breakfast, and the hour at which it was eaten, was the same as that of the previous morning. The same amount of time was allowed to elapse between breakfast and the start of the test as on the morning before when the control test was made. The test for renal function was carried out in exactly the same manner as it was on the previous day. Table V contains the data obtained before and after the administration of sodium rhodanate. They show that the renal function of the subject is high, and that it was not in any way disturbed by the sodium rhodanate. Thus, kidney damage is not likely to follow the administration of small amounts of this peptizing agent. As we have already seen, it may be used[1] even in nephritis.

TABLE V

	First Hour	Second Hour	Third Hour	Total
% of Injected Dye eliminated (control)	40	35	20	95
cc. of Urine	170	90	90	350
% of Injected Dye eliminated (after NaCNS)	50	30	15	95
cc. of Urine	120	70	230	420

Dr. Hauenstein performed another experiment which gave rise to several interesting bits of information about the action of sodium rhodanate. A volunteer consumed 190 cc. of alcohol mixed with ginger ale within two hours previous to the start of the experiment Then, during the next hour he was given three one-gram doses of sodium rhodanate in water solution. After the second dose of the peptizing agent the subject was very drowsy and fell asleep upon the least provocation. This is an interesting condition of affairs, for a parallel reaction was observed in the two other cases[2] that were reported. The tendency to sleep was probably not due to the approach of alcohol narcosis, for in each case the sleep lacked the depth of an alcoholic narcosis; and the patients' pulses became slower and stronger, rather than weaker. The action of the sodium rhodanate then is attributable to the quieting of stimulated sensory nerves by its peptizing action, which is followed by sleep due to natural causes plus the effect of the alcohol upon the brain. This argument will gain force as the discussion proceeds.

The third experiment, cited above, further established that sodium rhodanate does not disturb kidney function, for there was no sign of renal irritation. That sodium rhodanate tends to go selectively to disturbed areas seems to be strongly supported by the fact that after taking the medicine,

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[1] "Merck's Index," 420, 486 (1930).

[2] Bancroft and Rutzler: J. Phys. Chem., 35, 1185 (1931).

during the two hours that the patient was under observation, there was no detectable amount of sodium rhodanate in the urine. The previous drinking resulted in diuresis, for the specific gravity of the urine fell from 1.020 to 1.005, and finally to 1.003 during the experiment; so the cause of the absence of sodium rhodanate was not a lack of flow of urine. The patient felt no bad effects at any time as a result of this treatment. At 3:30 in the afternoon, about midway through the experiment, the patient overturned a sphygmotonometer without noticing that he had done so. One hour 20 minutes later the junior author saw him and talked with him; at this time it was not apparent that the patient had been drinking.

Sollman[1] says: "Stimulant doses of alcohol increase the rate and depth of respiration (even in sleep) by reflex and central stimulation. This may aid in the therapeutic use of alcohol as a stimulant. With narcotic doses the respiratory center is depressed." In two of the cases which were treated with sodium rhodanate the narcotic stage, as defined by Sollman, was not reached; while in the third case a few of the symptoms were discernible. It is interesting to note that there was neither vomiting nor other gastric difficulties in any of these three cases.

On page 545 we find: "Somewhat larger doses (45-90 cc. of alcohol for man, diluted) produce at first the same effects followed in an hour or less by decreased amplitude and force of the pulse, with progressive fall of the systolic pressure, and unaltered or rising diastolic pressure." The heart rate generally is increased; but there may be no change if the patient keeps quiet. Even under this circumstance, if the dose is large, the heart rate may increase (this means increasing pulse rate). The blood pressure behaves the same on larger doses as it does on smaller doses. In all three of the cases that have been investigated during the course of this research there was a slight fall in the systolic blood pressure and a small rise of the diastolic blood pres-

TABLE VI

Time from Start of Experiment in Minutes	Pulse Rate Case 1	Pulse Rate Case 2	Pulse Rate Case 3	Respiration Rate Case 1	Respiration Rate Case 2	Respiration Rate Case 3
0	88	76	81	28	13	21
18		76			14	
25			80			18
28	92			14		
36		72			13	
43			74			18
53	86			18		
60			70			18
78		72			16	
85	72		62	16		16
93		70			17	
120			62			18

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[1] "A Manual of Pharmacology," 542 et seq. (1917).

sure, thus checking in with the experiences of others. But, the sodium rhodanate shows an antagonistic effect toward the alcohol in the behavior of the pulse and respiration rates. The data are given in Table VI. The pulse rate fell markedly in two of the three cases, and definitely in the third case. Further, the pulses were strong rather than feeble. These data, being in opposition to the general trend of events after the ingestion of large quantities of alcohol, can safely be accounted for on the basis of the antagonistic action of sodium rhodanate toward alcohol. In the two cases (one and three) in which the alcohol was the most effective, sodium rhodanate caused a decrease in the rate of respiration; in the other case there was a slight increase in the rate of respiration. The facts necessary to explain this increase are at hand. Up to 36 minutes after the start of the experiment the respiration rate was about 13 which is close to normal; this gives rise to the fair assumption that the alcohol was not acting as a stimulant for the respiratory center, although well before that time its intoxicating action was evident. The stimulation due to reversible coagulation may be simulated by the stimulation due to reversible peptization.[1] The increase in rate of respiration in case two is therefore very likely due to the action of the sodium rhodanate alone, since this compound raises the rate of respiration when it is the only medicine ingested, as we have already seen.

The case for the antagonistic action of sodium rhodanate to alcohol now appears to be materially strengthened; that is, alcohol acts to reversibly agglomerate certain protein colloids of the nervous system, and sodium rhodanate repeptizes them.

A young 7.25 kilogram dog was given an intravenous injection[2] of 24 cc. of a 10% solution of sodium rhodanate. About ten minutes after the injection the animal vomited. The heart rate increased somewhat; and the rate of respiration increased almost immediately after the injection. Although it vomited three more times, the dog did not seem to be depressed by this treatment. Two weeks later the same animal was injected intravenously with 30 cc. of a 20% solution of sodium rhodanate. This resulted in vomiting and defecation almost immediately. However, under anesthetics dogs apparently do not vomit when given sodium rhodanate; there is some evidence that suggests that even small doses of alcohol tend to inhibit the vomiting due to sodium rhodanate. All of this points toward the idea that the action of sodium rhodanate on the vomiting center is that of peptization, especially in view of the fact that three-gram doses do not cause any unpleasant gastric sensations when administered to human beings.

Since the first paper of this series was published[3] Dr. H. C. Stephenson has performed an experiment which shows definitely that "nembutal" is antagonized by sodium rhodanate, as the theory demands that all anesthetics

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[1] Bancroft and Rutzler: Proc. Nat. Acad. Sci., 17, 186 (1931).

[2] The authors greatly appreciate the willingness of Dr. H. C. Stephenson, Professor of Materia Medica in the New York State Veterinary College at Cornell University, to help us with this and other experiments.

[3] Bancroft and Rutzler: J. Phys. Chem., 35, 1185 (1931).

should be antagonized to a small or large degree. A Boston bulldog weighing 7.9 kilograms was given an intraperitoneal injection of 3.47 cc. of "nembutal C" which is an experimental liquid preparation circulated, for trial, by the Abbott Laboratories. The solution contained one grain of "nembutal" per cc. The dog was lying down and was slightly "dopey" in 14 minutes; it was unable to walk after 57 minutes. There was only a light anesthesia accompanied by a little excitement. At this time eight cc. of a 10% solution of sodium rhodanate was injected into the femoral vein. The animal immediately became very excited; 12 minutes later the excitement subsided, and the animal was lying limp on the operating table. Four minutes after this condition of affairs set in five cc. more of the 10% solution of sodium rhodanate was injected into the femoral vein. This was done to be doubly certain that the excitement was due to the sodium rhodanate. The dog immediately became very excited again; this time the excitement subsided in eight minutes. If it is not a coincidence, it is interesting that the time of excitation is almost directly proportional to the amount of sodium rhodanate administered.

While it is true that the anesthesia was not deep and that the antagonism of the peptizing agent toward the agglomerating agent was not great, the important thing is that the theory demands that "nembutal" and sodium rhodanate act in opposite manners, and the experiment shows that they are actually antagonistic.

Since the last report[1] the work on anaphylaxis has been checked, using both egg white and horse serum as antigen. The results were the same as those reported before; sodium rhodanate acts as a protecting agent against anaphylaxis, but when mixed with the antigen the anaphylactic reaction is greatly intensified. We are not offering any explanation of the effect of the mixed dose.

Sodium rhodanate, at one end of the lyotropic series, and sodium citrate, at the other end of the series, act in opposite directions in their effect on the water output of rabbits.[2] The theory tells us that these two compounds should either act oppositely, or any given action of one of them should be very much greater than that of the other. Sodium citrate causes a retention of water, while sodium rhodanate increases the elimination of water. Because of its peptizing action one might expect a slight increase in the permeability of the kidneys as a result of the continued use of sodium rhodanate.

5. Ephedrine

Dr. G. H. A. Clowes says[3] that sodium rhodanate brings dogs out of "sodium amytal" anesthesia more rapidly than they would normally recover consciousnesss, but that ephedrine is more efficacious than sodium rhodanate in this respect. This fact might appear to create a dilemma that would

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[1] Bancroft and Rutzler: J. Phys. Chem., 35, 1185 (1931).

[2] Moraczewski: Compt. rend. soc. biol., 91, 702 (1924).

[3] Private communication.

give rise to an embarrassing situation. However, if the reversible agglomeration theory of anesthesia is correct and accounts for the facts, the best way out is for ephedrine to be a peptizing agent for proteins.

The general method of experimentation adopted for the study of the colloid chemistry of the nervous systems gives us the means by which such a thing as ephedrine can be classified. A 2% egg white sol was prepared using dried egg white and distilled water. The sol was filtered in order to take out the coarser particles. Small test tubes were prepared by sealing over one end of a number of short pieces of seven-millimeter glass tubing. Exactly 0.0040 gram of ephedrine sulphate was weighed into one of these tubes, 0.0206 gram into another, and 0.018 gram of sodium rhodanate into a third. Using a pipette, 0.7 cc. of the cloudy egg white sol was placed in each of the three tubes; a fourth tube was prepared into which was placed only the egg white sol. The contents of each tube were thoroughly mixed by closing the open end and inverting them several times. Ten minutes after these sols were prepared the least turbid (most peptized) one was that which contained the sodium rhodanate; the difference in turbidity between this system and the one containing the larger amount of ephedrine sulphate was slight. The tube containing the smaller amount of ephedrine sulphate was indistinguishable from the blank. A few hours later the general situation was the same, except that the smaller amount of ephedrine had peptized the protein slightly, as was evidenced by the fact that it was not quite so turbid as the blank. The amounts of ephedrine (in the tube containing the larger quantity) and of sodium rhodanate were tripled; there was very little, if any, change in the turbidity of the two sols which were almost clear before adding more of the two peptizing agents.

Since the system containing the larger amount of ephedrine sulphate cleared up almost as much as that containing sodium rhodanate, and the amounts of the two reagents were about the optimum quantities, an interesting comparison can be made between the two. The system containing the sodium rhodanate was 0.308 molar in respect to that salt; whereas, the system with the ephedrine sulphate in it was only 0.068 molar. Allowing in a rough manner for the difference in turbidity of the two sols, ephedrine sulphate appears to be approximately four times as powerful a peptizing agent as is sodium rhodanate. It is not inconceivable that upon other protein substrates ephedrine might have a slightly greater or a slightly lesser peptizing action than it does on albumin. Differences are to be expected, but qualitatively the action should be one of peptization of proteins in general.

There is further evidence that ephedrine peptizes reversibly agglomerated proteins of the nervous systems. The bronchial spasm produced by injecting peptone into the body is promptly stopped by injecting ephedrine.[1] Likewise, ephedrine is useful in treating severe and recurrent bronchial asthma[2]. Althausen and Schumacher report[3] that, as one would expect, hay fever and

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[1] Kreitmair: Klin. Wochenschr., 5, 2403 (1926).

[2] McDermot: Can. Med. Assoc. J., 16, 422 (1926).

[3] Archiv Int. Med., 40, 851 (1927).

asthma are relieved by ephedrine. In view of the action of sodium rhodanate on the vomiting center, it is interesting to note that these men found that vomiting occurred in 30% of the cases when ephedrine was used. Another symptom that they noticed was insomnia. Having postulated that sleep is on the agglomeration side, it is quite easy to see that ephedrine, by virtue of being an excellent peptizing agent, prevents sleep by keeping certain colloids in the brain from becoming agglomerated. Clowes[1] recommends ephedrine sulphate and caffeine sodium benzoate to antidote the long post-operative sleep due to "sodium amytal."

From what we now know, ephedrine, in the living organism, should peptize proteins more efficiently than an inorganic salt, all other things being equal, because it is almost undoubtedly more soluble in the lipoids than inorganic salts. That in turn means that it can get to the proteins more readily to exert its peptizing action than can sodium rhodanate, for instance. In bringing ephedrine into the fold, the capacity of this theory for the unification of what otherwise must be isolated facts is again illustrated strikingly.

The colloid basis is the only one which at the present time can successfully bring under one heading and make clear the reason for the similarity of the medicinal actions of the chlorides, bromides, iodides, rhodanates, ephedrine, and perhaps some other drugs with which we have not dealt up to the present time. Even the small number of things that are pointed out here (no attempt has been made to review the literature completely) as illustrating the likeness of the actions of these drugs should have shown people from the inductive method alone that there was an underlying general principle, and that that principle is the peptization of reversibility agglomerated protein colloids of the nervous systems.

The general conclusions supported by this paper are as follows:

1. The lyotropic series, Claude Bernard's theory of anesthesia, and the action of sodium rhodanate in many disorders of the nervous systems have provided a background which justifies the therapeutic classification of the alkali chlorides, bromides, iodides, and rhodanates as a single group.
2. This group of drugs acts, in the main, by virtue of the peptization of reversibly agglomerated proteins of the nervous systems.
3. Numerous examples of the therapeutic action of these compounds are discussed in order to show the close relationship between them.
4. Henceforth the German of thiocyanate, rhodanate, will be used in order to avoid the confusion that sometimes occurs between thiocyanate, thiosulphate, and cyanide.
5. Potassium salts should not be used therapeutically unless the specific action of the potassium ion is desired. The toxicity of the potassium ion is again pointed out.
6. Sodium rhodanate is comparatively non-toxic.
7. Sodium rhodanate raises the rate of respiration slightly when administered in sufficient quantities to human beings and dogs; this appears to be due to the over-peptization of the colloids of the respiratory center.

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[1] Clowes et al: Proc. Soc. Exp. Biol. Med., 26, 399 (1929).

8. Sodium rhodanate apparently does not disturb the renal function.

9. Alcohol is very definitely antagonized by sodium rhodanate, as shown by work on human beings.

10. Injections of large amounts of sodium rhodanate apparently cause vomiting as a result of the over-peptization of the colloids of the vomiting center.

11. Sodium rhodanate tends to go selectively to partially agglomerated areas for there is a delay in the excretion of the compound when a person is under the influence of alcohol.

12. People under the influence of alcohol go to sleep when given large doses of sodium rhodanate, because the peptizing agent quiets the sensory nerves; at the same time reversible agglomeration occurs in the brain as in sleep.

13. "Nembutal" is definitely antagonized by sodium rhodanate, as it should be.

14. Further experiments support the view that sodium rhodanate counteracts weak anaphylactic shock.

15. Ephedrine brings dogs out of "sodium amytal" anesthesia better than sodium rhodanate does.

16. The peptizing action of ephedrine on albumin is very strong.

17. Ephedrine is about four times as powerful a peptizing agent for albumin as sodium rhodanate.

18. Clinical evidence suggests that ephedrine acts in many cases by virtue of its peptizing action.

Cornell University.

GLASS ELECTRODE DETERMINATION OF SODIUM IN NaCl-KCl MIXTURES*

BY FRANK URBAN AND ALEXANDER STEINER

It has been shown by Horovitz[1] and Schiller[2] that a glass electrode can also function as a Na, K, Zn, or Ag electrode. In the presence of more than one ion, a mixed electrode potential is obtained, which, according to Michaelis and Fujita,[3] and Horovitz,[4] may be represented by the equation

$$E = \frac{RT}{F} \ln \sqrt{\frac{\Sigma \alpha_{ik} c_{ik}}{\Sigma \alpha_{ia} c_{ia}}} \tag{1}$$

where c_{ik} and c_{ia} indicate concentrations of cation and anion of salt i; α_{ik} and α_{ia} distribution coefficients of the cation and anion of salt i.

In our studies of mixtures of NaOH, NaCl and KCl, we kept KCl and NaCl constant in a given series of mixtures and varied NaOH only. It was found that log c_{Na} plotted against E always gave a straight line. Moreover, a change in c_{KCl} caused a parallel displacement of this straight line.

We attempted to derive this straight line from the Michaelis-Horovitz equation. For alkaline solutions containing NaOH, NaCl and KCl:

$$E = \frac{RT}{F} \ln \sqrt{\frac{\alpha_{Na} c_{Na} + \alpha_K c_K}{\alpha_{OH} c_{OH} + \alpha_{Cl} c_{Cl}}} \tag{2}$$

In studying a series of mixtures of NaCl and NaOH, such that the sum of $c_{NaCl} + c_{NaOH}$ was kept constant, we observed that the glass electrode potential remained nearly constant. The following mixtures were used:

M NaOH	+	M NaCl	=	Mols per liter
.233		2.096		2.329
.466		1.863		2.329
.932		1.397		2.329
1.864		0.465		2.329
2.329		—		2.329

On the basis of this observation, it may be permissible to put $\alpha_{OH} = \alpha_{Cl}$. By substitution in (2)

$$E = \frac{RT}{F} \ln \sqrt{\frac{\alpha_{Na} c_{Na} + \alpha_K c_K}{\alpha_{OH,Cl} (c_{OH} + c_{Cl})}} \tag{3}$$

But $c_{OH} + c_{Cl} = c_{Na} + c_K$. Substituting in (3) and dividing by $\alpha_{OH,Cl}$:

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* From the Laboratory of Biological Chemistry, Washington University School of Medicine, Saint Louis, Missouri.

[1] K. Horovitz: Z. Physik, **15**, 369 (1923).

[2] H. Schiller: Ann. Physik, (4) **74**, 105 (1924).

[3] L. Michaelis and A. Fujita: Z. physik. Chem., **110**, 269 (1924).

[4] K. Horovitz: Z. physik. Chem., **115**, 424 (1925).

$$E = \frac{RT}{F} \ln \sqrt{\frac{\alpha'_{Na} c_{Na} + \alpha'_K c_K}{c_{Na} + c_K}} \tag{4}$$

Neither equation (2) or (4) represent our experimental findings.

The glass[1] used by us had the following composition:

Li	70%
Na_2O	15%
K	very small amount
CaO	6%
$MgO - Al_2O_3 - HBO_3 - Fe_2O_3 - BaO$	9%

The equation proposed by Horovitz[2] for the potential of the glass electrode in alkaline solutions containing Na^+ is:

$$E = \frac{RT}{F} \ln c_{Na} \sqrt{\frac{\alpha_{Na}}{\alpha_{Si} K_{Gl}}} \tag{5}$$

When potassium ions are introduced into such a solution, the Na^+ distribution coefficient α_{Na} changes. If we assume that the number of sodium ions on the surface is in adsorption equilibrium with the number of sodium ions in solution,[3] then, upon the addition of potassium ions to the solution, some of the latter will be driven into the interface, displacing a number of sodium ions. If we apply the adsorption isotherm to this polar adsorption, the number of potassium ions adsorbed (per unit area) will be $k'.c^{1/n}$; and the Na^+ distribution coefficient will now be equal to $\alpha_{Na}(1 - k.c^{1/n})$. The isotherm does not contain a correction for the adsorption of the solvent and, furthermore, it does not hold in concentrated solutions. It is very probable that the true adsorption isotherm shows a pronounced maximum.[4] With these reservations, we substitute the corrected sodium ion distribution coefficient in (5):

$$E = \frac{RT}{F} \ln c_{Na} \sqrt{\frac{\alpha_{Na}(1 - kc^{1/n})}{\alpha_{Si} K_{Gl}}} \text{ or} \tag{6}$$

$$E = \frac{RT}{F} \ln c_{Na} + \frac{RT}{2F} \ln \frac{\alpha_{Na}}{\alpha_{Si} K_{Gl}} + \frac{RT}{2F} \ln(1 - k\,c^{1/n}) \tag{7}$$

It may logically be objected that α_{Na} cannot be independent of c_{Na}, even in solutions in which Na^+ is the only predominant cation. This objection is justified. We found a constancy of α_{Na} between 0.004 and 1.0 M NaOH. Above and below these concentrations, α_{Na} is no longer constant. The theoretical reasons for the constancy of a distribution coefficient have been discussed by Freundlich.[5]

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[1] Glass and analysis by Kimble Glass Co., Vineland, N. J.

[2] Z. physik. Chem., **115**, 424 (1925).

[3] Similar views have been brought forward by B. von Lengyel: Z. physik. Chem., **153A**, 425 (1931); and by K. Lark-Horovitz: Naturwiss., **19**, 397 (1931).

[4] Evans: J. Phys. Chem., **10**, 290 (1906), quoted by Freundlich.

[5] Freundlich: "Kapillarchemie," p. 251 (1931).

Equation (7) is in agreement with our findings. The glass electrode potential, in alkaline solution containing both Na^+ and K^+, is linearly related to log c_{Na}, as long as c_K is kept constant in the mixtures. A change in c_K causes a displacement, the slope 2.303 RT/F = 0.05912 remaining constant. The value of the slope was found to be equal to 0.060 v. (Average of 5 determinations). The term $0.0296 \log_{10} (1 - k\,c^{1/n})$ represents the parallel displacement due to K^+. $0.0296 \log_{10} \frac{\alpha_{Na}}{\alpha_{Si} K_{Gl}}$ represents the intercept, in the absence of K^+.

The linear relationship between E and log c_{Na} can be made the basis for a potentiometric determination of Na in the presence of K. If to an unknown mixture of NaCl and KCl, we add a known amount of NaOH, the potential found satisfies (7).

$$E_1 = m \log (x + c_1) + b \tag{8}$$

x = unknown NaCl (mols), c_1 = NaOH added. For an amount c_2 of NaOH added,

$$E_2 = m \log (x + c_2) + b \tag{9}$$

Subtracting (9) from (8):

$$E_1 - E_2 = m \log \frac{x + c_1}{x + c_2} \tag{10}$$

m being known[1] from a series of calibration determinations, equation (10) may be solved for x.

This can be done conveniently by plotting both $(E_1 - E_2)/m + \log (x + c_2)$, and $\log (x + c_1)$ against x (for various values of x) (Fig. 1). The abscissa representing the intersection of these two curves is the desired value for the unknown amount of NaCl in the original NaCl-KCl mixture.

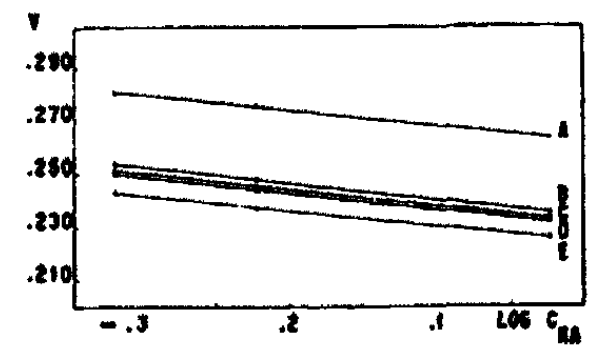

FIG. 1

As a reference electrode, a H_2 electrode was used, mainly for the purpose of eliminating liquid junction potentials. The potentials of the H_2 electrode were calculated from NaOH activity coefficients according to Harned.[2] The small salt error was neglected.

When the E.M.F. of the cell glass electrode-solution-H_2 electrode was plotted against log c_{Na}, parallel straight lines were also obtained.[3] (Fig. 2).

These are more convenient to use for the calculation of x, as the H_2 electrode potential does not have to be calculated. The procedure is the same as before, with the exception that m in (8) and (9) now represents the slope of the line obtained when log Na is plotted against EMF of the whole cell; while E_1 and E_2 represent the EMFs of the cell.

The following mixtures were analyzed in the latter manner.

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[1] The value of m depends on the electrode used; E_1 and E_2 should therefore be determined with the same electrode, which was used for determination of m.

[2] H. S. Harned: J. Am. Chem. Soc., **47**, 682 (1925).

[3] Activity coefficient deviations are apparently within the percentage error of the method.

Mixt.	Mols NaOH	Mols KCl	NaOH found	Error
A	0.25	0.125	0.26	4 %
B	0.25	0.25	0.242	3.3%
C	0.25	0.50	0.247	1.2%
D	0.25	1.00	0.245	2.0%
E	0.25	2.00	0.266	6.4%
			average	3.6%

Sufficient NaOH was added to make c_1 and c_2 0.233 N and 0.698 N respectively. A third point was obtained by adding sufficient NaOH to make c'_2 0.349 N.

The following cell potentials were observed: (Fig. 2).

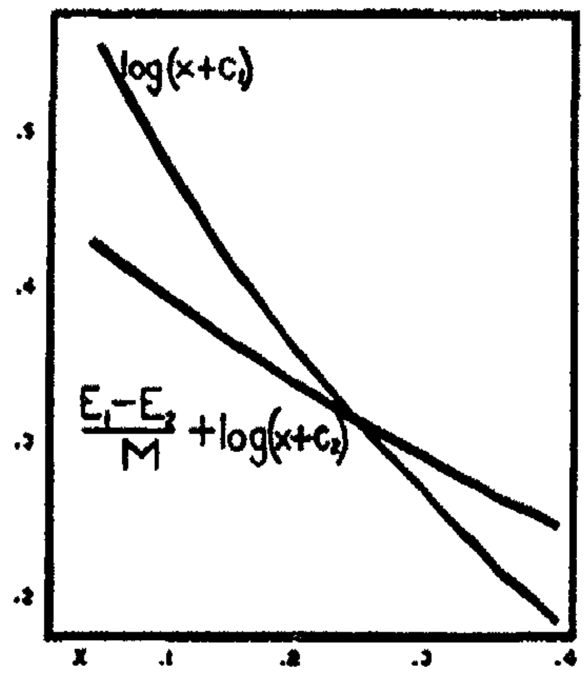

FIG. 2

N NaOH added	$c_1 = 0.233$	$c'_2 = 0.349$	$c_2 = 0.698$
Mixture A	0.5025 0.5025	0.5150 0.5150	0.5440
B	0.5295 0.5291	0.5429 0.5430	0.5720 0.5721
C	0.5320 0.5319	0.5455	0.5745
D	0.5329 0.5330	0.5460 0.5465	0.5770 0.5740
E	0.5402	0.5535	0.5814

Glass electrode potentials calculated form NaOH activity coefficients. (Fig. 3).

NaOH added	$c_1 = 0.233$	$c'_2 = 0.349$	$c_2 = 0.698$
Mixture A	−0.2804	−0.2754	−0.2631
B	−0.2536	−0.2474	−0.2351
C	−0.2509	−0.2449	−0.2326
D	−0.2499	−0.2441	−0.2315
E	−0.2427	−0.2369	−0.2257

Normal H_2 potential = 0.

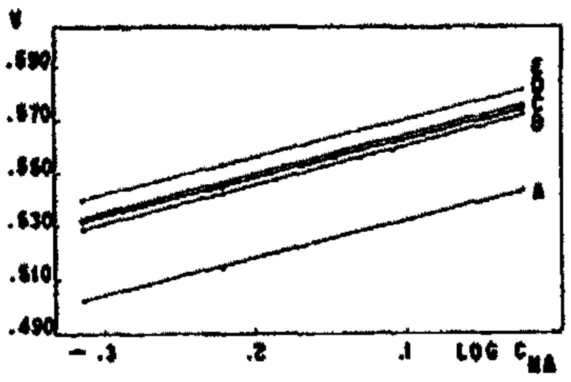

FIG. 3

In order to decrease the percentage error, c_1 and c_2 should be approximately of the order of magnitude of x.

All determinations were carried out in an oil bath at 25°C ± 0.01°. Hydrogen was purified by passing over platinized asbestos at red heat. Solutions were kept under oil during the determination, to protect them from CO_2. Readings were made by connecting electrodes in series with a 5 m.f. condenser to the EMF leads of a Leeds-Northrup type K potentiometer, so that at balance the condenser was unchanged. A $10^{-8.8}$ amp. sensitivity galvanometer was used, 0.2 millivolt giving a detectable deflection.[1] All leads were carefully insulated. As a rule, equilibrium was reached within less than 15 minutes. The glass electrode was of the Haber type, filled with 0.1 HCl; a Ag, AgCl electrode, properly screened from light was used. The ruggedness of this type makes it useful in alkaline solutions.

Summary

(1) A method for the detn. of Na in mixtures of NaCl and KCl by means of the glass electrode has been outlined.

(2) An equation for the mixed electrode potential has been developed.

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[1] G. H. Bishop: Proc. Soc. Expt. Biol. Med., **21**, 260-2 (1930).

EFFECTS OF DISSOLVED SUBSTANCES ON THE SOLUTION TEMPERATURE OF A PHENOL-WATER SYSTEM

BY J. L. CULBERTSON AND E. S. PALMER

Introduction

Since the time of Hofmeister[1] numerous studies have been made of the so-called Hofmeister or lyotropic ion series. Various explanations of the lyotropic action have been offered, the earliest of which was the theory that the different degrees of hydration of the ions was responsible for the varying magnitude of their effects on aqueous systems. Buchner[2] studying gelatin gels concluded that polyhydrol molecules of water had a greater peptizing influence than simple H_2O molecules. Hence the ions would appear to influence the association of water. Gortner and his co-workers[3] extracting protein from wheat flour with potassium halide solutions obtained results which agree with the conclusions of Buchner. Kruyt and Robinson[4] determined the solubilities of quinone, hydroquinone, and various nitroanilines in aqueous inorganic salt solutions. The distinct lyotropic series found for the salts is explained by postulating orientations of several kinds in the neighborhood of the ions and the molecules of the solute. The present investigation was made to determine the effect of dissolved substances on the solution temperature of a phenol-water mixture having a weight ratio of 36:64. Preliminary study of the system by Culbertson and Grafton[5] indicated the probable trend of results of such an investigation. Taylor[6] found that inorganic salt solutions in their effect on the solution temperature of phenol-water systems formed a lyotropic series. The present investigation was initiated for the purpose of studying the effects of a group of dissolved substances on this system over a considerable range of concentrations.

Experimental

Materials. Mallinckrodt C. P. quality phenol was redistilled and both the first and last portions rejected. This purification was deemed sufficiently thorough to permit recovery of the used phenol from the salt containing aqueous solutions by two such fractional distillations.

The salts were used as found in the original containers. The KCl, KI, KNO_3, and KCNS were Mallinckrodt's C. P. quality, the KBr was Merck's C. P. quality, and the K_2SO_4 were Baker's C. P. quality.

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[1] F. Hofmeister: Arch. exp. Path. Pharm., 24, 247-60 (1888).

[2] E. H. Buchner: Rec. trav. chim., 46, 439-44 (1927).

[3] R. A. Gortner, W. F. Hoffman and W. B. Sinclair: Colloid Symposium Monograph, 5, 179-98 (1928).

[4] H. R. Kruyt and C. Robinson: Proc. Koninklijke Akademie van Wetenschappen, Amsterdam, 29, 1244-50 (1926).

[5] J. L. Culbertson and C. M. Grafton: 1927, Unpublished data.

[6] W. W. Taylor: Proc. Roy. Soc., Edinburgh, 49, Pt. 3, 198-209 (1928-29).

The organic acids used, malonic and succinic, were Merck's C. P. quality and were used directly from the original containers.

Apparatus. A test tube large enough to admit a thermometer, the latter graduated to tenths of a degree, and a spiral glass rod for stirring purposes, was immersed 10-12 cm. in a variable temperature bath. Means of slowly heating or cooling the bath under close control were provided. Uniform agitation of the phenol-water system contained in the test tube was found necessary and was provided by imparting a reciprocating motion to the glass spiral by means of an electric motor.

Procedure. In all experimental work the basic phenol-water solution consisted of a 36:64 weight ratio. A quantity of this solution was placed in the inner tube of the apparatus and the solution temperature obtained by slowly heating the bath with continuous agitation of the mixture. Since the solution temperature is determined by observing the change from an opaque to a clear system an arbitrary condition of transparency must be chosen. Such a condition represented by a solution temperature of 65.6°C. was selected as permitting greatest accuracy. Duplicate determinations showed an agreement of ±0.1°.

TABLE I

Salt	KBr		KCl		KI	
	Conc.	Temp. Rise	Conc.	Temp. Rise	Conc.	Temp. Rise
	0.118	0.70°C.	0.114	0.70°C.	0.163	0.65°C.
	0.248	1.15	0.272	1.30	0.252	0.95
	0.509	2.00	0.490	1.50	0.513	1.45
	0.857	2.50	0.751	2.85	0.734	1.90
	1.022	3.50	0.993	3.60	1.009	2.55
	1.884	5.77	1.685	5.86	1.565	3.45
	2.072	6.38	1.975	6.53	2.048	4.40
	4.165	10.46	3.973	11.45	4.023	7.63
	7.894	18.66	7.011	18.41	7.997	13.05
	11.999	26.76	12.070	31.0	16.045	21.95

Salt	KNO_3		K_2SO_4		KCNS	
	Conc.	Temp. Rise	Conc.	Temp. Rise	Conc.	Temp. Rise
	0.131	0.50°C.	0.062	0.45°C.	0.260	0.32°C.
	0.252	0.85	0.125	1.05	0.505	0.50
	0.546	1.50	0.236	1.65	1.063	0.65
	0.751	2.05	0.346	2.10	2.043	0.95
	0.998	2.55	0.519	3.20	4.724	1.15
	1.397	3.15	1.028	5.72	8.229	1.45
	2.253	4.81	2.054	9.72	16.006	1.85
	4.038	7.98	4.008	16.63		
	8.181	13.99	6.002	24.18		
	16.011	25.07	8.020	29.7+		

After the solution temperature of the pure phenol-water system was determined a new mixture was prepared from a known weight of the basic solution and a small weighed quantity of one or more additional substances. The new solution temperature was determined and the temperature rise induced by the added substances was noted.

Results. I. Effect of Dissolved Salts on the Solution Temperature of the basic Phenol-Water System.

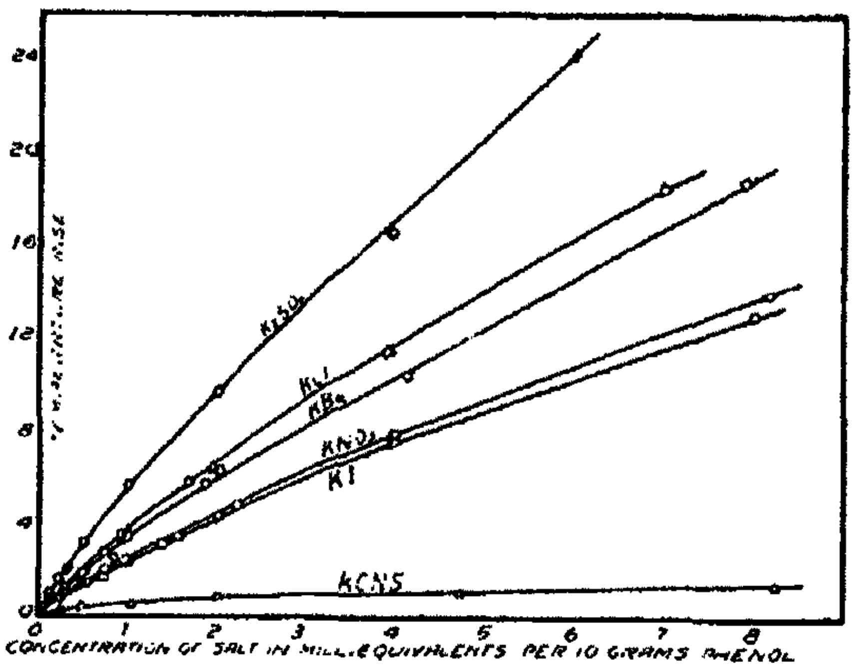

FIG. 1

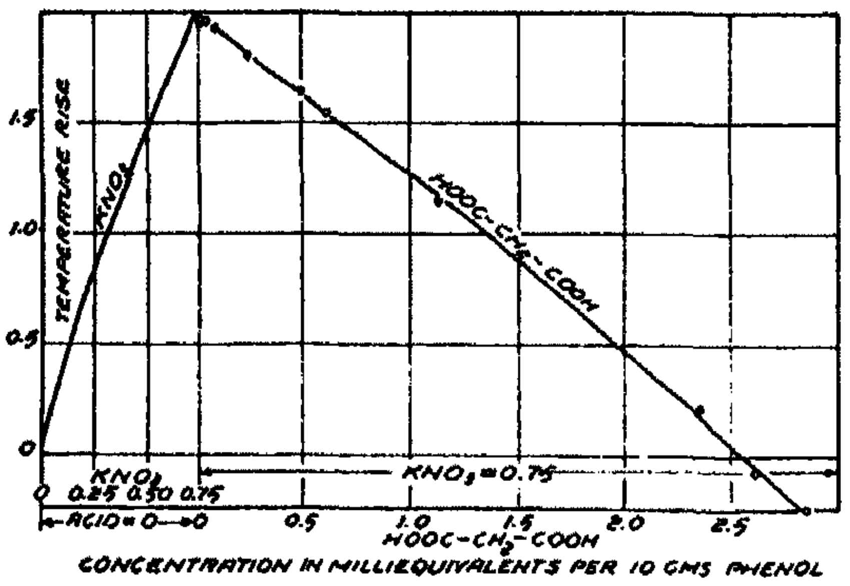

FIG. 2

Six inorganic salts were studied by the methods outlined above. The results obtained are given in Table I.

These data are represented graphically by Fig. 1. Concentrations in all experimental results in this paper are expressed in milliequivalents per 10 grams of phenol. It should be noted that the lower concentrations included in the table are not plotted in the figure because of limitations imposed by the coordinate scales used. It may be mentioned that check runs over several hours time proved that errors resulting from evaporation were negligible.

II. Effect of Malonic and Succinic Acids on the Solution Temperature of a Phenol-Water System.

These data were obtained by adding a definite quantity of a salt (as indicated in the table) to a 36% phenol-water solution and determining the solution

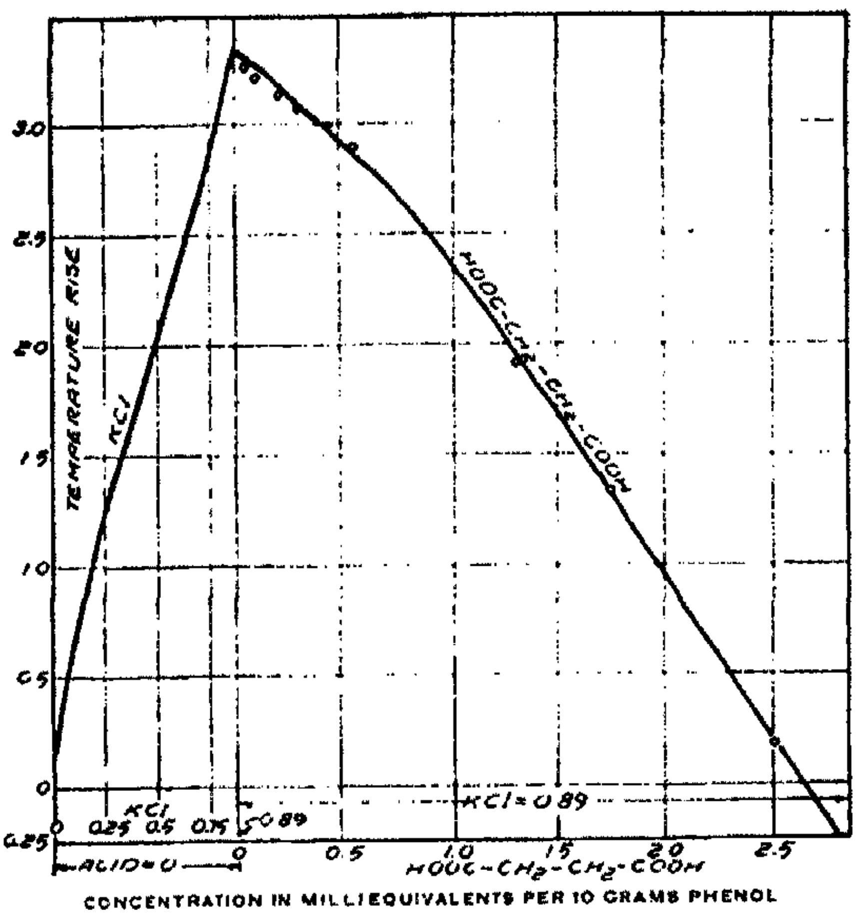

Fig. 3

Table II

Malonic Acid
$HOOC\text{-}CH_2\text{-}COOH$

KNO_3* = 0.750 milliequivalents per 10 grams of phenol throughout

Conc. Acid	Temp. Rise by Acid	Temp. Rise by Acid and Salt
0.0279	−0.04	1.96
0.0796	−0.07	1.93
0.2392	−0.20	1.80
0.5009	−0.36	1.64
0.6360	−0.45	1.55
1.137	−0.85	1.15
2.350	−1.82	0.18
2.614	−2.08	−0.08
2.852	−2.25	−0.25

Succinic Acid
$HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH$

KC_1** = 0.890 milliequivalents per 10 grams of phenol throughout

Conc. Acid	Temp. Rise by Acid	Temp. Rise by Acid and Salt
0.0301	−0.02	3.30
0.0593	−0.06	3.26
0.0758	−0.07	3.25
0.1002	−0.10	3.22
0.2198	−0.18	3.14
0.3177	−0.24	3.08
0.4366	−0.34	2.98
0.5530	−0.42	2.90
1.315	−1.40	1.92
1.764	−1.98	1.34
2.583	−3.14	0.18
3.332	−4.17	−0.85

* The temperature rise of this mixtures was 2.00° before the acid was added.
** The temperature rise of this mixtures was 3.32°.

temperature. A small weighed quantity of one of the organic acids was then added to the solution and the change in the solution temperature was noted. A Beckmann thermometer was substituted for the tenth degree thermometer used in the above work thus giving an accuracy of ±0.05°. The results are tabulated in Table II and illustrated graphically in Figs. 2 and 3. Portions of the curves showing low concentrations of the KCl and KNO_3 are also included for comparative purposes and to aid in locating the origins of the acid curves.

Discussion

Fig. 1 indicates clearly, throughout the concentration range employed, the usual lyotropic anion series, the magnitude of the effect of the separate ions being in the order of $SO_4 > Cl > Br > NO_3 > I > CNS$. Quantitatively the differences between ions are not at all uniform as the results of other investigations of lyotropic action show. Kruyt, in the investigation noted above, attributes the lyotropic action of salts to the orientation of water molecules around the ion, together with the undoubted differences in degree of hydration of the ions. It is our desire to correlate the effects of this series of ions with an additional property of such systems and for this purpose we have determined the effects of the malonic and succinic acids on two of the phenol-water-salt systems. As shown in Fig. 2 the malonic acid was added to a phenol-water-potassium nitrate mixture whose solution temperature was 2.0°C. above that of the standard phenol-water system. Similarly the succinic acid was added to a phenol-water-potassium chloride mixture whose solution temperature was 3.32°C above that of the standard mixture. (See Fig. 3). With increasing concentration of the acid in each case the solution temperature is lowered until within the concentration ranges employed it drops below the solution temperature of the standard mixture.

In the interpretation of these results, attention is called to the values of the surface tensions of the aqueous solutions of the salts and acids used. These values are shown in Fig. 4. Those for the salt solutions were taken from International Critical Tables[1] while those for the acids are due to King and Wampler.[2]

It would appear that a proper interpretation of the surface tension values should also be capable of application to the solution temperature effects noted. The orientation of water molecules in itself cannot account for the increased surface tension of the salt solutions, for orientation when it occurs must of necessity tend to reduce surface tension. This does not however indicate that water molecules cannot be oriented by the ions present for the ions due to their polar character would be expected to enhance surface energy values. The increase however would be minimized by any orientation which occurs. The organic acids being less polar in character than water itself

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[1] International Crit. Tables, 4, 466.

[2] H. H. King and R. W. Wampler: J. Am. Chem. Soc., 44, 1894-1902 (1922).

Note: Concentrations are expressed in terms of molal values in the article to which reference is made. In Fig. 4, they are plotted as molar concentrations. The resultant error does not change the general relationships.

cause lowered surface tensions in their solutions. These relations are qualitatively in agreement with the effects of the dissolved substances on the solution temperatures.

According to Harkins[1] when two highly immiscible phases are in contact the interfacial tension is high. Lower interfacial tensions accompany greater mutual solubility. It is no doubt permissible in this case to assume that the salts which increase the surface tension of the water phase-air interface also increase the water phase-phenol phase interfacial tensions and that the organic acids decrease this interfacial tension. We would then conclude from the results of the present investigation that the solution temperatures of the aqueous solution-phenol systems are in direct dependence upon the surface tensions of the aqueous solutions involved. It does not follow however that solubilities and therefore interfacial relationships in such cases may always be predicted from free surface tensions. Illustrating this point in the field of colloidal solutions is the fact that casein is made more soluble in water by the presence of the iodide ion. Following the ideas of Kruyt[2] we would conclude

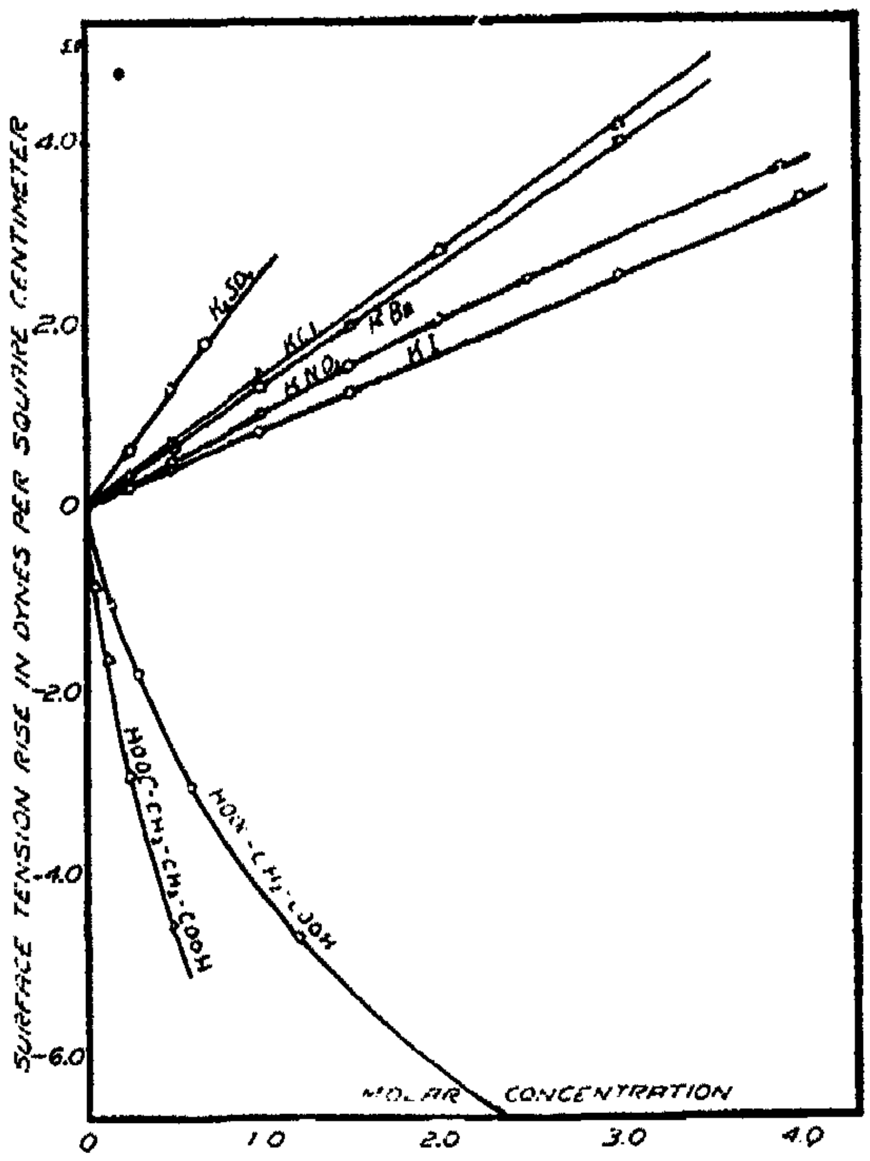

FIG. 4

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[1] W. D. Harkins, F. E. Brown and E. C. H. Davies: J. Am. Chem. Soc., 39, 354, 541 (1917).

[2] H. R. Kruyt: "Colloids," translated by H. S. van Klooster, 2nd Ed., p. 258.

that in such cases the nature of the orientation of the water molecules is such that interfacial energies are lowered by the presence of the ion in spite of free surface tensions that are higher than that of water. We propose to study the interfacial tensions of the water-phenol and other systems in order to test the relationships suggested here.

Summary

1. The effect of a number of dissolved substances upon the solution temperature of a phenol-water system has been determined.

2. The relationship of these values to the surface tensions of the aqueous solutions is noted and an interpretation suggested.

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THE FREE ELECTRICAL CHARGES ON DROPLETS OF INSOLUBLE LIQUIDS IN WATER

BY ROBERT DUBOIS AND ALEX H. ROBERTS

Using a null-point method for measuring the free electrical charges on coarse suspensions in liquid media, McBain and Williams[1] obtained results indicating that the number of charges on air bubbles and benzene droplets suspended in dilute, aqueous cetyl sulphonic acid solutions was only about 1/100,000th the number which would be produced by the electrolytic dissociation of all the molecules in a close-packed, monomolecular layer of cetyl sulphonic acid covering the interface. On the other hand, measurements of the "surface conductivity" of thin films of stearic acid on water led McBain and Peaker[2] to the conclusion that if the increased electrical conductivity near the surface can be ascribed to the presence of free, mobile hydrogen ions dissociated from the insoluble fatty acid layer, then about one-seventh of the close-packed monomolecular film consists of fatty acid ions instead of molecules*.

The discrepancy in the magnitudes of the surface charges on these two similar interfaces, as determined by the different types of experiment, is of the order of 10,000-fold. Similar large discrepancies (100-fold to 100,000-fold) were found by Usher[3] for the charges on suspended gamboge particles measured by several independent methods. In view of these conflicting conclusions the writers undertook to apply the method of McBain and Williams to other liquid-liquid interfaces and to make a critical study of the method and of the factors influencing the apparent surface charge density on small drops. The first experiments were especially directed toward the determination of the apparent charge at a stearic acid-water interface for direct comparison with the results deduced from surface conductivity data.

I. Experiments With Vertical Electrical Field

In order to measure the free electrical charge on small drops by the null-point method, a large number of droplets of some insoluble liquid are generated in water (or other medium) and a single one of these is observed through a telescope as it moves up or down between two electrodes connected to a source of direct current. The natural tendency of the drop to rise or fall because of the difference in density of the two liquids is balanced by a counter-electromotive force until the drop remains stationary in the field of observation. The total free charge, e, on the drop is then calculated by equating the electrical pull, F, on the drop and the gravitational force, F_g, acting in the oppo-

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* In a communication to the Bunsen Gesellschaft (May, 1931) McBain and DuBois show that part of the observed surface conductivity must be contributed by the fixed charge on the film itself. The revised calculations give a smaller fraction of dissociated fatty acid ions in the film but do not change the order of magnitude of the free charge.

site direction. The value of F_g can be determined by measuring the vertical velocity, V, with which the drop rises under the influence of gravity alone and applying Stokes' law in the form

$$F_g = 6\pi r \eta V. \qquad (1)$$

The radius of the drop, r, may be calculated by use of the Stokes formula,.

$$r^2 = \frac{9}{2} \frac{\eta V}{(s-s')g}, \qquad (2)$$

where η is the viscosity of the medium, s and s′ are the densities of medium and drop respectively, and g is the gravitational constant. The values of r thus determined in our work were confirmed by a few direct measurements with a telescope fitted with a pair of parallel, adjustable cross hairs and a micrometer eyepiece with calibrated scale.

The electrical force due to a field of strength, X, acting on the drop is Xe, and, according to our assumptions, at equilibrium,

$$F = Xe = F_g = 6\pi r \eta V, \qquad (3)$$

from which may be calculated the values of e in electrostatic units (or its equivalent, N, the total number of electronic charges on the drop) and the surface density of charge σ (= $N/4\pi r^2$).

We shall call the ratio V/X the mobility of the drop, since, as will be shown later, this is practically identical with the cataphoretic velocity of the drop in a horizontal electrical field of unit potential gradient.

Apparatus. A form of apparatus was developed (Fig. 1) which made it possible to generate the drops in a tube separate from that in which the observations were made but connected to it by tubes just large enough to allow free circulation between the two parts of the apparatus. The cell shown was made of Pyrex and was mounted firmly on a solid concrete bench. The distance between the two platinum electrodes was adjustable and was measured accurately with a travelling microscope. A 150-volt direct-current generator served as a source of potential. The polarity of the electrodes could be reversed instantly and the potential difference between the electrodes could be varied quickly and continuously by the use of three 2000-ohm dial-type potentiometers connected in series.

The region between the electrodes was illuminated obliquely from the rear by a beam of light passing through a system of condensing lenses. A water filter prevented heating effects and convection currents in the liquid being illuminated. The drops moving through the water in this part of the apparatus were observed through a short-focus telescope rigidly mounted and equipped with two adjustable, horizontal cross hairs and a micrometer eyepiece and scale, which was calibrated before use. The telescope was always focussed about midway between the electrodes and in the center of the tube in order to avoid streaming effects near the walls.

The diameter of the vertical tubes was 17 mm., their length 19 cm., the separation of the electrodes 3.00 cm., and the length of the connecting tubes 6 cm.

Procedure. The liquid medium (for most of the work conductivity water of specific conductivity 0.6 to 1.0 × 10^{-6} mho.) was poured into the tubes to a height of a centimeter or two above the upper connecting tube and a few cubic centimeters of the insoluble liquid were added to the "generating tube." A large number of small drops were generated by the use of a glass stirrer rotating at high speed. A swarm of droplets passed through the lower connecting tube to the "observation tube." The stirrer motor was disconnected and the liquid allowed to come to rest. A glass plunger in the upper connecting tube was lowered and served to check circulation of the liquid. Disturbances in the observation tube rapidly disappeared and within a minute all the drops were rising steadily through the water in straight lines.

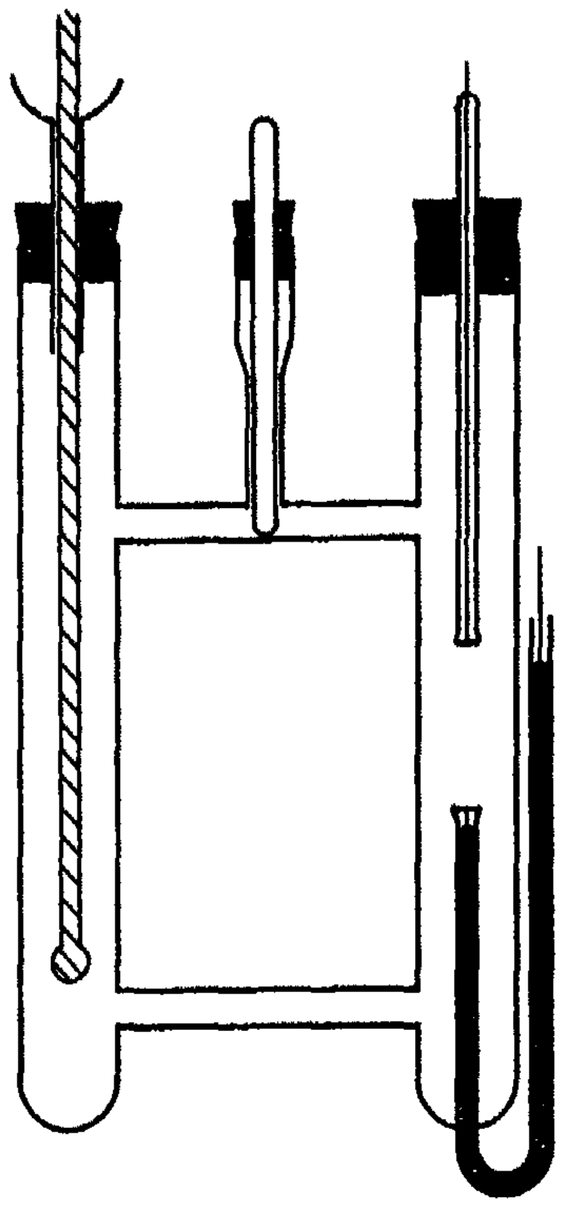
Fig. 1

A known electrical field was then applied. (In all the measurements reported the lower electrode was positive, since the drops in all cases were found to be negatively charged.) Some drops were retarded in their upward motion, some were reversed, while others were held motionless. One of these stationary drops would be selected for observation. The electrical circuit was then opened. The drop immediately rose under the influence of gravity and was timed as it moved between the cross hairs intersecting the field of view. Observations were made on ten to fifteen drops and their mean velocity used in the subsequent calculations. The measurements were repeated with various potential gradients.

The Electrical Charge on Dissociable Interfaces: Fatty Acids in Water. Early experiments with drops of melted stearic acid in water kept at a constant temperature just above the melting point of the fatty acid were abandoned because of persistent and unavoidable convection currents. In order to work at room temperature we have employed as a substitute a saturated solution of stearic acid in pure benzene. Since they contain a polar carboxyl group, fatty acid molecules are probably adsorbed at the surface of the drops to form a complete layer of molecules oriented perpendicular to the surface and with the –COOH groups turned toward the water. We should thus be dealing with an effective stearic acid-water interface.

Observations were also made on drops of oleic acid in water. Table I gives a typical set of readings. Table II summarizes the results obtained with fatty acids in water.

TABLE I

Stearic Acid—Water Interface

D = field intersected by cross hairs = 0.123 cm.
Potential gradient = 25 volts/cm.
A = Reading Number
B = Time of natural rise of droplets through D cm.—in seconds

A	B	A	B	A	B
1	4.1	6	4.8	11	4.4
2	4.6	7	4.8	12	5.2
3	4.6	8	4.7	13	4.2
4	4.5	9	4.4	14	4.8
5	5.2	10	4.4	15	4.6

Mean time 4.62 seconds
Corresponding mean velocity 0.0266 cm./sec.
Radius (taking $\eta = 0.01$, $s = 1.0$, and $s' = 0.875$) 0.00312 cm.
Total drop charge 18.8×10^{-5} e. s. u.
$= 3.94 \times 10^{5}$ electronic charges
Electronic charges per cm.^{2} = 3.21×10^{9}

TABLE II

Oleic Acid and Stearic Acid in Water
(Drops timed over a distance 0.123 cm.)

Material	Potential Gradient X (volts/cm.)	Mobility of drop V/X (cm./sec./volt/cm.) $\times 10^3$	Radius of drop r (cm.) $\times 10^3$	Total drop charge N (electronic charges) $\times 10^{-5}$	Charge Density σ (electronic charges) $\times 10^{-9}$
Oleic acid	8.3	0.76	1.62	1.5	4.4
	16.7	0.75	2.27	2.0	3.1
	25	0.68	2.66	2.1	2.4
	33.3	0.56	2.80	2.3	2.4
Stearic acid	8.3	1.08	1.82	2.4	5.7
	16.7	1.07	2.56	2.2	3.9
	25	1.06	3.12	2.9	3.2

The charges per square centimeter on these two fatty acid surfaces are seen to be of the same magnitude as the number found for cetyl sulphonic acid by McBain and Williams.

The total number of molecules in one square centimeter of a close-packed, monomolecular film is 4×10^{14} in the case of stearic acid (area per molecule taken as 25 sq. A. U.) and 2.3×10^{14} for oleic acid (area taken as 44 sq. A. U.).

For drops of the same size stearic acid appears to carry a 25% greater charge than oleic acid. In each case the number is about 1/10,000th to

1/100,000th that possible for a complete layer of ions. This fraction indicates, therefore, the proportion of the surface covered by free (ionic) charges.

The Electrical Charge on Non-dissociable Interfaces: Tetradecane-Water and Tetrahydronaphthalene-Water. To test whether the observed electrification of the drops was a specific effect attributable to the dissociation of hydrogen ions from the fatty acid molecules, measurements were made on two inert, non-polar hydrocarbons, normal tetradecane and tetrahydronaphthalene. The sample of tetrahydronaphthalene contained impurities which were almost completely removed by steam distillation and washing with conductivity water.

Table III shows the rather surprising result of these experiments; namely, that the number of charges per square centimeter is approximately the same for these inert liquids as for the fatty acids, if drops of the same size are compared. This is more plainly shown in Fig. 5.

TABLE III

Hydrocarbons in Water

Material	Potential Gradient X (volts/cm.)	Mobility of Drop V/X (cm./sec./volt/cm.) $\times 10^2$	Radius of Drop r (cm.) $\times 10^3$	Total Drop Charge N (electronic charges) $\times 10^{-5}$	Charge Density σ (electronic charges) $\times 10^{-9}$
n-Tetradecane	25	0.81	1.99	1.9	3.8
	33.3	0.84	2.34	2.3	3.4
Tetrahydronaphthalene	8.3	0.90	4.26	4.5	2.0
	16.7	0.92	6.10	6.7	1.4
	25	0.78	6.86	6.3	1.1
	33.3	0.75	6.71	6.7	0.9

Effect of Electrolyte on the Apparent Charge. The practical uniformity in the charge carried by the various substances studied suggested an alternative source of the electrification; namely, adsorption of ions from the conductivity water. Large electrokinetic effects are known to occur with minute concentrations of electrolytes. Lachs and Biczyk[4] in streaming potential experiments with glass capillaries in contact with "pure" water found that relatively large contact potentials were produced even with exceedingly small concentrations of dissolved material in the water (0.146 volt for water of specific conductivity 0.72×10^{-6} mho.).

Accordingly drop charges were measured with the same materials suspended in KCl solutions of various concentrations. Stronger solutions than those mentioned below could not be used because of the sweeping through the field of large gas bubbles liberated at the electrodes by electrolysis. From the results, as shown in Table IV and Fig. 3, it is seen that the addition of electrolyte to water has increased the electrical charges on the drops and this increase is roughly proportional to the concentration of the added KCl. That this

TABLE IV

Collected Results of Charge Measurements with Vertical Electrical Field

Material	Potential Gradient X (volts/cm.)	Mobility of Drop V/X (cm./sec./volt/cm.) $\times 10^3$	Radius of Drop r cm. $\times 10^3$	Total Drop Charge N (electronic charges) $\times 10^{-5}$	Charge Density σ (electronic charges) $\times 10^{-9}$
Oleic acid	8.3	0.76	1.62	1.5	4.4
	16.7	0.75	2.27	2.0	3.1
	25	0.68	2.66	2.1	2.4
	33.3	0.56	2.80	2.3	2.4
Stearic acid	8.3	1.08	1.82	2.4	5.7
	16.7	1.07	2.56	2.2	3.9
	25	1.06	3.12	2.9	3.2
Stearic acid in 0.00001 N KCl	8.3	1.37	2.04	3.3	6.3
	16.7	1.18	2.68	3.7	4.1
	25	1.14	3.24	4.4	3.3
Stearic acid in 0.0001 N KCl	8.3	2.14	2.56	6.5	7.9
	25	1.58	3.80	7.5	3.9
Tetradecane	25	0.81	1.99	1.9	3.8
	33.3	0.84	2.34	2.3	3.4
Tetradecane in 0.00001 N KCl	25	1.03	2.24	2.7	4.3
Tetrahydronaphthalene	8.3	0.90	4.26	4.5	2.0
	16.7	0.92	6.10	6.7	1.4
	25	0.78	6.86	6.3	1.1
	33.3	0.75	6.71	6.7	0.9

Results of McBain and Williams

(Cetyl sulphonic acid-water interface)

Air bubbles	36.6		1.0	2.0	12.4
Air bubbles	13.3		1.5	2.4	8.3
Benzene drops	36.6		4.1	5.9	2.8

larger charge was actually due to ionic adsorption was demonstrated by the marked decrease in conductivity of the electrolyte solutions shown by independent measurements made before and after the drops of insoluble liquid had passed through them.

Experiments with Reversed Phases: Water in Tetrahydronaphthalene. The apparatus was modified as shown in Fig. 2 to permit its use with the phases reversed, in which case the drops tend to fall through the dispersion medium. Observations were made on drops of water suspended in tetrahydronaphthalene.

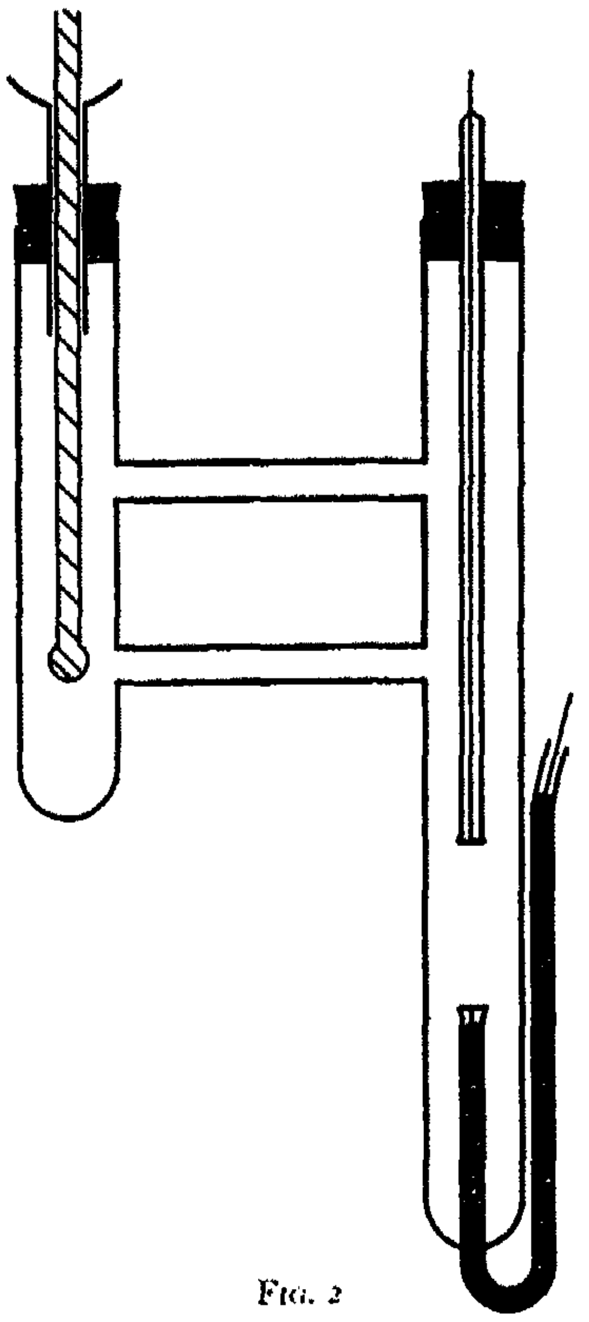

Fig. 2

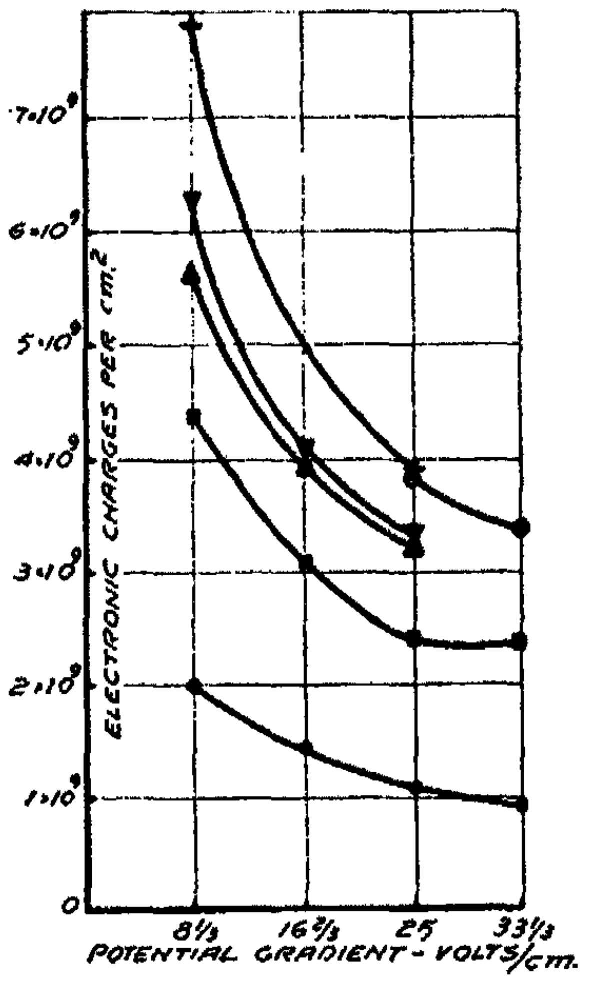

Fig. 3

■ Oleic Acid in Water
▲ Stearic Acid in Water
▼ Stearic Acid in 0.00001 N KCl
\+ Stearic Acid in 0.0001 N KCl
○ n-Tetradecane in Water
● Tetrahydronaphthalene in Water

When potential gradients up to 33 volts/cm. were applied, no effects whatever were produced on the motion of the water drops. The droplets continued to fall with unchanged velocity. This result is in harmony with the view that electrokinetic effects depend on the dissociation of free ions from the interface or from an adsorbed ionic layer at the interface and require an ionizing solvent for the external medium. With water drops in tetrahydronaphthalene the same interface exists as with the phases reversed but with the difference that in the former case both the adsorbed ions giving a charge to the interface and the free ions in the solution compensating this charge are self-contained within the drop and are not relatively displaceable in the electric field.

The Variation in Surface Density of Charge with Radius of Drop. Table IV and Fig. 3 show that the value of the charge density obtained in any series of experiments depends on the potential gradient used, whereas one would expect a constant charge per unit area on drops such as these where the radius of curvature is large compared with molecular size. Now combination of equations 2 and 3 with the formula for charge density,

$$\sigma = e/(4\pi r^2 \times 4.774 \times 10^{-10}), \qquad (4)$$

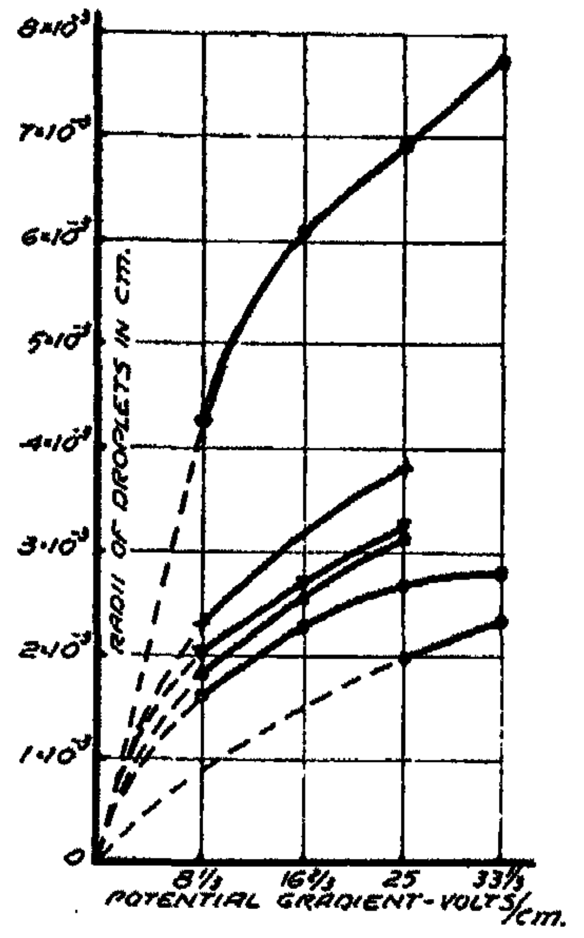

Fig. 4

- ■ Oleic Acid in Water
- ▲ Stearic Acid in Water
- ▼ Stearic Acid in 0.00001 N KCl
- \+ Stearic Acid in 0.0001 N KCl
- ○ n-Tetradecane in Water
- ● Tetrahydronaphthalene in Water

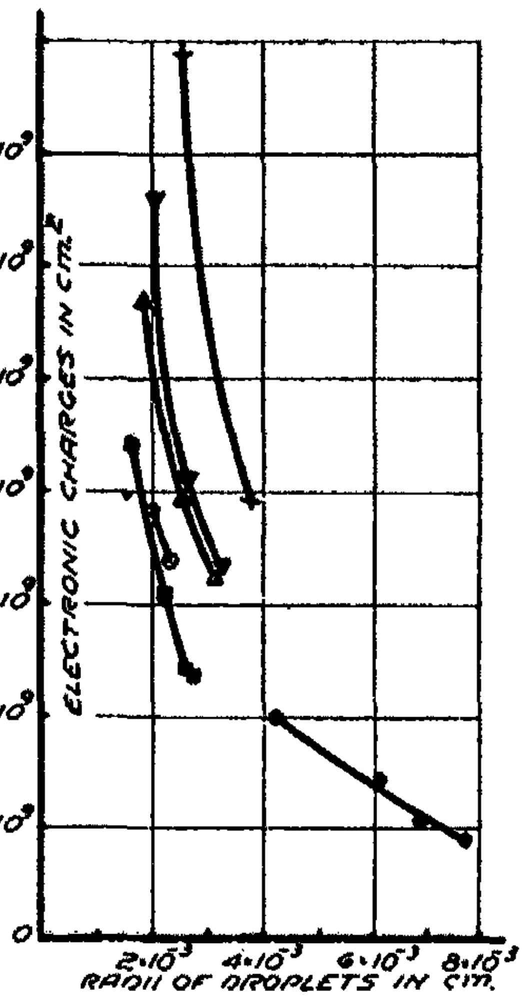

Fig. 5

- ■ Oleic Acid in Water
- ▲ Stearic Acid in Water
- ▼ Stearic Acid in 0.00001 N KCl
- \+ Stearic Acid in 0.0001 N KCl
- ○ n-Tetradecane in Water
- ● Tetrahydronaphthalene in Water

leads to the conclusion that the radii of drops just balanced by the electric fields should be directly proportional to the potential gradients, if the charge density is constant; that is,

$$r / X = K\sigma \qquad (K = s\text{-}s')\, g/3 \times 4.774 \times 10^{-10}). \qquad (5)$$

The relations experimentally obtained are plotted in Fig. 4 and it is apparent that r/X is actually varying, though the slope of each curve seems to be approaching a constant limiting value with the larger drops, corresponding to a constant, minimum value of the charge per unit area. Potential gradients of the magnitude employed probably do not themselves affect the charge density, but merely select drops of a certain size. The free electrical charge per square centimeter appears, therefore, to be a direct function of the radius of the drop rather than of the field strength.* A hint as to the form of the function is given by the observations of various workers (see the paper of Abramson[5] for an extensive list of references) that the electrical mobilities of very small drops are independent of the size. Equations 6 and 4 show that if V' is independent of r, σ must be a hyperbolic function of the radius. This is consistent with the forms of the curves in Fig. 5, which show a striking increase in the charge densities of the smaller drops.

II. Experiments with Electrical Field perpendicular to the Gravitational Field

McBain and Williams believed that their method must give only minimum values for the electrical charges because the assumptions underlying the calculations do not take account of possible electrosmotic streaming effects due to the migration of ions of opposite sign past the stationary drop. They point out that as a necessary consequence of the Laing formulation[6] of electrical conductivity, there must be a movement of the solvent with respect to any charged particle which is held stationary by mechanical constraint (gravity, in this case). This amounts to superposition on the gravitational force of an additional, frictional force acting on the drop in a direction opposite to that of the electrical field.

It should be possible to evaluate this frictional force, which we shall denote by the symbol F_{eo}, by measuring the cataphoretic velocity of the drops in a horizontal electrical field. The electrical force, Xe, exerted on a drop by a horizontal field of strength X must also be the force exerted in the opposite direction on the ions which have dissociated from the surface of the drop, since the system is electrically neutral. Now when equilibrium is reached the force impelling the droplets or ions through the medium is just balanced by the frictional drag of the medium, and both the droplets and the ions will have attained constant velocities. Since the opposing electrical forces (on drop and ions respectively) are equal, the resulting frictional effect of each on the medium must be the same, so that no resultant motion is imparted to the medium. Stokes' law should therefore be applicable to the migration of the particles or drops and the electrical force determinable from the observed velocity V'.

$$Xe = 6\pi r \eta V' \qquad (6)$$

On the basis of this reasoning equation 3 must be rewritten

$$Xe = F_g + F_{eo}. \qquad (7)$$

If the droplets to which equations 6 and 7 apply have equal radii and the same materials are used, the values of Xe may be equated and the value of the force F_{eo} calculated from the remaining quantities, all of which are known.

Apparatus. In order to make the measurements suggested we made use of the apparatus represented in Fig. 6. The drops were generated as before and

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* Very large gradients might have the effect of displacing adsorbed ions normally held immobile in smaller fields, thus increasing the mobilities of the drops and their charge densities.

observed as they moved in the region between the two electrodes. The arms containing the electrodes were connected by open tubes to the observation tube to prevent the development of back hydrostatic pressure in case electrosmotic currents should be set up. An additional pair of parallel cross hairs was installed in the telescope perpendicular to the original pair, and the width of the field intercepted by them was accurately measured. Vertical and horizontal velocities of a given drop could then be measured simultaneously by the use of two stop-watches.

Procedure and Results. A series of measurements was made with drops of a benzene solution of stearic acid suspended in conductivity water. The freshly formed drops rose steadily upward through the field of view. When the electrical field was applied, the droplets at first moved rapidly in the direction of the positive electrode and then slowed down to constant velocities. About ten to fifteen seconds sufficed for attainment of the steady state. The two forces, gravitational and electrical, were now acting at a right angle to each other, resulting in a diagonal motion of the drops across the rectangular field defined by the cross hairs.

The results of the observations are given in Table V. Column 5 shows the charge density calculated from the horizontal velocity by use of equation 6. Column 6 shows the corresponding value read off the grapn of Fig. 5 for the charge density found on a drop of the same size in the vertical field measurements.

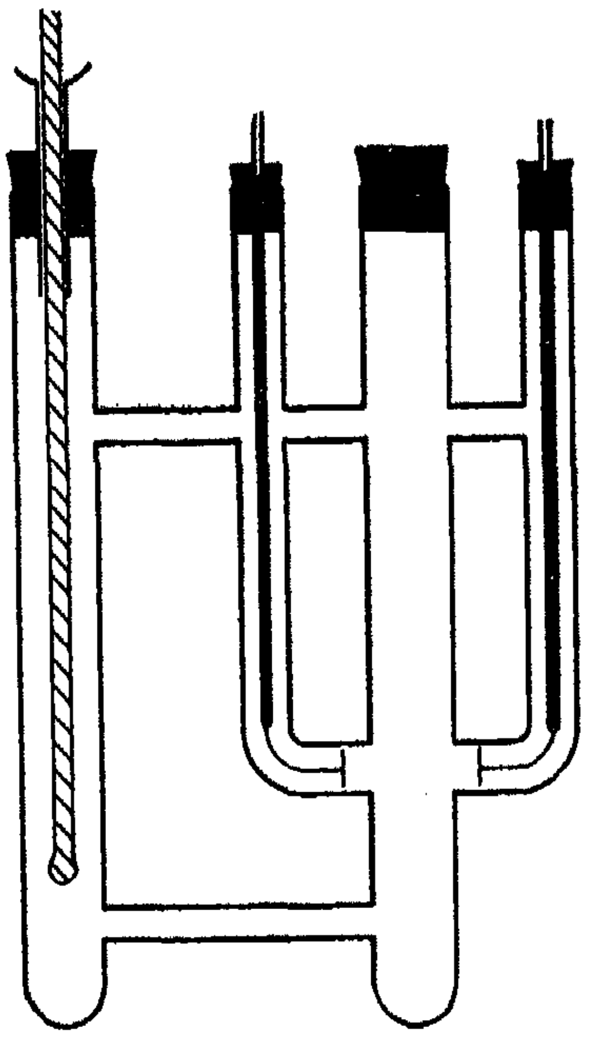

Fig. 6

Table V demonstrates that within the limits of accuracy obtainable in the experiments the charge densities determined by the two methods are practically identical. The null-point method of McBain and Williams is thus shown to be valid for the measurement of the mobilities of charged particles in a liquid medium and therefore constitutes a convenient means of determining cataphoretic velocities.

Whether the drop charges deduced from these experiments are true values, however, is open to question. It has been suggested[1] that the frictional resistance to the motion of the drop through the electrical field may be much greater than that calculated by the Stokes formula used, and a much larger number of electrical charges would be required to account for the velocities measured. This would require replacing the simple formula for frictional resistance by a different function of radius and velocity which would take

TABLE V

Comparison of the Charges measured by Horizontal and by Vertical Electrical Fields

(Stearic acid-Water)

Drops timed through horizontal distance 0.123 cm.
Drops timed through vertical distance 0.128 cm.
Horizontal potential gradient 25 volts/cm.
Distance between electrodes 3 cm.

Drop	Vertical Velocity cm./sec. V	Radius cm. r	Horizontal Velocity cm./sec. V'	Charge Density (hor. field) $\times 10^{-9}$ σ'	Charge Density (vert. field) $\times 10^{-9}$ σ	Ratio σ'/σ
1	0.016	0.0024	0.017	2.7	4.0	0.7
2	0.047	0.0041	0.035	3.3	2.5+	1.3
3	0.016	0.0024	0.023	3.6	4.0	0.9
4	0.015	0.0023	0.036	6.0	4.1	1.5
5	0.024	0.0030	0.026	3.3	3.3	1.0
6	0.021	0.0028	0.017	2.4	4.1	0.6
7	0.023	0.0029	0.022	2.9	3.4	0.8
8	0.016	0.0024	0.017	2.7	4.0	0.7
9	0.019	0.0026	0.028	4.0	3.7	1.1
10	0.018	0.0026	0.026	3.8	3.8	1.0
11	0.016	0.0024	0.013	2.1	4.0	0.7
12	0.019	0.0026	0.018	2.6	3.7	0.7
13	0.029	0.0032	0.028	3.3	3.2	1.0
14	0.051	0.0043	0.041	3.6	2.5+	1.4
15	0.027	0.0031	0.033	4.0	3.2	1.3
16	0.027	0.0032	0.032	3.8	3.2	1.2

Mean ratio σ'/σ = 1.0

account of the distance between the charges of opposite sign which are being displaced relative to each other.

It should be noted that such a substitution would probably alter all the values of the drop charges in the same proportion and would therefore not rob of significance relations discovered between the relative values of the charges on the drops, particularly the similarity in the charges found on interfaces of dissimilar chemical nature.

Summary

1. The null-point method of McBain and Williams has been used to measure the free electrical charges on small drops of various insoluble liquids in water and electrolyte solutions.

2. The charges per square centimeter on fatty acid-water interfaces were found to be 1/100,000th the number possible for a surface completely covered with fatty acid ions.

3. Drops of liquid hydrocarbons in water showed practically the same charge as that found for the fatty acids.

4. The electrical charges were increased by the addition of potassium chloride to the water. Measurements of conductivity showed that adsorption had taken place on the drops.

5. Drops of water in a liquid hydrocarbon were unaffected by an electrical field.

6. Independent measurements of cataphoretic velocity with a horizontal electrical field and the same materials gave values for the charge densities differing but slightly from those obtained by the null-point method.

7. The densities of charge on drops of various sizes were found to increase rapidly with diminishing radius.

References

[1] McBain and Williams: Colloid Symposium Annual, 7, 105 (1930).
[2] McBain and Peaker: Proc. Roy. Soc., **125A**, 394 (1929).
[3] Usher: Trans. Faraday Soc., **21**, 404 (1925).
[4] Lachs and Biczyk: Bull. de l'Académie polonaise des Sciences et des Lettres, A1930 360.
[5] Abramson: J. Phys. Chem., **35**, 289 (1931).
[6] Laing: J. Phys. Chem., **28**, 673 (1924).

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June, 1931.

THE COHERER METHOD OF DETERMINING HEATS OF ADSORPTION*

BY SAMUEL LENHER AND G. HARVEY CAMERON

Introduction

The direct determination of heats of adsorption of gases on solids is of importance in the field of contact catalysis. Heats of adsorption can be calculated from the Clausius-Clapeyron equation applied to adsorption isotherms. This method, however, has all the disadvantages of an indirect calculation. Calorimetric determinations of heats of adsorption have been made by several investigators[1] using finely divided catalysts. While the calorimetric method yields valuable results it is so cumbersome that its application has been limited.

A method of great experimental simplicity for measuring heats of adsorption has recently been described by Palmer.[2] Two loosely touching metallic (or carbon) filaments are caused to cohere by applying a small potential difference across the junction, the resistance of which decreases markedly as a result of the act. Palmer assumes that the action of the coherer is due to the evaporation of an adsorbed film of the gas in which the coherer is immersed and that the heat of adsorption of the gas on the filaments can be computed from the minimum voltage required to cause coherence.

The use of the coherer should present distinct advantages for the investigation of heats of adsorption, for the technique allows only true surface films to play a part in the measurements. Adsorption is assumed to take place on the relatively non-porous surface of a fine metal filament which can be easily heat-treated and which should remain with an unchanged surface activity throughout a series of measurements. The cohering test in vacuum is taken as a test of the cleanness of the surface from the gas studied or from contamination.

Experiment Details

The apparatus (see Fig. 1) was similar to that described by Palmer.[2] The coherer consisted, in most of the work, of tungsten filaments 0.02 mm. in diameter welded to heavier tungsten leads. One of these was sealed into the bulb, F: the other was sealed through a ground glass stopper which permitted adjustment of the contact. The potential was applied by charging the con-

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* Contribution No. 69 from the Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware.

[1] Foresti: Gazz., 53, 487 (1923); Beebe and Taylor: J. Am. Chem. Soc., 46, 43 (1924); Garner and McKie: J. Chem. Soc., 1927, 2451; H. S. Taylor and Kistiakowsky: Z. physik. Chem., 125, 341 (1927); G. B. Taylor, Kistiakowsky and Perry: J. Phys. Chem., 34, 748 (1930); Flosdorf and Kistiakowsky: 39, 1907 (1930); Keyes and Marshall: J. Am. Chem. Soc., 49, 156 (1927); Garner and Kingman: Nature, 126, 352 (1930).

[2] Palmer: Proc. Roy. Soc., 106A, 55 (1924); 110, 133 (1926); 115, 227 (1927); 122, 487 (1929).

denser, C, of 0.0192 microfarads capacity by the potentiometer P and connecting it at once to the coherer. The insulation of the condenser was tested with a Dolezalek electrometer; the loss of charge in one minute was 0.24 per cent at one volt. The chromel-alumel thermocouple, T, at 100-200°C. supplied a small potential to test the junction for coherence.

The bulb was heated with a flame several times while evacuating to remove volatile impurities, and the filaments were heated electrically before each series of measurements. All switches were of the mercury cup type. The apparatus was sufficiently removed from X-ray machines and other sources of electrical disturbance to avoid coherence from effects of this kind.

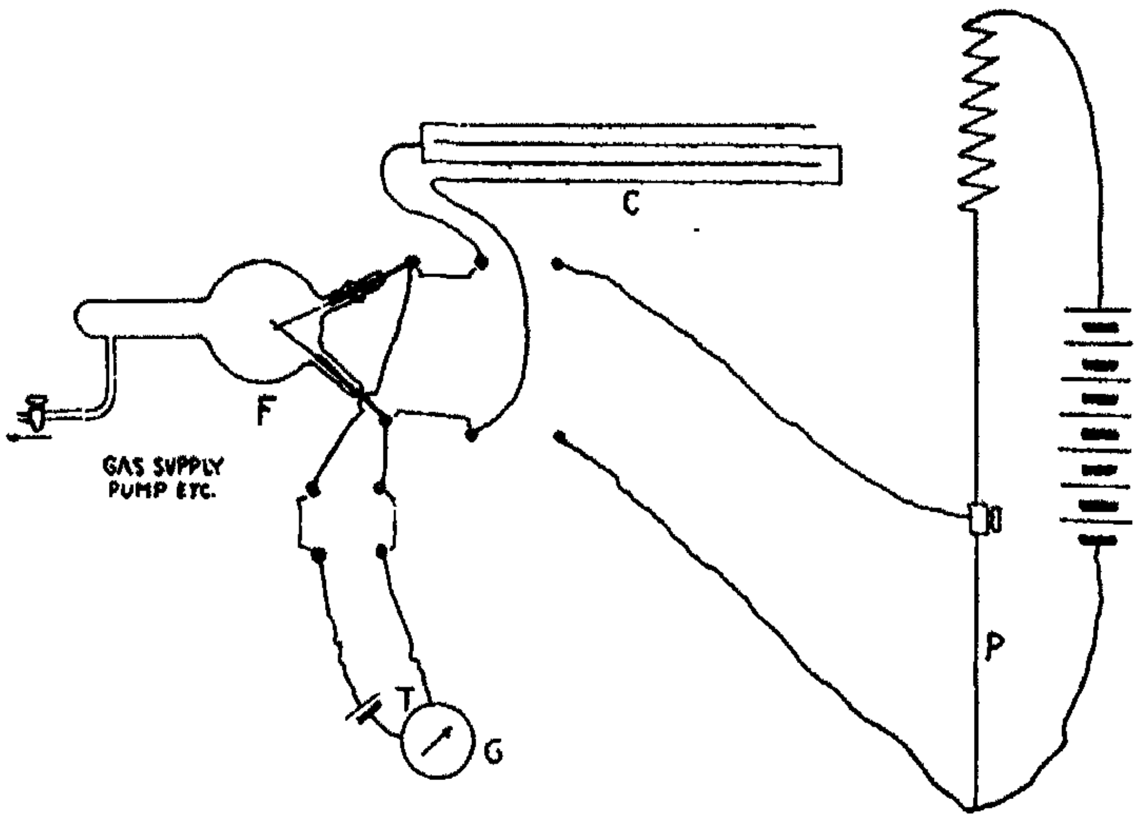

Fig. 1
Coherer Circuit

The bulb was evacuated with a mercury pump; pressures were read on a McLeod gauge and a mercury manometer. The gases used, oxygen, nitrogen, and hydrogen, were taken from commercial cylinders and stored in evacuated bulbs in contact with anhydrous magnesium perchlorate. Nitrogen and hydrogen were freed from oxygen by passing over hot reduced nickel. In some of the experiments a liquid-air trap was attached immediately in front of the bulb F to remove water and mercury vapor.

In spite of careful attention to all the precautions mentioned by Palmer, reproducible cohering voltages could not be obtained. The cohering voltages in vacuum, and at various pressures of nitrogen, hydrogen, and oxygen were equally erratic. For example, in one of a large number of experiments the apparatus was evacuated and hydrogen admitted. The filaments were glowed at a bright red heat. At a pressure of 115 mm. the filaments cohered once out of six times at 1.0 volts and four out of five times at 1.5 volts. The following day, under the same conditions, out of six trials at each voltage they cohered twice at 0.5 volts, once at 2.0, once at 3.0, three times at 6.0, and five times at 7.0 volts. New filaments were put in and glowed out in hydrogen; out of 30 attempts the filaments cohered only three times at voltages between 0.5 and 4.0 volts after which coherence could not be obtained at all even at 16 volts. It was observed several times that a pair of filaments would cohere at a comparatively low voltage but after tapping off would not cohere again until a higher voltage applied. Although a great variety of conditions was tried no reason for the erratic behavior could be found.

Discussion

Even under the most carefully controlled experimental conditions it has been found impossible to obtain reproducible effects, and consequently Palmer's results have not been confirmed. If Palmer's assumed mechanism for the action of the coherer were correct, it should be possible to repeat the operation at a given voltage any number of times provided the surface was not altered by the cohering act. We found, on the other hand, that some factors other than the voltage were instrumental in determining whether coherence occurred or not. In other words, the filaments rarely cohered every time the potential was applied at any voltage and no more frequently at five volts than at one volt in many cases. Furthermore, the lapse of time between applications of the potential seemed to play a part in determining the subsequent behavior. We observed also in many cases a weak coherence; i.e., the resistance of the junction as indicated by thermocouple and galvanometer did not drop to the usual low value.

Palmer's assumed mechanism was based on the work of Branly[3] who experimented with a coherer consisting of two plane metallic discs separated by a thin sheet of a solid dielectric. Branly believed that the action of this coherer was to be attributed to a sudden increase in the conductivity of the dielectric, and consequently that in the ordinary form of coherer the contacts must be separated by an insulating layer which becomes conducting under the influence of a small potential and regains its insulating power when the contact is tapped.

Shaw and Garrett[4] measured the force required to break a coherer contact and found it to be of the order of magnitude of the tensile strength of the metal. They calculated that there was sufficient heat developed to weld the minute areas in contact and concluded that this was the correct explanation of the effect. On this basis it seems probable that the gaseous atmosphere would influence the potential required to actuate the coherer by altering the character of the surface, especially after the filaments had cohered a few times. This might account qualitatively for some of the effects observed by Palmer.

The heat treatment of the tungsten filaments used by Palmer was not sufficient to remove the oxygen from the stable film of tungsten oxide on a tungsten surface according to the work of Langmuir.[5]

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[3] Branly: Compt. rend., **155**, 933 (1912).

[4] Shaw and Garrett: Phil. Mag., **8**, 165 (1904).

[5] Langmuir: Trans. Faraday Soc., **17**, 608 (1922).

In a recent theoretical paper based on the quantum mechanics Ehrenberg and Hönl[6] have shown that metallic contact is not essential to coherence. Their work indicates that the resistance of a contact has already dropped to a very low figure when the surfaces are still of the order of 10 Ångströms apart.

Heats of adsorption calculated by Palmer from "critical" cohering voltages do not agree even in order of magnitude with the findings of other investigators. Table I shows the striking disagreement between Palmer's values and those of Taylor, Kistiakowsky and Perry[7] for the heats of adsorption of several gases on platinum. The latter measurements were made calorimetrically on a powdered catalyst.

TABLE I

	Heat of Adsorption in Calories/gram mol.		Heat of liquefaction of the gas in calories
	Palmer	Taylor, Kistiakowsky and Perry	
Hydrogen	160	12,000	200
Sulfur dioxide	5340	25,000	5800
Oxygen	1200	120,000	1950
Carbon dioxide	750	30,000	1440

Summary

The repetition of some of Palmer's experiments on the coherer method of determining heats of adsorption has given very erratic values for the cohering voltages of tungsten filaments in hydrogen, oxygen, nitrogen, and in vacuum. Objections are raised to the mechanism of the cohering act assumed by Palmer which are based on the present experiments and on the work of previous investigators.

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[6] Ehrenberg and Hönl: Z. Physik, **68**, 289 (1931).

[7] Taylor, Kistiakowsky and Perry: J. Phys. Chem., **34**, 799 (1930).

THE SYSTEM:LITHIUM SULPHATE-ALUMINUM SULPHATE-WATER

J. P. SANDERS AND J. T. DOBBINS

Introduction

The alkali elements cesium, rubidium, potassium and sodium form alums with aluminum. Cesium forms the most stable alum, the stability decreasing with increase in atomic weight from cesium down to sodium. Since lithium has a lower atomic weight than sodium and is also a type element, it is of interest to know if this element forms an alum under any conditions. Previous investigators seem uncertain as to the formation of an alum by lithium and aluminum.

The system, lithium sulphate-aluminum sulphate-water has not been studied to any great extent. Kralovansky[1] stated that lithium aluminum sulphate—$Li_2SO_4.Al_2(SO_4)_3.24H_2O$,—is formed on evaporation of a mixed solution of lithium sulphate and aluminum sulphate below 11.° Rammelsberg[2] was not able to prepare the double sulphate and states that it does not exist. Schreinemakers and de Waal[3] made a more systematic study of the system and found that only the solid phases, $Li_2SO_4.H_2O$ and $Al_2(SO_4)_3.18H_2O$ are present at 30°. They found that when an unsaturated solution containing equivalent quantities of lithium sulphate and aluminum sulphate was evaporated at constant temperature crystals of $Al_2(SO_4)_3.18H_2O$ alone separated.

As Kralovansky claimed to have obtained a lithium alum at 11° it was thought that possibly it might become a stable phase at a temperature below that at which Schreinemakers and de Waal worked. Therefore, the isotherm at zero centigrade, was determined.

Experimental Procedure

A series of solutions was prepared from lithium sulphate and aluminum sulphate by adding solid lithium sulphate to solutions of varying concentrations of aluminum sulphate in some cases and solid aluminum sulphate to solutions of lithium sulphate in others until a solid phase remained in contact with solution. These solutions were kept immersed in an ice box containing crushed ice and water for six months. During this time the solutions were shaken several times each day.

Sampling

The solutions were sampled by pipetting and weighing small quantities of the clear solution from the bottles and making up to a known volume.

The residues were sampled by dipping the solid from the bottles, draining the liquid, weighing the wet solids, dissolving and making to a known volume as in the case of the liquids.

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[1] Schweigger's J., **54**, 349 (1928).

[2] Sitzungsber. Akad. Wiss. Berlin, **1848**, 385.

[3] Chem. Weekblad, 3, 539 (1906).

Methods of Analysis

Sulphates—The sulphates were determined by precipitating with excess lead nitrate in solution and titrating the excess lead nitrate with sodium molybdate according to the method used by Wiley[4] for the volumetric determination of lead. This method was tested satisfactorily before the analysis of this system was undertaken.

Aluminum—The aluminum was determined by the precipitation of aluminum with lithium chloride and igniting the precipitate to $2Li_2O.5Al_2O_3$. The procedure consists in adding an excess of lithium chloride solution to the sample of aluminum and making the solution just alkaline with ammonium hydroxide. The precipitate is washed, ignited and weighed as $2Li_2O.5Al_2O_3$.

Lithium—The lithium was calculated from the sulphate in excess of that equivalent to aluminum.

The composition of the solid phase was determined from analysis of the wet residue, by use of tie-lines.

Experimental Results

TABLE I

Composition of Solutions and Corresponding Residues in the System: Lithium Sulphate-Aluminum Sulphate-Water at Zero

Solution		Residue	
$Al_2(SO_4)_3$ per cent	Li_2SO_4 per cent	$Al_2(SO_4)_3$ per cent	Li_2SO_4 per cent
27.02	0		
26.30	0.99		
23.30	4.51		
20.15	8.63		
19.31	10.10	40.10	3.55
19.00	10.61	36.51	5.09
18.14	11.40		
17.80	12.80		
16.60	14.65	38.01	5.79
16.10	15.90	30.81	13.10
13.35	17.05	11.55	26.55
11.43	18.52	5.48	54.01
9.09	19.59	2.56	61.03
7.49	20.09		
6.39	20.67		
4.73	21.96		
2.31	23.39		
0	25.43		

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[4] Ind. Eng. Chem., Anal. Ed., 2, 124 (1930).

Discussion of Results

The results are plotted in Fig. 1. The values are plotted as a three-component system: lithium sulphate-aluminum sulphate-water. The curve represented by continuous lines and points represented by circles indicate the results obtained at zero degrees. The curve of Schreinemakers and deWaal is represented by broken lines and points by X. Curve aP$_3$ shows the various concentrations of lithium sulphate and aluminum sulphate in contact with $Al_2(SO_4)_3.18H_2O$ as solid phase and curve P$_3$b the concentrations with $Li_2SO_4.H_2O$ as solid phase. There is no indication of the existence of a lithium alum at this temperature.

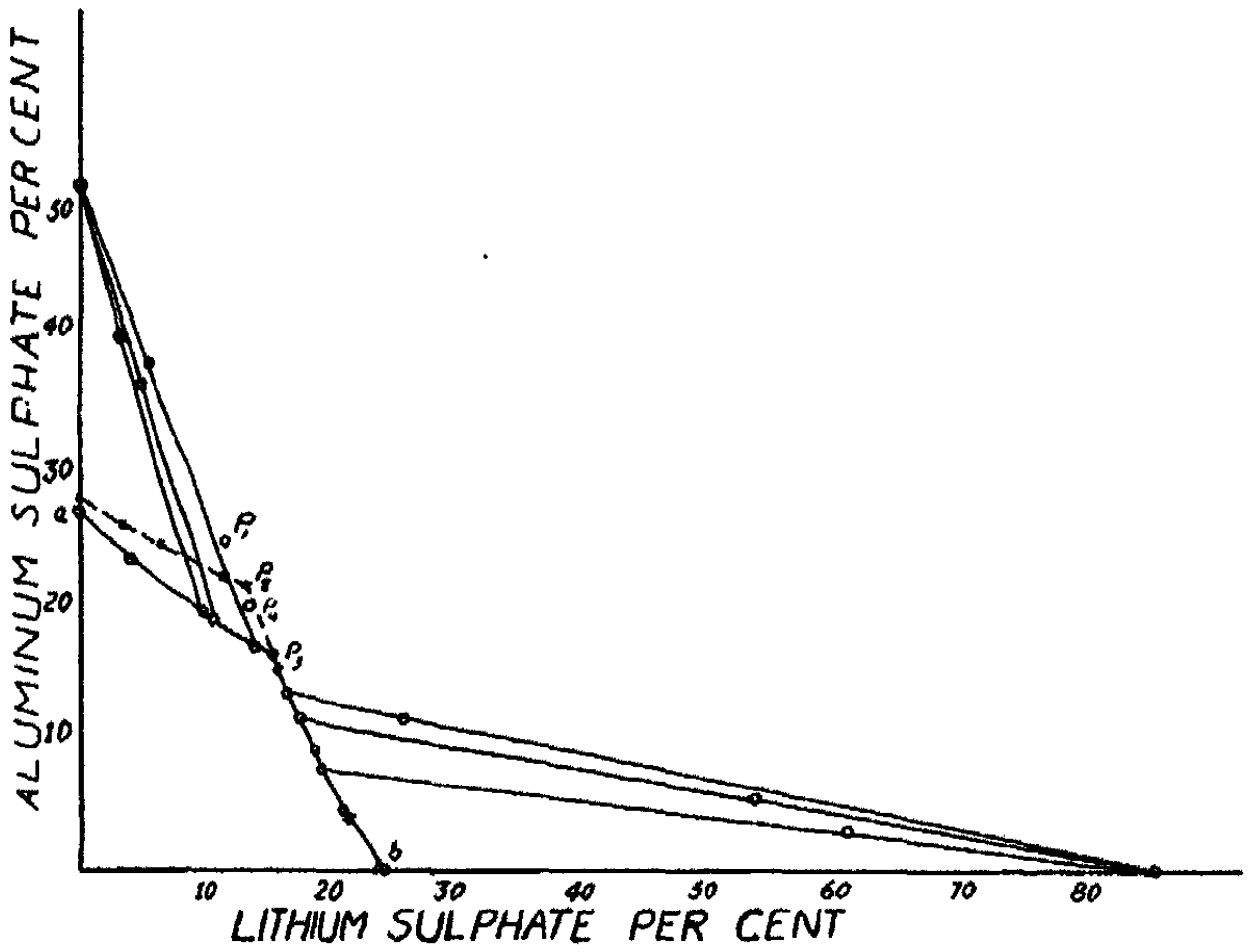

FIG. 1

Mutual Solubilities of Lithium Sulphate and Aluminum Sulphate in Water at Zero and 30 and 50 Degrees.

The results indicate that the solubility of each salt decreases with the increase in concentration of the other. On comparing the results with those found by Schreinemakers and de Waal at 30°, it will be seen that a change of temperature does not have very much effect on the solubility of lithium sulphate in the presence of aluminum sulphate, whereas, the lowering of the temperature decreases materially the solubility of aluminum sulphate in the presence of lithium sulphate. Lithium sulphate is slightly more soluble at zero degrees than at 30°.

After the completion of the investigation of the system at zero degrees and comparing the results with those obtained by Schreinemakers and de Waal at 30°, it was decided to determine the transition point for the system at 50°. At this point the solution was found to contain 24.74 per cent of aluminum sulphate and 11.93 per cent of lithium sulphate. The transition point at 50° is represented by P_1; that at 30 degrees by P_2 and that at zero degrees by P_3 in Fig. 1. When the concentrations at the transition points at the three temperatures are compared, it is seen that as the temperature rises the lithium sulphate becomes less soluble and the aluminum sulphate more soluble. The transition point was determined at 25 degrees, the point is represented by P_4. The solution contained 19.75% $Al_2(SO_4)_3$ and 13.55% Li_2SO_4.

Conclusions

1. In the system lithium sulphate-aluminum sulphate-water no lithium aluminum alum exists as a stable solid between zero and fifty degrees.

2. Lithium sulphate mono-hydrate and aluminum sulphate octodecahydrate are alone stable solid phases in contact with aqueous solutions between zero and fifty degrees.

3. The salts depress mutually the solubility of each other.

4. Change of temperature does not have much effect on the solubility of lithium sulphate in presence of aluminum sulphate. The lowering of the temperature decreases the solubility of aluminum sulphate in the presence of lithium sulphate.

5. The increase in temperature displaces the transition point in the direction of higher concentration of aluminum sulphate and lower concentration of sodium sulphate.

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ANILINE AND METHYL CHLORIDE*

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One finds the statement in reference books of organic chemistry[1] that methyl chloride acts upon boiling or hot aniline to produce a mixture of the hydrochlorides of methyl aniline and dimethyl aniline, the statement being based upon the work by A. W. Hofmann[2] in which he investigated the action of methyl chloride, bromide, and iodide upon aniline. No claim has ever been made, so far as the authors are aware, that aniline and methyl chloride will react with each other at room temperature.

In the course of Phase Rule investigations in this laboratory, using the methods and apparatus of Bancroft and Barnett,[3] we had occasion to investigate the action of methyl chloride gas upon liquid aniline and we observed that there is a slow interaction between the two even at 25°C. A ten-gram sample of aniline, for instance, in the presence of an atmosphere's pressure of methyl chloride, showed in the course of six hours the formation of a perceptible amount of a solid phase which had the appearance of a reddish-purple slush. Methyl chloride continued to be taken up slowly, so that at the end of 40 days 88% of one equivalent of the gas had been consumed, and at the end of 102 days the reaction apparently had come to a stop with 99.5% of one equivalent of methyl chloride bound by the aniline. At this point 5.398 milligrams of methyl chloride were held by the aniline, which represents 540 milligrams per gram aniline. The calculated amount is 543 milligrams of the gas per gram aniline, assuming the combination to be that of one mole of methyl chloride with one mole of aniline. At the completion of the reaction the content of the reaction flask was a solid mass of magenta color.

This reaction, naturally enough, proceeds much more rapidly at elevated temperatures; a sample of 1.97 grams aniline, for instance, held at 105°C., combined with 88% of one equivalent of methyl chloride in the course of forty-eight hours. The resulting solid had the same appearance as in the previous experiment carried on at room temperature, except that a little solid sublimed into the upper regions of the reaction flask, forming white, needle-like crystals. The increased speed of the reaction was due in part to the smaller aniline sample used, giving a relatively larger surface, but the principal factor was the increased temperature.

Aniline is soluble in ether; methyl aniline hydrochloride is insoluble. A sample of 1.45 grams aniline, treated for a convenient length of time (but

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*This work is done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of research established by August Heckscher at Cornell University.

[1] Beilstein: "Handbuch der organischen Chemie," **12**, 72 (1877).

[2] Ber., **10**, 594 (1877).

[3] Bancroft and Barnett: J. Phys. Chem., **34**, 449 (1930); Belden: J. Phys. Chem., **35**, 2164 (1931).

not until the reaction was complete) with methyl chloride, was extracted with ether to remove the unconverted aniline. The resulting solid material was readily soluble in water and gave instantly a silver chloride precipitate when dropped into silver nitrate solution, which showed the solid to be a hydrochloride. Methyl chloride gas, bubbled through silver nitrate solution, clouds the silver nitrate little, if any, in the course of an hour.

The purple appearance of this solid might suggest a considerable conversion of the original aniline into a colored substance. The purple material proved to be insoluble in ether, and soluble in water and ethyl alcohol. The hydrochloride of the previous paragraph was dissolved in water and then neutralized with N/20 sodium hydroxide, using brom thymol blue indicator whose color change could be seen even in the presence of the magenta coloration. The resulting methyl aniline (and perhaps dimethyl aniline) was extracted with ether, leaving in the water layer the purple coloration and the sodium chloride resulting from the neutralization. On evaporation of this solution on a steam bath, the color intensified slightly and proceeded to disappear, leaving at dryness sodium chloride crystals and almost nothing else. We conclude from this that during the reaction of aniline with methyl chloride a small amount of an aniline dye of intense color is formed and that there is not a considerable conversion into this colored substance.

We were interested further to learn the nature of the reaction, if any, between methyl chloride and biuret. We found that methyl chloride and biuret appear not to react at all with each other in this same apparatus at temperatures up to 100°C. We tried passing the gas over powdered biuret in a U-tube at temperatures up to the decomposition point (190°C.) of the solid; the product of the reaction of biuret with methyl chloride should be one or more molecules of HCl, which could be readily identified by passing the gas through silver nitrate solution. Above 140°C. we obtained a noticeable evolution of HCl gas. However, the weight of the solid decreased during the process, which is not what should happen if biuret is being converted into methyl biuret. We surmised that the one molecule of water with which biuret crystallizes had not been removed completely in drying the solid. After drying the solid more carefully to a constant weight, we were unable to obtain evidence of any reaction with methyl chloride up to 180°C., at which temperature the biuret commenced to sublime out of the U-tube.

The conclusions to be drawn from this paper are these:

1. Methyl chloride reacts with aniline slowly at room temperature to form a magenta-colored solid. The solid is principally methyl aniline hydrochloride with a small amount of intense dye.
2. The same reaction occurs much more rapidly at 105°C.
3. Methyl chloride does not react with dry biuret at any point below 180°C.

The authors are indebted to the Roessler and Hasslacher Chemical Company for methyl chloride (Arctic Gas).

Cornell University.

NEW BOOKS

The Industrial Development of Searles Lake Brines. *By John E. Teeple. 23 × 16 cm; pp. 182. New York: Chemical Catalog Company, 1929. Price: $3.00.* In the preface the author says: "My associates really include all the men who actually contributed to the manufacture or marketing of the products, or to research, or to design and construction of the plant. Many of their names will be found on the pages in connection with specific parts of the work. But it was an organized piece of cooperation in which it would be difficult and probably useless to evaluate just what each one of us contributed, beyond saying that we saw it all and were a part of it."

"This book has two purposes. First, to add to the record of scientific literature certain phase rule diagrams and data. This information was necessary to the work of Trona; it belongs to the American Potash and Chemical Corporation, was done at their initiative and was paid for with their money. It has now largely served its original purpose, and normally would have spent the rest of its existence buried in their files. The American Potash and Chemical Corporation in consenting to the publication of these data has performed a courteous act. One could wish that other chemical corporations would likewise release data from their files when it can be done without furnishing ammunition to direct competitors. Scientific information is about the only valuable commodity we are accustomed to bury for fear someone else might derive benefit from it.

"The second purpose of the book is to give a short story of the application of research, technology and common sense to the development of a potash and borax business. This story of the diagnosis of a situation in an industry and the course of development which led to success is not such an uncommon thing; in fact it is all in the day's work, so why write a book about it? The answer lies in the very peculiar attitude that was manifested toward the development of a potash industry in this country. During the World War potash was news. Anyone could be sure of making the front page by talking about potash and how this country was becoming independent of Germany. With peace came a change. College professors, bankers, business men, chemists and ministers of the Gospel now granted interviews freely to prove that this country could not hope to produce potash successfully in times of peace. Many of the interviews, possibly inspired, were circulated by a well-known advertising agency. The opposition to American potash was apparently deep seated, based on faith and belief rather than on facts or logic. Few things are more aggravating and often harmful than loud and dogmatic assertions that a given thing cannot be done, coming from people who obviously are in no position to judge whether it can be or not. I think we all react to this in much the same way; we look back of the loud speakers to see who is broadcasting; that tells us who is most afraid that the thing can be done; then we proceed to do it. The plant at Trona undertook to manufacture two staple products, potash and borax, in competition with two world monopolies. Today it has by far the largest borax plant in the world, and one of the largest potash plants. This was accomplished without governmental assistance from tariff or otherwise, and the business is profitable and still young. Since the record that it could not be done was so voluminous it seems well to make note of the fact that it has been done.

"This book does not contain detailed descriptions or processes, nor scale drawings or apparatus. *The former are not so antiquated nor the latter sufficiently obsolete to permit* their publication yet. Anyone intelligent enough to use that kind of information will know better than to expect it here," p. 7

The crystallized salts in Searles Lake consist of halite ($NaCl$), trona ($Na_2CO_3.NaHCO_3.2H_2O$), hanksite ($9Na_2SO_4.2Na_2CO_3.KCl$), borax ($Na_2B_4O_7.10H_2O$) and glaserite ($3K_2SO_4.Na_2SO_4$). On the equilibrium diagrams there occur in addition: burkeite ($2Na_2SO_4.Na_2CO_3$) and the unnamed salts $Na_2CO_3.K_2CO_3$, $K_2CO_3.2KHCO_3.3H_2O$, $Na_2B_2O_4.2NaCl.4H_2O$, $Na_2B_2O_4.2Na_3PO_4.36H_2O$, and $Na_2B_2O_4.2Na_3AsO_4.36H_2O$.

"To consider some of the evaporation problems for a moment, probably the most serious one was foaming. We are all familiar with this phenomenon in commercial evaporation and there are several well-known methods for handling such liquors, but I have never seen such pernicious, persistent and aggravating foam in a regular operation. At times the condenser water was actually richer in potash than the raw brine fed to the pans. Unless this could be controlled either the losses of potash from partly evaporated liquor would be enormous, or the pans must be operated at such slow rate that production would be negligible.

"In my first report I find the following comment: 'At present in the plant they are adding a small amount of oil to the pans to cut down the foaming. This, too, is a tradition. I did not find out who started it, on what theory it was based, or what work had been done to indicate whether it was beneficial or not.' The use of oil on foamy liquids is very common and often effective, but why in this case use only an amount which was entirely inadequate? Why not add a proper amount to control the foam, rather than simply tease it? I asked the people in authority at the plant and the oldest operators. No one knew, or rather everyone knew but their explanations did not agree or did not sound reasonable. A majority felt sure, from tradition, that it would not do to add more oil, and they were right, as traditions often are. One may have great respect for traditional conclusions but they are not entirely satisfying, so at a later date when we had small laboratory pans for studying the problem a trial of the oil showed that there was no foaming so long as a thin film remained on the surface. This film tended to disappear but a further addition of oil sufficient to keep a film always present kept the foam under complete control, evaporation proceeded at full speed and there was no obvious disadvantage; score—experiment 1, tradition 0. The experimental result was exactly what one would expect, so we next started a full-size single-effect evaporator in the plant with instructions to run it at top speed and make sufficient additions of the oil to keep a slight film always present on the surface and control foaming. This was done, and for several hours that pan had no trouble with foam, and produced high-grade concentrated liquor at a rate never before seen by the awed beholders. The operation was a complete success—in the evaporation house—but the patient died in the crystallizing house. After about twenty-four hours spent in excavating filters, centrifugals, and other equipment which seemed buried under layers of concrete, the plant resumed operations, and we knew why you should never add enough of that oil to stop foaming.

"I have mentioned that burkeite forms sparkling crystals of very high luster. The film of oil acts as a flotation agent and selects the burkeite crystals for attachment, then floats them over with the concentrated liquor to the crystallizing house where the mixture of crystal and oil acts like concrete. Tradition was finally right, without the faintest idea why.

"In studying the question of foaming it seemed reasonable to suspect organic matter in the brine as the cause. Synthetic brine containing all known constituents excepting organic matter could be evaporated without difficulty. Natural brine after treatment with absorbent carbon like Darco no longer foamed. In searching the watershed for organic matter which might be responsible, I selected greasewood as the probable source. The leaves of this very common plant appear as if coated with a varnish, easily soluble in very dilute alkalies, and a very small addition of this solution to a synthetic brine produces an excellent imitation of foamy natural brine. Probably a number of different organic materials are responsible, and more recent work at the plant by W. A. Gale indicates that the organic matter may be sodium salts of humic acid, and that its function is probably foam stabilization rather than foam formation, because its removal has little effect on surface tension.

"We found many substances which would prevent foam, such as cholesterin, capric acid, pine oil, turpentine, rosin, turkey red oil, and amyl alcohol, most of these being impracticable for use under vacuum evaporation. Finally R. W. Mumford worked out a practical one. The way to control this foam is to add soap or a fatty acid. This ended foaming as a serious trouble and made it certain that we should use steam evaporation and and not be compelled to resort to solar evaporation or some other makeshift," p. 36.

"Aside from the fixed charges incurred in obtaining ownership and in developing the 2500 acres of salt body in the lake, the only cost of raw material for the plant is the cost of pumping. Any basis for depletion charge which might become effective within a generation is very difficult to figure. Amortization of cost of the property should be accomplished well within the life of the plant, but in fact this amortization becomes a daily and not a per gallon charge, and we are left in the very peculiar situation of being able to disregard the amount of raw material used. Whether we obtain a 20 per cent or a 100 per cent recovery of the potash and borax in the brine used means little to us, a few cents per ton at most, so long as the losses are confined to raw brine on which no real work has been done. In evaluating mother liquors to see whether they should be discarded we can select a datum level of about 5 per cent KCl and 3 per cent borax. Anything below that level would naturally be discarded at once as worse than valueless. Anything richer than that has a value only equivalent to its excess content above the datum level minus any detriment or disadvantage from impurities that may be incurred by its use. This value also may easily be negative and the liquor should be discarded. I stress this point because chemists are so often urged to conserve resources and save everything, as though 100 per cent yields and no waste products were a sort of religious slogan that would pave the way to heaven. I can't quite agree with that point of view at all. A chemical plant is not a place for collecting and keeping family heirlooms on account of the sacred memories attached to them; it is a place for making things, and the best way to make things is by judicious waste of the unimportant so that you have room and time to devote entirely to the thing you are making. If there are those whose consciences might be hurt by such waste they may be reassured in this case, for all discarded materials are thrown directly back into the lake, just like little fishes, and so saved for posterity," p. 46.

"Probably I do not make the same distinction between chemical engineers and chemists that is commonly made. From both one demands a certain knowledge of chemistry and a certain ability in the technic of handling materials. The distinction lies largely in the amount of material they need to have in hand in order to be at their very best level of thought. Both are engaged in the chemical transformation of matter, but a good chemical engineer thinks best and works best when he is dealing with tons. He can visualize and arrange his equipment better, his manipulations go more smoothly, his whole manner of thought is freer and clearer if he pictures a regular succession of tons of material flowing through an operation. A man well-adapted to development work, however, probably thinks best in pounds or hundreds of pounds. A chemist thinks best and works best in grams. You can convert a chemist into a chemical engineer by once getting him thoroughly interested in the idea of tonnages. If his mind is at all adapted to that quantity of matter his interest will be awakened and he will learn the technic of handling tons without a great deal of difficulty. On the other hand, it is not difficult to convert a chemical engineer into a chemist by interesting him in the quickness and accuracy with which he may obtain information from working only with grams instead of tons. If his mind is at all adapted to that quantity he will master the technic of handling grams. To my mind it is largely a question of the quantity of material the individual mind likes to consider at one time. To carry the comparison a little farther, I suppose we should say that a physical chemist is one who works best and thinks best with molecules rather than with grams or tons, probably not to exceed ten or a dozen molecules at one time, and the modern physicist is at his very best inside the spacious confines of a single atom," p. 51.

"This is about all of the story to be told at present. The corporation is producing and marketing to-day between 20 per cent and 25 per cent of all the potash in America, but its output would make no real impression on the amount that America ought to use. It is making and marketing nearly half the borax and a considerable per cent of the boric acid that the whole world uses, but borax has extremely valuable properties, and if it is kept where it belongs, in the class of cheap chemicals, the world will use to advantage several times its present consumption. There is plenty of room for expansion and it seems probable that most of the borax of the near future will come from sources like Searles Lake, rather than from colemanite and other borax minerals as it did ten or fifteen years ago," p. 63.

The first part of the book is entitled history and development and the chapters are headed: Searles Lake; early history; solubility and double salts; early plant operation;

special features of the operation; the present plant. The second part is entitled equilibrium data and diagrams. "There will be found included sixteen systems of two components, thirty-eight of three components, twenty-five of four components, six of five components, and one of six components, one component always being water. Some systems are given at a single temperature, others at four or five temperatures over a considerable range. This obviously does not exhaust the subject; far from it. Only those are given which we found it necessary to work out for our own purposes, and naturally not all of those."

The development of Searles Lake was an economic and scientific triumph for Teeple and for those who had confidence in Teeple. Teeple richly deserved the Perkin medal, which fortunately was awarded to him before his death. He succumbed to an operation which his friends had expected would put him back in really good health once more. This book is valuable for the scientific data that it contains. It is also valuable because it is so written that it will give to those who did not have the privilege of knowing Teeple personally some conception of the charm, ability, and personal honesty of the man.

Wilder D. Bancroft

Oceanography. *By Henry B. Bigelow. 21 × 14 cm; pp. x + 263. Boston and New York: Houghton Mifflin Company, 1931. Price $2.50.* The chapters are entitled: introductory; submarine geology; physical and chemical problems of the sea water; relationship between oceanography and meteorology; life in the sea; economic value of oceanographic investigations; physical, chemical, geologic, and biologic unity in the sea.

"In practice oceanography falls most conveniently into three chief divisions: (*a*) the geological; (*b*) the physical-chemical; (*c*) the biological." It is therefore a rational order of presentation "to consider first the problems of the shape and composition of the basins that hold the oceans (i.e., submarine geology); next, those associated with the physical character and chemical composition of the waters that fill these basins (physics and chemistry of sea water); and third, those of the nature and activities of the animals and plants that inhabit the waters (life in the sea)," p. 11.

"An exact knowledge of the topography of the bottom would go far toward establishing the possibility of great rockslides on the steeper submarine slopes, a question recently raised by the puzzling rock formations in the Alps, Appalachians, and other mountain chains," p. 14.

"This matter of depth and of the local variations in crystal stability is of equal interest to the palaeontologist, and to the zoögeographer, because of its bearing on possible former land connections which have been postulated to explain the distribution of terrestrial animals and plants as at present existing; no less to account for the continental separations by which different floral and faunal areas (once continuous) are now isolated from one another. Changes in the depth of epicontinental seas, and in the degree to which the great oceans have been in free communication with one another in the past, equally concern the marine biologist as factors controlling the dispersal-routes of many marine organisms, and as affecting the ocean currents that transport animal and plant species," p. 16.

"Lime rocks have certainly been the most widely discussed of marine sedimentary formations, and in some cases, as with an oyster bed, or a reef of corals, or a swarm of Globigerinae, the progress of the event by which lime is added to the sea floor may be easily observed. But great quantities of limy mud are also being laid down in tropical seas, the minute amorphous particles of which seem not to be the simple fragments of shells of defunct animals. Whether bacteria are responsible for the formation of these muds, as formerly supposed, or whether they result from chemical or mechanical precipitation quite independent of bacteria, or whether, after all, they are simply the end product of the breakdown of exposed limestones, beach sand, etc., as has recently been maintained, is still a moot question. This question, however, is of great theoretic interest, not only for its bearing on events now taking place in the sea, but in connection with the formation of oölitic limestones, and in relation to the relative importance of salt and fresh-water situations as sites for the formation of limestones, now and in the past," p. 29.

"Problems equally broad arise in connection with the siliceous deposits, for with silica constantly contributed by the rivers to the sea, and with no return loss either to the atmosphere or to the land (except in regions of elevation), it seems that the silica of the earth is now tending to accumulate on the sea floor. The geologist is, therefore, as deeply interested as is the biologist in the factors that cause such accumulation of silica to take place most rapidly in cold water, and at great depths, as signboards to the conditions under which similar events occurred in the seas in past geologic ages. Among these siliceous deposits the radiolarian-bearing sediments demand special attention, both in relation to the depth at which they were deposited, as just mentioned, and because knowledge of the conditions under which they were laid down is vital to our understanding of the geosynclinal rocks, hence of the world's mountain chains.

"The formation of phosphatic concretions and of glauconite on the sea bottom of today also needs fresh examination for its bearing on the origin of phosphatic and potash rocks: it is in the sea, too, that the key to the riddle of the source and mode of formation of dolomite is most hopefully to be sought," p. 31.

"The problem of iron in modern marine deposits is important because of its bearing on the question, what part of the iron ores now being mined in sedimentary rocks were originally laid down with the latter, or in what part they entered subsequently, as secondary intrusions? Are deposits of this sort being laid down anywhere today? What, if anything, have bacteria to do with the segregation of iron in the sea? How does the common association of iron with manganese in modern deep-sea deposits bear on this problem? How sound are the chemical reactions that have been proposed to account for the deposition of either of these minerals, and what conclusion must we draw, as to the depths of the Paleozoic seas, from the distribution of iron, in deep and in shoal water, in the modern sediments?" p. 34.

"The studies of the chemistry of sea water that are at present in progress, like those of its physics, chiefly aim at enlarging our factual knowledge of regional variations, and our understanding of events that take place in the cycle of matter there, rather than at clarifying the nature of chemical processes as such. Thus they bear to the science of physical chemistry as a whole a relationship more subsidiary than do oceanic biology or physiology to current attempts to fathom the riddle of life," p. 51.

"The distribution of oxygen in the sea is so closely associated with the general problem of vertical circulation that it is best mentioned here. It seems certain that the intake of oxygen occurs exclusively at and near the surface, (*a*) in the surface film, or within the *upper few feet where their bubbles are entrapped by breaking waves, and (b) throughout* the upper illuminated zone where plants carry on photosynthesis; no sources are known from which the water can absorb free oxygen in the deeper levels. Quantitative data as to the rapidity with which any deficiency in oxygen is renewed from these sources of supply (particularly the efficiency of the latter out in the open sea) are therefore present desiderata. The relative importance, from the standpoint of oxygen intake, of coastlines of different characters, with their different types of wave action and of turbulence, offers an interesting problem. How effective a source of oxygen supply for the surrounding neighborhood is, for instance, a rocky headland upon which the surf beats constantly? We have yet to learn how deep simple turbulence is able to maintain the oxygen supply close to the saturation point in different regions under different conditions," p. 86.

"If there were no means of renewing oxygen from above, the underlying water would soon be absolutely stripped of this vital necessity, as the deeps of the Black Sea actually are. And within the last few years it has been found—(notably by the 'Carnegie' and by the 'Dana') that the mid-depths are, in fact, decidedly poor in oxygen in mid and low latitudes in the Pacific—also over large areas in the tropical Atlantic; so poor indeed, that one is inclined to marvel at the wealth of animal life that exists there. But, underlying this oxygen-poor stratum, the bottom waters of the ocean basins carry a much richer load of this gas. In the present state of our knowledge, it seems that the only way in which stratification of this sort can be maintained is by sinking currents carrying down into the deeps, water that has become saturated with oxygen near the surface in high latitudes, coupled with the consumption in the mid-stratum, rapid enough nearly to denude of its oxygen the water that is brought up from below by rising currents. But we urgently need information as to whether these mass sinkings of oxygen-laden water are as strictly confined to the Arctic and Antarctic, in their respective winters, as now seems probable; also how this water continues so nearly uniform in oxygen over vast areas on the sea floor in spite of the wide local variations in abundance of animals that are constantly consuming it there; and how far it is safe to deduce the drifts for the deepest stratum from the variations in the concentration of oxygen that do exist there," p. 87.

"Some substances are at present known to exist in sea water solely because they have been detected in the bodies or skeletons of marine animals and plants, which could only have obtained them from their aqueous environment. As examples of this we might mention the vanadium recognized in the blood of Ascidians and of Holothurians; the cobalt in the tissues of lobsters and muscles; the nickel in mollusks; and the lead that has been found in the ash of various marine organisms," p. 109.

"Various explanations have been proposed for the chemical events by which the preponderance of calcium and of carbonates, which characterizes river water, is so uniformly altered into the preponderance of sodium and of chlorides that characterizes the sea water, everywhere, and at all times, even under the most diverse conditions. But we believe no one would seriously maintain that any of the explanations are adequate," p. 113.

"Another contrast having far-reaching biologic effects is that between the specific gravity of the medium in which organisms live on land—the air—and in the sea. Thanks to the fact that sea water has almost the same specific gravity as protoplasm (or protoplasm as sea water if one prefer) no marine animal or plant needs the mechanical support against the pull of gravity that every organism of any considerable size must have on land if it is not to collapse of its own weight. Thus no alga needs, or has developed, a rigid woody skeleton. And as marine animals have never required strong frameworks to support themselves, their internal or external skeletons can be adapted entirely to other ends, such as protection (as in the case of many mollusks) to provide stiffness as among the horny corals, to maintain body form against resistance of the water while swimming or for the attachment of muscles as among fishes and crustaceans. Comparison of the frame of a whale (which suffocates of its own weight if left stranded on the beach by the ebbing tide) with that of an elephant or a dinosaur shows at a glance how much less is necessary in the one case than in the other. In spite of their great muscular power, even the largest sharks have still feebler and wholly cartilaginous skeletons without any hard bones, while even a more striking case of strength without framework is afforded by the giant squids, animals proverbially active, swift and muscular, though with only the rudiment of any sort of skeleton. No morphological development of this sort would be possible on land. As a corollary of this, there is no gravitational limit to the size of animals in the sea, the only theoretic limit being their need of taking in, through the surface (and usually through a very small part of it), enough food to support the entire bulk and enough oxygen for its vital requirements. With relief from the force of gravity, the sea supports animals as large today as it ever has, and heavier than any that have existed on land," p. 141.

"It is still a mystery how fishes and other marine animals are able to direct their long journeys, often in darkness, and always through a medium in which temperature and chemical composition are so nearly uniform over long distances that the most delicate tests are needed to reveal any difference at points many miles apart. The problem here is akin to that of bird-migration, but an even more puzzling one," p. 149.

"The question by what mechanism the cell is able to select out of the water those rare substances that, as it now seems, are of vital importance, opens the whole problem of the specific affinity of different cells for particular chemicals that forms the basis for all the structures that protoplasm manufactures. We might mention the secretion by diatoms of silica (an element relatively rare in sea water) in such great quantity that at times they may almost exhaust the water of it; the ability of seaweeds to draw iodine and potassium from the surrounding water so much more efficiently than man can, that until other sources for these substances were discovered it was far more economical to obtain them from the ash of seaweeds than it would have been to concentrate them direct from the water by any method yet perfected or likely to be developed: the ability of certain unicellular animals (Radiolaria) to build their shells of strontia, a substance so rare in the water that only recently have analyses revealed its presence there. If any seaweed made equal use of gold, the commercial extraction of the latter from sea water (on the average there are about five milligrams gold per cubic meter of water) would not be the will-o'-the-wisp it has actually proved. A more familiar example of the ability of the living cell to select particular substances from the outside is the secretion of *limy shells* by a *great variety of plants and* animals, an ability responsible for vast deposits of calcareous sediments, of limestone rock, and of the modern coral reefs. The question of the draft made by different vegetable cells of specific solutes for their nourishment, as of nitrates and of phosphates by diatoms: or of the same solutes in different proportion, is now under investigation at many hands," p. 163.

"The simplest task of marine bacteriology is perhaps to trace the direct service these lowly and minute organisms render to the larger in providing the latter with proteid food. That protozoans do feed on bacteria in the sea is established. In fact, recent studies suggest that in this passive way the bacteria that thrive on the organic debris accumulating in shoal waters, and the protozoa that prey upon these bacteria, are essential links in the food-chain of higher animals in coastal waters, where the echinoderms, mollusks, and others that feed on detritus gain their nourishment less from the latter direct than from bacteria and protozoa eaten at the same time," p. 167.

"We all need to know what part bacteria play in breaking down the more refractory organic substances that would accumulate on the bottom of the sea if there were not some mechanism to disintegrate them and to bring them into solution in the water. Specifically, what quantitative role do bacteria play in the sea, in the destruction of the agar from the stalks and fronds of seaweeds that is constantly taking place under water—a substance resistant to most bacteria? Bacteria of the sorts that do attack agar have recently been found in brackish and in salt water. But, so far, it has been only in the tropics that their presence in such situations has been established, whereas it is in higher latitudes (and lower temperatures) that the great concentrations of ordinary seaweeds exist, and the great overturn of agar and of similar hemicelluloses takes place. Thus it still remains an open question how far the annual disintegration of the millions of tons of kelp, and so forth, results from bacterial activity, or how far it simply reflects the solvent action of the sea water itself. We face this same problem with regard to the destruction of the chitin in the shells of dead crabs, shrimps, and other crustaceans, and of the oil from diatoms and copepods," p. 180.

Wilder D. Bancroft

Ausgewählte Untersuchungsverfahren für das chemische Laboratorium. *By L. W. Winkler. Vol. 29 of Die chemische Analyse founded by B. M. Margosches, edited by W. Böttger). 25 × 17 cm; pp. xviii + 155. Stuttgart: Ferdinand Enke, 1931. Price 17.50 marks; bound 19.50 marks.* This is essentially a somewhat miscellaneous collection of analytical and other methods devised by the author and described in various journals during the past thirty years or so. Few of these methods were ever fundamentally new but they all include some modification, either important or trivial, made so as to enable an older method to be carried out with simpler apparatus, or more rapidly or more accurately.

Most people interested in chemical analysis will find something to interest them in the book.

The first 24 pages deal with *determinations of density (gas, liquid, solid), melting point* and boiling point. In the next 55 pages come simple gas analytical methods and some selected volumetric methods are described while those remaining are concerned with gravimetric estimations. The latter include several solvent extraction processes for dealing with mixtures of alkali metal salts and alkaline earth metal salts.

The last third of the book is devoted to gravimetric precipitations. The manipulative procedure prescribed for all these is similar and in most cases involves slow precipitation from boiling, neutral solutions containing considerable amounts of ammonium chloride, a piece of cadmium foil being added to prevent bumping.

The fairly coarsely crystalline precipitates obtained in this way are filtered through a small pad of cotton wool in a small, more or less cylindrical, glass funnel ("Kelchtrichter"). The precipitates are weighed in the funnel after drying either at room temperature, 100° or 130° according to circumstances.

Throughout the book experimental procedure is described in the most minute detail.

H. Bassett

Alkalien und Erdalkalien in ausgewählten Kapiteln. (*Vol. 26 of Technische Fortschrittsberichte. Fortschritte der chem. Technologie in Einzeldarstellungen. Edited by B. Rassow, Leipzig). By Bruno Waeser 22 × 15 cm; pp. viii + 196. Dresden and Leipzig: Theodor Steinkopff, 1931. Price: 13.50 marks; bound 15 marks.* The object of this monograph is to give a summary of new developments in the technical preparation and utilisation of alkali metal compounds during the last decade. Only those compounds are dealt with, however, which have not already been considered in other volumes of the same series. The field covered in the volume under review is, in consequence, very restricted. This is particularly true of the alkaline earth compounds which take up 50 pages, of which a few calcium and barium compounds account for 45, the remaining five being required for strontium and beryllium.

The alkali metal compounds discussed are:—sodium and potassium carbonates and hydroxides (other than electrolytic), peroxides, borates, cyanides (thiocyanates, ferrocyanides, etc.), chromates, manganates, halogen compounds (other than electrolytic), phosphates (other than fertilisers), arsenates, sulphur compounds (except sulphate), silicates.

Three pages are devoted to lithium, rubidium and caesium. There are several interesting summaries of the economic situation in respect of some of the more important compounds such as the alkali carbonates, hydroxides and borates while in the case of most compounds a very brief outline is given of the method of preparation now in use. These are the only parts of the book likely to interest the general chemical reader.

The greater part of the book is taken up with short references to articles in the technical literature and to patents. The subject matter of the latter is given but the reader will find little guidance as to whether the patents are of any practical value and to what extent they are actually used. In the case of recent patent literature this is probably inevitable but those actually engaged in the alkali industry, for whom the book is intended, should find it useful and they will be in a position to judge such matters for themselves.

The reviewer regrets the tendency in modern German books for the spelling of long-established words such as caesium, cyanid to be altered to zaesium, zyanid. This will doubtless increase the number of words beginning with z but from all other points of view the change seems both undesirable and unnecessary.

H. Bassett

Heterogene Katalyse. *By Erwin Sauter. 22 × 15 cm; pp. x + 80. Dresden and Leipzig: Theodor Steinkopff, 1930.* In the preface the author says that although in chemical circles the view is still held that the field of catalysis is still quite obscure, he believes himself able to show that such an idea is no longer correct. "Admittedly it is hard to arrange the wealth of work on catalysis so that the simple and more general picture of catalysis is not blurred and masked by the incredible number of special observations. . . . It appears from the development that the chief problems of catalytic investigation are becoming more and more akin to those of theoretical physics."

After an introductory chapter dealing with the definition and classification of catalysts, with activation hypotheses and such-like things, the chapters dealing with heterogeneous catalysis proper are entitled: remarks on the preparation of catalysts; changes of state and properties of heterogeneous catalysts; how shall one characterize a contact catalyst with reference to the demands to be made upon it; the phenomenon of poisoning in contact catalysis, contact catalysis and sorption; selective contact catalysis; heat of activation at catalytic surfaces; reaction velocity and contact catalysis; instances of experimental technique.

On p. 7 the author says that in the majority of cases studied kinetically the reaction does not run practically to an end. Since the temperature usually does not rise very high in the catalytic conversions, unsupported catalysts may be used there, as in the case of Paal's colloidal palladium, p. 21. "The heats of adsorption are of the magnitude of the van der Waals forces; they are always then the heats of vaporization of the adsorbed substances," p. 38. According to Magnus the adsorption of carbon dioxide by charcoal decreases so rapidly with rising temperature as to become approximately zero at 400°, p. 43.

The author believes in chemical sorption which differs from ordinary adsorption and is the important thing in contact catalysis, p. 48. "Chemical sorption depends chiefly on two actions: 1. Between sorbent and sorbate there is direct electron action. According to the newer quantum theory there are formed an ionogenic and a homopolar bond, between which intermediate phenomena are possible. 2. Between sorbent and sorbate there is formed a co-ordinative bond (according to Werner compounds of a higher order occur). The sorbed molecule undergoes considerable deformation as it adds to the sorbent to form a new chemical molecule. It is essential that the chemical sorption leads only to the formation of a monomolecular surface compound, the peculiar lability of which was recognized especially by Volmer."

The author does not play quite fair in his statement that the intermediate compound theory has rather won out. He quotes the reviewer as assuming the existence of free radicals, p. 53. What everybody else has meant by the intermediate compound theory has been a compound formed by the catalyst with one or more of the reacting products. The author now implies that it covers the formation of monatomic hydrogen in presence of nickel or platinum. One can hardly believe that the author could make such a mistake as that and yet it is more painful to believe that he knew what he was doing.

On p. 47 it is recognized that carbon monoxide is not activated appreciably when adsorbed by platinum; but no attempt is made to account for this. *Wilder D. Bancroft*

Thermodynamik. *By W. Schottky. 26 × 17 cm; pp. xxv + 620. Berlin: Julius Springer, 1929. Price: 56 marks; bound 58.80 marks.* The author intends this to be the best book on thermodynamics ever writen. He claims to have discussed all points at length, which seems to be true. He differentiates quite sharply, p. x, between external and internal thermodynamics. External thermodynamics deals with reversible systems and usually with reversible cycles. Internal thermodynamics recognizes the existence of passive resistances to change and deals with would-be cycles which don't close.

The book is divided into three parts: general thermodynamics; physical thermodynamics; and chemical thermodynamics. The third part is more than three-quarters of the whole treatment. The chapters in the third part are: application of thermodynamics to chemical reactions; equilibrium conditions and the phase rule; theoretical and practical methods for building up reaction effects from thermodynamic data; regularities in special states and changes; chemical affinities and equilibrium conditions as given by measurable thermodynamic values; equilibria of higher orders and phase stability; changes while maintaining equilibrium; examples in the application of thermodynamics.

"It is now necessary to discuss an apparent contradiction which occurs in the assumptions underlying the discussion that has just been made. It was assumed that the end state could be carried back reversibly into the initial state. According to what has been said, that is only possible when the system passes through a series of thermal equilibria. The initial and end states must especially represent thermal equilibria, which is therefore necessary in the actual cases to be discussed, because otherwise the state and consequently the entropy cannot be characterized by a relatively small number of independent variables.

"On the other hand, the initial state might change into the final state through irreversible stages following chronologically without there being any change in the external conditions —since we are dealing with closed systems. We must therefore have a system in thermal equilibrium which can show spontaneous changes that carry it over spontaneously into another state. According to our definition that means that it was not a system in thermal equilibrium.

"A clearing-up of this contradiction and thereby the possibility of applying all these considerations is evidently given only when the original state involved a partially retarded system and did not strive to attain an irreversibly reached end-state because it is kept from taking the necessary steps by some sort of retardations which keep it from passing through the various steps. If these retardations were absolute and were never to be lifted, the whole discussion would become hopeless. Its application is limited to cases where the retardations can be over-ruled arbitrarily without perceptible thermodynamic expenditure," p. 56.

"The only significant definition of the solid state is the one that the smallest particles of the body in question are not freely movable relatively to one another, but are to be found in a stable arrangement, which it takes up again when disturbed," p. 95.

"The variations from the law of Dulong and Petit show the regularity that the specific heat per gram atom is too large at high temperatures and too small at low temperatures. The significance of the variation upward is hard to explain and people are not agreed as to it. . . . The theoretical explanation of the variations which come out too low are more successful since Nernst has shown that the specific heats of all substances decrease in the same way as the temperature falls toward the absolute zero and approach zero as the temperature falls toward the absolute zero. The quantum theory accounts for this by postulating a finite magnitude of energy differences between the lowest and the next higher of the possible quantum states of the vibrating atom and establishes a relation between the size of these energy jumps and the otherwise-determined self-frequency of the atom vibrations," p. 99.

It is doubtful whether the discussion of the relation between the maximum surface tension of mercury and the single-potential difference will be especially helpful, p. 122. No suggestion is offered as to a possible line of attack on the problem.

The author is quite enthusiastic over the activity concept and introduces it on all occasions. This is the more extraordinary because he admits, on p. 290, that the only object in introducing the activity concept is to enable one to continue to use the simple relations which either hold or seem to hold for dilute gases and dilute solutions.

The discussion of the variations from the ideal gas laws, p. 296, is not helpful. "The method of accounting for the variation from the ideal gas laws by introducing the chemical potentials and the activities [he puts the chemical potential and the activity on the same thermodynamic level] is a purely formal one and is often looked upon as unsatisfactory. There have of course been attempts to account for the variations admitted by the introduction of a instead of x on a molecular-theoretical basis by assuming special chemical interactions, which lead to the formation of new molecular types, for each of which the laws of ideal solutions hold. It is true that is possible in this way to account for almost all the phenomena, but it seems unjustified from the thermodynamic and molecular-theoretical view-point to exaggerate the chemical view-point to the extent of a general application of such a process. It is simply another formalism which has not even the advantage of being convenient. The attempt to handle liquid mixtures by means of the van der Waals equation of state is in fact scarcely less formal than the method of activities, because it involves at present empirical coefficients. It is not denied that the van der Waals equation may often be a convenient starting-point for an analytical presentation of the experimental data, though it is hard to say what the constants in the formulas mean and impossible to predict them.

"In view of the prevailing uncertainty whether the [abnormal] behavior of a solution is due chiefly to interactions of a chemical nature (solvation, polymerization, etc.), or of a physical nature (ionic forces, van der Waals forces), or to different kinds of interactions occurring simultaneously, it is better for the present to stick to the treatment by residual work or activity, which does not explain anything but gives a good description of the thermodynamic results. In cases, however, where the molecular state or the kind and influence of the physical interactions seem to be established by many experiments (for instance, formation of double molecules of organic acids in non-aqueous solvents, dissociation of strong and weak electrolytes), the predictions from the activities on the basis of this more exact knowledge and their comparison with the empirically determined data offers an especially convenient and comprehensive test of the special molecular assumption. Of course one must never let the convenient presentation of the data by empirical activities interfere with special conceptions in regard to possible molecular states and prevailing interacting forces, the working out of which must always remain the goal of investigations [wine bricks are now sold with strict injunctions not to put them in water].

"Widespread misconceptions make it desirable to say again here that the introduction of activities in no way denies the occurrence of chemical interactions. Activities (or residual work) do away with the need of making *insufficiently-grounded,* special assumptions as a basis for the presentation of the subject. The activity concept permits the limitation of the discussion to what is known empirically." This seems to be a very roundabout way of saying that the introduction of the activity concept puts all the disturbing factors out of sight and makes it possible to forget that they exist.

On p. 360 are given activity-concentration curves for acetone and carbon bisulphide, both curves lying above the ideal ones and a similar diagram for acetone and chloroform in which both curves lie below the ideal ones. No conclusion is drawn in either case. A mere statement of the activities is sufficient. To the layman it is not clear why pressure-concentration curves would not have been equally inadequate.

The question of the salting-out of a non-electrolyte is handled very briefly, p. 439. "The solubility of a non-electrolyte in aqueous solution is in general decreased by addition of an electrolyte, a phenomenon which is known as salting-out and which finds many practical applications. Thermodynamically speaking, the addition of an electrolyte increases the activity of a dissolved non-electrolyte. With volatile non-electrolytes there is consequently an increase in the partial pressure." Lash Miller did better than that over thirty years ago and without making use of activities. He showed definitely what Schottky probably assumes but certainly does not state, that the electrolyte and the non-electrolyte must be mutually insoluble. Miller's demonstration was general and did not necessitate one of the components being an electrolyte.

"If we dissolve solid naphthalene in benzene, we should expect heat and volume effects corresponding very closely to the heat of fusion of naphthalene and to the volume difference between solid and liquid naphthalene. The same thing must hold for all solutions of naphthalene in all liquids with which it forms ideal solutions. Gehlhoff has confirmed this prediction for the heats of solution. He obtained heats of solution of 4400-4800 cal/mol when naphthalene was dissolved in benzene, ether, aniline, etc., while the heat of fusion is 4560 cal/mol." One would have liked to see the conclusion drawn that naphthalene is present as a liquid and with some of the properties of liquid naphthalene even in dilute solutions. The corollary to that would have been that sodium nitrate is present as a liquid and with some of the properties of liquid sodium nitrate even in dilute aqueous solutions. As another the author might have felt reckless enough to say that sulphuric acid is present as a liquid and with some of the properties of liquid sulphuric acid even in dilute aqueous solutions. Even if he had got as far as this, he would probably have balked at saying that lead sulphate dissolves in sulphuric acid because it is soluble in liquid sulphuric acid. It is quite certain that a complex salt would have been invoked or possibly a change in activity.

On p. 592 there is given what purports to be a rigid thermodynamic deduction of Nernst's distribution law, which omits all reference to the increasing mutual solubility of the two liquids on addition of the third component.

It seems to the reviewer that the author is a man who has picked up his physical chemistry on the side and who has never really mastered the subject. The book cannot be recommended to the progressive chemist. The author's presentation is not even a masterpiece of style. *Wilder D. Bancroft*

Practical Physical Chemistry. *By A. Findlay. 22 × 14 cm; pp. xii + 312. London: Longmans, Green and Company, 1931. Price: 7 shillings, 6 pence.* In the fifth edition of this well-known book the form of the last edition and much of the old material have been retained. Some additions have been made, the most important dealing with potentiometric measurements, and experiments have been added to illustrate the conception of activity. Very few of the new experiments involve anything fresh in the way of experimental technique, and consequently the book cannot be regarded as entirely representative of modern experimental methods. The use of the thermionic valve in potentiometric measurements is described but there is no mention, except in a foot-note, of its employment in the determination of electrical conductivity, and the chapter dealing with the latter subject is unaltered. The book would have gained in value if some of the more rarely used approximate methods, especially of determining osmotic activity, had been omitted and the space devoted to a fairly full treatment of more accurate methods. In spite of this however there is no doubt that the book will continue to be of the greatest value as an introduction to the study of experimental physical chemistry. *C. S. Salmon*

Thermodynamics. *By A. W. Porter. 17 × 11 cm; pp. v + 93. London: Methuen and Co., 1931. Price: 2 shillings, 6 pence.* The author intended this monograph to "enable a reader to understand the logical foundations of the subject, and not only to see the kind of applications that are made of thermodynamic principles in various parts of physics, but to be able safely to apply them himself to further problems." He has succeeded admirably. An enormous amount of information is packed into very small compass, partly by fine writing and partly by a free use of the "language" of mathematics. Not that more than a knowledge of the elements of calculus is required, but the reader must be able to use such knowledge freely.

The outlook is physical rather than chemical, though the chapter on "equilibrium" deals briefly with the isochore, the isotherm and the phase rule. Classical notation is employed in preference to that of the G. N. Lewis school, the "Free Energy" of which is called the "Gibbs function" in this work, and there is no reference to "activity." The foundations of the subject are, however, exceptionally well presented. *L. J. Hudleston*

Errata

Victor K. LaMer, T. H. Gronwall and Lotti J. Greiff:
J. Phys. Chem., 35, 2245 (1931).

p. 2246 footnote (a) $E'' = E + \ldots$ should read $E_0'' = E + \ldots$

p. 2249 footnote (j) definition of f_0 should be

f_0 = activity coefficient at 0 conc. of solvent salt

equation (I.-29) $\sum\limits_{m=i}^{\infty}$ should be $\sum\limits_{m=1}^{\infty}$

p. 2251 equation (14′) should read

$$\psi_3(x, x) = q_2 \int_x^{\infty} \xi(u, x)\, \psi_1(u, x)\, \psi_2(u, x)\, u^2\, du + \frac{q_3}{6} \int_x^{\infty} \xi(u, x)\, (\psi_1(u, x))^3\, u^2\, du$$

equation (16′) should read $X_3(x) = (1/6) \int_x^{\infty} \xi(u, x)\, (\psi_1(u, x))^3\, u^2\, du$

equation (18′) should read $Y_3(x) = (1/x^6) \int_x^{\infty} x^5 X_3^*(x)\, dx$

p. 2252 equation (25′) last term $(d_n - d_{n-1})$ should read $(d_n + d_{n-1})$

p. 2254 equation (1) $\sum\limits_{j=1}^{z}$ should read $\sum\limits_{j=1}^{2}$

p. 2262 Table III (e) 1.4339 should read 1.4239

p. 2265 Table V(b) fifth item, first column

343.7−0.1 should read 343.7+0.1

p. 2271 equation 10

0.47532 should read 0.47528

0.32769 should read 0.32766

p. 2272 footnote (av) p. 476 should read p. 376

p. 2275 Table VIII the following changes should be made:

Valence Type	a[3] Å	Δt calc. +Error	$\frac{\theta}{(-z_1z_2)10^{-8}\kappa}$	a[3] Å	Δt calc. −Error	$\frac{\theta}{(-z_1z_2)10^{-8}\kappa}$	a[3] Å
1,−3	2	0.00069	1.215	^{c}10.00	0.00067	2.426	<1.00
		0.00133	1.728	2.50	0.00131	2.161	^{c}1.75
		0.01344	2.672	2.01	0.01342	2.680	1.99
	4	0.00070	0.608	>10.00	0.00068	1.822	2.00
		0.00136	1.082	> 6.00	0.00134	1.512	3.00
		0.00250	1.258	4.40	0.00248	1.427	3.53

p. 2279 Table IX

under Barium Nirate Series B[26] column $10^{-8}\kappa$

change 0.2239 to 0.02239
0.3305 0.03305
0.4276 0.04276
0.5835 0.05835

under Barium Nitrate[27] Most Probable a[1] = 2Å column Δt_t

change 0.00539 to 0.00535 column $\Delta t_t - \Delta t_0$
change av. 0.00045 to av. 0.00044
Most Probable a[3] = 3.10Å col. $\Delta t_t - \Delta t_0$
change av. 0.00009 to av. 0.00008

under Potassium Sulphate[29]
Most Probable a[1] = 2.8Å col. Δt_t
change 0.01536 to 0.01436

under Barium Chloride reference to[27] should be to[29]

under Barium Chloride[30] Most Probable a[1] = 2.6Å col. Δt_t

change 0.02760 to 0.02736
0.01047 0.01056
0.02053 0.02071
0.03047 0.03060
0.04029 0.04032
0.05005 0.04989

p. 2280 Table X

under Xantho-Cobaltic Chloride[31]
Most Probable a[1] = 1.5Å col. $\frac{\theta}{(-z_1z_2)10^{-8}\kappa}$
change 1.06778 to 1.06792 col. $\Delta t_t - \Delta t_0$
change −0.00092 to +0.00092

p. 2283 equation (18) last term should read $-0.30764\frac{q_3}{(10^8a)^3}(\ldots.)$

p. 2287 reference [4] (1927) should read (1929)

p. 2288 reference [9] p. 558 should read p. 358
[15] (1925) should read (1924)
[30] (1925) should read (1910)

Gronwall, LaMer and Sandved:
Physik. Z., 29, 358 (1928).

p. 367 equation 34 expression $-(m-1-10^{-3}c\,\partial V/\partial n)$ should read
$-(m-1-10^{-3}cm\partial V/\partial n)$

THE HEAT OF ABSORPTION OF HYDROGEN BY PALLADIUM BLACK AT 0°*

BY LOUIS J. GILLESPIE AND HENRY A. AMBROSE

The only direct measurements of the heat of absorption of hydrogen by palladium that have the appearance of accuracy are those of Mond, Ramsay and Shields.[1] These authors discussed the earlier work of Favre.[2]

From pressure measurements at varied temperature, the heat of absorption (change of heat content) has been calculated by Moutier[3] and by Dewar,[4] using the data of Troost and Hautefeuille[5] and of Roozeboom,[6] respectively, and by Gillespie and Hall,[7] using their own data. Both Moutier and Dewar found the heat evolved upon absorption to increase with rising temperature; Gillespie and Hall found the opposite behavior.

There is also some discrepancy as to the value of the heat calculated for 0°; Dewar finding about 9323 cal/mole H_2, and Gillespie and Hall finding about 6000 for the first hydrogen solution, 8860 for the horizontal isotherms, and about 9740 for the second hydrogen solution, the integrated value up to the composition of Pd_2H being 8780. The heat measured at 0° by Mond, Ramsay and Shields increased only very slightly with the hydrogen content, was assumed constant, and the average value found to be 9210, if a certain correction was introduced which seemed necessary,[7] or 9362, if the correction was omitted.

The agreement between the heat measured by Mond, Ramsay and Shields and that calculated by Dewar is probably fortuitous, as Dewar used only three points for the calculation of the three necessary parameters.

A difficulty, likely to be present in heat measurements in all systems in which a variety of phases is capable of existence, is that in the heat measurements, necessarily rapid compared with the measurements of equilibrium pressure, phases may be formed other than those that can remain in phase equilibrium, and can then persist during the measurement of the heat. When these other phases have different heats of formation from those of the equilibrium-phases, an error will result in the reported heat measurement.

It is evident that more calorimetric data are desirable. When, in some preliminary experimentation, we found that nearly or quite the whole of the

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* Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 270.

[1] Mond, Ramsay and Shields: Phil. Trans., **191A**, 105 (1898).

[2] Favre: Compt. rend., **68**, 1306 (1869); **78**, 1257 (1874).

[3] Moutier: Compt. rend., **79**, 1242 (1874).

[4] Dewar: Proc. Chem. Soc., **1897**, No. 183, 197.

[5] Troost and Hautefeuille: Compt. rend., **78**, 686 (1874); Ann. Chim. Phys., [5] **2**, 273 (1874).

[6] Hoitsema: Archives néerlandaises, **30**, 44 (1896); Z. physik. Chem., **17**, 1 (1895). He reported his own, and Roozeboom's data.

[7] Gillespie and Hall: J. Am. Chem. Soc., **48**, 1207 (1926).

pressure-composition isotherm of Gillespie and Hall could be traced by merely adding hydrogen to palladium, without resorting to the heat treatment used by them, it seemed that we were in a favorable position to undertake heat measurements.

Experimental

The palladium black was prepared from palladosammine chloride by the method of Gutbier[8] as before.[7] One variation of technique was made in preparing the black, which may have been responsible for the greater ease of absorption of hydrogen:—after the bulk of the ammonium chloride (formed in the reduction of the palladosammine chloride by hydrogen) had been removed in a current of carbon dioxide, the palladium weighed and introduced into the apparatus and the further small quantities of ammonium chloride removed by heating in a vacuum to the boiling point of mercury (as in the previous procedure), the palladium was further heated nearly to the softening-point of the pyrex container, the mercury diffusion pump still being connected. Further traces of ammonium chloride were seen to leave the palladium; and there seems to be no doubt that our palladium was freer from ammonium chloride than that of Gillespie and Hall.

With this palladium their isotherm could be traced up to a point on the second rising portion of the isotherm, with or without the aid of heat treatment. Sometimes it happened that hydrogen driven off by heat did not all return to the solids on subsequent cooling, but this was the exception, and heat treatment never produced a pressure appreciably lower than the value on their isotherm.

In order to avoid certain difficulties, the heat was measured when palladium and hydrogen were brought together within a container of constant volume; thus we measured a change of energy. The desired changes of energy and of heat content were then computed for the constant-pressure, constant-temperature change of state:

$$H_2 + 4\ Pd = 2\ Pd_2H \text{ (all at } 0°, 1 \text{ atm.)}, \qquad (1)$$

where Pd_2H gives the average composition of two solid solutions.

The essential features of the apparatus are shown in Fig. 1. Palladium black, three times treated with hydrogen and then each time exhausted at a high temperature (in the capsule A) is contained in the sealed capsule A, provided with a thin flattened top. After the introduction of the capsule, a measured quantity of hydrogen is introduced into the tube B, which is closed by the steel stopcock I. The volume of that part of the container of hydrogen outside the ice calorimeter has been made very small in comparison with that of the tube B. The calorimeter assembly includes the ice calorimeter C; a radiation shield D of copper, silvered on the inside; and the ice-bath E, insulated with felt two inches thick. The whole assembly is mounted on a base that can easily be raised into the position shown in the figure, or lowered. When in the low position, the ice-bath is filled with ice, the calorimeter given

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[8] Gutbier: J. prakt. Chem., (2) 79, 235 (1909).

time to cool to 0° and then a layer of ice is formed on the inside wall of the calorimeter by immersing a tube cooled in liquid air in a layer of mercury (not shown) in the inner tube of the calorimeter. Then the assembly is raised to the position shown and the calibrated capillary tube F, which is provided with a vernier reading to 0.1 mm., is connected at the ground-glass joint. The average mass of mercury per millimeter of capillary is 0.003052 g.

When the creep had become steady, the glass capsule A was shattered by means of the device H. By turning a nut, a long pointed rod, passing through a packing-gland, was forced down against the top of the capsule, breaking it without a failure. The creep was in the same direction as the motion of mercury in the calibrated capillary that attended the reaction. The average creep was determined before and after the reaction, and the creep per minute, multiplied by the time of the observation, was subtracted from the total motion observed. This correction was usually less than one percent.

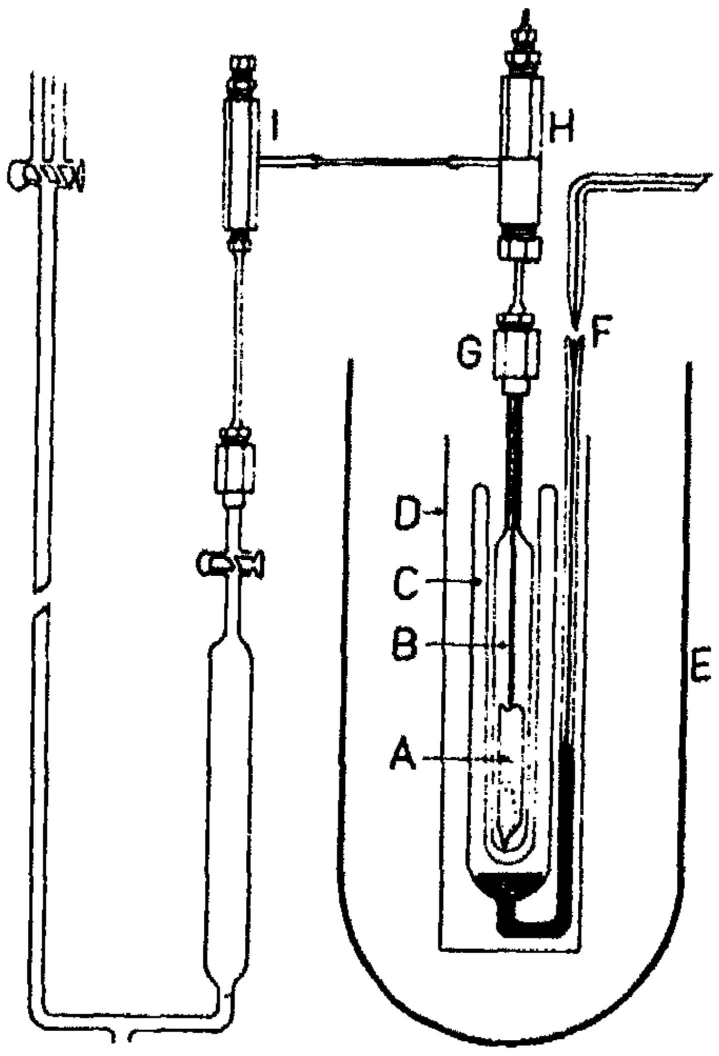

Fig. 1
Essentials of the Apparatus

For computing the heat from the motion of mercury, the conventional value of the calorimeter constant was used: 0.01546 grams of mercury per cal_{15}. This value was checked to about 1 percent by dropping known weights of water and of copper at known temperatures into the calorimeter.

The number of moles of hydrogen absorbed was computed from the quantity originally put in the reaction tube and the final pressure and volume (measured after breaking the capsule, by adding a known quantity of hydrogen and applying the ideal gas law).

Results

Table I gives the mass of palladium black and the moles of hydrogen absorbed, also the loss of energy, the loss of energy per gram of palladium, and the composition of the solids in moles of hydrogen per gram of palladium. The initial pressure never exceeded 2 atm., and the effect of a change of pressure from 2 to 1 atm. on the energy or heat content of hydrogen is negligible, as ascertained by the use of an exact equation of state. The effect of this change of pressure on the energy or heat content of the solids can also be neglected. Hence the change of energy or of heat content per unit mass of palladium is determined by the composition.

TABLE I

The Experimental Results

Run	g. Pd	Moles H_2	$-\Delta U$	$-\Delta U$/g.Pd	$10^4 \times$ moles H_2/g.Pd
1	2.1072	0.001474	12.91	6.127	6.99
2	2.0900	0.001804	15.87	7.593	8.63
3	0.8573	0.001623	14.01	16.460	18.93
4	2.0724	0.000184	1.18	0.571	0.89
5	3.2991	0.001215	10.51	3.186	3.68

For comparison, the data of Mond, Ramsay and Shields were recalculated on the assumption that hydrogen entered the calorimeter at 23°, by subtracting $23 \times C_p$ and the value of RT was also subtracted to obtain $-\Delta U$. Table II gives the recalculated values.

TABLE II

Data of Mond, Ramsay and Shields (Recalculated)

Run	$-\Delta U$	Moles H_2	$-\Delta U$/g.Pd	$10^4 \times$moles H_2/g.Pd
1	14.62	0.001663	8.78	9.98
2	28.40	0.003232	17.05	19.40
3	41.22	0.004679	24.75	28.09
4	43.97	0.004982	26.40	29.91

Discussion of Results

In Fig. 2, the loss of energy in calories per gram of palladium is plotted against the composition for both sets of data; our observations being indicated by the centers of plain circles, and those of Mond, Ramsay and Shields by the centers of circles with marks. The straight line shown was determined by the method of least squares for all points lying on the horizontal portion of the pressure-composition isotherm (between about 0.9×10^{-4} and 27.7×10^{-4} moles H_2/g. Pd.)[9]. Within these limits the slope of the line, which is the loss of energy per mole of hydrogen, appears constant, as we should expect. The

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[9] The equation found is $-\Delta U = 8740n - 0.01$, where n is the number of moles of hydrogen per gram Pd.

two lower points of Mond, Ramsay and Shields lie in this region and fall on our line. Their two higher points correspond to the second rising portion of the isotherm, and are high, qualitatively in accord with the finding of Gillespie and Hall from pressure data, that the heat is higher in this region. The lowest point of the curve corresponds to the first rising portion of the isotherm and is also low, but the experimental error is so great, owing to the fact that the heat measured was only 1 cal., that this point cannot be used to verify the conclusion from the pressure data that the heat is lowest in this region. Indeed, our calculations (not here reported in detail) show that our data as a whole (but not including this inaccurate point) indicate that the heat in this region is not lower than that in the region of the horizontal isotherms, provided our average precision is better than 0.8 percent. However, the calculations show that this average precision cannot be better than 0.5 percent, and the finding of Gillespie and Hall, that the heat along the first rising isotherm is the lowest per mole, is not definitely proved or disproved by the present work. To decide this, the apparatus would have to be rebuilt, to permit the introduction of a greater mass of palladium.

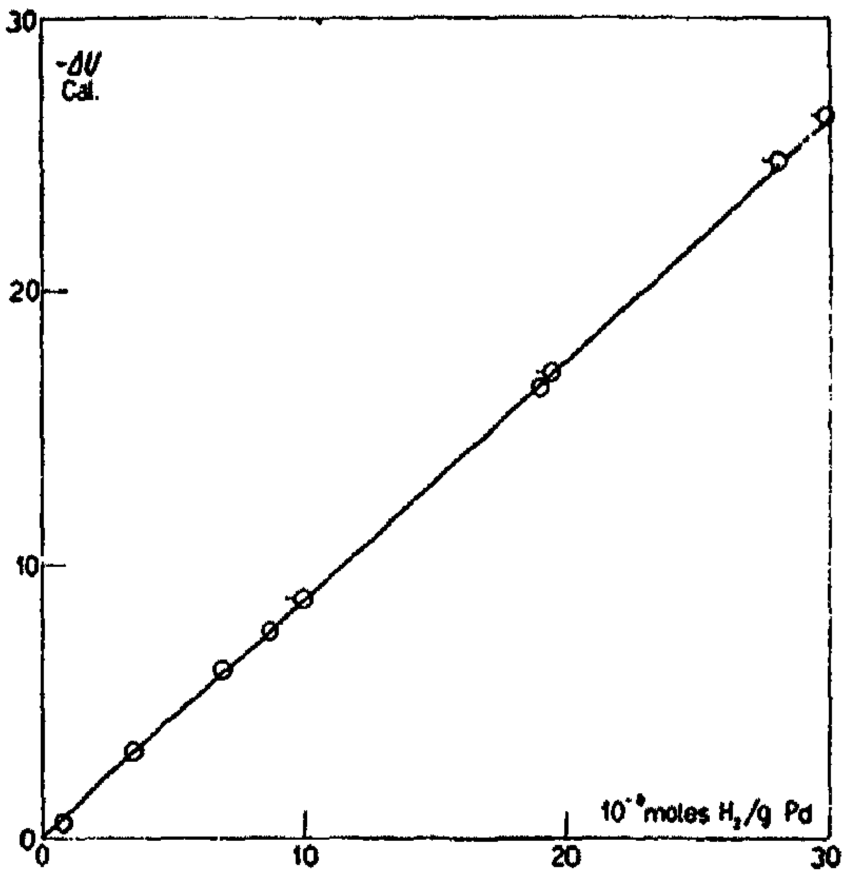

FIG. 2
The loss of energy in calorie per gram of palladium plotted against the composition.

In any case, the integrated value up to the composition of Pd_2H does not suffer seriously in precision owing to this uncertainty, since only about 3.8 percent of the heat is liberated along the first rising isotherm. The values we obtain for the heats attending the change of state (1), which are obviously, from Fig. 2, in agreement with the appropriate data of Mond, Ramsay and Shields, are $-\Delta U = 8740$, and $-\Delta H = 9283$.

The integrated value calculated by Gillespie and Hall for $-\Delta H$ is only 8780, 5.4 percent lower. Some of this can be traced to the empirical deviation plot used by them. In drawing this plot, they removed curvature at the lower temperatures in order to keep close to the datum for 0°. This procedure we have found inconsistent with the rational equation:

$$\log p = \text{A} - \text{B} \log T - C/T. \qquad (2)$$

This equation assumes (1) the ideal gas law for the gas, (2) that the partial molal volume of hydrogen in the palladium is negligible compared with the molal volume of the gas, and (3) that the change of heat capacity attending the evaporation of hydrogen from the palladium is constant. Assumption (1) we have verified by the use of an exact equation of state for hydrogen;[10] assumption (2) is valid, according to the density measurements of Wolf;[11] and assumption (3) is certainly safer than the assumption that the change of heat capacity is not only constant but also zero, which assumption leads to the disappearance of the term in log T and often is satisfactory for chemical equilibria. Application of equation (2) to the pressure data given for the horizontal isotherms by Gillespie and Hall in their Table I gives the following results. Least squaring with equal weights of the data for all temperatures gives for $-\Delta H$, 8940 cal., only 3.7 percent lower than our result; and similar treatment of the data without the datum for 0° gives 9534 cal., which is 2.7 percent high. The values of the pressure so calculated for 0° are 3.87 and 3.39 mm., respectively, instead of the experimental value found, 4 mm. Their experimental value at 0° is doubtless somewhat too high, and the measured heat now reported must be regarded as better than the value they derived, as it appears to agree with the calculated heats within the uncertainty of the calculation.

Summary

The loss of energy attending the absorption of hydrogen by palladium black has been directly measured in an ice-calorimeter. Such of the data of Mond, Ramsay, and Shields as correspond to compositions not exceeding that of the second solid phase (Pd_2H plus excess hydrogen) are in excellent agreement with our data.

The loss of heat content found for the reaction

$$H_2 + 4\ Pd = 2\ Pd_2H\ (0°, 1\ \text{atm.}),$$

where Pd_2H gives the average composition of the two solid phases formed, is 9280 cal_{15}. A recomputation of the data of Gillespie and Hall indicates that this value is in agreement with their pressure data within the uncertainty of the computation, which is several percent and principally due to the experimental error in measuring the small pressure at 0°.

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[10] Using the extension of equation (2) to gases not ideal, given, with equations for latent heats, by Gillespie: Proc. Am. Acad. Arts Sci., 66, 153 (1930).

[11] Wolf: Z. physik. Chem., 87, 575 (1914).

CONTRIBUTIONS TO THE CHEMISTRY OF BERYLLIUM

Beryllium III. Electrolysis of Solutions of Beryllium Compounds in Liquid Ammonia

BY HAROLD SIMMONS BOOTH AND GILBERTA G. TORREY

Introduction

In preceding articles[1] the electrolysis of solutions of beryllium salts in various non-aqueous solvents has been discussed. The only solvents from which beryllium salts gave a deposit of metallic beryllium were several organic derivatives of ammonia. The beryllium salts were very soluble in these solvents but the solutions possessed a high internal resistance so that extremely long periods of electrolysis were required to produce any quantity of beryllium metal. Also these solvents continually formed colloidal, brown, organic products which often adhered to the cathode and tended to prevent the deposition of pure metal. However, this slight success with the organic derivatives of ammonia encouraged the use of anhydrous liquid ammonia itself as a solvent. While this solvent presents greater manipulative difficulties, still it could not form colloidal organic decomposition products and should permit the deposition of pure metallic beryllium.

History of Liquid Ammonia as Solvent

Liquid ammonia has long been known as an excellent solvent for inorganic salts and various elementary substances, particularly the alkali metals. Gore, and Franklin and Kraus,[2] have determined the solubilities of many salts in liquid ammonia and state that the most soluble salts are the nitrates, chlorides, bromides, and iodides while the sulfates, carbonates, fluorides, and oxides are generally insoluble. Several investigators have determined the conductivities[3] of some of these solutions, chiefly those of the alkali metals, but they have rarely been interested in the possible electrode products. Since the solubility in liquid ammonia of only a few beryllium salts has ever been determined and apparently the solutions have never been electrolyzed, it seemed possible that this might be a means of preparation of metallic beryllium that had been overlooked by previous workers.

The chief objection to the use of liquid ammonia as a solvent is the difficulty of handling the solutions which must be maintained in an air-tight apparatus at a low temperature. A new solution must be prepared for each experiment and prolonged treatment of one solution is impossible. A paste

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[1] J. Phys. Chem., 35, 2465, 2492 (1931).

[2] Weyl: Pogg. Ann., 121, 601 (1864); 123, 350 (1864); Gore: Proc. Roy. Soc., 21, 140 (1872-3); Seely: Chem. News, 23, 169 (1871); Franklin and Kraus: Am. Chem. J., 20, 820 (1898).

[3] Franklin and Kraus: Am. Chem. J., 23, 277 (1900); Kraus and Bray: J. Am. Chem. Soc., 35, 1315 (1913); Cady: J. Phys. Chem., 1, 707 (1897).

of solid carbon dioxide in ether or acetone is the best available cooling agent that will maintain the pressure of the solutions below atmospheric during electrolysis, but requires constant replenishing during the experiment.

On the other hand, ammonia possesses the striking ionizing properties characteristic of water and forms solutions of low resistance. Also ions travel much faster[4] in ammonia than in water thus improving the conductivities of salt solutions even if the concentrations are less than in water solutions. Its most important advantage in working with beryllium salts is the absence of hydroxyl groups which react with the beryllium salts to form hydrolyzed, slightly ionized compounds from which no metal can be deposited. The usual by-products of electrolysis of solutions in liquid ammonia are gases, N_2 and H_2, so that there should be no troublesome residual products to contaminate the deposited metal. Thus ammonia offered a solvent of many advantages and it seemed possible that the difficulties formerly met in attempts to separate metallic beryllium by electrolysis of its salts in solution, might be overcome in this medium.

Apparatus

A special apparatus had to be devised for the electrolysis of solutions in liquid ammonia. In the first experiments the apparatus described in a previous article (Beryllium I, loc. cit.) was used. This, however, required a cooling bath around the tube containing the solution. The only cooling bath which would keep the ammonia condensed was a paste of solid carbon dioxide in ether which gives temperatures in the neighborhood of −78°C. This cooled the solution far below the boiling point of liquid ammonia and consequently lowered the possible conductivity of the solution. Since beryllium is a very light metal and requires considerable time for any weight of the metal to be deposited under even the most favorable conditions, it seemed advisable to maintain the solutions at the highest possible temperature. This was accomplished by allowing the ammonia to boil off from the solution and to be recondensed by a cooling agent kept above the solution. Due to the bubbles of escaping ammonia gas this method also affords continual stirring.

The apparatus consisted of a large tube (T) containing the electrolyte, a Dewar Flask (D) sealed above the electrolyzing tube, and suitable connections to source of ammonia, suction, manometer and current. A pint vacuum flask was sealed to a long tube of 5 mm. internal diameter and connected by an inner seal to a tube 24 mm. in diameter. This larger tube carried two sidearms and a large conical joint (J) by which the electrolyzing tube could be attached. Platinum wires were sealed in at the two sidearms and were insulated by a glass capillary down to the point where the electrodes were welded on. A mercury manometer (M) served to indicate the pressures prevailing in the apparatus. The whole apparatus could be maintained evacuated for any desired length of time. The tube (T) was always oven dried and the whole apparatus repeatedly evacuated and rinsed with dry air before use.

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[4] Franklin and Cady: J. Am. Chem. Soc., 26, 499 (1904).

In the early work the lower end of the electrolyzing tube was merely rounded off like a test-tube but later it was deemed necessary to wash the deposited metal with liquid ammonia. This was accomplished by connecting the electrolyzing tube to a side flask (F), by means of glass tubing extending from the bottom of the electrolyzing tube to the upper part of F. Since this connecting tubing was not cooled during the electrolysis the ammonia gas which volatilized from the surface of the liquid in the connecting tube into the side flask gradually expanded and caused violent bumping as it was forced back through the solution by its own increasing pressure. The low temperature of the liquid ammonia solution made it dangerous to transfer the residual liquid through a stopcock after the completion of a run so a mercury seal was designed to close off the connecting tubing and side flask during electrolysis and yet leave an easily opened exit for the residual solution and the subsequent liquid ammonia washings.

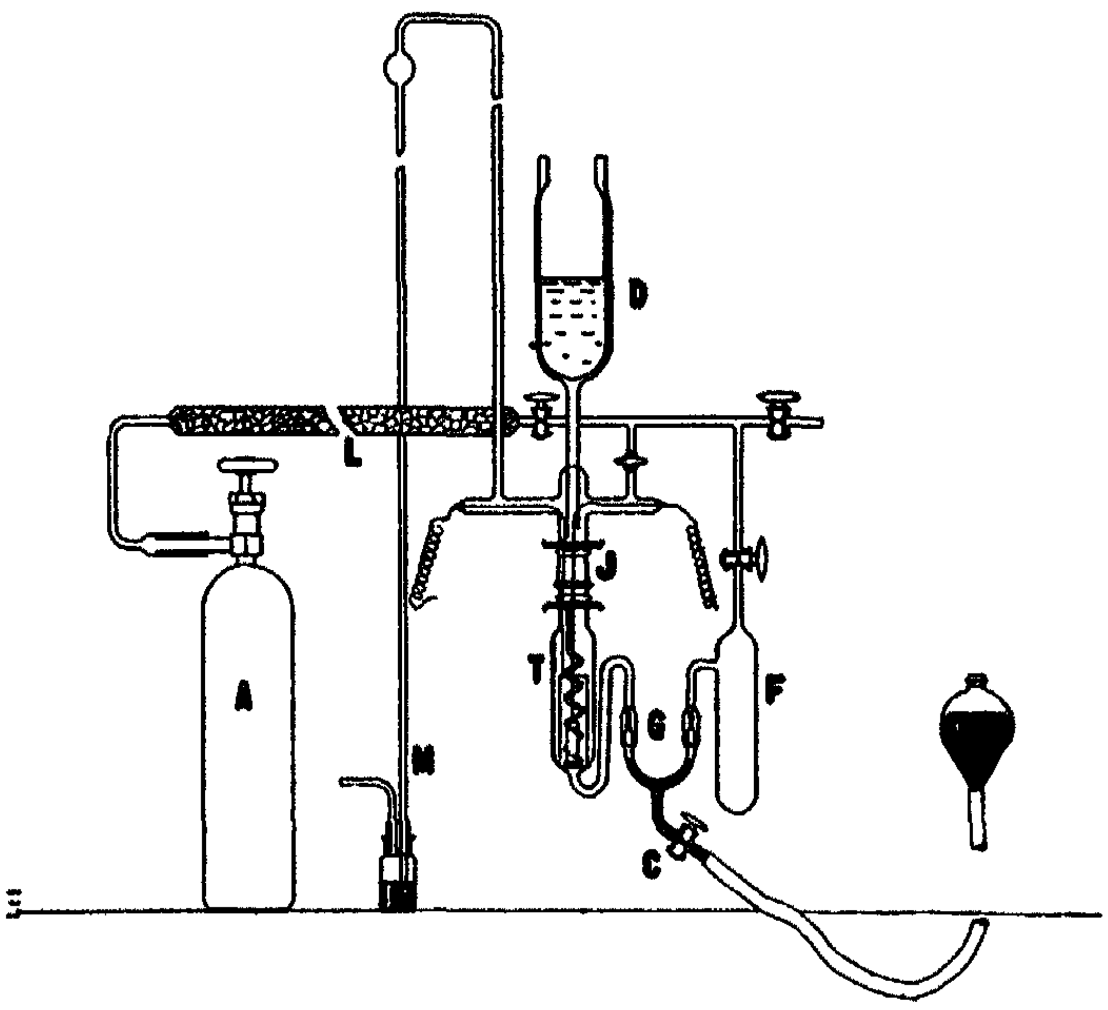

FIG. 1

The mercury seal consisted of two small ground joints, (G), into which ground conical floats fitted snugly when pushed into position by the rise of mercury. These valves were joined by a U-tube of 7 mm. glass and connected through a T to a stopcock (C) which regulated the flow of mercury supplied by an auxiliary leveling bulb. The conical floats were loaded with mercury but were often violently driven into place by the sudden boiling of the ammonia solution as it was transferred. They were later filled with powdered metallic iron and held in position over tiny glass-point supports at the bottom of the tube by means of an external magnet. The electrolyzing flask, mercury seal and side flask were sealed together as a unit which could be placed in the oven for drying. This unit was attached to the rest of the apparatus through the conical joint and a flat joint (not shown in the cut) on the residue flask.

Platinum electrodes were used throughout the work. The anode was a small piece of platinum sheet rolled into a small cylinder and insulated from the large platinum cathode which surrounded it by a glass spiral. Although the electrodes were placed as close as two or three millimeters, the glass spiral prevented short circuiting between the electrodes and yet offered very little hindrance to the passage of current.

Solvent Purification. Solutes

Dry ammonia from a tank (A) of the pure gas was passed through a four foot tube of quick lime (L) and condensed directly over the sample to be electrolyzed.

In their determinations of solubilities of inorganic salts in liquid ammonia, Franklin and Kraus (loc. cit.) reported the sulfate, basic carbonate, chloride and oxide to be insoluble. Fluorides, sulfites, phosphates are in general insoluble so the selection of a suitable salt for solution in liquid ammonia was quite a problem. The iodide and bromide[1] are rather hard to prepare. Anhydrous beryllium chloride, nitrate and acetylacetonate were prepared as described in Beryllium I. To prepare the double fluoride of beryllium and ammonium,[2] beryllium basic carbonate was dissolved in pure hydrofluoric acid, the calculated amount of ammonium fluoride added, and the mixture evaporated in a platinum crucible in a stream of dry carbon dioxide. The resulting double fluoride was crystalline, and was preserved in a desiccator over phosphoric anhydride until needed.

Practically all the beryllium salts are extremely hygroscopic and must be handled in a dry atmosphere to prevent contamination with the products of hydrolysis.

Other investigators have reported several ammoniates[3] of beryllium chloride which Franklin and Kraus, under the conditions of their method of determining solubilities, could not have detected. However, no one had noticed any definite solubility of the chloride in ammonia. Since this was the most easily available anhydrous salt further trial of its solubility in liquid ammonia was undertaken. Even if the salt dissolved in very small quantity it was thought that it might furnish a sufficient number of ions to produce metallic beryllium on electrolysis. The solubility of the double fluoride had never been determined but it was hoped that this salt also might be a suitable salt for electrolysis. The acetylacetonate is one of the few salts of beryllium that is not readily hydrolyzed and so is most satisfactory from the standpoint of ease of handling. Beryllium nitrate dehydrated by heating in a bath of fused ammonium nitrate was found to be a satisfactory solute.

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[5] Lebeau: Compt. rend., 126, 1272 (1898); Ann. Chim. Phys., (7) 16, 457 (1898).

[6] Lebeau: Ann. Chim. Phys., (7) 16 489 (1898).

[7] Mieleitner and Steinmetz: Z. anorg. Chem., 80, 71 (1913); Ephraim: Ber., 45, 1322 (1912); Lebeau: loc. cit.

Behavior of the Various Salts in Liquid Ammonia

For the first tests of the solutions in liquid ammonia the simple apparatus described in the preceding articles was used. Ammonia was condensed over samples of the salts and the conductivity, electrode products, and general behavior of the solution determined before trying the experiment in the larger apparatus.

1. *Solutions of Beryllium Acetylacetonate.* This salt dissolved slowly in liquid ammonia. When electrolysis was first started the solution carried 0.2 A/sq. dm. at 10 volts potential but this value slowly increased during three hours to a value of 2.0 amperes. After three hours further electrolysis the conductivity dropped to the initial value. At first a small amount of gas was evolved at the anode, later copious evolution of gas was observed at both electrodes and gelatinous, brown precipitate was deposited at the cathode. There was no indication of deposition of metal on the cathode.

2. *Solutions of Beryllium-ammonium Fluoride.* Solutions of this salt in liquid ammonia carried only 0.015 amperes/sq. dm. with 10 volt potential. With 115 volts potential there was much gassing at both electrodes apparently due to boiling solvent. The conductivity rapidly increased from 0.2 amperes/sq. dm. to 4.70 amperes in the course of five minutes. There was a slight indication of deposition of metal which formed a gray fog on the walls of the tube but the electrolysis had to be discontinued because of the excessive gassing at this high voltage.

3. *Solutions of Beryllium Chloride.* Ammonia was condensed over pure, anhydrous beryllium chloride[1] which absorbed a considerable amount of ammonia before any liquid phase appeared. The volume of the salt increased markedly due to formation of the ammoniates. With 10 volts potential the solution carried 0.2 amperes/sq. dm. but this value rapidly increased to 2.5 amperes, which was the constant value maintained during the rest of the run. Much gas was evolved at both electrodes and a black material deposited on the cathode to which it adhered loosely. The ammonia was evaporated off and the tube filled with absolute alcohol. This dissolved the residual beryllium chloride leaving the black deposit contaminated with some white transparent crystals not completely removed by repeated washings with alcohol. The black material readily dissolved in sulfuric and hydrochloric acids and in sodium hydroxide, with evolution of gas as long as it was in contact with the platinum electrode. The metal is brittle, adheres very slightly to the cathode, and under the microscope has a distinct metallic lustre and crystalline structure.

The presence of ammonium chloride in the alcoholic solution was detected microscopically on evaporation of the wash alcohol. The white crystalline salt, partly soluble in alcohol, is probably a product of the reaction of beryllium chloride with ammonia but its constitution was not determined.

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[1] When E. C. Franklin was Visiting Professor in the Morley Chemical Laboratory, the senior author called our observations to his attention and supplied him metallic beryllium. He initiated studies on the halides and similar salts of beryllium in liquid ammonia. This work was continued on his return to Stanford University and published by F. W. Bergstrom: J. Am. Chem. Soc., 50, 652, 657 (1928).

Since the solutions of beryllium chloride in liquid ammonia seemed the most suitable they were tested on a larger scale in the specially designed apparatus. A sample of beryllium chloride was introduced into the well-dried apparatus, the electrodes adjusted, and the system evacuated for several minutes to remove all permanent gases. The refrigerant was placed in the inner vessel of the Dewar flask (D) and dry ammonia passed slowly into the apparatus from the tank. The gaseous ammonia rose through the inner-sealed tube into the evacuated space between the two walls of the Dewar flask, was condensed, and dripped down on to the sample of chloride contained in the electrolyzing tube. Ammonia evaporated from this until the tube and chloride were cooled to the temperature of boiling ammonia and then it collected around the chloride. The chloride slowly swelled due to absorption of ammonia. The solid beryllium chloride slowly dissolved but not with sufficient speed to indicate ready solubility.

During electrolysis ammonia constantly boiled off from the solution, passed into the Dewar flask and was recondensed into the solution. The drops of liquid ammonia ran down the spiral which was used to insulate the electrodes, and thus prevented splashing of drops into the solution and loss of salt on the walls of the tube.

The copious gassing around the electrodes was due to boiling ammonia as there was very little non-condensable gas formed during the electrolysis. From 388 cc. of gas obtained during an experiment only three cubic centimeters of gas were left after absorption in sulfuric acid; from 461 cc. about 4.5 cc. were left unabsorbed. The small amount of gas made impractical a determination of its nature. This electrolysis had been run at high current densities so it is probable that some hydrogen had been give off at the cathode. On completion of electrolysis the mercury seal was lowered until the mercury stood just below the level of the connecting U-tube in the seal. All stopcocks were closed, the ether-solid carbon dioxide refrigerant was brought up slowly around the side flask (F) and the liquid ammonia solution siphoned over as a result of the condensation of the ammonia gas. Violent agitation of the conical floats was obviated by insulating the connecting tubing and by holding the cones securely in place by means of a magnet. After the solution had been completely drawn over, the stopcocks to the back line of the apparatus were opened and the ammonia allowed to vaporize and pass back into the main apparatus where it was condensed by the upper Dewar flask and by a refrigerant around the electrolyzing flask. The electrodes were then soaked in the recondensed ammonia for fifteen minutes to permit solution of residual salt and the ammonia siphoned over into the side flask as before. This process was repeated until constant conductivity indicated the metal was clean. The ammonia was evaporated from the side flask, the apparatus was evacuated and dry air admitted slowly. The electrodes were then removed for examination and should have been free from any beryllium compounds that might have been formed by hydrolysis during exposure to air. Apparently ammonium chloride was formed during the electrolysis but it was readily soluble in liquid ammonia.

Since the metal tended to scale off from the electrode and to be carried away by the rush of the ammonia solution as it was transferred to the side flask, it was difficult to collect.

Effect of Current Density on Deposit

As it was difficult to collect completely the metal which was deposited on the cathode due to its lack of adherence several experiments were tried in an attempt to produce an adherent deposit of beryllium. It was thought that the current density might affect the nature of the deposit so one run was made at low current densities. Ammonia was condensed over beryllium chloride until the lower 2.5 cm. of the cathode were covered with solution. The total exposed surface of the cathode was about 30 square centimeters. With a line voltage of 2 volts only one milliampere could be forced through the solution. When the voltage was maintained at 3.6 volts which is just about the decomposition voltage of beryllium chloride, the current density was 0.02 amperes/sq. dm. The run was continued for twenty-five hours. The mercury seal was then lowered, the solution of ammonia and beryllium chloride siphoned over, and the electrodes washed three times. After the ammonia had been recondensed and the liquid allowed to stand over the electrodes for several minutes the ammeter readings for the second and third washings were consistently two milliamperes so the metal was thought to be clean. On opening the apparatus the cathode was found only slightly coated with metallic beryllium. Apparently either the solution of ammonium chloride that is formed as the electrolysis continues is sufficiently acid to dissolve off the metal which is readily soluble when in contact with platinum, or the voltage used was so close to the decomposition voltage that very little metal was deposited. The lower part of the cathode carried metallic beryllium that was perfectly clean.

During another run the current density was maintained at 0.6 amperes/sq. dm. for three hours. Successive washings of the metal gave ammeter readings equivalent to 0.1 ampere, 0.02 and 0.006 amperes per square decimeter. This metal was contaminated with fragments of white material where the solution had splashed up from the boiling liquid.

With high current densities the metal is deposited in small nodules that flake off the cathode easily. Apparently the current density is not the only factor that influences the nature of the deposited beryllium.

Attempt to prepare Pure Metallic Beryllium

Since the attempt to prepare adherent beryllium did not produce metal that would entirely remain on the cathodes, some other method of obtaining pure beryllium in quantity had to be devised. Since the metal tended to suspend in the ammonia solution as it is siphoned away after an experiment it was necessary to arrange some means of collecting the loose metal. A dried cellulose thimble was placed around the electrodes to catch the particles of metal that might drop from the cathode. The sample of beryllium chloride was placed outside the thimble with the idea that no material that had been hydrolyzed during the exposure to air could get into the thimble and contaminate the deposited metal. Ammonia was condensed over the whole surface of the cathode and the thimble. The total electrode surface at the cathode was about twenty square centimeters and carried 1.3 amperes/sq. dm. at 8 volts potential. The electrolysis was continued for five hours. After electrolysis the thimble and electrodes were completely covered with liquid ammonia and washed four times with freshly condensed ammonia. The resulting metal was quite pure. Under the microscope only occasional very fine particles of white residue could be observed in the crevices of the metal.

Physical and Chemical Nature of the Metallic Beryllium

The metallic beryllium is deposited unevenly over the surface of the cathode as a dark gray or black coating. Under the microscope the metal appears in small, warty nodules. These are usually grouped in small clusters of varying size, and resemble heavy warty nickel deposited from aqueous solutions. The nodular fragments are very readily crushed and separate into tiny microscopic particles consisting of small crystals of undetermined form. Some authors have stated that the metal is readily malleable but the pure metal obtained by us is frangible. It is possible that the metal, like chromium, occludes large quantities of hydrogen during its deposition and this prevents its cohering. Under the microscope the metal appears in small, highly refracting crystals grouped irregularly in small rounded lumps which are hollow and seem to have been produced around a nucleus by successive deposition layers.

From its chemical behavior the metal is probably very pure. Previous authors have stated that beryllium is soluble in hydrochloric acid and in strong alkali hydroxides. The metal obtained by this method is insoluble in these reagents and only dissolves in aqua regia slowly on heating with repeated quantities of the acids. The only simple way to dissolve the metal is to place it in contact with metallic platinum and use concentrated hydrochloric acid in which the metal is then readily soluble. If a trace of impurity is present the metal dissolves readily in sulfuric acid, in hydrochloric and in sodium hydroxide with evolution of gas. In this matter of solubility the metallic beryllium which we have prepared resembles pure metallic zinc which likewise is very difficult to dissolve except in contact with a metal lower in the electromotive series. On this basis alone it seems likely that the metal is extremely pure. Obviously it cannot be contaminated with platinum and no carbon is present in the electrolyte. As far as we have found it does not react with pure water, or if so, extremely slowly.

Determination of the Decomposition Voltages of Solutions of Beryllium Chloride in Liquid Ammonia

An attempt was made to determine the decomposition voltage of the saturated solution while the pressure of ammonia was continually varying but the temperature of the solution seemed to have a very noticeable effect on the decomposition voltage. Therefore it was necessary to maintain the temperature constant in order to obtain values that furnished a smooth plot for the decomposition voltage. The pressure of the solution was taken as a criterion of the prevailing temperature of the solution and was kept at a very definite value during two determinations of the decomposition voltages. The pressure of the solution was controlled by careful addition of small amounts of solid carbon dioxide to the refrigerant in the Dewar flask. An empty Dewar flask was kept around the electrolyzing flask to protect it from air currents but the solution was not cooled by any external means. A point on the mercury manometer was marked and the readings taken only when the pressure of the solution was exactly at that point. One operator controlled the temperature while the other made the readings of the voltage and amperage. Readings were made for every tenth of a volt change. Determinations were made at a pressure of 350 mm. and 550 mm. The curve plotted from the values of the voltage and amperage at 350 mm. pressure showed no sharp break while that at 550 mm. gave a decomposition voltage break at 3.5 volts. As the voltage in another experiment was maintained at 3.6 volts and small amounts of metal were deposited this value is apparently very near the actual decomposition voltage of this solution. The slight break on the 350 mm. curve was in practically the same position. The temperatures of these solutions may be roughly calculated by comparing the pressures with those determined for liquid ammonia by Brill.[1] This gives a temperature for the 550 mm. solution of −40°C. and for the 350 mm. solution of −48.8°C. These values are only approximate as the presence of the solute would somewhat alter the temperature for a given vapor pressure.

Current Efficiency

The current efficiency of this method of preparing metallic beryllium has not yet been obtained. The fact that some of the metal failed to adhere to the cathode made the ordinary method of determining current efficiency useless. The particles of metal were so small in some cases that they were readily carried away by the washings of liquid ammonia and lost.

4. Solutions of Anhydrous Beryllium Nitrate and Ammonium Nitrate in Liquid Ammonia

The meager solubility of beryllium chloride in liquid ammonia encouraged the trial of beryllium nitrate as solute. Beryllium nitrate, dehydrated in fused NH_4NO_3 as described in Beryllium I, slowly formed a heavy, viscous solution when NH_3 gas was condensed over it. With 8 volts the solution carried 60 A/dm²., but for extended runs the current density was reduced to 8 A/dm². Smooth, adherent metal was deposited on the cathode. After repeated washings with alcohol minute traces of white material adhering to the metal remained and could not be removed. The metal while in contact with platinum dissolved slowly in hydrochloric acid and was tested microchemically, the

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9 Ann. Physik, 21, 170 (1906); Chem. Abs., 1, 268 (1907).

test proving the absence of any possible transferred platinum from the anode and giving clear evidence that the deposited metal was pure beryllium. Excess ammonia gas may be allowed to evaporate from the solution until a solution stable at room temperature is obtained. This solution is clear to slightly opaque and stable for extended periods if protected from moisture. More NH_3 may be condensed over it for further electrolysis or the heavy viscous solution may be electrolyzed at room temperature. This solution affords an easily controlled method of obtaining metallic beryllium.

Summary

Metallic beryllium may be obtained by a new method in a high degree of purity by electrolysis of solutions of its compounds in liquid ammonia. The metal itself is so pure that it can only be dissolved with difficulty in ordinary reagents. A special apparatus has been devised for electrolysis at the boiling point of ammonia solutions and has been modified to permit the washing of the deposited metal by liquid ammonia. The decomposition voltage of the $BeCl_2$-NH_3 solutions has been measured and the effect on the nature of the deposited metal of different current densities investigated.

Electrolysis of liquid ammonia solutions of beryllium nitrate dehydrated in fused ammonium nitrate and containing some of the latter, gave coherent, adherent deposits of metallic beryllium. Even when the solution became concentrated by evaporation to a viscous mass at room temperature, beryllium could still be deposited from the bath.

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THE ACTION OF FLUORINE ON CERTAIN AROMATIC COMPOUNDS AND A THEORY OF RING SUBSTITUTION*

BY STEPHEN FRANCIS WHEARTY, JR.

The Theories of Substitution and Orientation in the Benzene Ring

When halogens act on benzene derivatives containing side chains there will be substitution in the nucleus or side chain depending upon conditions. In the case of bromine and toluene the facts may be summarized as follows:—[1]

"1. Ring and chain substitution in the dark, temperature effect.
2. Chain substitution in the sunlight.
3. Chain substitution in the dark with H_2O or dilute NaOH.
4. Chain substitution with PCl_5.
5. Chain substitution with sulphur as a carrier.
6. Some chain substitution in the dark with H_2O or dilute NaOH.
7. Ring substitution with $FeCl_3$, ICl, $SbCl_3$, etc.
8. Ring substitution by electrolysis.
9. Some ring substitution in the dark with H_2O or dilute NaOH."

Various explanations have been offered to account for these phenomena, that of Bruner[2] perhaps being the first of real significance. He maintains that nuclear substitution is due to a dissociation of the halogen molecule into atoms or ions and assumed that chain substitution is due to molecular halogen only. This hypothesis is favored by reaction velocity measurements since both side chain and nuclear substitution processes apparently take place according to the requirements of the equation for a unimolecular change.

Bancroft[3] enlarges upon Bruner's theory by assuming that nuclear substitution is caused by negative halogen ions and that side chain substitution is caused by positive ions. His five assumptions are as follows:—

"(a) There is a slight reversible dissociation of bromine into positive and negative particles or gaseous ions.

$$Br_2 = Br^{\cdot} + Br'$$

(b) There is a slight reversible reaction between bromine and the positive gaseous ion.

$$Br_2 \, . \, Br^{\cdot} = Br_2 + Br'$$

(c) Substitution takes place in the ring when the negative gaseous ions are present in excess; otherwise it takes place in the side chain.

(d) The addition products of benzene are to be considered as analogous to the chain substitution products of toluene.

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* This work was done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Bancroft: J. Phys. Chem., 12, 417 (1908).

[2] Z. physik. Chem., 41, 513 (1902); Cracovie: Bull. Akad. Sci., 1907, 691; 1910, 516, 560.

[3] Bancroft: J. Phys. Chem., 12, 417 (1908).

(e) There is a reversible dissociation of the halogen carriers with formation of so-called gaseous halogen ions. Whether these ions are positive or negative depends on the nature of the carrier."

"Of these assumptions the first and fourth are not new; the first half of the fifth has been made implicitly by everybody who has tried to account for halogen carriers without postulating the formation of an intermediate compound. It was explicitly made by Bruner. The second half of the fifth assumption is new but it is a necessary consequence of the first part of the assumption."

"The second assumption is new, so far as I know, and is made because I cannot get along without it. The third assumption is also new but it is a necessary consequence of the first two assumptions."

"I will now show how these assumptions apply to the cases we have to account for. At low temperatures and in the dark, there will be a formation of $Br_2.Br^{\cdot}$ and consequently an excess of Br'. The relative excess will be greater, the greater the concentration of the bromine. We should therefore expect ring substitution in concentrated solutions with an increasing percentage of substitution in the side chain as we start with a more and more dilute bromine solution. This is exactly what was found by Bruner . . . With rising temperature we get increasing dissociation of $Br_2.\ Br'$, the ratio of $Br^{\cdot}$ to Br' increases, and consequently we get an increasing percentage of benzyl bromide among the reaction products. This was also found experimentally by Bruner. . . . Sunlight will increase the dissociation of Br_2 and $Br_2.\ Br'$ and therefore bring the ratio of $Br^{\cdot}$ to Br' up very close to unity and consequently under the third assumption we shall get side chain substitution only, provided the intensity of the light is sufficient. In diffused light we shall of course get a state of things intermediate between the results for darkness and bright light. Both of these predictions have been confirmed experimentally."

"With a carrier such as ferric chloride our fifth assumption calls for a reversible dissociation into gaseous halogen ions and ferrous chloride. With iron we can, of course, only have negative gaseous halogen ions and the equilibrium will be represented by the equation

$$FeCl_3 = FeCl_2 + 2Cl'$$

Under these conditions there will be enough negative gaseous ions to overbalance any positive ions which might come from the chlorine gas and we should expect to get ring substitution even in boiling toluene and even when the system is exposed to bright sunlight. This is exactly what happens."

"With the chlorides of iron, antimony, molybdenum and aluminum, there can be no question but that the chlorine is the negative radical. With iodine monochloride, however, the matter is more open to doubt. Since chlorine is a more powerful oxidizing agent than iodine, we might reasonably expect that iodine would be the positive radical and chlorine the negative radical. The margin of safety is not large however and the experimental results are just what we should expect under these circumstances. Iodine monochloride as carrier does substitute in the ring; but the dissociation is not sufficient to prevent substitution in the side chain in boiling toluene, especially if the concentration of iodine monochloride or monobromide is low. Of course, if one were to decrease sufficiently the concentration of ferric chloride as carrier there would come a point at which side chain substitution would also occur in boiling toluene in spite of the iron; but no such point has been determined experimentally."

"While iodine monochloride is on the line, phosphorus pentachloride is apparently over it and either forms positive gaseous chlorine ions only or an equal quantity of positive and negative gaseous chlorine ions. It makes no difference which reaction we postulate

$$PCl_5 = PCl_3 + 2Cl'$$

or

$$PCl_5 = PCl_3 + Cl^{\cdot} + Cl'$$

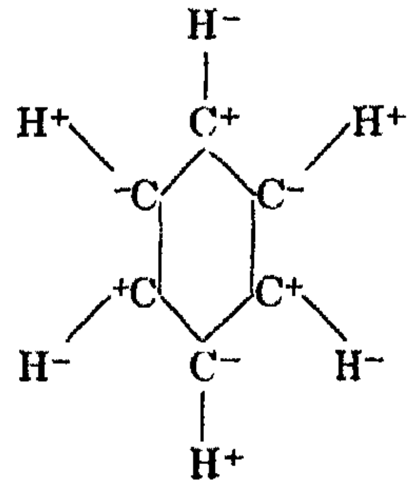
Either one will account for the formation of benzyl chloride by the action of chlorine and phosphorus pentachloride on toluene. Since phosphorus pentachloride accelerates the rate, we must look upon it as a halogen carrier. This differs from the case of iodine monochloride because side chain substitution takes place with phosphorus pentachloride and chlorine in sunshine. Willgerodt has shown that phosphorus pentachloride, chlorine and benzene form benzene hexachloride, so that its behavior with benzene corresponds to the behavior with toluene. . . ."

"It would strengthen the argument if it were possible to show why negative chlorine substitutes in the ring and positive chlorine in the side chain."

Another explanation to account for the mechanism of substitution is that of Holleman.[1] He accounts for side chain substitution by assuming that the replacement is due to molecular halogen. Nuclear substitution on the other hand he postulates as being the result of the action of a perhalide.

Fry[2] criticizes these theories and takes the opposite view to that of Bancroft by assuming that nuclear substitution is due to positive halogen and side-chain substitution to negative halogen.

Using the electronic conception of positive and negative valence to the atoms composing the benzene nucleus, Fry maintains that the following model represents the formula for benzene in which the hydrogen atoms in the 1,3,5 positions function negatively and those in the 2,4,6 positions function positively.[3]



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[1] Rec. Trav. chim., 27, 435 (1908).

[2] "The Electronic Conception of Valence and the Constitution of Benzene" (1921).

[3] Z. physik. Chem., 76, 385, 398, 591 (1911).

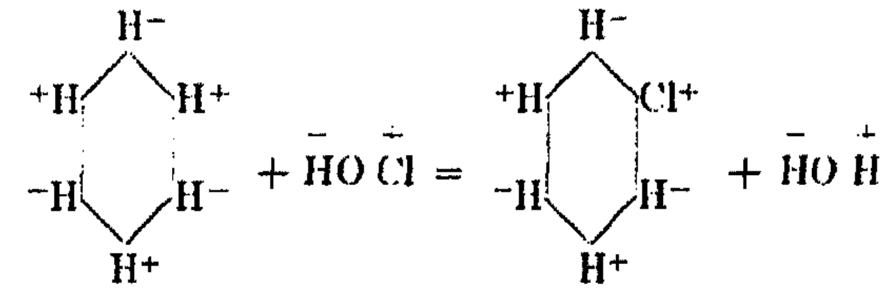
Evidence of the existence of positive chlorine has been furnished by Noyes[1] and Stieglitz[2] while the positivity of chlorine in the 2,4,6 positions has been pointed out by Chattaway and Orton.[3] Also there is proof of the alternate negativity and positivity of the nuclear hydrogen atoms.[4]

On the basis of evidence such as this, Fry has formulated his theory to account for the mechanism of side chain and nuclear substitution and the processes of orientation following the Brown and Gibson rule.[5]

"Now the application of the electronic conception of positive and negative valences to the constituent atoms of the benzene molecule and to the principles of the Brown and Gibson rule, not only rendered possible an interpretation of the rule, but also indicated a mechanism according to which substitution must take place in one way rather than in another way. This was a consequence of the evidence, both theoretical and experimental, that in benzene the hydrogen atoms in positions 1,3, and 5 are negative, while the hydrogen atoms in positions 2,4, and 6 (relatively speaking) are positive. Accordingly, when substituents are of the same sign or polarity they occupy positions which are meta to each other, but if two substituents are of opposite sign or polarity they will occupy positions either ortho or para to each other. The extension of these principles, and the electronic conception of valence to the *phenomena* and conditions of nucleus and side chain substitution may afford not only an explanation of the phenomena, but also indicate a possible and a probable mechanism of the process."

Because of the fact that the presence of moisture, low temperature and the absence of sunlight favors nucleus substitution and also because these factors cause the stabilization of hyprobromous and hypochlorous acids, Fry concludes that these substances are intermediates in nuclear substitution. The halogen therefore comes from the hypoacid and is positive. On the other hand the conditions which favor side chain substitutions i.e., high temperature, sunlight and absence of water also cause hypobromous and hypochlorous acids to act as oxidizing agents and Fry points out that side chain substitution is essentially an oxidation-reduction reaction.

Accordingly the mechanism of nuclear substitution is as follows:—



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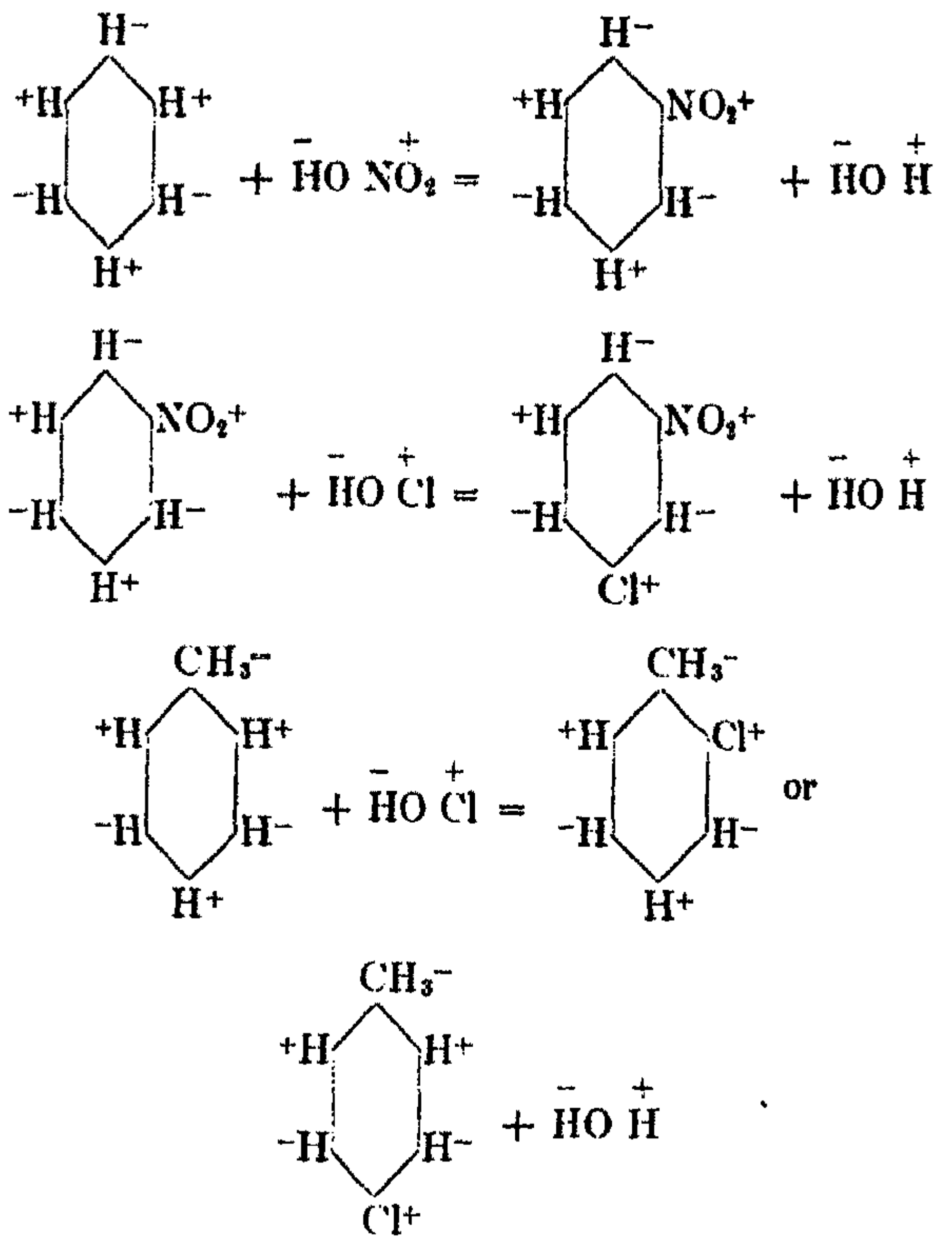
[1] J. Am. Chem. Soc., 23, 460 (1901); 35, 76 (1913); 42, 991 (1920).

[2] J. Am. Chem. Soc., 23, 797 (1901).

[3] J. Chem. Soc., 75, 1046 (1899); Ber., 32, 3572 (1899).

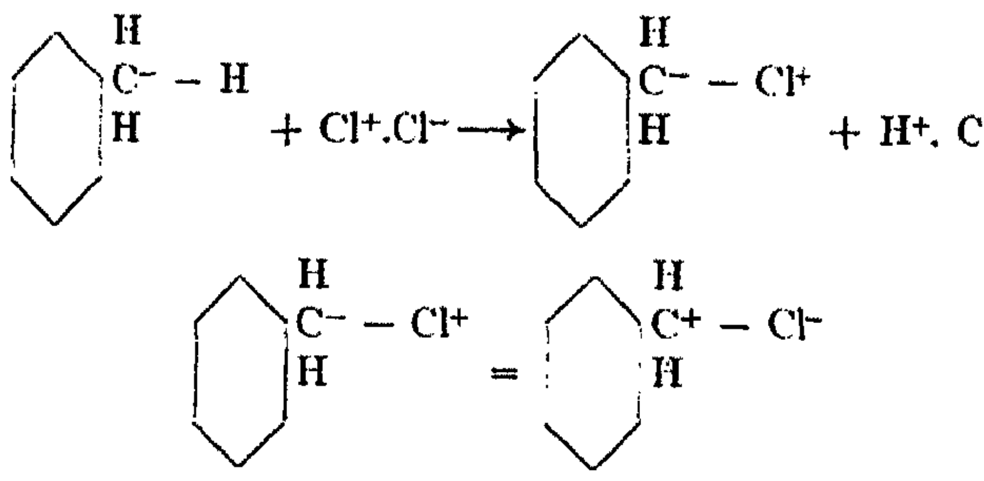
[4] J. Am. Chem. Soc., 38, 1324 (1916).

[5] "Electronic Conception of Valence and the Constitution of Benzene," 133 (1921).



It can be seen from this that the sign of the group already in the ring determines the position of the entering group. The NO_2 groups directs into meta position and the CH_3 group directs into ortho-para positions, this is in accord with the Gibson and Brown rule.

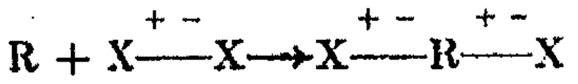
The mechanism of the side chain substitution may be summarized as an intra-molecular oxidation-reduction process.



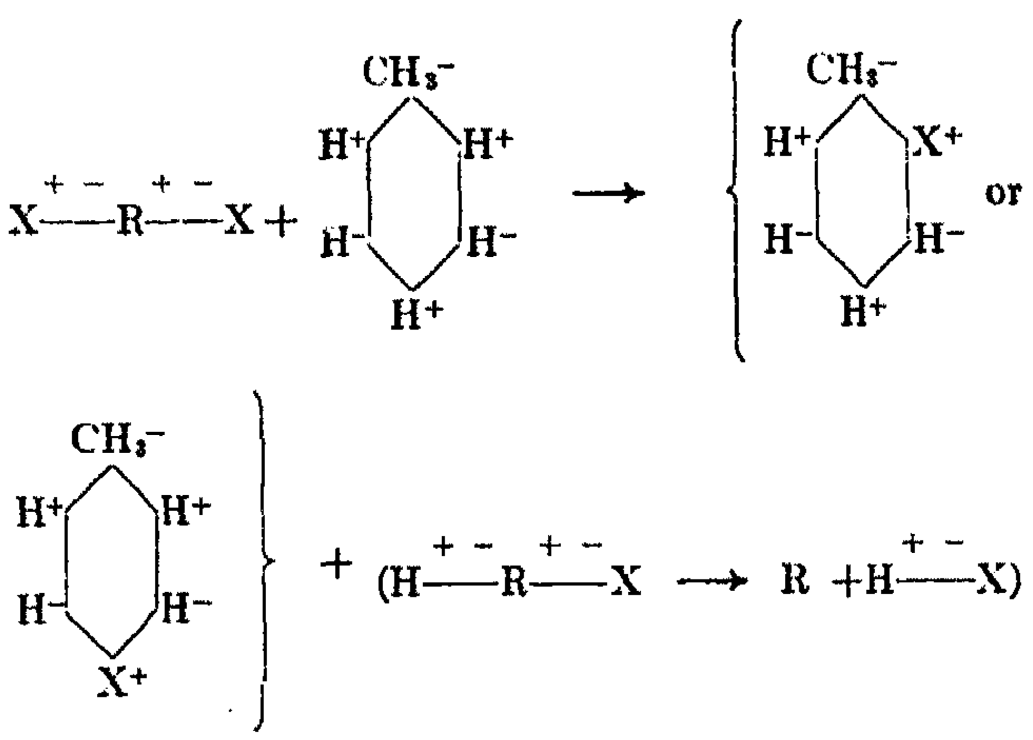
Fry correlates this change from positive halogen to negative halogen in the side chain when halogenation occurs in the sunlight, by the fact that heat or sunlight will also convert $HO^- Cl^+$ to $H^+ Cl^-$ with an evolution of oxygen. In other words the halogen is reduced in both cases.

He explains the action of halogen carriers as follows:—[1]

"R represents any halogen carrier such as water, pyridine, iodine chloride, phosphorus-, antimony-, and molybdenum-trihalides, or any other compound containing an atom which in uniting with chlorine or bromine, X_2, increases its valence from (n) to (n + 2) as follows:—



$$R + \overset{+}{X}—\overset{-}{X} \rightarrow \overset{+}{X}—\overset{-\,+}{R}—\overset{-}{X}$$



"It should be observed that the halogen acid eliminated during the course of the substitution is of the type $\overset{+}{H} - - \overset{-}{X}$, and not $\overset{-}{H} - - \overset{+}{X}$, the latter electromer never having been identified. If neither oxidation nor reduction has occurred during nucleus substitution then the elimination of $\overset{+}{H} - - \overset{-}{X}$ is conclusive evidence that the substituted halogen atom is positive, the reaction having preceded as indicated above. . . ."

Fry's ideas have been criticized from time to time. Holleman[2] states that "on studying this hypothesis more closely it seems to me that there are so many objections against it, that it cannot be accepted." Brunel[3] raises objections to the electronic conceptions of valence put forward in Fry's work. "The chemical evidence advanced in support of this hypothesis in as far as it deals with simple phenomena is quite unconvincing. Any application of the theory involves the constant use of assumptions that render it too elastic to be proved or disproved by these applications."

Another one of the earlier theories developed to explain substitution in carbon chains, orientation in the benzene ring etc., is that of Flürscheim.[4] He goes back to the accepted ideas of the physicist as regards the structure

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[1] "Electronic Conception of Valence and the Constitution of Benzene," 138 (1921).

[2] J. Am. Chem. Soc., 36, 2495 (1914).

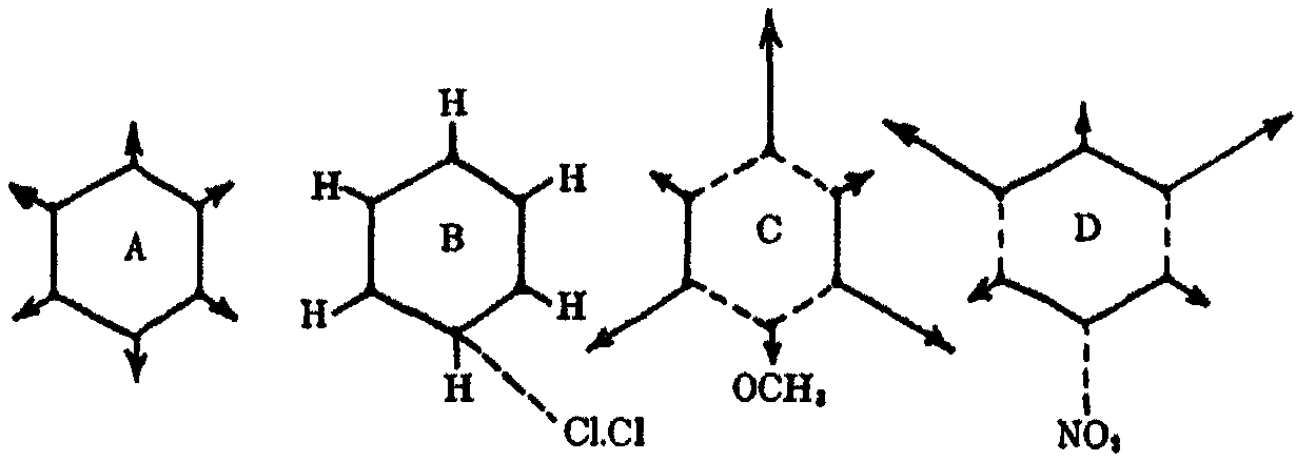
[3] J. Am. Chem. Soc., 37, 722 (1915).

[4] Chem. Ind. Review, 3, 246 (1925).

of the atom i.e., the Rutherford-Bohr-Sommerfeld conception of the rotation of electrons around a positive nucleus in orbits governed by the quantum theory and explains the behavior of a substance under certain conditions on the basis of "reactivity."

"Accordingly, in addition to external factors, such as temperature, medium, concentration, reactivity is governed by three internal factors:—the amount of affinity (quantitative factor "q"), the kind of affinity (polar factor "p") available at each reacting atom and the magnitude of any steric hindrance (steric factor "s") affecting each reacting atom" .... The nature of the affinity of all atoms in a molecule is modified, by a substituting atom, in the direction of the nature of the affinity of the latter, and it has been found that the extent to which atoms in direct combination modify the kind of each other's affinity ("p") is a direct function of the affinity content of the bond between them ("q")."

Using this idea that the reactivity is governed by the three internal factors "p," "q," and "s," Flürscheim interprets and predicts orientation in the benzene ring, the degree of hydrolysis of salts of tautomeric acids and bases, the relative order of electrolytic dissociation constants of acids and bases, the thermionic dissociation of quaternary salts and bases and the mobility of substituents. He explains benzene substitution and orientation as follows,[1] "The equilibrium principle when applied to benzene, leads to formula A, in which we have a symmetrical distribution of free and bound affinity. The amount of residual affinity at each carbon atom is less than at ethylene carbon, but more than at methane carbon. Consequently, the hydrogen atoms are more saturated even than in methane, and substitution is preceded by molecular addition exclusively at one of the six equivalent carbons (see formula B). Substitution of one of the hydrogens creates a new equilibrium with an asymmetric distribution of affinity. Thus the unsaturated, bivalent oxygen of methoxyl in anisol makes a bigger affinity demand on nuclear carbon than did the hydrogen of which it has taken the place, and this results in a shifting of bound and free affinity as shown in formula C, wherein the strong lines denote bonds with an affinity content greater than in benzene, dotted lines bonds with a lesser affinity content, and long and short arrows, respectively, amounts of free (residual) affinity greater and smaller than in



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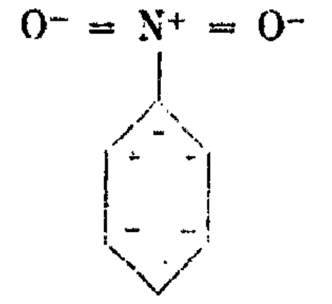
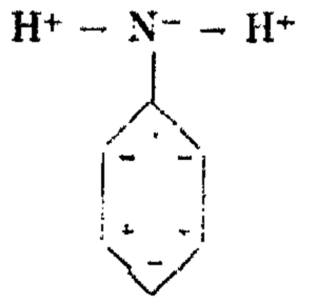
[1] Chem. Ind. Review, 3, 248 (1925).

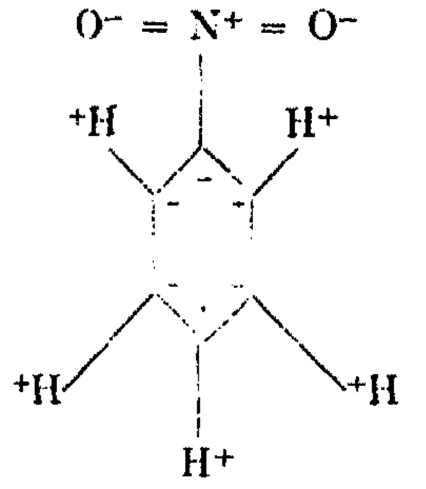
benzene. It is seen that residual affinity is reduced at the meta carbons and increased at the ortho and para carbons, to which latter a substituting reagent must be attracted. When, on the other hand, nitrobenzene, with its highly saturated pentavalent nitrogen, is considered, the distribution is reversed, as shown in formula D, leading to meta substitution."

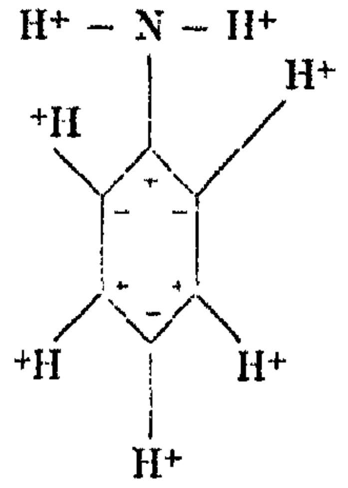
Other workers in this field of benzene substitution have been principally concerned with the mechanism of orientation. Vorländer[1] put forth the assumption that the atoms of a radical may exhibit an alternate polarity which may be indicated by means of the signs + and − attached to the radical. He writes the formulas for nitrobenzene and aniline as follows:—





and points out that the carbon-nitrogen bonds in these two cases are not of the same type. He assumes each hydrogen to be positive, which means that in the case of nitrobenzene the positive NO_2 group replaces the positive hydrogen and the general character of the benzene system is retained. However, in the case of aniline the carbon-nitrogen union is different and Vorländer assumes a strain to exist in the aniline molecule. He indicates the difference between the two by using long and short lines in his structural formula:—





These formulas show that the hydrogens in the ortho, para and meta positions are different depending upon the substituent present. Vorländer uses this mechanism to explain the difference in the substitution processes in the two compounds. According to him, if a negative substituent is attached to a carbon atom of positive polarity, this substituent will be readily removed and easily replaced by another negative substituent. In the case of the three nitro-bromobenzenes,

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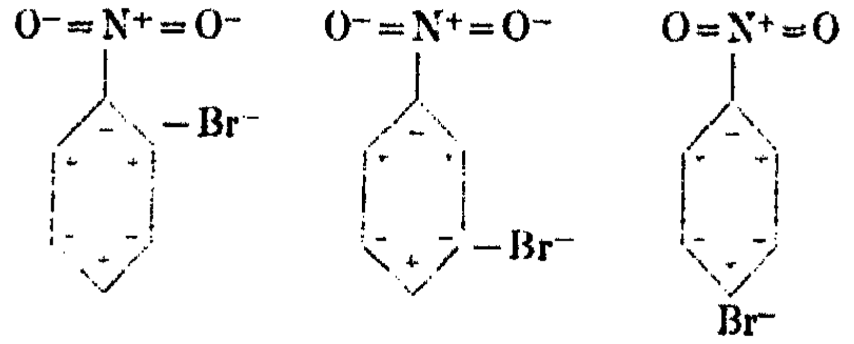
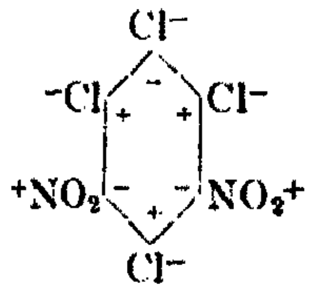
[1] Ber., 53, 263 (1919); J. prakt. Chem., 87, 90 (1913); Ber., 37, 1646, 1651 (1904); 46, 3450 (1913); Ann., 341, 1 (1905); 155, 251 (1906).



the bromine in the meta position is attached to a carbon atom of like sign; this makes it far less reactive than the bromine atoms in the ortho and para positions.

A confirmation of Vorländer's ideas is found in 1,2,4,6-tetrachloro-3,5-dinitro-benzene,



In this compound the only chlorine attached to a negative carbon atom is the one in the 1-position. The others can be removed by various groups, but the one in the 1-position is inactive.

It should be noticed that according to this theory the halogens in the nucleus are negative.

An orientation theory which leads to the same results as those of Vorländer's is "the induced alternate polarity" principle in chains of atoms and first brought out by Lapworth.[1]

He postulates that the laws involving changes in carbon compounds are necessary changes from the operation of the laws of free valencies arising from some point of dissociation or excitation. If some disturbance occurs at one carbon atom in a chain there will be a shift in the valence conditions surrounding each atom and it is assumed that this shift is manifested by the alternate atoms in the chain acting as similar seats of excitation. Any disturbance in the valence conditions of one atom in a chain sets up a constraint and the atom strives to regain its normal condition by redistributing the valencies elsewhere.

While enlarging upon his ideas, Lapworth brings in the conception of the "key atom." This is the atom which is supposed to cause the alternating induced effect evidenced by peculiar properties of the compound. Gough and Thorpe[2] illustrate this point by showing that when ortho and para xylylene dibromides interact with potassium cyanide in alcohol solution, the end products are dicyanides; and no monocyanide is isolated in either case. On the other hand meta xylylene dibromide under the same conditions easily yields a monocyanide. The alternating polarities are shown as follows, the underlined bromine atom being the "key atom":—

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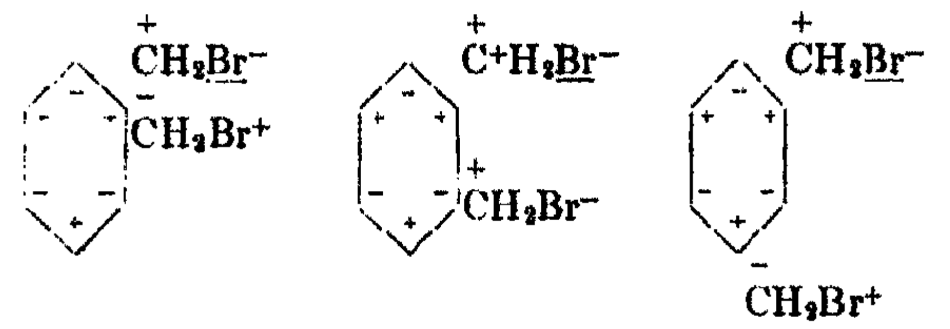
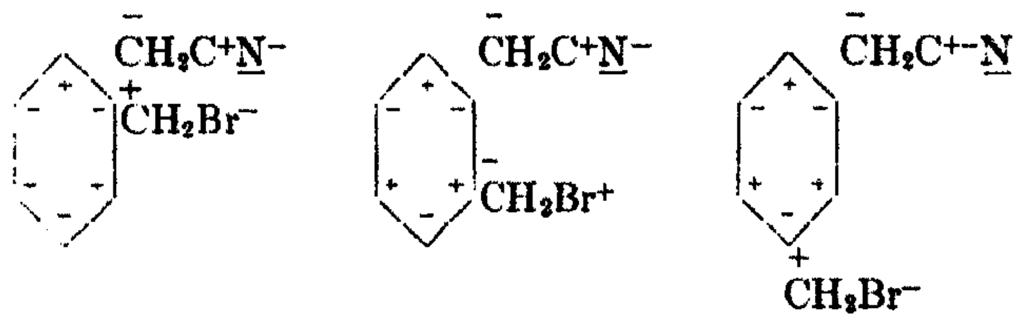
[1] J. Chem. Soc., 121, 416 (1922).

[2] J. Chem. Soc., 115, 1155 (1919).



When a cyanide radical is introduced in place of this bromine atom, the new "key atom" is the nitrogen atom. This new "key atom" accentuates the negative nature of the bromine atoms in the ortho and para positions but tends to neutralize the normal negativity of the bromine in the meta derivative. This is probably the reason for the fact that the monocyanide is formed from the meta compound.

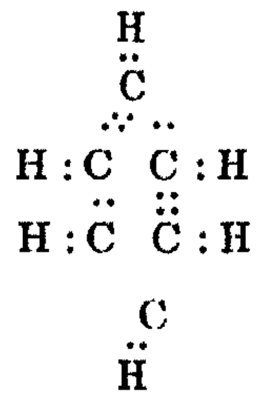


Although the theory of induced alternate polarities fits in nicely with a great many cases, the concept of the "key atom" leaves much to be desired. After the facts are known the "key atom" may be selected but the advantage of a theory is to predict the facts and this cannot be done when there is no means of selecting from several atoms present the one to be designated as the "key atom."

The basic features of Lapworth's theory were brought out long before the modern conceptions of valence were introduced,[1] but later on[2] he showed that his ideas might be made to agree with Lewis's ideas of atomic structure.

Another view of the whole subject based on the modern conceptions of atomic structure has been developed by Kermack and Robinson.[3] Their conclusions are the same as those of Lapworth but they give a definite conception of the "key atom."

The formula for benzene based on Lewis's idea of shared electrons is as follows:—



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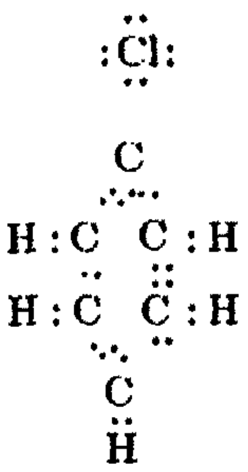
[1] J. Chem. Soc., 73, 445 (1898).

[2] J. Chem. Soc., 121, 423 (1922).

[3] J. Chem. Soc., 121, 427 (1922).

If a substituent such as chlorine, which tends to complete its octet of electrons, is introduced a shift of electrons throughout the ring occurs thus:—



The carbon atoms in the 1,3,5 positions are rendered unstable and those in the 2,4,6 positions stable. This then tends to favor meta substitution.

On the contrary if the substituent in the NO_2 group the carbon atoms in the 2,4,6 positions are made unstable because in this case the oxygen atoms tend to form stable octets and thus alternately the carbon atoms in the 1,3,5 positions are stable. This leads to ortho-para substitution.

Although this is not the whole story it serves to point out the similarity to the alternating polarity idea of Lapworth and defines the "key atom" as the atom that will form a stable octet grouping.

A complete outline of this theory as it has been developed by Robinson, Kermack, Ingold and others is given by Ingold.[1]

Besides the above mentioned effect of induced alternate polarities, called the "inductive effect" the substituent may exert its influence in the molecule through a "tautomeric effect" and a "direct effect."

When there are unshared electrons adjacent to the aromatic nucleus tautomeric electron displacements are made possible and these give negative charges to the ortho and para carbon atoms. This tautomeric effect explains why the chlorine atom in benzene monochloride directs into ortho-para positions while on the basis of the inductive effect alone it should direct into the meta position.

The "direct effect" is always present but has to be considered only when the inductive and tautomeric effects balance each other. The fundamental idea here is that the permanent electro-chemical nature of the substituent will change the electron—availability at the various positions in the aromatic nucleus by an effect acting through space in addition to the atom to atom relay. Once originated however its distribution will be in the order ortho, meta, para rather than ortho, para, meta as in the case of the inductive effect. These three effects are nicely illustrated by numerous examples of cases of substitution and orientation.

Ingold[2] describes the attack of the reagent molecules as follows:—"Two internal factors relating to the reagent may be expected to contribute to the

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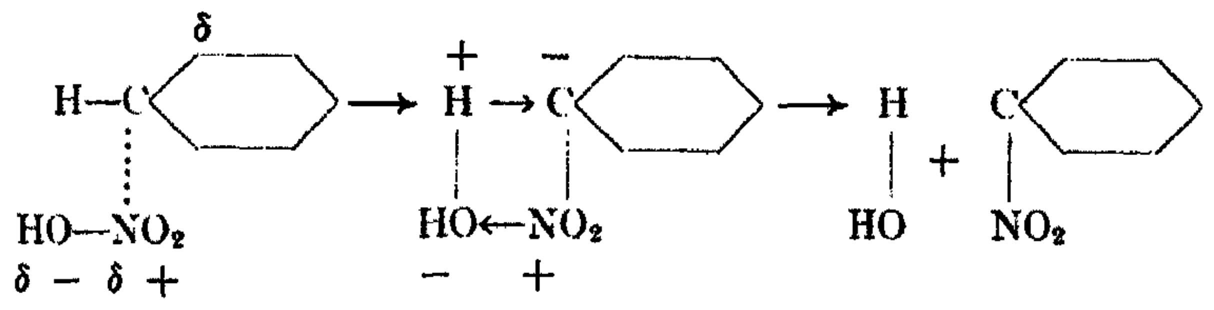
[1] Rec. Trav. chim., 48, 797 (1929).

[2] Rec. Trav. chim., 48, 808 (1929).

facility with which the ordinary substituting agents attack an aromatic nucleus. These are first the polarization, or capacity for polarization, of the attacking molecule and secondly the proton—affinity of the anionic portion ultimately eliminated in combination with hydrogen. The collaboration of the two factors has been pictured for nitration by means of the following illustrative scheme, in which, once molecular addition to the negative carbon atom has been effected (the orientation), the tendency of hydrion and hydroxide ion to form undissociated water determines the completion of the reaction (the substitution):



". . . . . When the atom to be replaced is not hydrogen (which is normally stable as its positive ion), but is an atom or group such as chlorine which is most stable as its negative ion, a group of *positive-* centre- seeking, or, to use Brönsted's term, "basic" reagents (HNRR′, $O\bar{R}$, $\bar{S}R$, $^{-}\bar{S}$, etc.) became especially effective in leading to substitution. . ."

The above mechanism illustrating the introduction of the NO_2 group is similar to that of Fry. The symbol "δ" represents the electron repulsion or attraction necessary to start the reaction. In the case of halogenation Ingold, Smith and Vass[1] state "In explanation of the process of halogenation, Fry, Cofman, Francis and others have supposed that the halogen molecule ionizes, the positive ion being the active agent. Whilst, however, it seems unlikely that such a decomposition involving the exclusive appropriation of electrons by one atom, would take place without external excitation, the electron repulsion of a negative centre (e.g., in an aromatic nucleus) might supply the necessary stimulus by tending to divest a halogen atom of its shared electrons during combination, leaving the other halogen atom to escape as negative ion. Thus, the activity of a molecular chlorinating agent, X.Cl, should increase with the electron affinity of X, and similarly for bromination and iodination, which agrees with the fact that bromine chlorides is a powerful brominating agent, but does not chlorinate, that iodine monochloride iodinates. . . ."

The fact that iodine trichloride is a chlorinating agent is explained on the basis of the theory of "singlet" linkings. Prideaux[2] writes the formula for iodine trichloride thus:—

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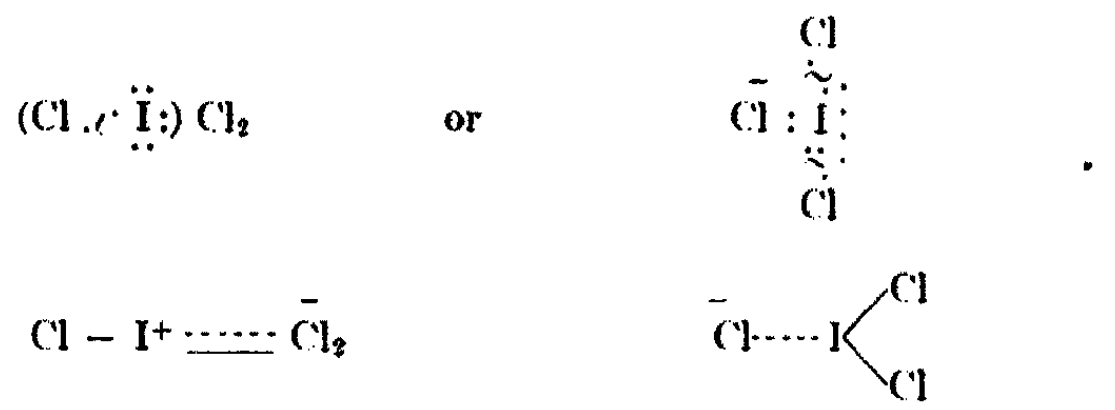
[1] J. Chem. Soc., 130, 1245 (1927).

[2] Chem. Ind., 42, 672 (1923).



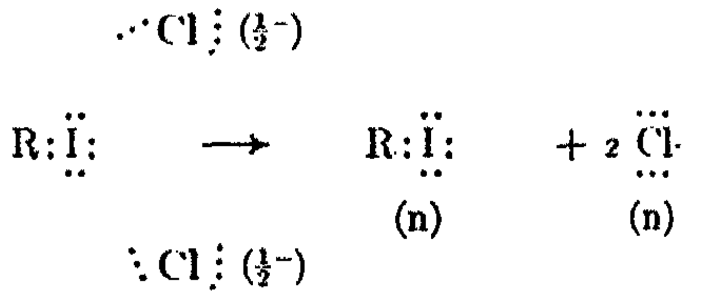
$$(\mathrm{Cl}\,.\!\cdot\,\underset{\cdot\cdot}{\ddot{\mathrm{I}}}:)\,\mathrm{Cl}_2 \quad \text{or} \quad \bar{\mathrm{Cl}} : \overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{I}}} \vdots$$

$$\mathrm{Cl} - \mathrm{I}^+ \cdots\cdots \bar{\mathrm{Cl}}_2$$

in which the binding electrons attached to the negative chlorine atoms are furnished by the iodine atom. This leaves the iodine atom positive and the chlorine atoms negative.

Ingold and Ingold[1] explain halogenation by compounds of this nature as follows:—

"It has also to be remembered that the dissociation of a reagent into neutral atoms, or radicles, may lead to substitution in positions determined by the consideration that those neutral atoms (e.g., Cl) which have to gain electrons to form their stable ions will seek out negative centres, and in this respect simulate a positive group, and vice versa. This may well be the mechanism of chlorination by phosphorus pentachloride, iodine trichloride and aryliodide dichlorides each of the two loosely held chlorine atoms in these compounds being regarded as bound by a single electron and as in a state of incipient atomic dissociation of the following kind:—



$$\begin{matrix} \cdot\cdot\mathrm{Cl}\,\vdots\,(\tfrac{1}{2}^-) & & & \\ \mathrm{R}:\underset{\cdot\cdot}{\ddot{\mathrm{I}}}: & \longrightarrow & \underset{(n)}{\mathrm{R}:\underset{\cdot\cdot}{\ddot{\mathrm{I}}}:} & +\,2\,\underset{(n)}{\dddot{\mathrm{Cl}}\cdot} \\ \because\mathrm{Cl}\,\vdots\,(\tfrac{1}{2}^-) & & & \end{matrix}$$

"Thus it happens that chlorine although *negative* (0.5 unit charge) in the original group, tends to separate as a neutral atom which so desires an electron that it simulates a positive group. Thus the apparent anomoly of negative chlorine leaving positive iodine or phosphorus to become attached to negative carbon is explained."

Studying the halogenation of phenol from the reaction velocity viewpoint Soper and Smith[2] show that the reaction between phenol and hypochlorous acid involves the phenoxide ion and the un-ionized hypochlorous acid and that in the case of iodination the main reactions are those between the hypoiodous acid and ionized and unionized phenol.

Experiments on the electrolytic oxidation of aromatic compounds[3] show that a negative hydroxyl group is introduced into the nucleus in the same positions as those into which a positive nitro group would enter. Oxidation

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[1] J. Chem. Soc., 129, 1310 (1926).

[2] J. Chem. Soc., 129, 1582 (1926); 2757 (1927).

[3] Fichter and Alder: Helv. chim. acta, 8, 74 (1925).

at the anode gives a neutral hydroxyl radical which contains one electron less than the number required to form the stable group and will therefore seek out the negative centers of the aromatic nucleus. This is similar to the behavior of a positive group.

From reaction velocity measurements it has recently[1] been shown that the general electron drift influence is usually the predominating factor in determining aromatic reactivity. Moreover, Bradfield and Jones[2] indicate from reaction velocity measurements that groups keep their relative reacting powers under widely differing reaction conditions.

Another aid to the study of substitution processes is the investigation of the local electrical fields in the neighborhood of the various atoms. "Such an investigation can be carried out in certain cases by measurement of the electrostatic dipole moment of the molecule and though the electrical polarization of the normal 'resting form' of the molecule which is that measurable by purely physical methods, may be radically different from that of the 'activated form' of the molecule at the moment of reaction there is remarkable agreement between the theoretical deductions drawn from such measurements and the known facts of aromatic substitution."[3]

The mass of evidence for and against each of the theories presented, is enormous. There seems to be agreement on several points but in general the problem is still a very complex one.

The following ideas on the subject seem to have been accepted by most everyone:—

(1) The chlorine molecule when reacting with benzene dissociates into positive and negative ions; the positive ion enters the nucleus and the negative ion unites with the positive hydrogen to form HCl. In this process the benzene is activated in some manner.

(2) The modern electronic views of atomic structure, together with the modern conceptions of electro-valence, co-valence and coördinated valence are applicable to aromatic substitution and orientation.

(3) Because of the facts of ortho, para and meta substitution the substituent causes an alternate induced polarity along the nuclear carbons. This involves a key atom in the case of groups such as CH_3, NO_2, etc.

However, although these several points seem to be generally accepted they have not met with universal approval. Because of this, new terms and new theories are constantly being introduced in attempts to solve the problem. Indeed it is the opinion of some people that introducing these various conceptions of co-valence, semi-polar linkages, induced alternate polarities, etc., leads only to confusion. For instance, Cranston[4] points out that there has been no uniformity in the choice of symbols to represent the various types of linkages used in the development of the electronic theory of valence. As a

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[1] Shoesmith and Slator: J. Chem. Soc. 129, 216 (1926); Olivier: Rec. Trav. chim., 41, 646 (1922); 42, 516 (1923); Berger and Olivier: 46, 517 (1927); Berger: 46, 545 (1927).

[2] J. Chem. Soc., 1928, 1010.

[3] Waters: Science Progress, 23, 649 (1929).

[4] J. Soc. Chem. Ind., 47, 208 (1928).

result of this it very often happens that two people, supporters of the same theory, are unable to comprehend each other. Also these new conceptions are probably making the problems far more complicated than they actually are. Fry[1] in showing why chemists are inclined to impose upon structural formulas an octet system of valence notation says: "Most chemists, I believe, are more partial to the Lewis-Langmuir conception of electronic shells than to the Bohr conception of electronic orbits. A possible reason for this attitude may be the fact that the cubical octet conception is primarily and fundamentally an outgrowth and a pictorial elaboration, in terms of atomic structure, of the original conception of Abegg and Bodländer, who, in 1899, stated that atoms display different kinds of valency termed "normal" and "counter" valency of opposite polarity according as they are united with electropositive and electronegative atoms. Furthermore, it is a question in the minds of many chemists whether or not the Lewis-Langmuir valence conceptions and notations possess any more, or perhaps as much, truly chemical significance as that which characterizes the Abegg and Bodländer system."

"Now when we come to consider the actual chemical properties of atoms and molecules, no matter what attempts may be made to explain valency by an electronic pictorial notation, all that the chemist knows pragmatically about the valence of an atom may be embodied in the simple fact that if (n) be the empirically determined valence of a given atom, that atom may function in (n + 1) different ways. This has been fully illustrated in the numerous publications of the interpretations of a great variety of chemical reactions. This is also a direct and simplified modification of the conceptions of Abegg and Bodländer and it does not require the amplification and entailed ambiguity necessarily encountered when the cubical octet or other systems of electronic valence notation are imposed upon structural formulas. It enables us to correlate in a simple fashion the several ways in which atoms and radicals react, positively, negatively, and amphoterically, in strict conformity with the actual chemical behavior of the molecule as amply illustrated by the well established chemical reactions actually being dealt with such as ionization and electrolysis, hydrolysis, and oxidation-reduction processes. In fact, practically all chemical phenomena may be classified under these types."

There seems to be therefore a great demand for some simple workable theory that will explain the facts sufficiently well without going back to the fundamental conceptions of the structure of the atom. It is the purpose of this paper to call attention to the theory of substitution proposed by Bancroft in 1908, substantiate it and to show that slightly modified it will explain the facts of nuclear and side chain substitution in a simple manner.

One of the big objections to Bancroft's theory has been his postulation that the entering halogen is negative in ring substitution. Most all of the other theories have it as positive and this view point has been generally accepted as has been pointed out above. However there are still arguments in favor of the negative halogen. Flürscheim,[2] to cite one instance, when speak-

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[1] Chem. Reviews, 5, 559 (1928).

[2] Rec. Trav. chim., 48, 819 (1929).

ing of the recent theory of induced alternating polarities states that, "Since the new theory depends . . . . . on the assumption that the entering group has a positive charge this assumption may be refuted." Also the assumptions it is necessary to make when contradictions to the positive theory appear complicate the problem. Illustrations of this, already mentioned are the single linkages of Prideaux to explain chlorination by iodine trichloride and the "tautomeric effect" of Robinson, Kermack, Ingold, et. al., to explain why the chlorine atom in benzene monochloride directs into ortho and para positions when it should direct into meta position if positive. In addition reaction velocity measurements have shown that very often in benzene substitution the reaction is not a function of the halogen at all but that the unionized reactant is the predominating factor.

Purpose of This Investigation

It is the purpose of the first part of this paper to offer an explanation for the mechanism of the process of ring substitution and to uphold Bancroft's theory by showing that the entering halogen is negative. In the second part the theory will be extended and applied to cover cases where the substitution is not a function of the halogen alone.

Introduction to Experimental Part

When ferric chloride or chlorine and ferric chloride reacts with benzene or toluene to form chlorobenzene, the chlorine is certainly negative; but we do not know whether the ring hydrogen is positive or negative until we know whether the first step in the reaction is the replacement of hydrogen by chlorine or the reaction of hydrogen with chlorine. We can picture two quite different mechanisms:—

$$(1)\quad C_6H_6 + Cl_2 = C_6H_5Cl + [H + Cl = HCl];$$

$$(2)\quad C_6H_6 + Cl_2 = HCl + [C_6H_5 + Cl = C_6H_5Cl].$$

In the first reaction we have negative chlorine replacing a negative hydrogen and the replaced hydrogen reacting with the residual chlorine. This was the case postulated implicitly by Bancroft[1] in his theory of halogen substitution. In the second reaction negative chlorine reacts with positive hydrogen and the resulting phenyl radical, C_6H_5, combines with the residual chlorine.

When chlorine acts on benzene in the sunlight there is formed benzene hexachloride, which breaks down under suitable treatment into trichlorobenzene and hydrochloric acid.

$$C_6H_6Cl_6 \rightarrow C_6H_3Cl_3 + 3HCl.$$

In this case it seems certain that the primary reaction is the splitting off of hydrogen chloride and the residual chlorines combine with the C_6H_3 group to give trichlorobenzene. This is the more certain because the reaction takes

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[1] J. Phys. Chem., 12, 417 (1908).

place on boiling with alkali, which would of course tend to split off hydrochloric acid.

It is extremely probable that the six chlorines add on in pairs and not simultaneously. On this assumption the reaction would take place in three stages theoretically though not practically:

$$C_6H_6 + 3Cl_2 = C_6H_6Cl_2 + 2Cl_2 = C_6H_6Cl_4 + Cl_2 = C_6H_6Cl_6.$$

If we had a substance which accelerated the splitting off of hydrogen chloride at the end of the first stage, the reaction would be written

$$C_6H_6 + Cl_2 = C_6H_6Cl_2 = C_6H_5Cl + HCl.$$

If ferric chloride were such a substance, the chlorination of benzene in presence of light and of ferric chloride would involve the same first stage and we could say that Equation 2 was right. Unfortunately it turns out experimentally that ferric chloride is not that kind of a catalyst. Some benzene hexachloride was heated in an electric furnace to over 200° with and without ferric chloride. In both cases there was a small amount of hydrogen chloride evolved; but there was no catalysis by the ferric chloride. This indicates that Equation 2 does not hold for the chlorination of benzene in presence of ferric chloride. If Equation 1 is the only other possibility, and it seems to be, then Equation 1 must hold for the chlorination of benzene in the presence of ferric chloride, stannic chloride, aluminum chloride, etc., and the ring hydrogen in benzene and toluene must be negative relatively. On the other hand a negative proof is not very satisfactory and it was therefore hoped that the action of fluorine on benzene might be helpful if it were found possible to make the reactions take place slowly.

Preparation of Fluorine

The method of preparing fluorine was essentially the same as that worked out by Argo, Mathers, Humiston and Anderson,[1] later modified by Meyer and Sandow[2] and by Simons.[3] The apparatus used during the first part of the work was that set up by Jones[4] in this laboratory but later a cathode pot of larger capacity kindly loaned us by Professor Frank C. Mathers of Indiana University was employed. Several other changes were made also; these will be pointed out later.

The cell (Fig. 1) consists of a magnesium pot which serves as cathode, heated electrically by a nichrome element, and a magnesium diaphragm or bell through the top of which is suspended the anode, a carbon rod. The diaphragm serves to prevent the union of hydrogen and fluorine generated at their respective electrodes. A thin magnesium plate is placed over the lower part of the diaphragm in order to deflect any hydrogen rising from the bottom of the pot. Several holes are drilled in the diaphragm to allow for

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[1] Trans. Am. Electrochem. Soc., 35, 335 (1919).

[2] Ber., 54, 759 (1921).

[3] J. Am. Chem. Soc., 46, 2175 (1924).

[4] J. Phys. Chem., 33 801 (1929).

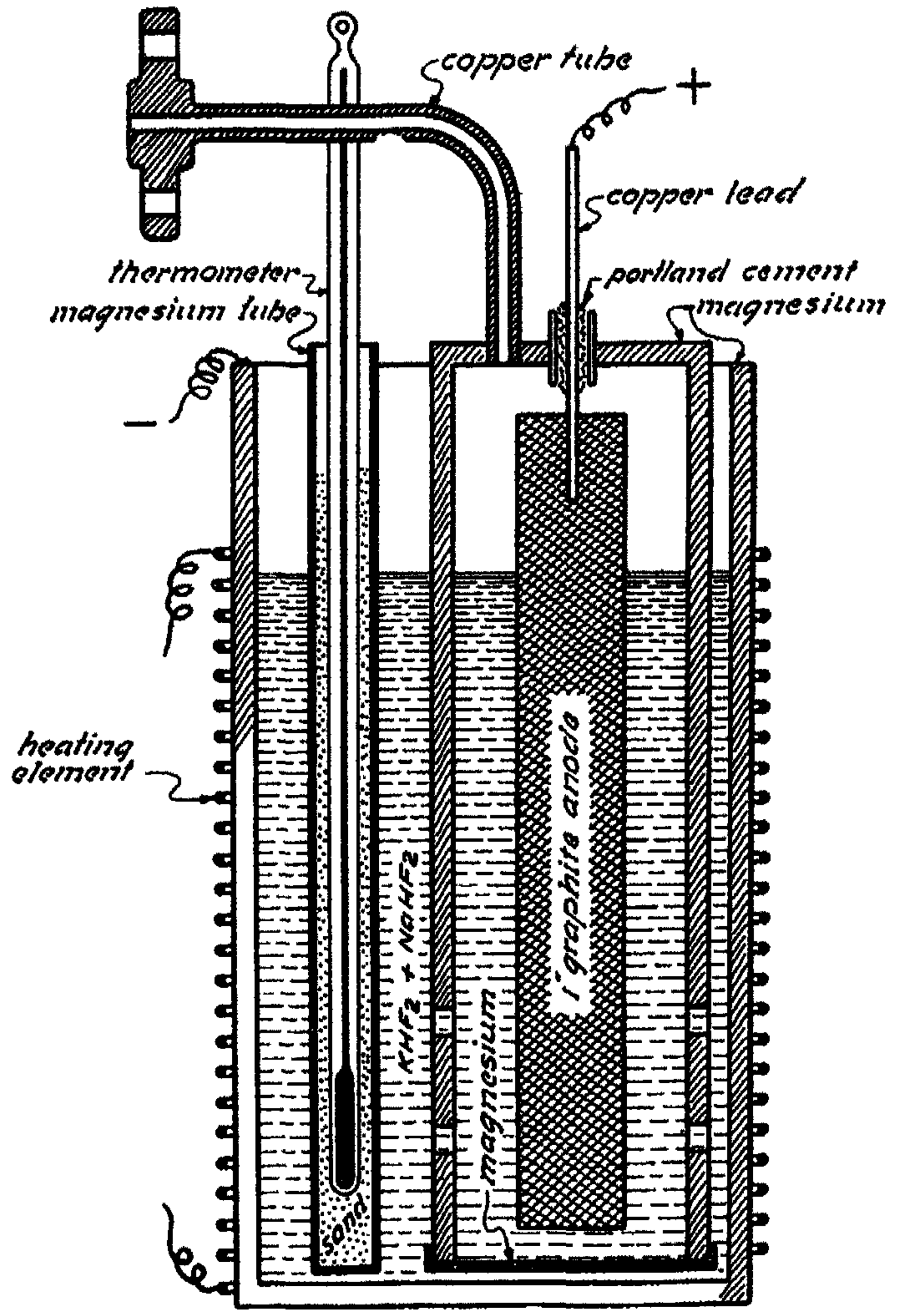

FIG. 1

circulation of the electrolyte. The anode is connected to the electrolyzing circuit by a heavy copper wire driven into a hole in the end of the carbon. In order to insulate the copper lead from the diaphragm the space around it is filled with pasty Portland cement and then baked at 200°C. This seal holds the anode rigid and will withstand the action of fluorine for several months before breaking down. The temperature of the bath is determined by a thermometer incased in a magnesium well immersed in the electrolyte.

The cathode pot is 4⅝ inches internal diameter and 8⅜ inches high; the diaphragm is 7 inches high by 2 inches internal diameter. Both pieces are

1/4 inch in wall thickness. The anode is a one-inch graphite rod 6½ inches long. The thermometer well was made by drilling a 5/16 inch hole almost through a 1/2 inch magnesium rod 9 inches long.

A 1/4 inch copper tube leads off from the top of the anode compartment and connects to a purification train by means of a copper flange union made gas tight by a gasket of thin copper. Because of the ease with which fluorine attacked the several soldered joints on the purification U tubes used by Jones, it was decided to employ a straight copper tube which would involve two threaded joints only. The threads corrode quickly so the apparatus remains gas-tight indefinitely. To save space this straight purification tube can be bent into a U. Sintered lumps of sodium fluoride are used in the purification train to take out hydrofluoric acid given off by the molten bath.

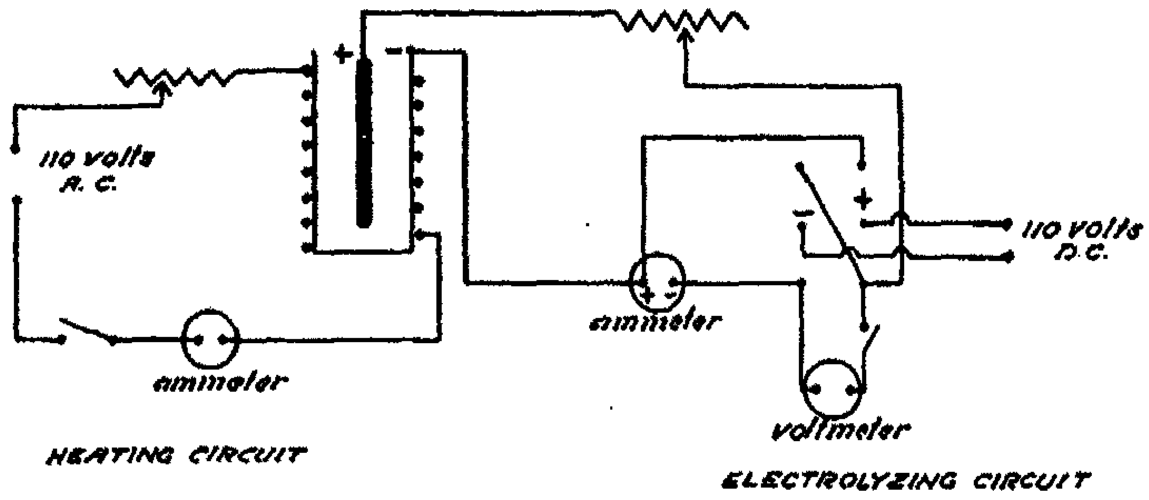

Fig. 2

In the past, workers in this field have used for the electrolyte either sodium or potassium bifluorides. In making a choice the following factors were taken into consideration:—

(1) Sodium bifluoride is cheaper than potassium bifluoride.

(2) Sodium bifluoride has more fluorine per gram.

(3) Potassium bifluoride is hygroscopic; sodium bifluoride is not.

(4) Potassium bifluoride tends to creep over the side of the pot and thus destroy the heat-insulating material and to short-circuit the heating unit.

(5) Sodium bifluoride decomposes before the melting point is reached; potassium bifluoride does not.

(6) A mixture of the two would give a lower melting point. This would save time in heating the bath and also save electrical energy.

It was decided to use a mixture of the two salts containing 35% sodium bifluoride. This mixture has a melting point of 170° which is 50° lower than potassium bifluoride alone and about the lowest of any combination of the two salts. There is little or no creeping by the electrolyte and the hygroscopic nature of the potassium bifluoride is diminished to such an extent that there is hardly any anode polarization by oxygen resulting from the electrolysis of water. However more hydrofluoric acid is given off than from a bath of potassium bifluoride alone so a larger purification train is necessary.

The bath is kept heated by an element connected through an ammeter and rheostat to the 110 volt A.C. line, (Fig. 2). Six amperes are used until the charge is molten and the electrolysis started. This is then reduced to about three amperes depending on the amount of fluorine left in the bath. When the electrolysis is started, the anode covers itself with a film of oxygen because the water in the bath electrolyzes out before any fluorine will be generated. This film is pierced by 110 volts when the current is reversed. The electrolysis is carried out at three amperes, the cell delivering about 900 cc. fluorine per hour. A charge of 3400 grams replenished from time to time to compensate for volume decrease was still in operation after over 100 hours of continuous usage. The fusion temperature starting at 170° for a fresh bath rises gradually as the fluorine is used up.

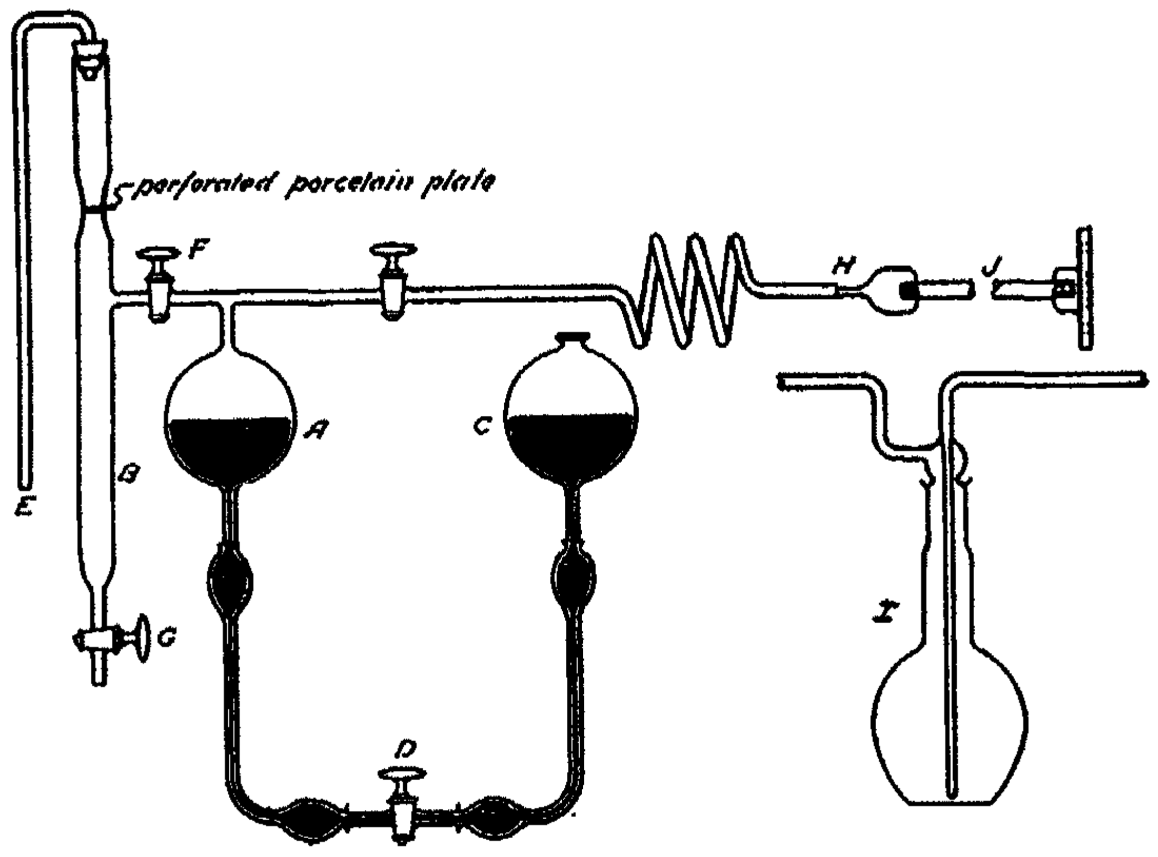

Fig. 3

Apparatus and Manipulation

The apparatus (with the exception of the generator) is shown in Fig. 3. The copper purification tube (J) is joined to the rest of the apparatus by a glass-on-copper seal at (H). This union may also be made by using glass tubing of slightly larger diameter than that of the copper, slipping it over the copper and sealing with paraffin wax. Fluorine from the generator is collected over mercury in a bulb of approximately 600 cc. capacity (A), and then run into the reaction chamber (B) by raising the levelling bulb (C). The rate of flow is regulated by the stop cock (D) and is estimated by the number of bubbles forming at the delivery tube (E) which dips into carbon tetrachloride. This arrangement is also used to indicate the rate of flow of fluorine into the reservoir from the generator. Stop cock (F) is opened and if the liquid levels inside and outside at the delivery tube are the same, fluorine is flowing into the reservoir as fast as it is being generated. This flow is regulated by stop cock (D). In this manner loss of fluorine, or contamination by air in case there are leaks in the apparatus is prevented. Because of the fact that leaks develop around the stop-cocks it is necessary to replace most of the apparatus about once a week. "Lubriseal" stop cock grease is used and although it is attacked by fluorine the action is not fast enough to set fire to the material and break the stop cocks as was the case with several other greases tried.

Two different types of reaction vessels are used depending on whether the material to be treated with fluorine is a liquid or a solid. In the case of solids the arrangement (B) is employed. Fluorine passes up through the material, the reaction product (if liquid) drips down and is drawn off through the stop cock (G). A fresh supply of reactant can be added from time to time through the top. With solutions a wash-bottle arrangement (I) proves to be satisfactory.

The Action of Fluorine on Benzene

When fluorine was passed into dry benzene at room temperature, small explosions occurred, CF_4 and HF were evolved and carbon deposited. However the action was made to take place quietly by diluting the fluorine with dry nitrogen in the proportion 1:1 and cooling the benzene to about 7°. Under these conditions the solution became murky and a thick material, with an odor somewhat like that of diphenyl, formed in the delivery tube. After prolonged fluorination the solution became very dark and some of the tarry material settled to the bottom. This was filtered off and the filtrate, shaken with dilute alkali until free from HF. No attempt was made to separate the fluorobenzene suspected of being present from the excess benzene by distillation, because of the fact that the two boiling points are very close together. However an attempt was made to establish the presence of fluorobenzene by nitration with 1:1 nitric-sulphuric acid mixture. This converts the benzene into the dinitro derivative,[1] m.p. 90°, b.p. 297°, and fluorobenzene into a 9:1 mixture of para and ortho nitrofluorbenzenes, m.p. of the mixture 18.55°.[2] Sodium methylate converts the latter compound quantitatively into the corresponding anisole m.p. 54°, with a separation of sodium fluoride.[3] No fluorobenzene could be detected by this method.

The solid material remaining was washed as well as possible with dilute alkali and then tested qualitatively for fluorine by a potassium fusion and precipitation of CaF_2 from faintly alkaline solution by $Ca(NO_3)_2$. Fluorine was found to be present by this method. No further analysis was attempted, but from the tarry nature of the material and the similarity of its odor to diphenyl it was assumed to be a fluor-substituted condensation product.

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[1] Kamm: "Qualitative Organic Analysis," 165 (1923).

[2] Holleman: Rec. Trav. chim., 24, 140 (1905).

[3] Holleman: Rec. Trav. chim., 23, 225 (1904).

The Action of Fluorine on Toluene

Toluene behaved similarly to benzene when diluted fluorine was bubbled through. No fluor-substituted toluenes could be detected and a tarry residue which gave a qualitative test for fluorine was formed as in the case of benzene.

The Action of Fluorine on Anisole

Anisole was chosen because it is supposed to have an active hydrogen atom. Nevertheless fluorine without dilution could be bubbled fairly rapidly through this material without a violent reaction taking place. No tarry material was formed in this case but the solution changed from colorless to dark red. By fractional distillation after refluxing to get rid of dissolved gases, the excess anisole was removed and the dark red liquid remaining gave a qualitative test for fluorine.

The Action of Fluorine on 1,3,5-Trinitrobenzene

Fluorine set fire rather readily to 1,3,5-trinitrobenzene but by dilution and careful regulation a reaction could be made to take place quietly. After many hours of endeavor the reaction was abandoned because although the mixture became sticky and pasty it seemed to burn away slowly.

The Action of Fluorine on Hexachlorobenzene

When fluorine was passed slowly over hexachlorobenzene a reaction took place which was evidenced by a heating of the reaction vessel and an evolution of chlorine. If however, the rate of flow was increased, small explosions occurred and carbon was formed. If the reaction chamber was cooled there seemed to be little or no reaction. It was necessary therefore to regulate carefully the flow of fluorine, reducing the rate when small explosions began yet having it flow fast enough to keep the reaction mixture warm. After many hours of fluorination a colorless sticky liquid of peculiar odor started to form. This dripped away from the sphere of action and was withdrawn for purification and analysis.

It was suspected that the mixture resulting from the fluorination consisted of some new compound or compounds, unattacked hexachlorobenzene, carbon tetrafluoride, fluorine and chlorine all in solution and carbon in suspension. This mixture was subjected to a fractional distillation, first however refluxing until there was no longer tests with starch iodide or blue litmus paper. The fractionation was not sharp but most of the material came over within two ranges 140°-150° and 230°-240°.

The Action of Fluorine on 1,3,5-Trichlorobenzene

When fluorine was passed over 1,3,5-trichlorobenzene in a manner similar to that used for hexachlorobenzene a sticky, oily liquid not dissimilar to that obtained above was formed and chlorine evolved. However to speed up the reaction a concentrated solution of 50 grams of 1,3,5-trichlorobenzene in carbon tetrachloride was made up and fluorine bubbled through this slowly at first and then rapidly for about 53 hours.

The mixture was subjected to a fractional distillation under reduced pressure, first however refluxing to get rid of the dissolved gases. At 2.5 cm. Hg. and 75° a pale yellow liquid came over; this had a boiling point of about 150° under atmospheric pressure but was not stable.

The Action of Fluorine on 1,2,4 Trichlorobenzene

Attempts to introduce fluorine into 1,2,4 or unsymmetrical trichlorobenzene failed, although the reaction was not studied under all conditions. Under ordinary conditions when fluorine was bubbled through the liquid, small explosions occurred as in the case of benzene and toluene and an odor was noticed similar to that formed when these two substances were treated with fluorine.

Method of Analysis

Because of lack of information in the literature concerning the properties, derivatives, etc., of the compounds suspected of being present, it was decided to run ultimate analyses for chlorine and fluorine. Of the several methods in use for halogens in organic compounds, that of Piccard and Buffat[1] for fluorine and that of Drogin and Rosanoff[2] for chlorine were judged to be the best. The first method calls for a potassium fusion at an elevated temperature to get the fluorine as potassium fluoride. The second method, excellent for chlorine, bromine, and iodine, consists in treating the material in alcoholic solution with sodium.

It was decided not to risk the loss of the small amount of material available for analysis by attempting the bomb reaction necessary in the Piccard and Buffat method for fluorine but rather to analyse for chlorine and fluorine simultaneously by a modification of the Drogin and Rosanoff method. Their scheme is followed exactly except that 40 W grams of potassium instead of 21.5 W grams of sodium and 135 W grams instead of 160 W grams of alcohol is used. W representing the weight of sample. An outline of the procedure is as follows:—

0.2 to 0.3 grams of unknown is dissolved in 135 W grams of alcohol (dried over sodium) and treated with 40 W grams of potassium. The reaction takes place in a Kjeldahl flask fitted with a reflux condenser. The potassium is added slowly thru the condenser and the flask gently heated to help dissolve any metal remaining. After cooling, the reaction mixture is diluted with 200 cc. of water and adjusted to neutrality. The separation of chlorine and fluorine is made on the basis of the solubilities of their calcium salts in slightly alkaline solution.[3] Chlorine is determined by precipitating it as AgCl with

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[1] Helv. chim. acta, 6, 1047 (1923).

[2] J. Am. Chem. Soc., 38, 711 (1916).

[3] Treadwell-Hall: "Quantitative analysis," II, 406 (1928).

a known amount of N/15 $AgNO_3$ and then titrating the excess $AgNO_3$ with N/15 NH_4CNS. Fluorine is determined gravimetrically as CaF_2.[1]

This method when tried with fluorobenzene gave results which were low. However it was thought to be satisfactory for the complex type of compound analyzed in this problem in view of the fact that complex compounds break up easily.

Results of Analyses

The results obtained from the analyses of the compounds produced by fluorination of hexachlorobenzene and 1,3,5-trichlorobenzene are as follows:—

A. From hexachlorobenzene

I. Fraction boiling at 230°-240°

	% Cl		% F
1.	53.7	1.	16.4
2.	53.7	2.	14.7

II. Fraction boiling at 140°-150°

	% Cl		% F
1.	46.4	1.	20.9
2.	45.3	2.	20.6

B. From 1,3,5-trichlorobenzene

I. Fraction boiling at 75° (2.5 cm. Hg)

	% Cl		% F
1.	35.5	1.	28.5
2.	35.1	2.	28.7

The theoretical proportions of chlorine and fluorine in the compounds that fit the closest to these are as follows:—

	% Cl	% F
$C_6Cl_4F_2$	56.3	15.1
$C_6Cl_3F_3$	45.2	24.2
$C_6HF_3Cl_2$	35.3	28.3

It has therefore been concluded that these new compounds have been isolated. Unfortunately there was not enough material for further investigation and identification but recently Kraay[2] and De Crauw[3] have prepared thru the diazo reaction 3,4-dichlorofluorobenzene b.p. 171°; 2,5-dichlorofluorobenzene b.p. 168° and 2,4,5-trichlorofluorobenzene m.p. 62°, and these compounds have properties similar to those of the compounds prepared above.

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[1] Treadwell-Hall: "Qualitative analysis," II, 406 (1928).

[2] Rec. Trav. chim., **48**, 1055 (1929).

[3] Rec. Trav. chim., **48**, 1061 (1929).

In the reaction between fluorine and hexachlorobenzene, the fluorine has of course displaced the chlorine, because there is no question of the formation of a stable chlorine fluoride. In the reaction between fluorine and symmetrical trichlorobenzene, one chlorine and two hydrogens are substituted by fluorine. From the fact that the hydrogens and chlorines behave much alike, it seems probable that we are dealing with a direct replacement in both cases.

Activation by Charcoal

Regardless of how we account for it, we know that sunlight activates chlorine and that this activated chlorine reacts with toluene to form benzyl chloride, benzyldichloride, and benzyltrichloride, all the substitutions occurring in the side chain. This is a commercial process and precautions must be taken to prevent the presence of iron. We know also that phosgene can be made from carbon monoxide and chlorine either under the influence of light or in the presence of charcoal. We know from the work of Jones[1] that charcoal does not activate carbon monoxide at all and that consequently the charcoal activates the chlorine. In the reactions between hydrogen and chlorine, it is the chlorine and not the hydrogen which is activated. The validity of this conclusion is supported by the fact that sunlight has no appreciable effect on the combination of hydrogen and oxygen to form either[2] water or hydrogen peroxide while it is known that monatonic hydrogen reacts with oxygen[3] to form hydrogen peroxide.

It was therefore expected that the chlorination of toluene in the presence of activated charcoal would give substitution in the side chain—nothing of the sort happened. When chlorine was passed into benzene and into toluene in the presence of activated charcoal ("Nuchar" No. 000 from the Industrial Sales Corporation) ring-substituted products were formed exclusively. The obvious explanation is presence of iron; but that seems not to be the right answer. In order to be sure that these results were not due to small traces of iron, the charcoal was heated almost to the melting-point of combustion tubing, and chlorine was passed through it for about four hours to drive off the iron as ferric chloride.

While it might not be possible to make charcoal behave like sunlight, we ought to be able to make sunlight behave like charcoal. Apparently the only way to account for the results, if we consider that iron has been ruled out, is to postulate that the charcoal activates the toluene, loosening one of the ring hydrogens more than the side-chain hydrogens. If this is the explanation, light which is absorbed by toluene should cause substitution in the ring to some extent. Curtis[4] has reported that ring substitution takes place in benzene and toluene if the reaction is carried out in a quartz flask placed a few centimeters from an iron arc; light from a carbon arc gives negative results. This

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[1] J. Phys. Chem., 33, 1415 (1929).

[2] Mellor: "Modern Inorganic Chemistry," 102 (1922).

[3] Traube: Ber., 15, 2434 (1882).

[4] J. Franklin Inst., 184, 875 (1917).

seems to prove that light of very short wave-length, such as is found in the spectrum of the iron arc activates the benzene and toluene, causing ring substitution. The results of Curtis have been confirmed, using the following procedure:—

Chlorination of Benzene

About 300 cc. of thiophene-free dry benzene was placed in a quartz flask fitted with a reflux condenser. The flask was then placed a few centimeters from an arc formed between two iron rods carrying 15 amperes. After about three hours, or until the delivery tube clogged, the reaction was stopped and the flask allowed to cool. The benzene hexachloride was filtered off and the filtrate distilled to get rid of the excess benzene.

The ring-substituted products were detected by their unmistakable odor and by the fact that hexachlorobenzene was formed in the vapor and caught in the condenser tube. This was recognized by its melting point.

Chlorination of Toluene

Dry redistilled toluene was treated in a manner similar to that used for benzene. The chlorotoluenes were partially separated from the excess toluene and benzyl chloride by fractional distillation under reduced pressure.

After converting the mixture to the corresponding acids by oxidation with $KMnO_4$ and separating the acids by fractional crystallization from ligroin[1] the presence of chlorotoluenes was confirmed by the melting point of the product.

It was not to be expected that ultra-violet light would give only ring substitution, as the charcoal does, because chlorine absorbs also in the ultra-violet, and is consequently activated also. In the visible spectrum the chlorine is activated and the benzene and toluene are not. Consequently we get zero substitution of the ring hydrogen in the visible spectrum and partial substitution in the ultra-violet.

These results with ultra-violet light do not prove that our chlorine-treated charcoal was free from iron. The assumption was a good working hypothesis because it permitted us first to predict and then to confirm the experiments of Curtis which seem to have been ignored by organic chemists because they did not fit in.

The general conclusions of this paper are as follows:—

1. Chlorine set free at the anode reacts primarily with the ring hydrogen.
2. The activation of chlorine by ferric chloride must give an essentially negative chlorine and this chlorine reacts primarily with the ring hydrogen.
3. Fluorine reacts with benzene hexachloride replacing chlorine. This must involve a displacement of chlorine.
4. The compounds $C_6Cl_4F_2$ and $C_6Cl_3F_3$ have been prepared by the fluorination of hexachlorobenzene.

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[1] Bornwater and Holleman: Rec. Trav. chim., 32, 231 (1913).

5. The compound $C_6HF_3Cl_2$ has been prepared by the action of fluorine on symmetrical trichlorobenzene. There is no reason as yet to postulate any difference between the substitution of chlorine and the substitution of hydrogen in this compound. On the other hand there seems to be no proof that there is no difference.

6. Ferric chloride is not a catalyst converting benzene hexachloride into trichlorobenzene and hydrochloric acid. Consequently, the chlorination of benzene in presence of ferric chloride does not involve a preliminary addition of two chlorines.

7. Since the conversion of the addition product, benzene hexachloride, into trichlorobenzene undoubtedly involves the reaction of half the added chlorine with the ring hydrogen, it is probable that the chlorination in presence of ferric chloride does not involve this reaction.

8. Activated charcoal, which has been treated red-hot with chlorine to remove iron, causes ring substitution with chlorine and toluene. This is probably due to activation of toluene.

9. Ultra-violet light activates toluene and benzene and causes some ring substitution. It of course activates the chlorine and causes side-chain substitution thereby.

10. When attached to an amino group, a phenyl group is known to be more negative than a methyl group. This is an argument in favor of considering the ring hydrogens as more negative than the side-chain hydrogens. The matter cannot be said to be proved definitely.

Acknowledgments

This problem was suggested by Professor W. D. Bancroft and carried out under his direction. The author welcomes this opportunity to express his appreciation for the many helpful suggestions and kindly criticisms offered by Professor Bancroft during the course of the investigation.

The author also wishes to thank Dr. N. C. Jones for his invaluable assistance with the fluorine cell.

Cornell University.

MIGRATION STUDIES WITH FERRIC OXIDE SOLS

II. Negative Sols

BY FRED HAZEL AND GILBERT H. AYRES

Introduction

The stability of suspensoid sols that have a positive charge is decreased to a marked extent when small amounts of a highly valent negative ion are added to the sol. Positive ferric oxide sols are coagulated by low concentrations of ferrocyanide ions. The strongly adsorbable nature of this ion together with its high valence bring about the recharging of a positive sol to the negative form when a higher concentration of the ion is present.[1]

Migration experiments with potassium ferrocyanide reported in the first paper of this series[2] illustrate in a striking manner the powerful action of the ferrocyanide ion. Relatively low concentrations of the electrolyte (for instance 0.01 millimols per liter of sol-electrolyte mixture) gave very stable negative sols. It can be assumed that all of the added electrolyte is adsorbed from these dilute solutions and that we are dealing with negative colloids stabilized by preferential adsorption of ferrocyanide ions. Having previously investigated the effect of added anions of different valence on the migration velocity of positive ferric oxide sols, it was thought interesting to study the migration of negative sols on addition of positive ions.

Experimental

A stock sample of sol was prepared by hydrolysis of ferric chloride. It was dialyzed for five days at a temperature of about 90° and then diluted with distilled water to 0.012 g. of iron per liter. Two sols, designated as A and B in the subsequent discussion, were obtained from the stock sample by adding equal volumes of potassium ferrocyanide solutions. The latter were of such concentration that sol A contained 0.025 millimols of the electrolyte per liter, while sol B contained 0.25 millimols per liter.

The data in the following tables show the effect of KCl, $BaCl_2$, $AlCl_3$ and $Th(NO_3)_4$ on the migration velocity (determined by the method described in the first article of this series) of negative ferric oxide sols.

Results

The strong tendency of ferrocyanide ions to recharge positive ferric oxide sols is shown in Table I. Data are given for four sols that have different hydrogen ion concentrations. Velocities of migration are expressed in μ/sec./v./cm. Concentrations of potassium ferrocyanide are given in millimols per liter of reaction mixture.

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[1] von Kohei Hakozaki: Kolloid-Z., 39, 319 (1926).

[2] Hazel and Ayres: J. Phys. Chem., 35, 2930 (1931).

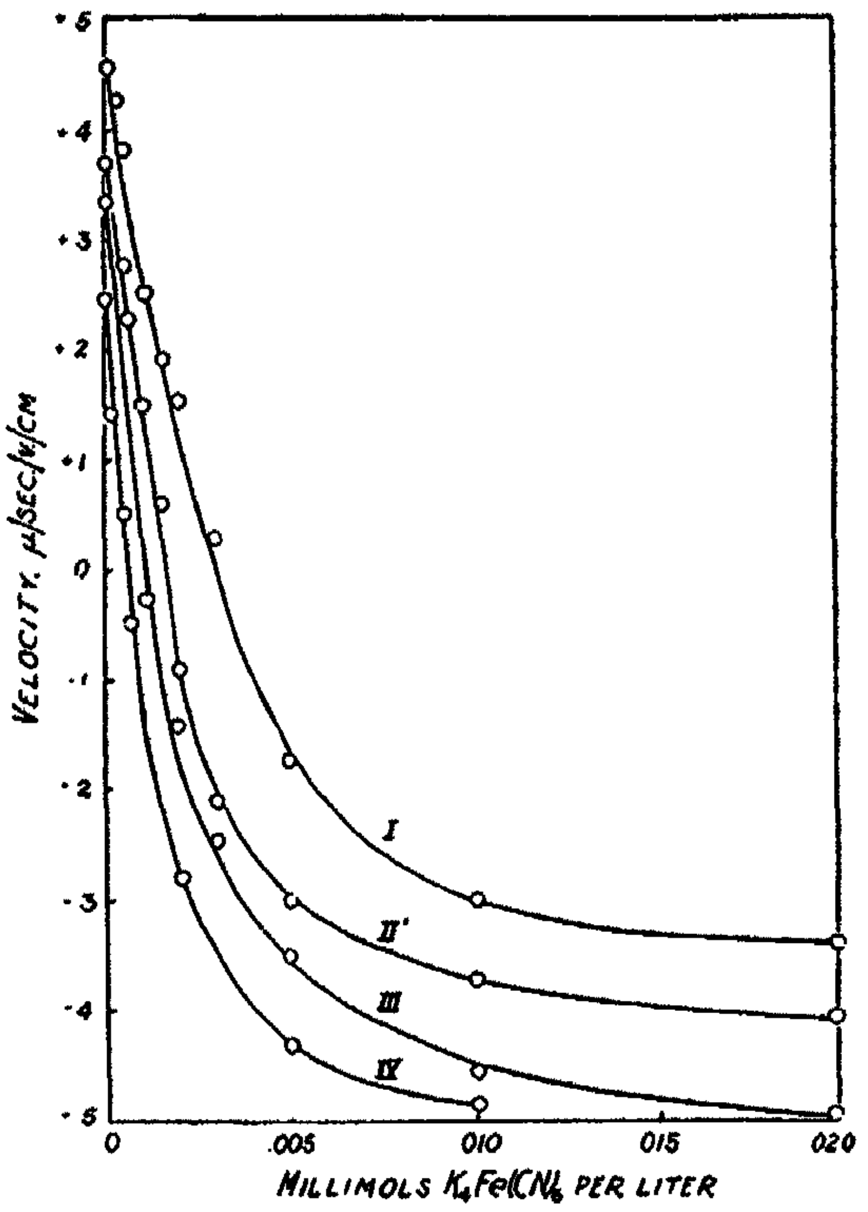

FIG. 1

TABLE I

Sol No.	Millimols $K_4Fe(CN)_6$ per liter	Velocity, μ/sec./v./cm.			
		Series I pH = 4.0	Series II' pH = 5.2	Series III pH = 6.4	Series IV pH = 7.3
1	0.0	+4.6	+3.7	+3.4	+2.5
2	0.00025	+4.3	+2.7	—	+1.5*
3	0.0005	+3.8	+2.3	+0.5*	—
4	0.0010	+2.5	+1.5*	−0.3*	±0.0*
5	0.0015	+1.9*	+0.6*	—	—
6	0.002	+1.6*	−0.9*	−1.4*	−2.8
7	0.003	+0.3*	−2.1	−2.4	—
8	0.005	−1.7*	−3.0	−3.5	−4.3
9	0.01	−3.0	−3.7	−4.6	−4.8
10	0.02	−3.4	−4.1	−5.0	—

* In this and following tables (*) indicates samples which showed precipitation by manifestation of distinct turbidity after two hours.

Fig. 1 shows these data graphically. The fact that the curves for the more acid sols are always above those for the less acid sols means that while the hydrogen ion stabilizes positive sols, it decreases the stability of negative sols.

The data in Table II are for sols A and B with potassium chloride. Both sols had a pH of approximately 5. Sol A recharged with 0.025 millimols of $K_4Fe(CN)_6$ per liter had a negative velocity of 3.9 μ/sec./v./cm. when no additional electrolyte was present. Sol B recharged with 0.25 millimols of $K_4Fe(CN)_6$ per liter had a negative velocity of 4.8 μ/sec./v./cm. under the same conditions.

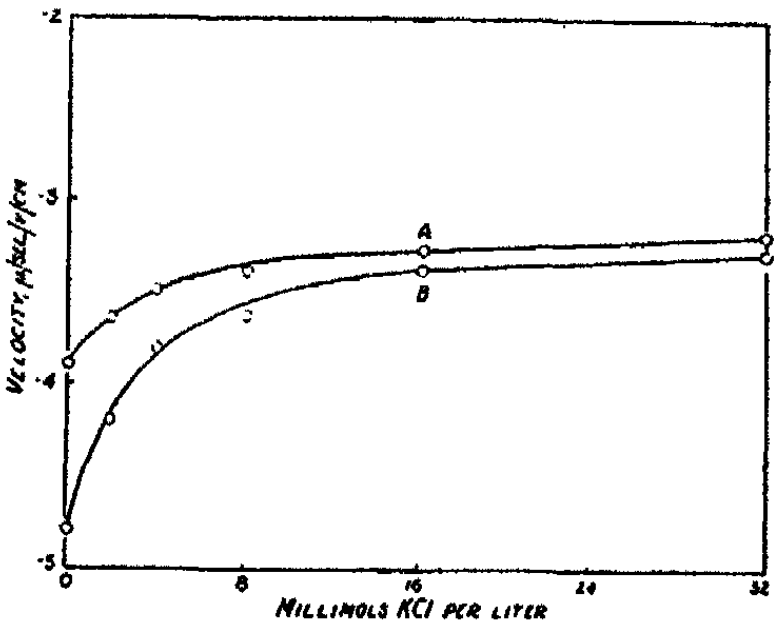

Fig. 2

TABLE II

Sol No.	Millimols KCl per liter	Velocity, μ/sec./v./cm.	
		Sol A	Sol B
1	0	−3.9	−4.8
2	2	−3.6	−4.2
3	4	−3.5	−3.8
4	8	−3.4	−3.6
5	16	−3.3	−3.4
6	32	−3.2	−3.3

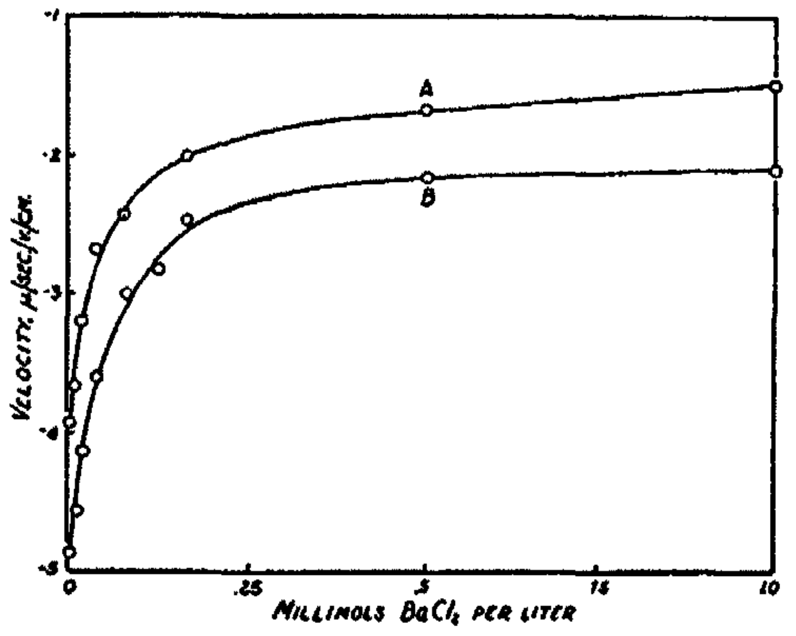

Fig. 3

These results were as expected. The presence of more ferrocyanide ions in the latter instance gave a greater density of charge per unit area of surface and this was accompanied by an enhanced migration of the particles in the electric field.

Fig. 2 shows a plot of the above data.

The results obtained with $BaCl_2$ are given in Table III and plotted in Fig. 3. It is to be noted that the discharging effect of the bivalent barium ions is greater than that for potassium ions.

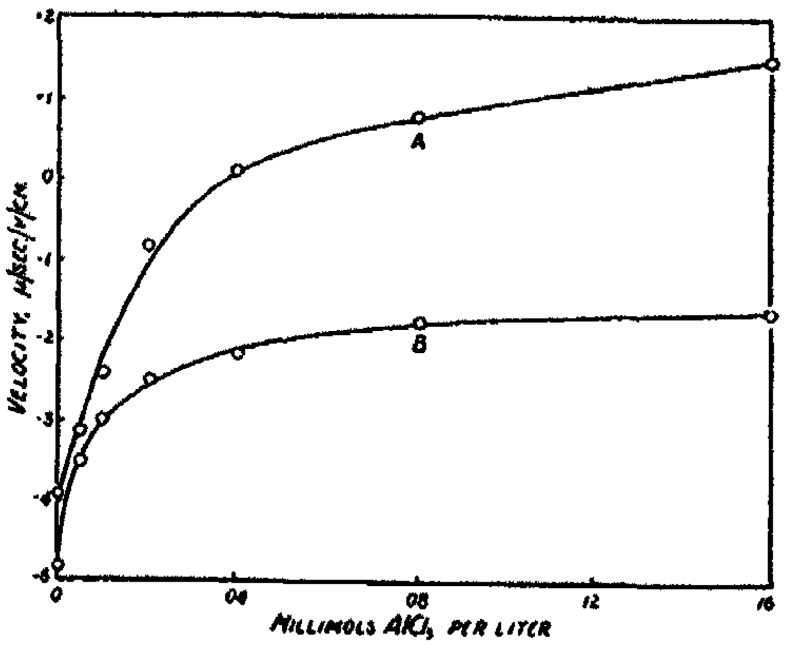

Fig. 4

Table III

Sol No.	Millimols $BaCl_2$ per liter	Velocity, μ/sec./v./cm.	
		Sol A	Sol B
1	0	−3.9	−4.8
2	0.01	−3.7	−4.6
3	0.02	−3.2	−4.2
4	0.04	−2.7	−3.6
5	0.08	−2.4	−3.0
6	0.12	—	−2.8
7	0.16	−2.0	−2.4
8	0.5	−1.7*	−2.2
9	1.0	−1.5*	−2.1*

Data for aluminum chloride are given in Table IV. Fig. 4 shows the results graphically. This electrolyte in the higher concentrations recharged sol A to the positive form.

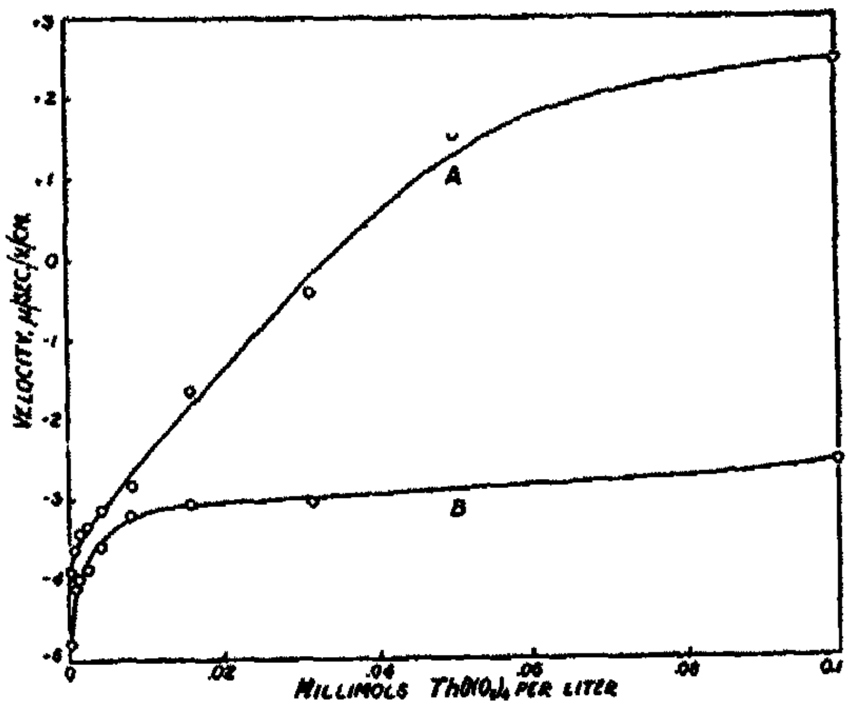

FIG. 5

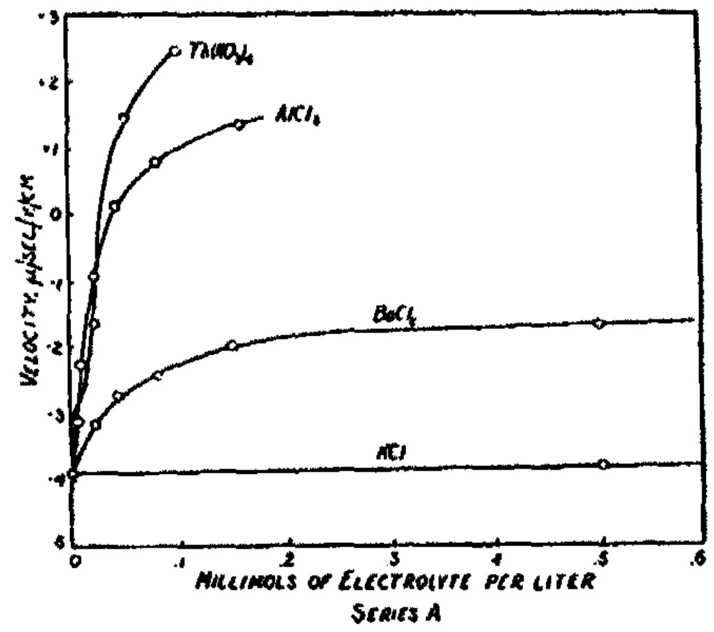

FIG. 6

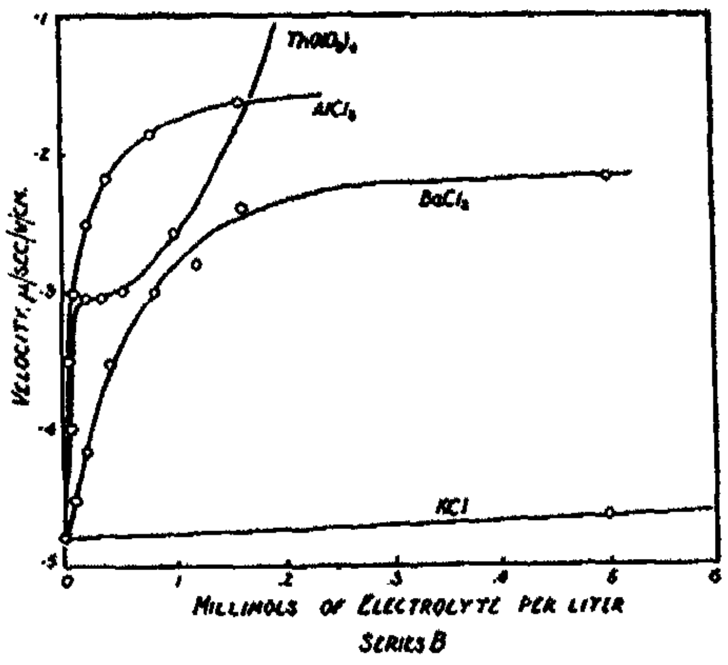

FIG. 7

TABLE IV

Sol. No.	Millimols $AlCl_3$ per liter	Velocity, μ/sec./v./cm.	
		Sol A	Sol B
1	0	−3.9	−4.8
2	0.005	−3.2	−3.5
3	0.01	−2.4	−3.0
4	0.02	−0.7*	−2.5
5	0.04	±0.0*	−2.2
6	0.08	+0.8*	−1.8*
7	0.16	+1.5*	−1.6*

The behavior of thorium nitrate is shown by the results incorporated in Table V and plotted in Fig. 5. The tetravalent thorium ion in sufficiently high concentrations is capable of recharging both sols positively. The curve for sol B in Fig. 5 does not show the recharging phenomenon; however, if the plot were extended to include electrolyte concentrations up to 0.3 millimols per liter this would be made clear. The actual course of the curve is given in Fig. 7 which also includes a graph of the $AlCl_3$, $BaCl_2$ and KCl data. Similar curves for sol A are shown in Fig. 6.

TABLE V

Sol No.	Millomols $Th(NO_3)_4$ per liter	Velocity, μ/sec./v./cm.	
		Sol A	Sol B
1	0.	−3.9	−4.8
2	0.0005	−3.7	−4.1
3	0.001	−3.5	−4.0
4	0.002	−3.4	−3.9
5	0.004	−3.2	−3.6
6	0.008	−2.8	−3.2
7	0.016	−1.6*	−3.2
8	0.032	−0.5*	−3.1
9	0.05	+1.6*	−3.0**
10	0.10	+2.4*	−2.6**
11	0.20	——	−0.8**
12	0.30	——	+1.1**
13	0.40	——	+2.7**

** These samples showed a peculiar white turbidity not characteristic of the appearance of the sols in which coagulation had been induced by other electrolytes.

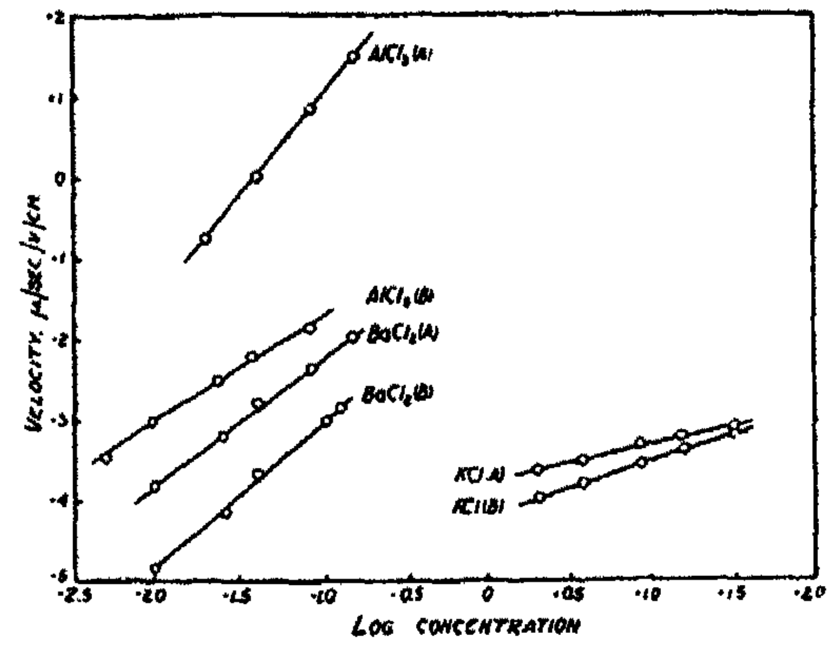

Fig. 8

The logarithmic nature of the curves is shown in Fig. 8. Th $(NO_3)_4$ does not give a straight line relationship when plotted in logarithmic form.

Discussion

It has been observed in the migration experiments with negative ferric oxide reported here and in the mobility studies with positive ferric oxide sols reported previously that the sols lose their stability when the particles migrate with a velocity in the range between approximately -2.0 and $+2.0$ μ/sec./v./cm. Therefore, it may be assumed that these values correspond to the critical potentials within which limits the particles have no real stability. Furthermore, since the critical velocities of positive and negative sols have equal values but opposite signs, we may assume roughly that at any velocities which are equal, and greater than the critical value, the sols have the same degree of stability.

In Fig. 1, curve I is for a sol pH 4.0 and curve II' is for a sol of pH 5.2. An inspection of the two curves shows that when the concentration of potassium ferrocyanide is 0.003 millimols per liter in the sol of pH 5.2 the stability of the sol is equal to that of sol pH 4.0 when the latter contains 0.006 millimols or twice as much of the electrolyte per liter. Both sols under these conditions have a stability represented by a negative mobility of 2.1 μ/sec./v./cm. Of course the stability of the sols at this velocity is not very great because of the close proximity to the critical value. However, we wish to choose the above conditions in order to make a comparison with potassium ferrocyanide flocculation data for sols of different acidities.

In Table VI the following symbols are used for degree of flocculation. In all cases three cc. of electrolyte were added to two cc. of sol.

–	indicates no turbidity after 72 hours.
+	precipitation or evidence of turbidity after 72 hours.
++	indicates complete precipitation in 2 hours.

It is evident that the sol of pH 5.4 is stable when the concentration of potassium ferrocyanide lies between 0.032 and 4.0 millimols per liter. Cataphoretic determinations made in a U-tube by observing a moving boundary show these sols to be negatively charged. In this case 0.032 millimols of the electrolyte per liter is the minimum concentration that will give a stable negative sol. On the other hand, a sol of pH 3.9 requires a minimum concentration of 0.06 millimols per liter to give a stable negative colloid. This concentration is approximately twice as great as for the sol of pH 5.4, which fact is in excellent agreement with the results obtained from migration experiments on sols of comparable pH values. The same agreement holds when we approach the region of coagulation from the positive side. Interpolation from the curves indicates that approximately twice as great a concentration

TABLE VI

(Concentration of sols: 0.6 g. Fe per liter)

m. mols $K_4Fe(CN)_6$ per liter	Flocculations* sol pH 5.9	sol pH 5.4	sol pH 4.6	sol pH 3.9	sol pH 3.4
0.006	−	−	−	−	−
0.008	+	−	−	−	−
0.010	+	−	−	−	−
0.012	++	+	−	−	−
0.014	++	+	−	−	−
0.016	+	++	−	−	−
0.020	+	++	+	−	−
0.024	+	++	++	+	+
0.028	+	+	++	++	++
0.032	−	−	++	++	++
0.036	−	−	+	++	++
0.040	−	−	+	++	++
0.044	−	−	−	+	++
0.048	−	−	−	+	++
0.05	−	−	−	+	+
0.06	−	−	−	−	+
0.07	−	−	−	−	+
0.08	−	−	−	−	+
0.09	−	−	−	−	+
0.10	−	−	−	−	+
0.11	−	−	−	−	+
0.12	−	−	−	−	−
4.0	−	−	−	−	−
20.0	+	+	+	+	+
40.0	++	++	+	+	+

* The potassium ferrocyanide solutions were made up in boiled distilled water and stored in blackened flasks. The salt was of reagent purity quality.

of the salt is required to reduce the velocity of sol pH 4.0 to the critical value as to decrease the stability of sol pH 5.2 to the same extent. The flocculation data show that 0.012 millimols per liter start the precipitation for the sol of pH 5.4 and 0.024 millimols for the sol with a pH value of 3.9. The curves and flocculation data both show that there is a greater concentration range of potassium ferrocyanide which produces instability with the more acid sols than with those of weaker acidity.

Fig. 1 also illustrates the futility of attempting to define an isoelectric point for colloidal iron oxide from a standpoint of pH. We have shown four different pH values all of which satisfy the criterion of zero mobility. A moment's thought will make clear that there might be an infinite number of pH values at which there could be an isoelectric condition. Therefore, it may be concluded that although hydrogen and hydroxyl ions play an important role as far as the stability of ferric oxide sols is concerned, they do not uniquely determine the stability. In the study of suspensoid sols the chief interest in these ions lies in their low valence yet strong adsorbability.

The curves in Figs. 2, 3, 4, 5, 6, 7, and 8 are graphical representations of data obtained on two sols which had been charged negatively by the addition of potassium ferrocyanide. Sol A containing 0.025 millimols of the salt per liter had a velocity of -3.9 μ/sec./v./cm. The concentration of electrolyte in sol B was 0.25 millimols per liter and the mobility had a value of -4.8 μ/sec./v./cm. The results of the addition of potassium chloride to the two sols are shown in Fig. 2. Because of its weak adsorbability fairly high concentrations of the monovalent potassium ion are required to decrease the mobility of the particles. At the lower concentrations the rate of diminution of velocity is much more marked (indicated by the slopes of the curves near the ordinate) for the sol with the greater negative charge. The same phenomenon is encountered when small concentrations of aluminum and thorium ions are added to the sols. With the barium ion the action is less pronounced but still real. This general behavior warrants some comment.

In order for a colloidal particle to migrate with a velocity u in an electric field, the frictional force, η u/d, must be overcome by the electric force Hq. When these two forces are equal we may write

$$\eta\, u/d = Hq \tag{1}$$

where η = the viscosity
u = the velocity
d = the thickness of the double layer
H = the potential gradient
q = the density of charge per unit surface.

Equation (1) may be written

$$\eta u/Hd = q$$

For a unit potential gradient and taking η as a constant in these dilute systems, we have

$$uk = qd \tag{2}$$

Equation (2) states that the migration velocity is directly proportional to the product of density of charge and thickness of the double layer.

Let us now consider the behavior of the potassium ion with two sols of different charge density. If we are permitted the simplifying assumption that q is effectively constant[3] for each sol on the addition of potassium ions, it follows that a decrease in velocity of the particles is a result of decreasing the thickness of the double layer. Sol A had a charge per unit surface which was smaller than that for sol B. On addition of four millimols of KCl to the former sol the thickness of the double layer is decreased because of electrostatic attraction between the ions of the inner and outer part of the layer. This is accompanied by a falling off of velocity. With sol B addition of the same concentration of potassium chloride results in a much greater decrease in d, attended by a larger decrease in velocity of the particles, because of stronger attraction between the ions in the two shells.

The curves of Fig. 2 show that after the addition of eight millimols of KCl per liter the velocity becomes practically constant. This may be interpreted to mean that further addition of the salt produces little change in d. The fact that the velocity curve for sol B always lies under the curve for sol A is reasonable. As has been pointed out, the velocity is proportional to the product of two factors, q and d. The thickness of the double layer is probably smaller at all concentrations of KCl in case of B, but the charge per unit surface is greater for this sol than for sol A. The product of q and d always has a greater value in the case of the sol with the larger charge density.

The same reasoning may be applied to the curves in Fig. 3, 4, and 5. An additional feature of interest that is brought out from inspection of the figures is the tendency for the curves for the monovalent ion to converge, those for the bivalent ion to remain practically parallel, while the curves for tri-and tetravalent ions diverge.

The course of the thorium nitrate curve with sol B shows an inflection at velocities around -3. Although the reason for this anomaly was not ascertained, it may be in some way connected with the fact that all of the sols having a mobility between -3.0 and $+2.7$ had a peculiar milky turbidity which was manifest immediately upon preparing the samples. Since the turbidity was not at all characteristic of the appearance of the sols in which coagulation had been induced by other electrolytes and since it was first encountered at velocities which were greater than the critical velocities, it might have been due to a chemical reaction between thorium ions and ferrocyanide ions which were present in excess. Thorium ferrocyanide is less soluble than aluminum ferrocyanide and barium ferrocyanide; the "regular" course of the curves is therefore obtained with the aluminum and barium salts. It may be pointed out that Powis[4] encountered a similar phenomenon, which did not readily lend itself to explanation, when arsenious sulfide sols were coagulated with thorium nitrate.

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[3] See however, Bull and Gortner: J. Phys. Chem., **35**, 309 (1931).

[4] Powis: J. Chem. Soc., **109**, 734 (1916).

Our data with KCl show for both positive sols[3] and negative sols that the critical velocities (±2.0 μ/sec./v./cm.) which were found with polyvalent ions were not reached. The course of the curves for monovalent ions indicates that extremely high concentrations would be required to reach the critical value. It is difficult to reconcile this behavior with the fact that moderate concentrations of KCl cause the coagulation of concentrated sols. However, it is to be expected that addition of a given increment of electrolyte would decrease the potential of the double layer to a less extent for a concentrated sol (there being more particles present to compete for the same number of ions) than for a dilute sol. Apparently with monovalent ions it is not necessary to reduce the potential as much to cause coagulation in concentrated systems as in dilute ones.

These results are in agreement with experiments by Powis[4] in which he determined the critical potentials of arsenious sulfide sols with potassium chloride, barium chloride, aluminum chloride and thorium nitrate. Powis gives the following ciritcal potentials for these electrolytes:

Electrolyte	P.D. in volts
Potassium chloride	0.044
Barium chloride	0.026
Aluminum chloride	0.025
Thorium nitrate	0.027 0.026 0.024

We quote from Powis' paper relative to the high critical potential of potassium chloride: "The results agree with the idea of a critical P. D. (the sols coagulated when the particles had the above potentials) as determining the stability or instability of a colloidal system in so far as barium chloride, aluminum chloride and thorium nitrate are concerned, but the behavior with potassium chloride suggests that electrolytes also exert a kind of salting out effect, so that when an electrolyte is used which has only a weak influence on the P. D., and therefore a relatively high concentration is required for coagulation, this coagulation occurs when the P. D. has a value so high that without this superimposed salting out effect the mixture would be quite stable. Since such an effect was not observed in the author's [Powis'] experiments with an oil emulsion where the number of suspended particles per unit volume was very small compared with the number in the colloidal arsenious sulfide, . . . it is perhaps only important when the concentration of suspended particles is very large."

The above argument suggests that if dilute arsenious sulfide sols had been used in the migration experiments, the critical potential with KCl might have agreed with the value common to ions of higher valence. Our data do not prove this argument but they do show that the critical potential with KCl for dilute sols is less than 0.035 volts and hence approaches the common value of 0.030 volts found for ions of higher valence. Powis does not venture an opinion regarding the reason for the value found with KCl being much higher than the values for the other three electrolytes which agreed closely with each other.

It is interesting to note in our experiments with ions having a valence greater than one that the critical velocities were approximately the same and correspond to a potential of roughly 30 millivolts. These experiments were with dilute sols. However, Powis[4] has found a value of 30 millivolts for a concentrated ferric oxide sol with sodium sulfate. It would seem from this that the concentration of the sol has little influence on the critical potential when polyvalent ions are employed.

Summary

1. The conversion of positive ferric oxide sols to negative sols by means of potassium ferrocyanide is shown in relation to the hydrogen ion concentrations of the systems.

2. The "isoelectric point" of this sol has been shown not to be uniquely determined by the hydrogen ion concentration of the system.

3. The effect of cations on the migration velocity of negative sols is illustrated.

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PARTIAL PRESSURE ISOTHERMS. I*

BY WILDER D. BANCROFT

It has been shown in recent papers[1] from this Laboratory that the changes of the partial pressures with changing concentration for two consolute liquids at constant temperature can be represented with an unexpected degree of accuracy by what the chemists call an exponential equation; and that the Raoult Law is a special case of this equation. Quite apart from any question as to the accuracy of the suggested equation, there is the difficulty that all the disturbing factors are lumped together. If these disturbing factors are to be unscrambled and assigned their relative values, it seems certain that a different method of attack must be adopted.

It will perhaps be easier to work from, rather than to, the Raoult Law. An ideal solution is defined as one in which two consolute liquids mix without volume changes or heat effects. For such pairs of liquids the Raoult equations hold over the whole range of concentrations,

$$\frac{N_1}{N_1+N_2} = \frac{p_2-p'_2}{p_2} \text{ and } \frac{N_2}{N_1+N_2} = \frac{p_1-p'_1}{p_1},$$

where the molecular weights are those in the vapor phase, p_1 and p_2 are the vapor pressures of the pure liquids and p_1' and p_2' are the corresponding partial pressures in the solutions. A corollary from these facts is that the molecular weights of the pure liquids are the same as those in the vapor phase.

If we drop the limitation that there are no disturbing factors, we shall have the van't Hoff formula holding for the upper end of the curve and Henry's law describing the lower end of the curve. For dilute solutions at the upper end of the curve, in which we compare the concentration of one component with the lowering of the partial pressure of the other component, we know that the form of the curve depends only on the molecular weight of the solute in the liquid phase and of the solvent in the vapor. The chemical natures of solute and solvent and solute are quite unimportant.

For dilute solutions at the lower end of the curve in which we compare the concentration of what we in the preceding paragraph have been calling the solvent with its own vapor pressure, the partial pressures depend on the chemical natures of both substances and on the molecular weight of what we are calling the solvent in the liquid phase. The general diagram[2] for two consolute liquids with no limitations is shown in Fig. 1. The upper right-hand part of the curve is the portions for which the Raoult formula holds, as is

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* This work was done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Bancroft and Davis: J. Phys. Chem., 33, 361; Dornte: 1332 (1929).

[2] Wilhelm Ostwald: "Lehrbuch der allgemeinen Chemie," 2 II, 617 (1902).

also section (a). The two portions (b) and (c) represent the cases in which the variations from the Raoult equation are positive and negative respectively. If there are no other disturbing factors beyond the polymerization and dissociation of the solute, curve (b) corresponds to dissociation and curve (c) to polymerization.

If two liquid layers are formed, we shall have (Fig. 1) a curve of the general type of (d), which has nothing necessarily to do with polymerization. Benzene and water are a rather extreme case of this type and nobody supposes that benzene becomes more polymerized when a layer of water is put beneath it. Salicylic acid and water do not form two stable liquid layers; but an instable system with two liquid layers can be realized experimentally. Consequently, we draw the conclusion that we may get a curve lying above the normal in case there is a tendency for a second liquid phase to occur and that this will be in addition to and independent of any polymerization which may occur.

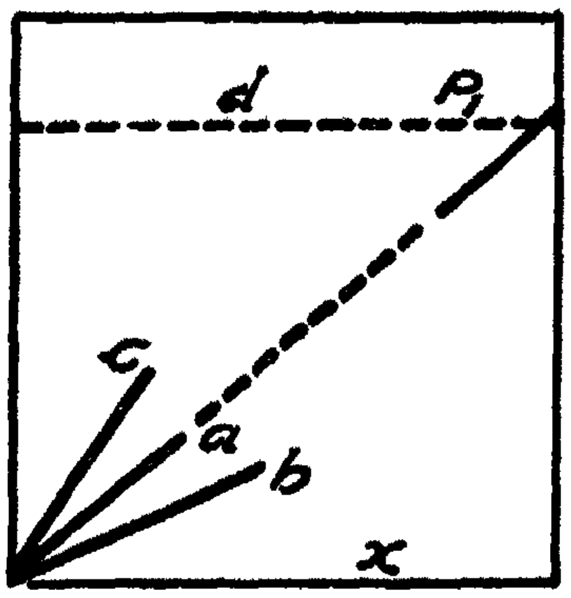

Fig. 1
(Ostwald)

If we are dealing with solutions of two consolute liquids in which the only disturbing factors are polymerization and dissociation we may write the Raoult equations as:—

$$\frac{N'_1}{N'_1+N_2} = \frac{p_2-p'_2}{p_2} \text{ and } \frac{N'_2}{N_1+N'_2} = \frac{p_1-p'_1}{p_1},$$

where N_1 and N_2 refer to the molecular weights in the vapor, and N_1' and N_2' to the molecular weights in the solution. We can then calculate the molecular weights to be used in these equations in order to make the curves straight lines. This has been suggested several times and has always proved unsuccessful.

Linebarger[1] was one of the first to make calculations of this sort; but Lehfeldt[2] criticizes the results and consequently the method. "In this way Linebarger found molecular weights [for acetic acid] which increased steadily

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[1] J. Am. Chem. Soc., 17, 665, 690 (1895).

[2] Phil. Mag., (5) 46, 59 (1898).

with the concentration of the acid, and by extrapolation found 240 for the molecular weight [$(CH_3CO_2H)_4$] of the pure liquid at 35°. My results for alcohol do not, however, at all confirm the accuracy of the method. On drawing smooth curves of partial pressure from the observations given in the tables above and treating them in the way just indicated, we get

Table I

Aggregation of the Alcohol

Molecules of Alcohol	Molecules in Benzene	Molecules in Toluene
10	6.0	2.0
30	5.7	2.6
50	5.3	4.2
70	5.0	5.7
90	4.9	6.0

"It will be seen that the two series disagree altogether, and that neither leads to any reasonable value for the aggregation of pure alcohol. I can only conclude that the partial pressure of the hydrocarbon vapour is not necessarily linear in mixtures, and that therefore the rule proposed by Linebarger for determining the molecular weights of liquids is not correct."

Ostwald[1] questions whether one partial-pressure curve can be a straight line if the other is not. The same objection has been expressed by Hildebrand[2] who says: "If Raoult's law holds throughout the whole range of composition for one component of a binary mixture, it holds for the other." This is probably true for all practical purposes; but it will be shown later that it is not theoretically necessary.

Hildebrand[3] has amplified upon Lehfeldt's criticism, discussing Dolezalek instead of Linebarger. "In order to account for positive deviations from Raoult's law, Dolezalek[4] has assumed that one of the components is associated, containing a certain proportion of double molecules which are dissociated into single molecules as this component is diluted with the other, each molecular species present, however, obeying Raoult's law when the 'true' mol fraction rather than the apparent mol fraction is considered. . . . Dolezalek has carried out such calculations for the systems benzene-carbon tetrachloride and ether-methyl salicylate, assuming the second-named component of each pair to be partly associated. . Even large values of K [the dissociation constant] are insufficient to account for the large deviations from Raoult's law that are found with many solutions, such as acetone-carbon bisulphide[5] and carbon bisulphide-methylal. . . . Möller[6] has derived expressions for more

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[1] "Lehrbuch der allgemeinen Chemie," 2 II, 632 (1902).

[2] "Solubility," 46 (1924).

[3] "Solubility," 78, 80, 82 (1924).

[4] Z. physik. Chem., 64, 727 (1908).

[5] Von Zawidski: Z. physik. Chem., 35, 129 (1900).

[6] Z. physik. Chem., 69, 449 (1909).

complicated reactions assumed in order to reproduce certain curve-pairs. For example, the solution ethyl iodide-ethyl acetate is assumed to contain triple molecules of the former and double molecules of the latter, while both components of solutions of carbon tetrachloride-ethyl acetate are assumed to form double molecules. In none of the systems which he considers, however, are the deviations very large, and the followers of Dolezalek have thus far discreetly avoided such systems as acetone-carbon bisulphide."

"A still greater difficulty with this type of explanation is presented by mixtures which form two liquid phases. Keyes and Hildebrand,[1] who investigated the system aniline-hexane, have pointed out that even the assumption of very complex molecules of aniline is insufficient to account for the extreme deviations here encountered. . . . If the aniline is assumed to be completely associated to form molecules of $(C_6H_5NH_2)q$, where q is an integer, then one single molecule forms $1/q$ associated molecules and if r_2 represents the corresponding number of hexane molecules, the 'true' mol fraction of hexane is $r_2/(r_2+1/q)$, and the activity of the hexane is $a_2=r_2/(r_2+1/q)$. . . .

"It would be expected, of course, that any such complex molecules would dissociate as the percentage of hexane is increased, giving lower values for the vapor pressures of hexane at the upper end than the curves represent, so that the curves represent maximum values. It is obvious that no reasonable value of q comes anywhere near explaining the actual behavior of this or any similar system. If the cause of the behavior lies in the 'association' of the aniline, it is evident that a very different kind of association must be pictured, an association not into relatively simple complexes which are able to mix with the other component so as to obey Raoult's law, but rather an association of the whole mass of aniline molecules to form a liquid in which the internal pressure or attractive force between the aniline molecules is so great as to resist dispersion into the hexane. . . .

"The advocates of the Dolezalek theory are often led to assume association in liquids which, according to all other criteria, are entirely normal or unassociated. Thus Schulze and Hock[2] explain the positive deviation of the total vapor pressures of benzene-stannic chloride by assuming the formation of double molecules of the latter to the extent of eighty-one percent in the pure liquid at 100°. At ordinary temperatures this association would have to become still greater. This is in absolute conflict with a large amount of evidence, presented in Chapter VIII, that stannic chloride is a quite normal liquid.

"The most striking example of the extent to which Dolezalek and his followers have been led by their enthusiasm for their 'chemical' explanation of all deviations from ideal behavior is found in a paper by Dolezalek[3] in which liquid solutions of nitrogen and argon are 'explained' by assuming polymerization of the argon to form double molecules!"

One difficulty with these calculations and with the criticisms of them is that they are based on an assumption that is very rarely if ever true, that the

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[1] J. Am. Chem. Soc., 39, 2126 (1917).

[2] Z. physik. Chem., 86, 445 (1918).

[3] Z. physik. Chem., 93, 585 (1918).

only disturbing factor is polymerization or dissociation. The occurrence of heat effects, and of tendencies to form two liquid layers has been ignored completely. We need not consider variations from the gas laws not accompanied by heat effects, because the validity of Raoult's law for ideal solutions shows that such disturbances have been eliminated. The question of solvates has been studied by many people, from Jones to Kendall; but never in connection with the other sources of error.

It will be wisest to consider the effects of each disturbing factor by itself, eevn though there will probably be few actual cases as simple as that. We will begin with solvation. If one molecule of the solute combines with one or more molecules of the solvent, this will be equivalent to increasing the concentration and will cause the variations from Raoult's law to become negative. Of course if several molecules of what we are calling the solvent combines with one of the other component, that is equivalent to decreasing the concentration along the other curve and to make the variations along it positive. We know that a compound, chloral hydrate, is formed, because chloral and water are not consolute liquids and mix only in presence of the compound. In the case of butyl chloral hydrate and water, two liquid layers are actually formed when the solution is heated. There are no data for this case and it is not a simple one because the two components are not consolute liquids. Acetic anhydride and water go so nearly completely to acetic acid even at the boiling-point that they are not especially interesting. Aniline and acetic acid would be a case in point; but acetic acid is polymerized both in liquid and in vapor.

Qualitatively the effects due to heats of dilution are easy to handle; but the quantitative treatment has not been solved satisfactorily except for special cases. Twenty-five years ago it was pointed out[1] that the low apparent molecular weights in finite solutions of sodium in mercury and of sulphuric acid potassium hydroxide in water were due in part to heat being evolved when the solutions are diluted. Conversely alcohol in benzene shows abnormally high molecular weights and heat is absorbed when the solutions are diluted.

Hildebrand[2] supports this view, though not enthusiastically or accurately. "A positive deviation from Raoult's law is generally accompanied by an absorption of heat when the pure liquids are mixed, and a negative deviation is generally accompanied by an evolution of heat upon mixing the pure liquids. The heats absorbed in the solution of solids in these cases are respectively greater or less than the heats of fusion."

Harrison and Perman[3] have actually made use of the relation. "In order to obtain an equation which included the heat of dilution, Trevor[4] suggested a form of the Gibbs-Helmholtz Equation,

$$PV = Q+T\frac{d(PV)}{dT},$$

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[1] Bancroft: J. Phys. Chem., 10, 319 (1906).

[2] "Solubility," 61 (1924).

[3] Trans. Faraday Soc., 23, 19 (1927).

[4] J. Phys. Chem. 9, 90 (1905).

Q being positive when heat is evolved on dilution. This equation can only be integrated when Q is zero or does not vary with temperature. Supposing Q equals a constant A, we have an integration,

$$PV = RT+A,$$

an expression which may be substituted in the van't Hoff equation,

$$PV = RT\frac{N}{n}\log\frac{\pi_0}{\pi_1},$$

giving

$$RT+A = RT\frac{N}{n}\log\frac{\pi_0}{\pi_1}.$$

"Bancroft[1] has shown that the taking into account of the heat of dilution, as is done in this equation, is sufficient to remove many anomalies from molecular weight determination, for which cumbrous and doubtful hypotheses had been devised. Thus sodium in mercury has an apparent molecular weight of 16, an impossible figure, raised to nearly 23 when account is taken of the heat of dilution; a similar simplification was observed in the case of sulphuric acid.

"The heat of dilutions of solutions of calcium and potassium chloride changes rapidly with temperature, as may be seen from the curves submitted. Nevertheless as merely an approximation, the above equation was applied to the case of a thirty percent calcium chloride solution at 40°C. The value of the molecular weight was given as 54 compared with 20 when no account was taken of the heat of dilution; 54 as against 111 (the theoretical mol.wt.) is not unreasonable, because it can be explained by postulating ionisation of the calcium chloride to the extent of about 50 percent. A value of 20 would require a special hypothesis such as 'removal' of the water from the solution due to hydrate formation.

"The above equation was applied to urea; data for the vapour pressure and the heat of dilution are given by Perman and Lovett.[2] In the case of a thirty percent solution, for which the heat of dilution is fairly constant with temperature, a true molecular weight of 59 is given instead of an apparent value of 67 (Theoret.60) obtained by neglecting the heat of dilution. For a sixty percent solution, for which the heat of dilution showed a far greater change with temperature, the corrected value was 57."

If heat is evolved on adding B to a solution of A and B, heat must be absorbed on adding A to a solution of A and B. Consequently one component must show positive deviations from the Raoult law, and the other component negative deviations whenever the heats of dilution are the predominent disturbing factors. It will be shown later in this paper that this criterion does not hold for benzene and alcohol; and that consequently another, more important, disturbing factor comes in. From the data with other available pairs of liquids, it is rather a question whether the heat effect is as important

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[1] J. Phys. Chem. **10**, 319 (1906).

[2] Trans. Faraday Soc., **22**, 1 (1926).

a factor as I had hitherto assumed it to be. On the other hand the tendency to form or not to form two liquid layers is apparently much more of a disturbing factor than anybody had ever assumed it to be.

We have already seen that a tendency to form two liquid layers means an abnormally high vapor pressure at the lower end of the curve. Mellor[1] makes the assumption that the upper portion of the curve is abnormal, Fig. 2, when there are two liquid layers, which is quite possibly true but which has not been proved. Mellor's diagram is a bit misleading because he is using it to represent partial pressures and total pressures as well. If the curves refer to partial pressures, the lower ends must come at zero. With a tendency to form two liquid layers both partial pressure curves will show positive variations, as though both substances were polymerized. In this respect this case differs from the one in which the formation of a compound of the components in other than a one to one ratio is the important disturbing factor; and from the case—apparently realized with some liquid alloys—in which the heat of dilution is the important disturbing factor. For these two cases the variations will be positive for one partial pressure curve and negative for the other

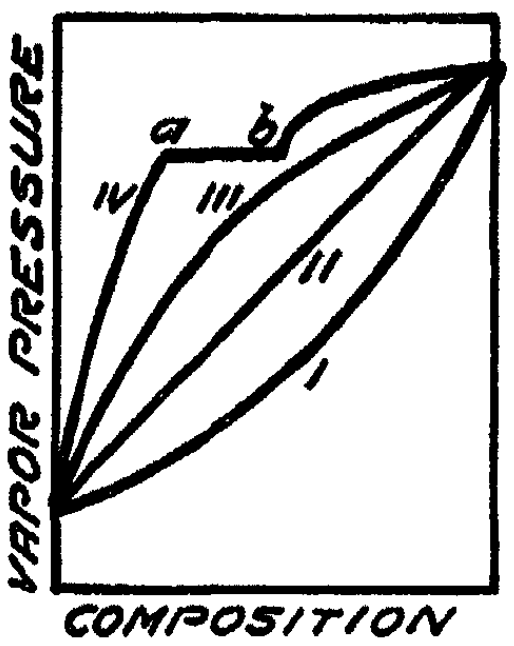

Fig. 2
(Mellor)

An increase in partial pressures with increasing tendency to form two liquid layers is probably what Hildebrand[2] has in mind when he says: "The evidence presented at length in Chapter VIII, indicates that the fundamental distinction between the normal and the associated liquids lies in the greater symmetry of the fields of force surrounding the molecules of the former, the field surrounding the latter being unsymmetrical or polar. The result is that the polar molecules have an abnormally great attraction for each other, producing greater cohesions, internal pressures, surface tensions and heats of vaporization, and tending to squeeze out, as it were, non-polar or slightly polar molecules from their midst. The result is an abnormally great fugacity for any non-polar molecules mixed with the polar ones, just as would be the case in a lesser degree if the high internal pressure were not accompanied by polarity. On account of the greater selective attraction of the polar molecules for each other, however, the squeezing-out effect may be greater than it would be in the case of high internal pressure alone unaccompanied by polarity. The result in either case is a strong positive deviation from Raoult's law with the accompanying effects upon solubilities. This tendency of the polar liquid to squeeze out the non-polar one is of course balanced by the thermal agitation,

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[1] "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 1, 555, Fig. 22 (1922).

[2] "Solubility," 85 (1924).

which, increasing as the temperature increases, tends to give the upper critical temperature of mixing of two liquids so much more common than a lower critical temperature."

The best way to find out the value of a hypothesis is to carry it to an extreme. Knowing the partial pressure isotherms for any pair of liquids we can calculate what the molecular weights should be in order to give the ideal curve if we make the explicit, though temporary, assumption that polymerization and depolymerization are the only disturbing factors. We can do this either from the Raoult formula $N_1/(N_1+N_2) = (p_2-p_2')/p_2$ or from the exponent in the case of the so-called Henry formula $N_2/(N_1+N_2) = (p_2'/p_2)^n$. Theoretically one should take the tangent at a given point in order to determine the exponent; but it is close enough for anything that we can do at present to take the slope of the curve between two adjacent points. In so far as these slopes are constant, the change of the partial pressures with the change of the molecular concentrations can be represented by a so-called exponential formula. The Raoult equation and the Henry equation deduced from it are necessarily identical for ideal solutions; but they are not necessarily identical and are not always identical for non-ideal solutions.

In Table II are given the data for ethyl alcohol and water at 25° as determined by Dobson[1] with the apparent coefficients of polymerization as calculated from the Raoult equation.

TABLE II

Ethyl alcohol and water at 25° (Dobson). Raoult's law.

x = mol fraction alcohol; $1 - x$ = mol fraction water.

p'_1 = partial pressure alcohol, p'_2 partial pressure water; mm. Hg.

A = apparent coefficient of polymerization of ethyl alcohol.

B = apparent coefficient of polymerization of water.

x	p'_2	A	$1-x$	p'_1	B
0.0	23.73	—	1.0000	0.0	—
0.0523	22.64	1.2	0.9477	10.5	3.9
0.0918	21.78	1.1	0.9082	16.66	3.9
0.1343	21.15	1.2	0.8657	22.27	3.6
0.6170	21.79	1.4	0.8330	24.90	3.6
0.2022	20.36	1.5	0.7978	26.85	3.3
0.2850	19.60	2.0	0.7150	35.73	2.7
0.3370	19.01	2.1	0.6630	32.16	2.2
0.4903	17.31	2.6	0.5097	36.64	1.6
0.5822	16.18	3.0	0.4178	39.53	1.5
0.7810	10.68	2.9	0.2190	47.40	1.1
1.0000	0.0	—	0.0	50.01	—

The apparent molecular weight of ethyl alcohol is only slightly above normal up to ten molecular percents of alcohol and rises to about three times normal in the concentrated solutions. The apparent molecular weight of

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[1] J. Chem. Soc., **127**, 2866 (1925).

TABLE III

Ethyl alcohol and water at 25° (Dobson). Henry's law.
x = mol fraction alcohol; $1-x$ = mol fraction water.
p'_1 = partial pressure alcohol; p'_2 = partial pressure water; mm. Hg.
$\%p'_1 = p'_1.\,p_1$; $\%p'_2 = p'_2/p_2$ $\qquad \log x = \bar{5}.3034 + 2.8 \log p'_1$
$\log(1-x) = 3.28 + 2.0 \log p'_2$

x	p'_1	p'_1 calc.	% p'_1	% p'_1 calc.	$\frac{\Delta \log x_1}{\Delta \log p_1}$
0.0523	10.5	10.54*	0.178	0.179*	
					1.2
0.0918	16.66	16.53*	0.282	0.280*	
					1.3
0.1343	22.27	22.41*	0.377	0.380*	
					2.0
0.1670	24.90	25.1	0.422	0.425	
					2.5
0.2022	26.85	26.9	0.455	0.456	
					2.8
0.2850	30.73	30.4	0.521	0.515	
					3.8
0.3370	32.16	32.3	0.544	0.547	
					2.8
0.4903	36.64	36.9	0.621	0.625	
					2.3
0.5822	39.53	39.2	0.670	0.664	
					1.7
0.7810	47.40	43.6	0.803	0.738	
					1.0
1.0000	59.01	47.6	1.000	0.801	

1-x	p'_2	p'_2 calc.	%p'_2	% p'_2 calc.	$\frac{\Delta \log (1-x)}{\Delta \log p'_2}$
1.0000	23.73	22.91	1.000	0.980	
					1.5
0.9477	22.67	22.30	0.969	0.954	
					1.6
0.9082	21.78	21.8	0.931	0.933	
					2.8
0.8657	21.15	21.3	0.904	0.911	
					2.5
0.8330	20.79	20.9	0.889	0.894	
					2.9
0.7978	20.36	20.5	0.871	0.875	
					2.1
0.7150	19.60	19.4	0.838	0.828	
					2.0
0.6630	19.01	18.7	0.813	0.797	
					1.6
0.5097	17.31	16.4	0.740	0.699	
					1.1
0.4178	16.18	14.8	0.692	0.633	
					1.7
0.2190	10.68	10.7	0.457	0.458	

* Calculated by equation $\log x = \bar{3}.44 + 1.25 \log p$.

water is practically normal up to twenty molecular percents of water and rises to about four times normal in the concentrated solutions. Taken by themselves these values are not impossible ones, though they are higher than those deduced from the surface tension relations.

In Table III are the same data calculated to show the slopes of the curves and also showing the degree of accuracy to be obtained by using exponential equations. Calculations have also been made on the basis of percentage partial pressures, because that makes it possible to compare data at two temperatures or for two different liquids.

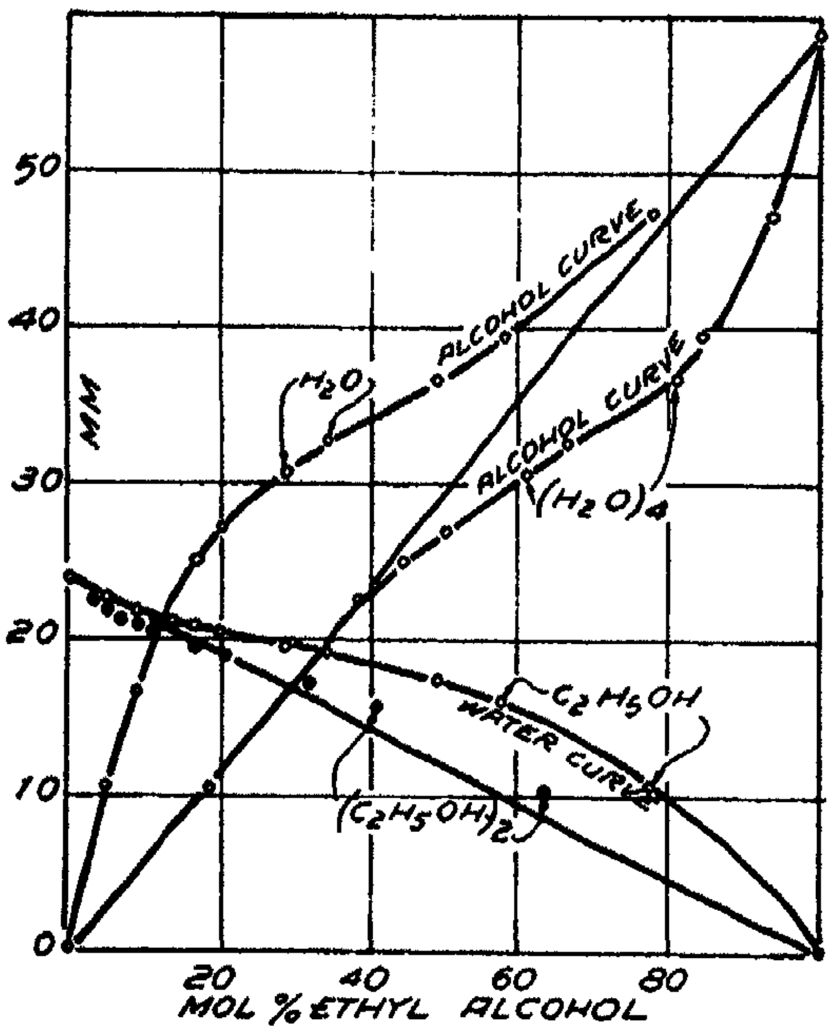

Fig. 3
Ethyl Alcohol and Water at 25° (Dobson)

The exponent for alcohol is not much above unity between five and nine molecular percents of alcohol, rises to a maximum of 3.8 with increasing alcohol concentration, and drops to unity between eighty and one hundred molecular percents of alcohol. Since the two end-points must lie on the ideal curve, there must be a maximum variation somewhere in the middle of the curve and the exponents may and often will approach unity at the two ends. It is probable that the maximum of 3.8 is due to experimental error.

The exponent for water shows an improbable value of 1.7 between twenty and forty molecular percents of water, dropping to 1.1 between forty and fifty molecular percents of water. It then rises to a maximum of 2.9 and falls off to about 1.5 between ninety-five and one hundred molecular percents of water.

From Tables II and III we are justified in drawing the conclusions that water shows a molecular weight of 18 in concentrated alcoholic solutions and that ethyl alcohol shows a molecular weight of 46 in dilute alcoholic solutions: but beyond that there is very little agreement. A strict application of our assumptions calls for a molecular weight of 72,$(H_2O)_4$ for the molecular weight of pure water from Table II while Table III shows no signs of such a result.

Dobson's data are shown graphically in Fig. 3. The left-hand curve for the partial pressures of alcohol, marked H_2O, represents Dobson's actual figures and is therefore the curve on the assumption that water is monomolecular throughout. It coincides fairly well with the ideal Raoult curve (the straight diagonal) down to at least fifteen molecular percents of water. From twenty molecular percents of water onwards there is no suggestion of an agreement between the experimental curve and the theoretical line. This variation cannot be due primarily to heats of dilution or to solvate formation, because the partial pressure curve for water shows positive variations also.

The curve of the alcohol pressures indicated as $(H_2O)_4$ is calculated on the assumption that liquid water is quadrimolecular over the whole range. It is evident that this assumption enables us to predict the facts satisfactorily from about sixty to one hundred molecular percents of water. Consequently the partial pressures of ethyl alcohol in aqueous alcoholic solutions can be represented over the whole range by assuming that the molecular weight of water varies suitably from 18,(H_2O), to 72,$(H_2O)_4$. I have not done this and have not tried to apply the mass law, because the subsequent study of the system, methyl alcohol and water, will show that liquid water cannot be represented by the formula $(H_2O)_4$.

If we look at the partial pressure curve for water in Fig. 3, we see that ethyl alcohol is monomolecular in dilute solution in water, as it should be. With increasing concentration, we get positive deviations. The circles with dots in them show the curve marked $(C_2H_5OH)_2$—which we get if we assume that ethyl alcohol is bimolecular throughout. There is, of course, an overcorrection at the water end; at the alcohol end the correction is not quite enough. If the polymerization were the only factor causing the abnormal curve, this would mean that pure liquid alcohol was more than bimolecular. This conclusion does not follow, however, if we scale down the apparent molecular weight of water as we are going to do.

In Tables IV-V and Fig. 4 are the data for methyl alcohol and water at 30.9° as Ferguson and Funnell.[1] In the dilute solutions of water in methyl alcohol, the partial pressures of methyl alcohol fall very well on the ideal line up to at least twenty molecular percents of water which means that water is practically monomolecular as far as that concentration. Along the lower left-hand portions of the curve there are positive deviations; but at ninety-five molecular percents of water, the apparent coefficient of polymerization is only 1.6. The right-hand alcohol curve—marked $(H_2O)_2$—which we get

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[1] J. Phys. Chem., 33, 1 (1929).

on the assumption that water is bimolecular throughout. This involves an over-correction from beginning to end and consequently the mean molecular weight of liquid water comes out much less than 36 from the data with methyl alcohol on the assumption that polymerization is the only disturbing factor.

The partial pressure isotherm for water with methyl alcohol considered as monomolecular does not lie much above the ideal curve and the calculated coefficient of polymerization does not go over 1.5 at any point. The circles with dots in them indicate the curve calculated on the assumption that methyl alcohol is bimolecular throughout. The bimolecular curve lies farther below the ideal curve than the monomolecular curve lies above. From the data as shown in Tables IV and V and plotted in Fig. 4 we are therefore justified in deducing that, so far as our knowledge now goes, both liquid water and liquid methyl alcohol are not polymerized to bimolecular values at 30.9°.

Except for the difference in temperature, which is only six degrees, liquid water must be the same whether we determine it by extrapolation from methyl alcohol solutions or from ethyl alcohol solutions, always supposing that we are not overlooking some important factor. Actually we get a value for the molecular weight of water of not to exceed 30 by extrapolation from methyl alcohol solutions and a value of about 72 by extrapolation from ethyl alcohol solutions, a difference which is far outside any experimental error. Consequently the partial pressures of ethyl alcohol in an aqueous alcohol solution are much higher over most of the range of concentrations than they ought to be from what is known about the molecular weight of water.

TABLE IV

Methyl alcohol and water at 30.9° (Ferguson). Raoult's law.
x = mol fraction alcohol; $1-x$ = mol fraction water.
p_1 = partial pressure alcohol; p_2 = partial pressure water; mm. Hg.
A = apparent coefficient of polymerization of methyl alcohol.
B = apparent coefficient of polymerization of water.

x	p'_2	A	1-x	p'_1	B
0.0	55.0	—	1.00	0.0	—
0.05	52.8	1.3	0.95	20.2	1.6
0.10	50.7	1.3	0.90	39.8	1.6
0.20	45.1	1.1	0.80	74.4	1.6
0.30	41.9	1.4	0.70	101.1	1.5
0.40	37.7	1.5	0.60	122.8	1.3
0.50	32.8	1.5	0.50	143.7	1.2
0.60	27.5	1.5	0.40	165.3	1.2
0.70	21.0	1.4	0.30	188.0	1.1
0.80	14.8	1.5	0.20	210.4	1.1
0.90	7.8	1.5	0.10	235.0	1.0
1.00	0.0	—	0.0	260.5	—

Table V

Methyl alcohol and water at 30.9° (Ferguson). Henry's law.
x = mol fraction alcohol; $1-x$ = mol fraction water.
p'_1 = partial pressure alcohol; p'_2 = partial pressure water; mm Hg.
$\%p'_1 = p'_1/p_1$; $\%p'_2 = p'_2/p_2$ $\log x = \bar{4}.99 + 1.25 \log p_1$
$\log (1-x) = \bar{3}.68 + 4/3 \log p'_2$

x	p'_1	p'_1 calc.	% p'_1	% p'_1 calc.	$\frac{\Delta \log x_1}{\Delta \log p'_1}$
0.05	20.2	23.3	0.078	0.089	
					1.0
0.10	39.8	40.4	0.153	0.156	
					1.1
0.20	74.4	70.6	0.286	0.271	
					1.3
0.30	101.1	97.7	0.388	0.375	
					1.5
0.40	122.8	122.9	0.471	0.472	
					1.4
0.50	143.7	141.7	0.553	0.567	
					1.3
0.60	165.3	170.1	0.635	0.653	
					1.3
0.70	188.0	192.3	0.722	0.738	
					1.2
0.80	210.4	214.1	0.808	0.822	
					1.1
0.90	235.0	235.1	0.902	0.903	
					1.0
1.00	260.5	255.9	1.000	0.982	

1-x	p'_2	p'_2 calc.	% p'_2	% p'_2 calc.	$\frac{\Delta \log(1-x)}{\Delta \log p'_2}$
1.00	55.0	55.0	1.0000	0.999	
					1.25
0.95	52.8	52.9	0.9602	0.961	
					1.3
0.90	50.7	50.8	0.927	0.923	
					1.01
0.80	45.1	46.5	0.820	0.847	
					1.8
0.70	41.9	42.1	0.762	0.765	
					1.5
0.60	37.7	37.5	0.685	0.681	
					1.3
0.50	32.8	32.7	0.596	0.594	
					1.3
0.40	27.5	27.6	0.590	0.503	
					1.01
0.30	21.0	21.2*	0.382	0.385*	
					1.2
0.20	14.8	14.6*	0.269	0.265*	
					1.01
0.10	7.8	7.8*	0.142	0.143*	

* Calculated by equation $\log (1-x) = \bar{2}.019 + 1.1 \log p$.

Since the deviations are positive both for ethyl alcohol and for water, the over-looked factor must be one which will affect both molecular weights similarly. This could occur if we had in solution a 1:1 hydrate of alcohol; but there is no independent evidence of this, and this would not be adequate, without some further assumption, to account for the differences between the alcohol and the water isotherms. It is not desirable to pile up assumptions when we have another explanation which does not need so much bolstering and for which we already have independent confirmation.

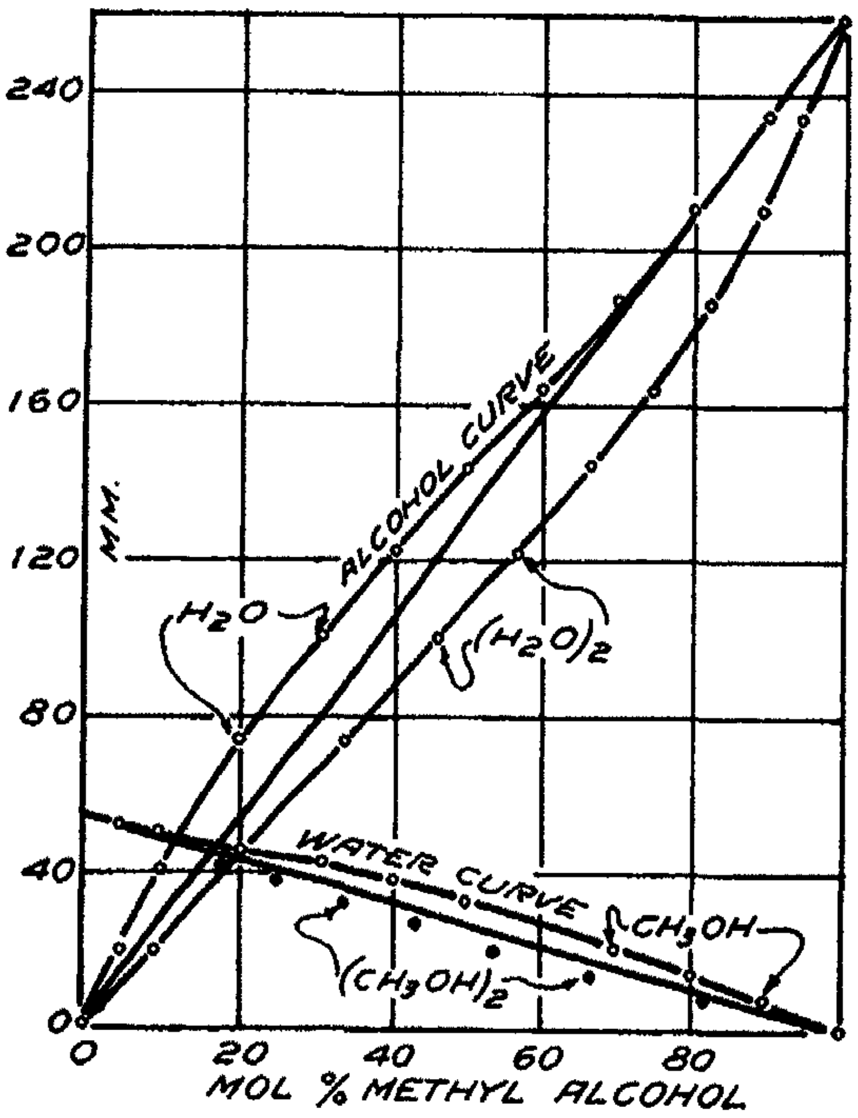

Fig. 4
Methyl Alcohol and Water at 30.9° (Ferguson and Funnell)

The obvious disturbing factor is the tendency for aqueous alcoholic solutions to separate into two liquid layers. We know that the higher alcohols are not completely miscible with water, that water and ethyl alcohol can be made to form two liquid layers on addition of certain salts, whereas there is apparently no record of this being possible with methyl alcohol and water. This is what one would expect because methyl alcohol has a CH_3 group in place of one H in water, whereas ethyl alcohol substitutes a C_2H_5 group and propyl alcohol a C_3H_7 group. We can therefore predict that the apparent polymerization of water dissolved in propyl alcohol will be greater than that of water dissolved in ethyl alcohol. Wrewsky[1] has data at 30.35°, which are

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[1] Z. physik. Chem., 80, 21 (1913).

therefore comparable with those of Dobson except in accuracy, and the accuracy is sufficient for our purpose. In the most concentrated solutions, about 84 and 91 molecular percents of water, the apparent polymerization coefficient of water is 8-10 in propyl alcohol as compared with 4 in ethyl alcohol and considerably less than 2 in methyl alcohol. When calculated in the same way the data of Beare, McVicar and Ferguson[1] give an apparent polymerization coefficient of, 8 for water in acetone.

A corollary of this is that propyl alcohol will be more abnormal in water than ethyl alcohol and ethyl alcohol than methyl alcohol. A glance at Fig. 5 will show that this is true. The ordinates are the partial pressures of water divided by the vapor pressure of pure water at the same temperature. This is done to minimize differences of temperature. There is of course nothing surprising about the higher alcohols being apparently more polymerized than the lower alcohols. It is what we have always believed. The catch will appear when we consider these same alcohols in benzene solution.

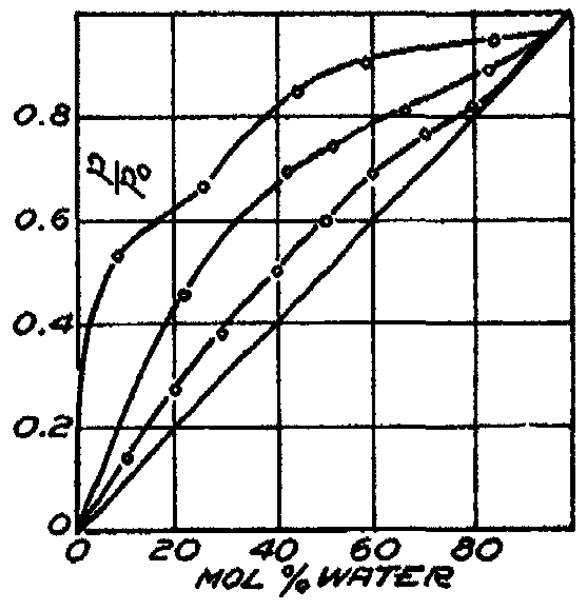

Fig. 5

Top Curve: Propyl Alcohol
Second Curve: Ethyl Alcohol
Third Curve: Propyl Alcohol
Fractional Pressures Water

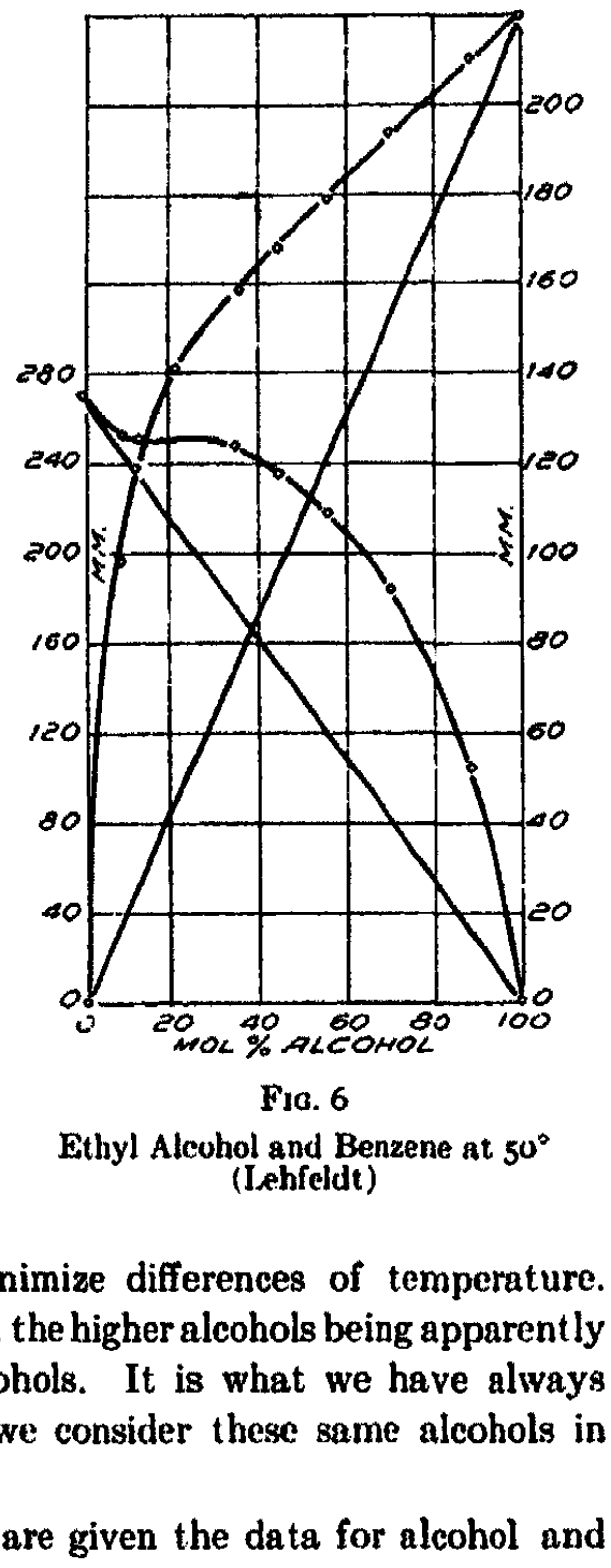

Fig. 6

Ethyl Alcohol and Benzene at 50°
(Lehfeldt)

In Tables VI and VII and in Fig. 6 are given the data for alcohol and benzene at 50° by Lehfeldt.[2] There are errors in Lehfeldt's determinations because the partial pressure of 255.3 mm for benzene containing 21.5 molecular percents alcohol is higher than the figures for the two more dilute

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[1] J. Phys. Chem., 34, 1310 (1930).

[2] Phil. Mag., (5), 46, 59 (1898).

solutions, which is of course impossible. Lehfeldt calculated his apparent molecular weights from a smoothed curve and not from his actual data. That accounts for his missing the fact that alcohol is not abnormal in very dilute solutions in benzene.

TABLE VI

Ethyl alcohol and benzene at 50° (Lehfeldt). Raoult's law.

x = mol fraction alcohol; $1-x$ = mol fraction benzene.

p'_1 = partial pressure alcohol; p'_2 = partial pressure benzene; mm Hg.

A = apparent coefficient of polymerization of ethyl alcohol.

B = apparent coefficient of polymerization of benzene.

x	p'_2	A	1-x	p'_1	B
0.0	270.9	—	1.000	0.0	—
0.088	251.9	1.3	0.912	98.5	8.4
0.121	250.2	1.7	0.879	118.8	8.6
0.215	255.3	4.6	0.785	141.6	8.5
0.355	247.2	5.7	0.645	158.7	4.7
0.444	235.8	5.4	0.556	168.6	4.1
0.561	218.3	5.3	0.439	179.3	3.5
0.697	184.3	4.9	0.303	194.1	3.3
0.886	104.6	4.9	0.114	210.4	3.0
1.000	0.0	—	0.0	219.5	—

From the partial pressures and the calculations in Table VII, we see that the apparent polymerization of alcohol in benzene increases rapidly up to about thirty-five molecular percents of alcohol, where the coefficient of polymerization is nearly six and then sags off to about five. These high apparent molecular weights are qualitatively in keeping with the heats of dilution. Gibbons[1] and I tried hard but unsuccessfully to account for the data quantitatively on the assumption that the heat of dilution was the important disturbing factor. It is clear enough now, fifteen years later, why we failed.

If we look at the curve for benzene in alcohol, we find to our surprise that the apparent polymerization of benzene in alcohol is much greater than the apparent polymerization of alcohol in benzene, the coefficient of polymerization of benzene running up to 8–9, while that for alcohol is only 5–6. If the heat of dilution were the important disturbing factor the apparent molecular weights for benzene should be low and not high. Consequently that is eliminated. Nobody believes that liquid benzene is polymerized to anything like eight-fold under any conditions, but if we throw out the benzene values we must throw out the alcohol values also, because they stand or fall together. Nobody will claim the existence of a 1:1 compound between alcohol and benzene as the cause of the difficulty and we are therefore forced to assume that the chief disturbing factor is the hypothetical tendency of ethyl alcohol and benzene to form two liquid layers.

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[1] J. Phys. Chem., 21, 48 (1917)

Table VII

Alcohol and benzene at 50° (Lehfeldt) Henry's law.
x = mol fraction alcohol; $1-x$ = mol fraction benzene.
p'_1 = partial pressure alcohol; p_2 = partial pressure benzene; mm Hg.
$\% p'_1 = p'_1/p_1$; $\% p'_2/p_2$ $\log x = 8.9750 + 3 \log p'_1$
$\log (1-x) = \bar{7}.814 + 2.5\, p'_2$

x	p'_1	p'_1 calc.	% p'_1	% p'_1 calc.	$\frac{\Delta \log x}{\Delta \log p'_1}$
0.088	98.5	97.7	0.449	0.445	
					1.6
0.121	118.8	108.6	0.541	0.495	
					3.3
0.215	141.6	131.7	0.645	0.600	
					4.1
0.355	158.7	155.5	0.723	0.709	
					3.7
0.444	168.6	167.5	0.768	0.763	
					3.8
0.561	179.3	181.1	0.827	0.825	
					3.9
0.697	194.1	194.7	0.884	0.887	
					3.0
0.886	210.4	210.9	0.959	0.961	
					2.9
1.000	219.5	219.6	1.000	1.001	

1-x	p'_2	p'_2 calc.	% p'_2	% p'_2 calc.	$\frac{\Delta \log(1-x)}{\Delta \log p'_2}$
1.000	270.9	298.2	1.000	1.101	
					1.3
0.912	251.9	287.3	0.930	1.061	
					13.3
0.879	250.2	283.1	0.927	1.045	
					7.1
0.785	255.3	270.6	0.942	0.999	
					6.1
0.645	247.2	250.2	0.913	0.923	
					3.1
0.556	235.8	235.8	0.870	0.870	
					3.1
0.439	218.3	216.4	0.806	0.799	
					2.2
0.303	184.3	183.9	0.680	0.683	
					1.8
0.114	104.6	125.1	0.390	0.462	

As there was no other evidence that benzene and alcohol tend to form a dineric system and since nobody has ever recorded any case of two liquid layers in such a system, the outlook for this hypothesis was pretty hopeless. By means of a flank attack the hypothesis has been established. Methyl alcohol is more like water and therefore less like benzene than ethyl alcohol. On the other hand propyl alcohol is less like water and therefore more like benzene than ethyl alcohol. If the chief cause of the abnormal molecular weights is the tendency to form two liquid layers, we can predict that methyl alcohol will be the most abnormal in benzene, ethyl alcohol less abnormal, and propyl alcohol the least abnormal of the three. We can also predict that it should be easier to form two liquid layers from methyl alcohol and benzene than from ethyl alcohol and benzene.

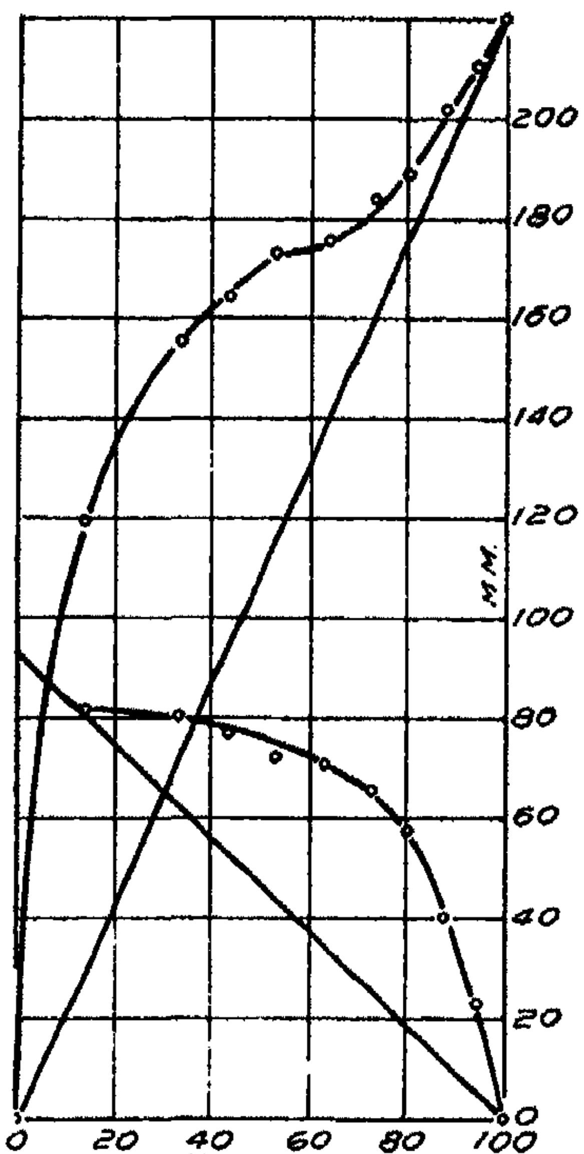

Fig. 7
Ethyl Alcohol and Toluene at 50°
(Lehfeldt)

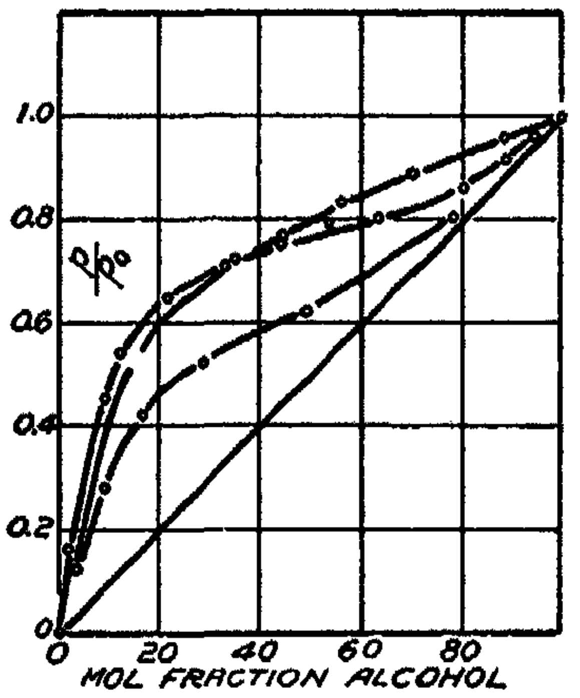

Fig. 8
Top Curve: Benzene
Second Curve: Toluene
Third Curve: Water
Fractional Pressures Alcohol

The second prediction was verified first because it was easier to do. Mr. Lee found that he could get two liquid layers with methyl alcohol and benzene by adding sodium iodide or anhydrous calcium chloride, both of which are soluble in methyl alcohol and insoluble in benzene. He was not able to get two liquid layers from solutions of ethyl alcohol and benzene.

Mr. Lee has also determined partial pressure isotherms for benzene and methyl alcohol and for benzene and propyl alcohol at 40°. He finds, as predicted, that the apparent polymerization of methyl alcohol is greater than that of ethyl alcohol, while the apparent polymerization of propyl alcohol is less. The apparent coefficients of polymerization for high alcohol concentrations are approximately: methyl alcohol, 7+; ethyl alcohol, 5; propyl alcohol, 4+.

If we obtain the degrees of polymerization of the liquid alcohols by extrapolation from water solutions, we find that the order of decreasing polymerization is $CH_3CH_2CH_2OH > CH_3CH_2OH > CH_3OH$. By extrapolation from benzene solutions we get the reverse order $CH_3OH > CH_3CH_2OH > CH_3CH_2CH_2OH$. Both orders cannot be right. The discrepancy disappears if we postulate that we are not measuring polymerizations but tendencies to form two liquid layers. On this basis the two orders should be different and we can predict which is which.

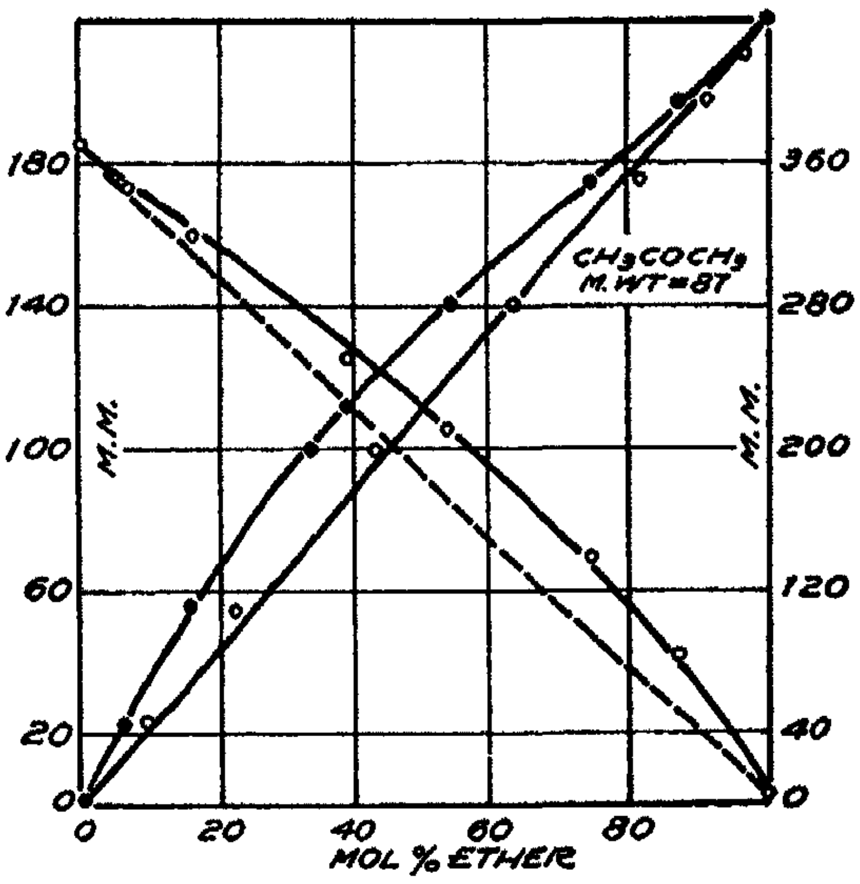

FIG. 9
Acetone and Ether (Sameshima)

A similar conclusion was reached by Perrakis[1] in 1925 from experiments on the lowering of the freezing-point of benzene by different alcohols. Over quite a range of concentrations, butyl alcohol lowers the freezing-point of benzene the most and methyl alcohol the least. "The flat portion of the curve, *which indicates the nearness of a state of non-miscibility*, is less and less marked as one passes up from methyl alcohol to normal butyl alcohol. This fact shows that *the miscibility of these alcohols with benzene increases as one passes up in the homologous series of the alcohols*. . . . Of all the substances that we have just studied, only o-cresol and phenol give *a good miscibility* with ethyl alcohol. These are *good solvents* of ordinary alcohol. . . whereas benzene and phenyl oxide are bad solvents of ethyl alcohol.

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[1] J. Chim. phys., 22, 290 (1925).

Perrakis also points out that in 1909 Faucon determined the freezing-point curves for formic, acetic, propionic, and butyric acids in water. The form of the curve gets flatter as one passes from formic to butyric acid, indicating the approach of non-miscibility. Perrakis comments on the fact that the apparent polymerization increases as one goes up in the homologous series for the acids in water and goes down for the alcohols in benzene.

Freezing-point curves are not as safe material on which to base conclusions as partial pressure isotherms because heats of dilution have a double effect.

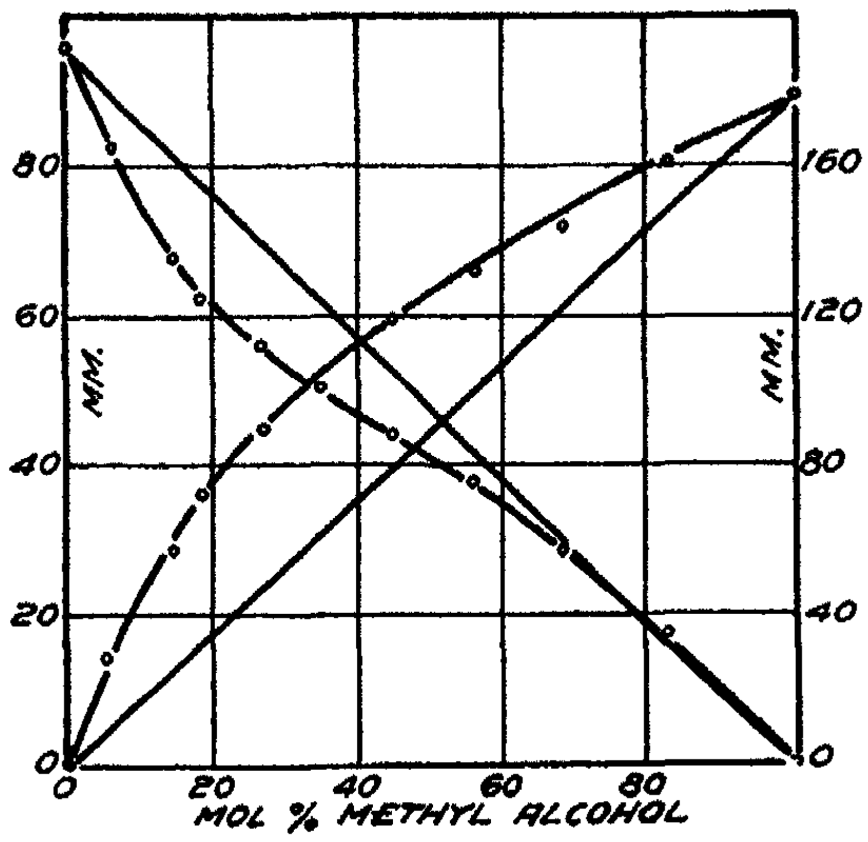

FIG. 10
Acetone and Methyl Alcohol (Morton)

They distort the partial pressure isotherms and in addition they distort[1] the freezing-point curves. In the cases cited, the effects are so large that they are not masked by the heats of dilution.

In Table VIII and Fig. 7 are given Lehfeldt's data for alcohol and toluene. They don't differ very much from those for alcohol and benzene. This is shown clearly in Fig. 8. The benzene curve is the most abnormal; then comes the toluene curve; and the water curve is the least abnormal of the three, though that is not saying much.

In Table IX and Fig. 9 are shown the data for acetone and ether at 30° by Sameshima.[2] This does not differ much from the methyl alcohol and water diagram, Fig. 4. Since the variations are positive in both cases, the chief disturbing factor cannot be polymerization or heat of dilution.

In Fig. 10 we have the data for acetone and methyl alcohol by Morton.[3] This is the only pair of this series in which the variations have opposite signs

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[1] Ewan: Z. physik. Chem., 14, 409 (1894).
[2] J. Am. Chem. Soc., 40, 1482, 1504 (1918)
[3] J. Phys. Chem., 33, 384 (1929).

TABLE VIII

Alcohol and toluene at 50° (Lehfeldt). Henry's law.
x = mol fraction alcohol; $1-x$ = mol fraction toluene.
p' = partial pressure alcohol; p'_2 = partial pressure toluene; mm Hg.
$\%p'_1 = p'_1/p_1$; $\%p'_2 = p_2/p'_2$ $\log x = \overline{10}.81 + 4 \log p'_1$
$\log (1-x) = \ddot{9}.4450+4.4 \log p'_2$

x	p'₁	p'₁ calc.	% p'₁	% p'₁ calc.	$\frac{\Delta \log x}{\Delta \log p'_1}$
0.138	117.9	120.9	0.530	0.551	
					3.2
0.334	154.8	150.5	0.705	0.687	
					4.6
0.437	164.1	161.3	0.748	0.735	
					3.8
0.533	172.8	169.5	0.787	0.772	
					6.2
0.634	176.1	177	0.802	0.806	
					3.4
0.736	184.0	183.7	0.838	0.838	
					3.5
0.806	188.8	188	0.860	0.856	
					1.3
0.885	202.6	201.7*	0.923	0.923	
					1.7
0.946	210.6	210.5*	0.959	0.960	
					1.3
1.000	219.5	218.8*	1.000	0.997	

1−x	p'₂	p'₂ calc.	% p'₂	% p'₂ calc.	$\frac{\Delta \log(1-x)}{\Delta \log p'_2}$
1.000	93.0	88.0	1.000	0.946	
					1.1
0.862	81.6	85.1	0.877	0.915	
					14.9
0.666	80.2	80.2	0.862	0.862	
					4.0
0.513	76.9	77.3	0.826	0.830	
					3.0
0.467	72.2	74.4	0.776	0.800	
					13.4
0.366	70.9	70.0	0.762	0.753	
					3.8
0.264	65.0	65.0	0.099	0.698	
					2.6
0.194	57.7	57.0**	0.020	0.612	
					1.3
0.115	38.9	39.2**	0.418	0.421	
					1.4
0.054	22.9	22.9**	0.246	0.246	

* Calculated by equation $\log x = \bar{4}.49 + 1.5 \log p'_1$

** Calculated by equation $\log (1-x) = \bar{4}.83 + 1.4 \log p'_2$.

TABLE IX

Acetone and ether at 30° (Sameshima). Henry's law.
x = mol fraction acetone; $1.x$ = mol fraction ether.
p'_1 = partial pressure acetone; p'_2 = partial pressure ether; mm Hg.
$\%p'_1 = p'_1/p_1$; $\%p'_2 = p'_2/p_2$ $\log x = \bar{4}.573 + 1.4 \log p'_1$
$\log (1 - x) = \bar{4}.57 + 1.22 \log p'_2$

x	p'_p	p'_p calc.	% p'_1	% p'_1 calc.	$\frac{\Delta \log x}{\Delta \log p'_1}$
0.0387	21.8	27.7	0.077	0.098	
					1.1
0.1327	66.2	66.3	0.234	0.234	
					1.3
0.2509	106.7	104.4	0.377	0.370	
					1.5
0.3454	132.4	131.3	0.468	0.464	
					1.5
0.4958	167.5	169.9	0.593	0.601	
					1.5
0.6507	201.2	201.3	0.712	0.730	
					1.3
0.7047	213.7	218.4	0.756	0.773	
					1.3
0.8381	243.1	247.2	0.860	0.875	
					1.1
0.9337	266.8	266.8	0.944	0.944	
					1.5
0.9528	270.6	270.9	0.957	0.958	
					1.3
0.9799	276.6	276.4	0.979	0.978	
					0.94
1.0000	282.7	280.5	1.000	0.993	

1 − x	p'_2	p'_2 calc.	% p'_2	% p'_2 calc.	$\frac{\Delta \log(1-x)}{\Delta \log p'_2}$
1.000	646.0	647.9	1.000	1.003	
					1.8
0.9613	632.5	627.4	0.979	0.971	
					1.0
0.8673	570.8	576.5	0.884	0.892	
					1.3
0.7491	510.2	513.2	0.790	0.794	
					1.5
0.6546	464.6	457.6	0.718	0.709	
					1.5
0.5042	390.3	369.6	0.604	0.572	
					1.5
0.3493	301.5	273.6	0.467	0.424	
					1.3
0.2953	266.0	238.3	0.412	0.369	
					1.3
0.1619	166.5	145.6	0.252	0.225	
					1.1
0.0663	71.0	70.1	0.110	0.108	
					1.4
0.0472	55.3	53.1	0.086	0.082	
					0.9
0.0201	20.8	26.3	0.032	0.041	

in the two cases. Consequently, the tendency to form a dineric system is not the chief disturbing factor in this case, as it has been in all the others. Further discussion of this system is postponed to a later time.

In Table X and Fig. 11 are the data for water and glycerol at 70° by Perman and Price.[1] While the curve does not lie far from the ideal line, it is to the right of it, which should mean a dissociation of water if we considered the variations to be due solely to polymerization or dissociation.

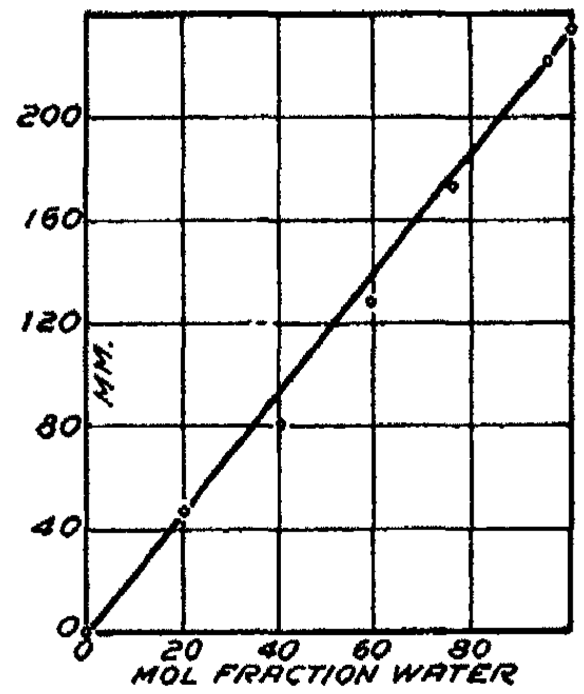

FIG. 11
Water and Glycerol at 70° (Perman and Price)

TABLE X

Water and glycerol at 70° (Perman and Price). Henry's law.
x = mol fraction water; p'_1 = partial pressure water; mm Hg.
$\%p'_1 = p'_1/p'$; $1.2 \log x = \bar{3}.625 + \log p'_1$

x	p'_1	p'_1 calc.	% p'_1	% p'_1 calc.	$\frac{\Delta \log x}{\Delta \log p_1}$
0.410	79.8	81.4	0.341	0.348	
					0.8
0.599	128.1	128.2	0.548	0.548	
					0.8
0.764	173.4	171.7	0.742	0.733	
					0.8
0.862	199.9	198.4	0.855	0.849	
					0.9
0.949	222.3	222.7	0.951	0.953	
					0.8
0.977	229.3	229.8	0.981	0.983	
					0.4
0.977	230.9	230.7	0.988	0.987	
					0.2
1.000	233.8	237.1	1.000	1.014	

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[1] Trans. Faraday Soc., 8, 68 (1912).

It has been shown conclusively that the effect on the partial pressures of the tendency to form two liquid layers is one that cannot be neglected and that it is the most important disturbing factor in the systems methyl alcohol, ethyl alcohol and propyl alcohol with water and with benzene or toluene. On the other hand it is apparently not the important factor in the system acetone and methyl alcohol or in the system water and glycerol. We are therefore justified in concluding that the mean molecular weights of liquid water, liquid ethyl alcohol, and liquid methyl alcohol are definitely less than corresponds to the bimolecular formula. This does not of course mean that water molecules corresponding to $(H_2O)_3$ or $(H_2O)_6$ cannot occur. A solution consisting of $5H_2O + (H_2O)_6$, for instance, would have a mean molecular weight of 33 which is less than the bimolecular value of 36.

This paper has a possible bearing on the Debye-Hückel theory. Debye and Hückel postulated that the only disturbing factor in the case of dilute solutions of certain electrolytes was the electrostatic effect of the ions. It was an eminently advisable assumption that the electrostatic effect was one of the disturbing factors or even that it was the most important of the disturbing factors; but they have never proved that it was the sole factor and most physical chemists have forgotten or have never realized that this unproven assumption underlies all the calculations in the Debye-Hückel theory.

In the case of water and salicylic acid (a weak electrolyte) we have an instable two-liquid layer system. It has been shown in this paper that the tendency to form two-liquid layers may introduce errors of at least seven hundred percent in systems in which the tendency to form two liquid layers is much less pronounced than with water and salicylic acid. There is no evidence as yet that a tendency to form two liquid layers occurs in the systems studied by Debye and Hückel or by their followers; but it is a possible source of error in view of the fact that we get two liquid layers with aqueous acetone and a great number of salts—admittedly at relatively high concentrations from the view-point of the modern orthodox physical chemist who considers a hundredth-normal solution as a concentrated one. It is also quite conceivable that it is the overlooking of an unsuspected source of error which causes the Debye-Hückel theory to break down, rather than an inadequate treatment of the electrostatic effect.

The general conclusions to be drawn from this paper are:—

1. Polymerization, dissociation, heats of dilution, and solvation—except when a 1:1 compound is formed—are disturbing factors which increase the apparent molecular weight of one component and decrease the apparent molecular weight of the other.

2. A tendency to form two liquid layers increases the partial pressures and the apparent molecular weights of both components.

3. Abnormally high molecular weights of both components have been observed with methyl alcohol and water, ethyl alcohol and water, propyl

alcohol and water, methyl alcohol and benzene, ethyl alcohol and benzene, propyl alcohol and benzene, ethyl alcohol and toluene, and in many other cases.

4. While ethyl alcohol might conceivably have a coefficient of polymerization of six in benzene, it is impossible to assume that benzene can have a coefficient of polymerization of eight in alcohol. Consequently these are not true molecular weights.

5. If the abnormal values for ethyl alcohol in benzene are due to the tendency to form two liquid layers, the abnormality should be and is greater with methyl alcohol. It should be and is less with propyl alcohol.

6. In benzene the order of apparent polymerization is: methyl alcohol > ethyl alcohol > propyl alcohol.

7. By addition of anhydrous calcium chloride or of sodium iodide to solutions of methyl alcohol and benzene, it is possible to obtain a separation into two liquid layers, whereas this could not be done with solutions of ethyl alcohol and benzene. These results were predicted.

8. Since butyl alcohol is not miscible in all proportions with water, it was predicted, successfully, that the apparent molecular weights of ethyl alcohol in water would be more abnormal than those of methyl alcohol and less abnormal than those of propyl alcohol.

9. In water the apparent order of polymerization is: propyl alcohol > ethyl alcohol > methyl alcohol. This is just the reverse of what was found, with benzene, proving that we are not dealing with a characteristic of the alcohols but with the differing tendencies to form two liquid layers in the two solvents.

10. From freezing-point measurements in benzene Perrakis showed that the apparent polymerization of the alcohols increases as one passes up the homologous series, while Faucon showed that it decreased for the organic acids, formic to butyric in water.

11. These results prove nothing as to relative polymerizations of ethyl alcohol in benzene and in water, because we cannot yet evaluate quantitatively the effects due to the tendency to form two liquid layers. The line of attack is probably through the internal pressures.

12. It seems to be proved definitely that the true polymerization coefficient of pure liquid water, of pure liquid methyl alcohol, and of pure liquid ethyl alcohol is distinctly less than two.

13. In the case of acetone and methyl alcohol, the variations from the ideal curve are positive for the methyl alcohol isotherm and negative for the acetone isotherm. Consequently this is a case in which the tendency to form two liquid layers is not the important disturbing factor.

14. In the water-acetone system at 25°, as studied by Beare, McVicar and Ferguson, the apparent polymerization coefficient of water reaches a value of

about eight, which is not surprising in view of the readiness with which aqueous acetone solutions break into two liquid layers on addition of a suitable third component.

15. In the water-glycerol system the variations from the ideal curve are slightly negative for the water isotherm.

16. In all the systems studied the effect of the tendency to form two liquid layers is negligible in very dilute solutions. On the other hand, it now appears as one of the most important factors in complicating the treatment of concentrated solutions.

17. It seems like retarding progress when the thermodynamicists treat all the disturbing factors under the single head of activity coefficients instead of trying to evaluate the single factors.

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TRIATOMIC OR MONATOMIC HYDROGEN

BY G. R. SCHULTZE

Articles dealing with the existence of triatomic hydrogen appear over and over again. Indeed the subject matter merits the greatest attention not only because of its chemical interest but also because of its relation to the problem of chemical valence. Further interest in this field has been occasioned by the recent developments in the field of wave mechanics, developments which have led to a very remarkable extension of our conceptions of interatomic forces and chemical bonds, particularly for homopolar compounds.

The more one becomes acquainted with these problems the more one realizes how little has actually been achieved toward the establishing of conclusive proof of the existence of triatomic hydrogen.

This note is written with special reference to a recent paper by J. L. Binder, E. A. Tilby and A. C. Grubb.[1] Without doubt the paper represents a good piece of research as far as a confirmation of facts already known and an extension of our knowledge of active hydrogen in general are concerned. But a proof of the existence of some sort of active hydrogen does not justify the assumption of the presence of triatomic hydrogen, since an explanation on the basis of monatomic hydrogen will still remain possible.

We know that the existence of monatomic hydrogen is well established by the fundamental investigations of Langmuir, Wood, and many others. The facts about monatomic hydrogen are summarized in an excellent monograph by Bonhoeffer.[2]

On the other hand Paneth, Klever, and Peters[3] have shown that the experiments presented by several investigators intended to prove the formation of triatomic hydrogen are open to question. They conclude that there really has been no proof to date for the existence of a neutral H_3-molecule.

Moreover the interpretation of the results obtained by Wendt and his co-workers[4] is mainly based upon two facts: (a) the contraction of the gas under influence of activating agents; (b) the existence of H_3^+ as was found by J. J. Thompson.[5] The contraction finds a satisfactory explanation in the 'clean-up effect'. The positive ray spectrum undoubtedly gives evidence of a charged H_3^+ ion, but its existence is far from being a proof of an uncharged H_3 molecule as Paneth (loc. cit.) has already pointed out.

Another argument in favor of the triatomic modification is to be found in the claims of differences in reactivity and stability between H and H_3. A

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[1] Canadian Journal of Research, 4, 330 (1931). Cf. also Chem. Abs., 25, 3917 (1931).

[2] Erg. Exact. Naturwiss., 6, 201 (1927).

[3] Z. Elektrochemie, 33, 102 (1927).

[4] J. Am. Chem. Soc., 42, 930 (1920); 44, 510 (1922).

[5] Proc. Roy. Soc., 89A, 1 (1913); also cf. A. I. Dempster: Phys. Rev., (2) 8, 651 (1916); Phil. Mag., 31, 438 (1916).

higher or lower concentration of atoms and, in particular, the fundamental influence of wall poisoning upon the formation of active hydrogen readily explain any observed effects which all together would only represent differences in degree and not in kind. Thus the writer of this communication was able to estimate for the active hydrogen an increase of average life of about 5 to 10 times as much as was assumed before simply by reducing the wall skin recombination by means of a negative catalyst.[6] On this ground no definite assertion can be made for the existence of either H or H_3 unless some specific reaction[7] for either one of the modifications is available.

Additional evidence for the monatomic structure of active hydrogen could be drawn from more definite conceptions taken from the kinetic theory and from our knowledge of the reaction kinetics of disintegration of active hydrogen. However, we need not go too much into detail.

One more point should be mentioned however. While the older theory of atomic structure permitted such a molecule as H_3[8], the more recent developments of wave mechanics point to a contrary conclusion.

The different forms of action of homopolar valence forces have been shown to be dependent upon the symmetry-properties of Schroedinger's Eigenfunction. The actual number of valences computed from the multiplicity of terms which correspond to a certain state, is given by the group-theoretical possibilities as limited by Pauli's Principle. Assuming certain resonance effects London has expanded his theory to the formation of hydrogen molecules[9] and has shown that only two possibilities are given: homopolar binding (i.e. formation of H_2-molecules) or elastic reflexion (i.e. H + H atoms). For a third hydrogen atom[10] an immediate application of Pauli's Principle results in an exclusion of a state in which all three electrons are characterized in exactly the same way. Only if the two H-atoms were bound antisymmetrically could the third one be attracted. An antisymmetrical combination, however. corresponds in the last analysis to an exclusively positive value of energy as derived from Broglie's equation which means repulsion of the atoms.

In conclusion may I add that I do not want to deny the possibility of an active form of hydrogen which may be attributable to an H_3 molecule although modern physics has furnished strong theoretical arguments against such a molecule, but I do not believe that a mere proof of the existence of some sort of activation is sufficient basis for the assumption of the existence of H_3 when one has a possible explanation by means of the well established atomic modification of active hydrogen.

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[6] v. Wartenberg and G. Schultze: Z. physik. Chem., 6, 261 (1930).

[7] Using perhaps Wrede's orifice method if the two forms of active hydrogen should happen to be chemically identical. Cf. also Harteck: Z. physik. Chem., 139A, 106 (1928).

[8] N. Bohr: Meddel. Vetenskapsakad. Nobelinst., 5, No. 28, 1 (1919).

[9] W. Heitler and F. London: Z. Physik, 44, 455 (1927).

[10] F. London: Physik. Z., 29, 559 (1928); Science Abstr.: 31, 909 (1928) No. 3170; W. Heitler and F. London: Z. Physik, 44, 468 (1927). F. London: Z. Elektrochemie, 35, 552 (1929).

Since this communication was sent in, the author's attention has been called to an article by Egon Hiedemann (Z. physik. Chem., **153A,** 210-240 (1931)) entitled, "Die Natur des 'dreiatomigen Wasserstoffes." The elaborate experimental work of this investigator has shown conclusively that triatomic hydrogen does not exist. To summarize the result of his work: he found that a hydride of silicon accounts for the activity which can not be explained by means of monatomic hydrogen. It would seem therefore that the question of the non-existence of triatomic hydrogen has been definitely settled.

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THE COLLOID CHEMISTRY OF THE NERVOUS SYSTEMS. III*
HISTAMINE

BY WILDER D. BANCROFT AND J. E. RUTZLER, JR **

There are people who are neither willing to trust their eyes nor to admit the verity of experimental results that fall logically into line and therefore act as checks one upon another. For the qualitative formulation of a theory one experiment repeated a great number of times lacks value almost totally in comparison to a large number of different experiments each of which fits the theory well. Were one to lose consciousness a hundred times by the agency of ether, it still would not teach him that sodium amytal is a good anesthetic, nor would he be able to predict that fact. So a single experiment repeated many times with the same result becomes a trustworthy tool, whereas a good theory is a whole workshop. So it is with a measure of real satisfaction that we are able to present this work on the action of histamine, because from several angles it supports strongly the contention[1] that histamine acts by the reversible agglomeration of the protein colloids of the sympathetic nervous system. This conclusion was drawn from the action of sodium rhodanate as an antagonist for histamine in rabbits. The object of this paper is to show in a variety of different ways that the previous contention as to the mode of action of histamine best explains the facts met with.

Dale and Laidlaw[2] report many interesting things about the action of histamine; we will consider the anesthetic effect first. In the case of the frog, it depresses the central nervous system; this condition is also found in rabbits and cats, for 25-milligram doses may cause a moderately deep narcosis in the rabbit, and ten milligrams a light narcosis in the cat. "When the injection is made subcutaneously, much larger doses are easily tolerated, both by the rabbit and the guinea pig. Twenty-five mgms. thus administered to a rabbit caused a gradual increase in rate of both heartbeat and respiration, the effect first becoming marked about 15 minutes after the injection. Defaecation, with semi-fluid faeces, and micturition occurred, and during the hour succeeding the onset of the symptoms the animal showed signs of prostration, with moderately deep narcosis. The attitude was sprawling, the head sunk on the table, the ears pale and cold. Recovery then set in, and in a few hours the animal was apparently normal."

"In the cat the discrepancy between the effects of intravenous and subcutaneous injections was not so marked. Intravenous injections (long

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*This work was done under the programme now being carried out at Cornell University and financed in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

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[1] Bancroft and Rutzler: J. Phys. Chem., 35, 1185 (1931).

[2] J. Physiol., 41, 318 (1910).

saphena vein) of two, four, eight and ten mgms. caused immediate vomiting and purging, profuse salivation, and laboured respiration, with a subsequent period of collapse and light narcosis, increasing with the dose. During this narcotic stage the pupils were markedly constricted. The cat which received ten mgms. intravenously, and which at the end of an hour had partially recovered, was then given a second intravenous injection of 20 mgms. This caused renewed vomiting and collapse, but the symptoms were rather less marked than those produced by the first injection of ten mgms. The animal, which had thus received 30 mgms. in all intravenously, recovered completely during the night. The effects of subcutaneous injections in the cat were similar, though naturally somewhat slower in onset. 50 mgms. injected into a cat subcutaneously produced vomiting in six minutes, followed by purgation, and subsequently collapse and mild narcoses very similar to the condition following smaller intravenous injections."

In a later paper[1] we find: "The normal rabbit or guinea pig is easily killed by a relatively small intravenous injection of histamine, but suffers little harm from a much larger injection when deeply under the influence of an anesthetic. The unanesthetized cat, on the other hand, recovers from the depressant effects even of very large doses, while in the same species under an anaesthetic even moderate injections of histamine often produce a fatal circulatory collapse and respiratory failure, from which the animal does not recover even after prolonged application of artificial respiration."

From the point of view of the theory of reversible agglomeration these actions of histamine at first appear to be paradoxical, for, while it anesthetizes both herbivora and carnivora, an anesthetic protects herbivora from histamine shock and synergizes the action of histamine in carnivora. However, these apparently opposing facts can be reconciled. In the case of herbivora we have seen that there is a large discrepancy between the toxicity of an intravenous and a subcutaneous dose of histamine, the intravenous dose being by far the more toxic. Since anesthesia may result from the subcutaneous administration of histamine, it becomes evident that the central nervous system is affected more readily by small concentrations of histamine than is smooth muscle and the sympathetic system. The shock effect is much greater as a result of the intravenous administration, which means that large local concentrations are necessary to cause agglomeration of the protein colloids in smooth muscle and sympathetic nerves.

The difference in effect between intravenous and subcutaneous injections must also mean that the rabbit and guinea pig detoxicate histamine fairly rapidly. If we assume that the anesthetic is taken up slightly by the sympathetic nervous system, its concentration may be low enough not to produce the condition of shock itself, and yet high enough so that the displacement by the histamine takes place too slowly to build up the shock concentration, even though intravenous injection is resorted to. This results in protection from the shock. In the case of carnivora the anesthetic prevents histamine

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[1] Dale and Laidlaw: J. Physiol., 52, 355 (1919).

from going into the brain, and forces it to concentrate in the sympathetic nervous system, with fatal results. Thus, with carnivorous animals the important thing seems to be the amount of histamine available; while with herbivorous animals the important thing appears to be the rate at which the histamine is supplied.

Dale contributes[1] many other facts about the action of histamine. Anesthetized cats and dogs showed a considerable fall of systematic arterial blood pressure upon the administration of histamine; this was due to a general vasodilatation. In perfusion experiments with isolated organs histamine behaves in exactly the opposite way, acting as a vaso-constrictor. Intact animals show severe bronchial constriction. The urinary bladder contracts upon the administration of histamine; this is due to stimulation by the drug of centers in the cord. A slow injection of histamine into a cat produced convulsive inspirations which appeared to be efforts at vomiting. Dale and Laidlaw observed that there was an abnormal agglutination of the blood platelets; they found that there is a large loss of blood volume, it being held by various organs and capillaries. The blood increases in hemoglobin content and in viscosity. These investigators emphasize the similarity of the action of larger doses of histamine and traumatic shock, which is almost surely accompanied by reversible agglomeration.[2]

In pointing out the likeness of histamine shock to anaphylactic shock Dale and Laidlaw say: "All available evidence goes to show that the anaphylactic antibody is of the nature of a 'precipitin' the interaction of which with the corresponding antigen results in a change in the state of dispersion of the colloidal particles. One of us has given reasons for believing that the occurrence of this reaction actually in the plain muscle fibres of the guinea-pig is the exciting cause of the contraction of the plain muscle, which gives to the anaphylactic 'shock' its characteristic type in that species. It is not inconceivable that a physical change of this type occurring in the endothelial cells would lead to relaxation of their tone and ultimately to abnormal permeability; indeed if the anaphylactic reaction, as exhibited in different tissues and species, depends always on the same type of interaction between antigen and antibody, this would almost of necessity follow. So that it is quite possible that the production by histamine, and by a whole group of other substances, of a complex including contraction of plain muscle with relaxation and permeability of capillaries, may depend on a common-type of physical change in protoplasm produced by all of them, the result of which receives different expression in terms of the physiology of different tissues."

Wells[3] also draws attention to the close resemblance of histamine shock to anaphylactic shock. Another item of interest is that histamine seems to have an additive effect on anaphylactic shock, which is what one would expect. Kopaczewski[4] cites the work of Dale, among others, in support of

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[1] Dale and Laidlaw: J. Physiol., **41**, 318 (1910); **52**, 355; Dale and Richards: 110 (1919).

[2] Bancroft and Rutzler: J. Phys. Chem., **35**, 3036 (1931).

[3] "The Chemical Aspects of Immunity," 209 (1925).

[4] Alexander: "Colloid Chemistry," **2**, 976 (1928).

his theory that shock is due to protein flocculation. He also mentions the "inversion of the electric charge of the globulins" as being associated with shock. All of these things are explained by reversible agglomeration.

The reaction of the isolated uterus to histamine[1] follows the precepts of colloid chemistry, and corresponds to the different effects that Dale and Laidlaw found, depending on whether histamine was injected subcutaneously or intravenously into a rabbit. The rapid addition of histamine to an isolated uterus preparation is more effective than slow application. The question of its activity seems to be related mainly to its concentration. Many agglomeration phenomena exhibit this same peculiarity. For in many cases it takes a good deal more of an agglomerating agent to coagulate a sol if the agent is added very slowly rather than all at once. So, here we have a striking resemblance to a well known colloidal action. Sollmann[2] says: "The stimulation [by histamine] is most marked in the uterus; the bronchioles are also highly sensitive; the intestine, arteries and spleen are less susceptible (one part of histamine in 700 parts of water causes complete inhibition or paralysis of the isolated intestine of the rabbit);[3] the bladder and iris do not respond." Sollmann then plays into our hand with the statement that calcium salts, which are agglomerants for protein sols, intensify the action of histamine upon the intestine. Here we have the agglomeration caused by histamine increased by the agglomeration brought about by calcium salts which is directly in line with this theory.

A difference between anaphylactic shock and the action of histamine is that the susceptibility of sensitized rabbits[4] and guinea-pigs to foreign proteins is increased three to ten times by the subcutaneous injection of quinine. It has, however, no harmful effect on the course of the intoxication produced by histamine. This is the consequence of the manifold colloidal changes in anaphylactic shock; whereas, as had been pointed out,[5] the colloidal changes accompanying histamine shock are probably simpler.

The conclusion of Schenk, who says[6] that histamine probably acts through a paralysis of the sympathetic system, or by an effect upon the myoneural junction, falls more into line with the conception that we hold concerning the cause for the action of histamine. Likewise Heubner[7] lists histamine as a capillary and nerve poison. There can be no doubt but that the sympathetic nervous system takes part in the shock caused by histamine, for Chauchard and Saradjichvili[8] found in experiments upon dogs that injections of histamine gradually increased the chronaxie of the cardiac inhibitory fibers of the vago-sympathetic nerve. The chronaxie gradually returned to

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[1] Oehme: Archiv exp. Path. Pharm., **72**, 76 (1913).

[2] "A Manual of Pharmacology," 362 (1917).

[3] Olivecrona: J. Pharmacol., **17**, 141 (1921).

[4] M. I. Smith: J. Immunol., **5**, 239 (1920).

[5] Bancroft and Rutzler: J. Phys. Chem., **35**, 1185 (1931).

[6] Archiv exp. Path. Pharm., **89**, 332 (1921).

[7] Archiv exp. Path. Pharm., **107**, 129 (1925).

[8] Compt. rend. soc. biol., **99**, 53 (1928).

normal after the injections were stopped. "If the dose [of histamine] is excessive, the vago-sympathetic nerve becomes inexcitable and the animal soon dies." Bancroft and Richter[1] have shown that reversible protein agglomeration causes a rise of the chronaxie which reaches a maximum when the pH of the medium in contact with the muscle-nerve preparation is very near the isoelectric point of the proteins involved. Likewise, Chauchard and Saradjichvili found that the chronaxie-time curve goes through a maximum after the injection of histamine. At first there does not appear to be any relation between these two sets of data; yet they are related in an important way. In the first case, the decrease of pH is proportional to the increase in the concentration of hydrogen ions. Further, more hydrogen ions are adsorbed as their concentration increases within limits, of course. In the second case, the experiment was performed *in vivo*, and the histamine was injected intraperitoneally. This means that more and more histamine will find its way into the blood stream, up to a maximum concentration, with the passage of time; therefore, time is related to concentration in this case. So we have the two curves showing a maximum at the optimum concentrations, the maximum indicating reversible agglomeration. We do not make the assumption that the maximum chronaxie corresponds exactly to the maximum amount of histamine in the blood.

Histamine causes a loss of water in *Spirosteum teres*,[2] and the organism dies. The dead protozoon is much shrunken, and presents the appearance of having undergone heat coagulation. This demonstrates again the property of agglomerating protein sols that is possessed by histamine. In connection with this, it is well to call attention once more to the fact[3] that histamine dihydrochloride causes horse serum to agglomerate. Such facts as these pretty thoroughly establish histamine as an agglomerating agent for proteins.

Experimental Study

1. Swelling Experiments *in vitro*

In order to study the colloidal effects produced by histamine upon the sympathetic nervous system, excisions were made of the superior cervical ganglia, which in bulk is the purest obtainable sympathetic nervous tissue, of rabbits. In dealing with sympathetic nerves there is the advantage that the situation is not complicated by the presence of lipoids; for the sympathetic nerves have no medullary sheaths.[4] We shall see later how this is of advantage. Cocaine, which is classed as an agglomerating agent, paralyzes the superior cervical ganglia of rabbits.[5] The agglomeration is reversible and responds to treatment as the theory demands, for some of the irritability is restored by washing the ganglia with physiological salt solution.

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[1] Proc. Nat. Acad. Sci., **17**, 310 (1931).

[2] Hopkins: Am. J. Physiol., **61**, 551 (1922).

[3] Bancroft and Rutzler: J. Phys. Chem., **35**, 1185 (1931).

[4] Burton-Opitz: "Elementary Manual of Physiology," 101 (1922).

[5] Dixon and Premankin De: J. Pharm. Exp. Ther., **31**, 415 (1927).

When gelatin swells it adsorbs water and increases in weight; were salts also adsorbed they would augment the increase in weight. Many proteins behave the same way. Peptization accompanies such an increase in weight, and agglomeration is indicated by a decrease in weight. So, if a ganglion increases in weight when immersed in one solution and decreases in weight in an equimolar solution of another compound, peptization can be assumed to have taken place in the first case, and agglomeration in the second case.

The superior cervical ganglia of a good-sized rabbit were removed,[1] after first pithing and bleeding the animal. The ganglia were removed as rapidly as possible after the animal was bled, and placed in a 15 cc. weighing bottle containing Ringer's solution. Because these ganglia are so small (weighing between 14 and 56 milligrams) a micro-balance was used; the weighings were made in a small tightly-stoppered weighing-bottle. The experimental method employed was to transfer the ganglion from the Ringer's solution to the weighing-bottle by means of metallic forceps with fine ends; the ganglion was touched four or five times to the side of the bottle containing the solution, at a point above the surface of the liquid. This procedure was repeated when the ganglion was removed from the bottle in which it was weighed. This took off most of the adhering liquid so that the true weight of the ganglion could be estimated quite accurately. Therefore, the weight of the weighing bottle and the ganglion minus the weight of the weighing bottle and some adhering liquid ("drip") is equal to the weight of the ganglion. The ganglion was immersed in a 0.0604 molar solution of histamine dihydrochloride or sodium rhodanate depending upon which one was being studied. After a given period of time the ganglion was removed from the solution and weighed in the manner described above. From the data obtained, the percentage change in weight was calculated. The ganglion was returned to the solution for a time and the process repeated.

The data obtained from the first experiment, which was made on two ganglia, one being placed in 0.0604 histamine dihydrochloride solution and the other in 0.0604 molar sodium rhodanate solution. It was evident from the change in size of these two ganglia during the experiment that the one in the sodium rhodanate solution had swelled, and the one in the histamine solution had decreased in size. The data are given in Table I, and are plotted graphically in Fig. 1, curves 1 and 4. The same experiment was performed on another sample from a different rabbit. The data obtained are given in Table II, and are plotted graphically in Fig. 2.

The experiment was repeated again with a change in the procedure; this time the ganglion was placed in 0.0604 molar sodium rhodanate after it had been in an equimolar solution of histamine dihydrochloride for five hours. The data obtained from this experiment are recorded in Table III, and are plotted graphically in Fig. 1, curves 2 and 3.

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[1] The authors wish to thank J. W. Papez, M.D., Assistant Professor of Anatomy at Cornell University, his assistants, and H. L. Rutzler for their advice and help with this part of the work.

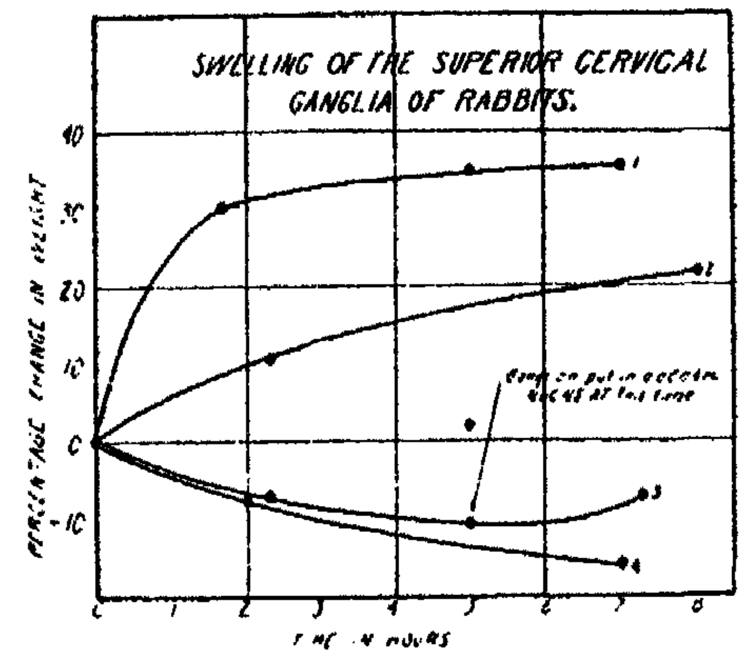

Fig. 1

Curve 1. Ganglion in 0.0604 M Sodium Rhodanate
Curve 2. Ganglion in 0.0604 M Sodium Rhodanate
Curve 3. Ganglion in 0.0604 M Histamine Dihydrochloride
Curve 4. Ganglion in 0.0604 M Histamine Dihydrochloride

TABLE I

Compound	Time in Hours	Weight Bottle + Ganglion in Milli-grams	Weight Bottle + Drip in Milli-grams	Weight Ganglion in Milli-grams	Increase in Weight in Milli-grams	% Increase in weight
0.0604 Molar Histamine Dihydrochloride	0	34.620	6.089	28.532	0	0
"	2	39.995	13.655	26.340	2.192	− 7.69
"	5	46.580	17.483	29.097	0.565	1.95
"	7	44.112	20.083	24.029	4.503	−15.80
0.0604 Molar NaCNS	0	19.106	4.809	14.297	0	0
"	1⅔	34.934	16.300	18.634	4.337	30.32
"	5	37.264	18.030	19.234	4.937	34.55
"	7	38.580	19.220	19.360	5.063	35.50

Upon examining Fig. 1, we find that the ganglia underwent an increasing positive change in weight with the passage of time, when immersed in the sodium rhodanate solution. This means that they increased in weight, which in turn signifies peptization of the protein colloids in the ganglia. This result falls in line with the fact that most of the natural proteins are peptized by the rhodanate ion. Curves 3 and 4 of Fig. 1 show that the ganglia immersed in the histamine solution underwent an increasing negative change in weight with the passage of time. This means that they lost weight, showing that the protein sols were agglomerated. Curve 3 tells us that the agglomeration

TABLE II

Compound	Time in Hours	Weight Drip + Ganglion in Milligrams	Weight Drip in Milli-grams	Weight Ganglion in Milli-grams	Increase in Weight in Milli-grams	% Increase in Weight
0.0604 Molar NaCNS	0	62.681	6.212	56.469	0	0
"	2¾	71.136	4.212	66.924	10.455	18.52
"	5	75.301	6.595	68.706	12.237	21.72
"	10	81.045	13.231	67.814	11.345	20.10
0.0604 Molar Histamine Dihydrochloride	0	31.485	2.897	28.588	0	0
"	2⅔	35.982	5.168	30.395	1.807	7.7
"	4⅔	30.028	2.685	27.343	−1.245	−4.36
"	7¾	33.665	4.436	29.229	0.641	2.24
"	11	31.361	3.238	28.123	−0.465	−1.63

TABLE III

Compound	Weight drip + Ganglion in Milligrams	Weight Drip in Milli-grams	Weight Ganglion in Milli-grams	Increase in Weight in Milli-grams	% Increase in Weight	Time in Hours
0.0604 Molar Histamine Dihydrochloride	17.099	1.425	15.674	0	0	0
"	18.266	3.709	14.557	—1.117	— 7.13	2⅓
"	15.633	1.613	14.020	—1.654	—10.55	5.0
Same sample put in 0.0604 Molar NaCNS	16.081	1.498	14.583	—1.091	— 7.02	7⅓
0.0604 Molar NaCNS	22.091	3.655	18.436	0	0	0
"	23.786	3.375	20.411	1.975	10.7	2⅓
"	26.572	4.118	22.454	4.018	21.8	8

brought about by histamine is reversible; for upon immersion of the ganglion in the solution of sodium rhodanate it gained weight as the theory says it should.

Thus, eliminating the possible sources of error presented by experimentation upon the intact animal, and dealing directly with one of the parts affected in histamine shock, the conclusion that this drug acts by agglomerating reversibly protein colloids of the sympathetic nervous system, becomes even more inevitable. But, in Fig. 2, while sodium rhodanate peptizes one of the ganglia of a rabbit, the agglomerating action of histamine is not very evident.

This is due to an interesting experimental error. In order to facilitate the explanation of the effects shown in Fig. 2 it is desirable first to introduce further data.

A rabbit was pithed and its cerebral cortex carefully removed. The blood vessels and dura were stripped from the surface of the sample, taking care to keep it wet with Ringer's solution all of the time. The specimen was cut into equal parts, the weight of which were sufficient for them to be weighed accurately on the ordinary analytical balance, which was used in this case. Swelling experiments then were performed on two of the sections using the method described for histamine and sodium rhodanate. The solutions used were a 0.0604 molar sodium rhodanate solution and a saturated solution of chloroform in water at 25°. The data obtained are presented in Table IV, and are plotted graphically in Fig. 3.

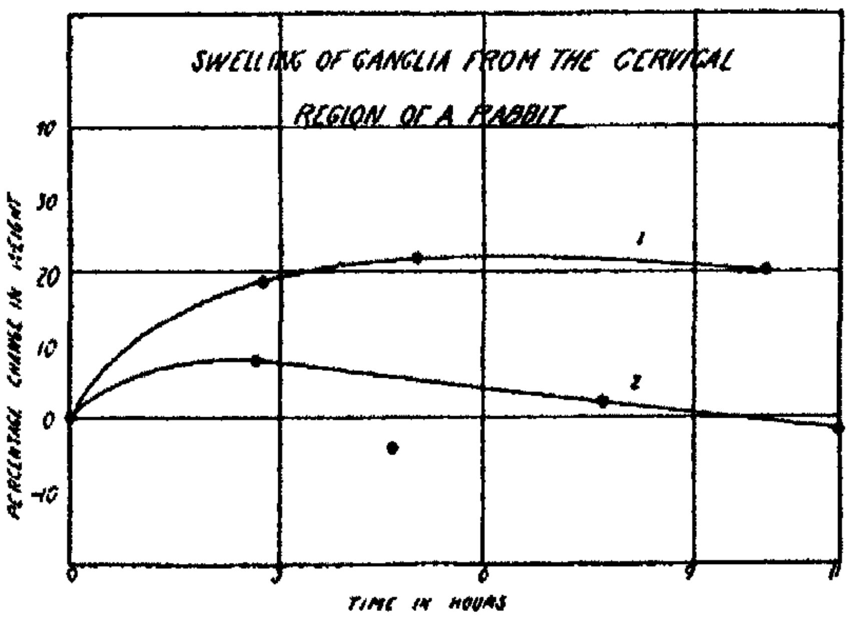

FIG. 2

Curve 1. Ganglion in 0.0604 M Sodium Rhodanate
Curve 2. Ganglion in 0.0604 M Histamine Dihydrochloride

TABLE IV

Compound	Time in Hours	Weight Bottle + Brain in Grams	Weight Bottle + Drip in Grams	Weight Brain in Grams	Increase in Weight in Grams	% Increase in Weight
0.0604 Molar						
NaCNS	0	22.4608	21.4701	0.9907	0	0
"	3¼	22.7864	21.5351	1.2513	0.2606	26.3
"	6	22.9637	21.5272	1.4365	0.4458	45.0
"	8½	23.0508	21.4915	1.5593	0.5686	57.4
"	30	23.8500	21.6180	2.2320	1.2413	125.5
Saturated $CHCl_3$						
Solution	0	16.9694	16.0811	0.8883	0	0
"	2½	17.4263	16.2780	1.1483	0.2600	29.3
"	5	17.5743	16.1976	1.3767	0.4884	55.0
"	8½	17.7244	16.2829	1.4415	0.5532	62.3
"	29½	17.9800	16.4200	1.5600	0.6717	75.6

The curves show that the cerebral cortex increases in weight both in a chloroform solution and in a sodium rhodanate solution. But, there cannot be peptization in both cases because chloroform is an agglomerating agent for protein sols. On the other hand, chloroform dissolves in lipoids, in which the cerebrum is rich. The specimen then is capable of taking up chloroform by a pure solvent action which accounts for the increase in weight upon immersion in a chloroform solution. The fat cannot dissolve a significant quantity of sodium rhodanate. Therefore, curve 1 of Fig. 3 shows that sodium rhodanate causes the proteins of the cerebral cortex to increase in degree of dispersion. That the effect is not due to the peptization of the lipoids is shown by the fact that a lecithin sol in distilled water is coagulated by sodium rhodanate. The general morphology of the two sections toward the end of the experiment bears out the conclusion that sodium rhodanate acted as a peptizing agent and chloroform merely dissolved in the fatty material. At the end of eight hours the section that had been in sodium rhodanate was much softer than at the start of the experiment; in fact it was jelly-like. The section that had been immersed in chloroform solution broke up into several large pieces, but was as firm as it was in the beginning. At another time we had occasion to immerse the whole cerebrum of a rabbit in water saturated with chloroform. At the end of 24 hours it had wrinkled up, was very hard to the touch, and had lost 9% in weight. The longer time of immersion in this case clearly brings out the coagulating effect of the chloroform. This thoroughly establishes the point in question.

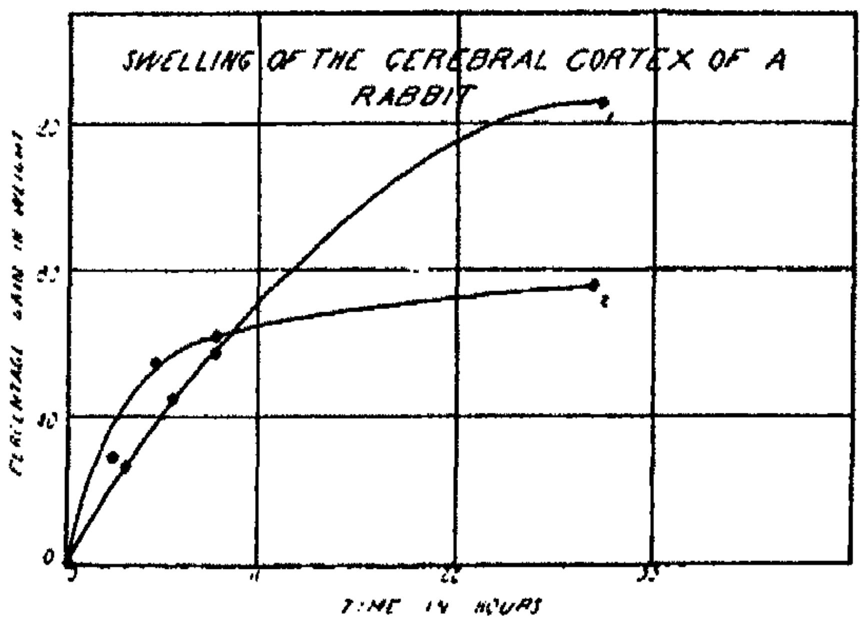

Fig. 3

Curve 1. Cerebral Cortex in 0.0604 M Sodium Rhodanate
Curve 2. Cerebral Cortex in Saturated Chloroform Solution

The bearing of the above discussion on the swelling curve in Fig. 2 for histamine on a ganglion from the cervical region should be apparent immediately—after citing two more facts about the specimen used. This ganglion weighed twice as much as any of the superior cervical ganglia that were used; further, the operator states that the ganglion was either a sensory ganglion from the cervical region or a superior cervical ganglion which included fatty material, due to faulty excision technique. In either case the increase in weight that the ganglion underwent in the histamine solution can be regarded safely as due to the dissolving of histamine in fatty material. The general shape of the curve indicates that after dissolving in the fatty material, the histamine began to agglomerate the protein colloids, for the final value shows that the ganglion lost weight. It is certain that this ganglion was not a pure specimen of sympathetic nervous tissue; which in turn suggests strongly that pursuing a line of attack such as this, one should be able to work out a qualitative method, based on colloid chemistry, for the differentiation of nervous tissues.

Since ephedrine is a very good peptizing agent for protein sols,[1] it should follow that ephedrine is useful in disturbances brought about by histamine and related drugs. Chen[2] reports that the fall in blood pressure in anesthetized dogs, brought about by histamine, peptone, and anaphylactic shock, is stopped, and the pressure raised, by the administration of ephedrine. Adrenaline exerts a similar action.[3] A 1 % solution of ephedrine hydrochloride arrests the heart in perfusion experiments; this arrest can be combated by two coagulating agents,[4] histamine and salts of calcium. This is, of course, a case of reversible peptization. As we have seen, peptone shock is very similar to histamine shock. Ephedrine quickly relieves the bronchial spasm brought about by injecting peptone.[5] It is quite possible that the bronchodilator action of ephedrine[6] is due to the "stimulation" of sympathetic nerves, which are inhibitory to this muscle. Ephedrine and ergotoxine being peptizing agent and agglomerating agent respectively [the action of ergotoxine is much like that of histamine] should exert opposite effects. Nagel[7] found that the pressor (increase of blood pressure) action of ephedrine is reduced by ergotoxine, and Curtis[8] succeeded in preventing it entirely.

In histamine poisoning the bronchioles are strongly constricted as a result of peripheral stimulation so that the lungs bloat as in anaphylaxis.[9] Another protein-agglomerating agent, barium chloride, causes profound constriction of the pulmonary artery[10] following perfusion with a 1/1000 solution.

2. Skin Reactions

This brings us to a study of the skin reactions produced by histamine and giant-ragweed pollen; it will be shown that in this case also sodium rhodanate

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[1] Bancroft and Rutzler: J. Phys. Chem., 35, 3036 (1931).

[2] J. Pharmacol., 26, 83 (1925).

[3] Niculescu: Chem. Abs., 8, 2745 (1914).

[4] Chen and Schmidt: "Ephedrine and Related Substances," 24 (1930).

[5] Kreitmair: Klin. Wochenschr., 5, 2403 (1926).

[6] Chen and Schmidt: "Ephedrine and Related Substances," 40 (1930).

[7] Archiv exp. Path. Pharm., 110, 129 (1925).

[8] J. Pharm. Exp. Ther., 34, 37 (1928).

[9] Sollmann: "Manual of Pharmacology," 362 (1917).

[10] Baehr and Pick: Archiv exp. Path. Pharm., 74, 41 (1913).

and ephedrine oppose the action of histamine. First, it is of interest to note that there is a rich supply of sympathetic vaso-constrictor nerves present in the arterioles of the skin.[1] Histamine exerts a local dilator effect[2] upon capillaries and upon the smallest arterioles and venules which border on the capillary system; there occurs also an opening up of a large number of capillaries of which no trace can be seen before the application of histamine. According to Wallace and Pellini[3] a widening, or paralysis, of the capillaries is produced by histamine; no visible structural change accompanies this process. Carrier[4] reports that adrenaline produces contraction of both arterioles and capillaries, while solutions of histamine from one part in 1000 up to one part in 10,000 produce dilation of the capillaries with hastening of the blood stream. Urethane, an anesthetic, dilates both capillaries and arterioles. Heubner[5] classifies histamine as a capillary and nerve poison, arsenic as a capillary and cell poison, and caffeine as a vessel poison. All three of these are active dilators of skin vessels; and from the point of view of this theory all are agglomerating agents for protein sols. The interesting thing here is that according to Sollmann and Pilcher,[6] "a comparison of the substances that do and do not produce urticaria shows that this is not related to vasoconstriction or vasodilation, or capillary paralysis; nor to acidosis; nor to various forms of inflammatory or sensory initation; nor to osmosis." That does not leave much but reversible agglomeration.

When histamine is applied to the scarified skin or to mucous membranes, it causes marked local urticaria which closely resembles that of skin reactions in persons sensitized to a foreign protein.[7] Sollmann and Pilcher[8] report several interesting things resulting from their study of skin reactions. The skin reaction to Witte's peptone as one would expect, is similar to that produced by histamine. Adrenaline when applied to scarification histamine wheals, antagonizes the histamine action; but the swelling does not undergo any noticeable change. On the contrary, the wheals produced by morphine were not antagonized to any extent by the application of adrenaline; it does not seem to make any difference whether the adrenaline is applied before or after the morphine. Calcium chloride, an agglomerating agent for protein sols, when applied to the scarified skin produces a reaction like histamine in respect both to the wheal and urticaria. "The production of urticaria by calcium is rather surprising in view of the employment of calcium therapy for the prevention of urticaria, for instance, after serum injection. However, the concentration and method of application are quite dissimilar in the two conditions." When the concentrations are properly adjusted, and using the

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[1] Dale and Richards: J. Physiol., 52, 110 (1918-19).
[2] Rich: J. Exper. Med., 33, 287 (1921).
[3] Arch. Int. Med., 28, 711 (1921).
[4] Am. J. Physiol., 61, 528 (1922).
[5] Archiv exp. Path. Pharm., 107, 129 (1925).
[6] J. Pharm. Exp. Ther., 9, 309 (1917).
[7] Wells: "Chemical Aspects of Immunity," 209 (1925).
[8] J. Pharm. Exp. Ther., 9, 309 (1917).

mucuna method for producing the reaction, morphine hydrochloride and histamine give almost identical skin reactions. Likewise, using this method, cocaine produced a number of small wheals. Lactic acid produces a fair wheal; but N/10 hydrochloric acid does not. There are no data given from which to figure whether or not the concentrations of lactic acid and hydrochloric acid were comparable; the hydrogen ion is an agglomerating agent for normal negative protein sols. The authors say that, "none of the reactions in man or in animals was modified in any way by the administration of iodides." Here again there are no data given, so one cannot judge whether or not the iodides, when administered, are capable of modifying the reactions; all that we know is that an unspecified dosage did not exert any effect.

If the skin reaction produced by histamine is connected with reversible protein agglomeration it is only reasonable to expect that sodium rhodanate will alleviate the condition when properly applied. Accordingly the skin on the right forearm of a volunteer[1] was carefully broken by means of a hypodermic needle. A couple of drops of a solution, of histamine dihydrochloride, containing 30 mg. per 100 cc. of distilled water, were applied carefully to the scratch. In about ten minutes a good sized wheal formed on the arm directly under the scratch; the irritation was accompanied by itching. A distinct area of redness (urticaria, or erythrema) soon appeared around the wheal. A 10% solution of sodium rhodanate was applied to the affected area 15 to 20 minutes after the application of the histamine. This resulted in a slight diminution of the reaction.

Another scratch was made below the first; to this was applied a couple of drops of the 10% solution of the sodium rhodanate, which caused a stinging sensation. When the arm was again dry, the scratch was found to have closed over almost entirely. It was opened up a little, and the histamine solution applied. It took about twice as long for the wheal to appear as it did in the first experiment. The edema was not quite so marked and the wheal was not as darkly colored as the first one; The erythrema was not as marked; and there was no itching.

These experiments were repeated twice in order to obtain a quantitative measure of the antagonistic action of sodium rhodanate toward histamine. Since quite a few scratches were made in this study a tabulation of the treatment received by each scratch will facilitate the description of the reaction, for the individual scratches can then be referred to by number. Table V contains these data. By using a magnifying glass it was found to be possible to break the skin by means of the hypodermic needle to approximately an equal depth in each case. The solutions were applied as before, a couple of drops usually being used. The histamine dihydrochloride solution contained 15 mg. per 100 cc. A 10% solution of sodium rhodanate was used. Dr. Denniston performed these experiments on the junior author. In each case when a solution was applied it was allowed to dry before any other solution was placed on the scratch.

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[1] The authors wish to thank H. P. Denniston, M.D., of Ithaca, who performed these experiments upon H. L. Rutzler.

TABLE V

Scratch Number	Treatment
1	Control
2	Sodium rhodanate solution followed by histamine solution after 5 minutes
3	Ringer's solution followed by histamine solution after 5 minutes.
4	Control
5	Histamine solution applied at the same time that it was applied to 2 and 3.
6	Ringer's solution followed by histamine solution.
7	Sodium rhodanate solution followed by histamine solution.
8	Control
9	Control
10	Histamine solution alone.
11	Histamine solution alone.

The controls, scratches number, 1, 4, 8, 9 did not form wheals, and the erythrema was negligible. Two minutes after the histamine solution was applied to scratch number 5 there was a perceptible reaction; while scratch number 2 showed no reaction until four minutes had elapsed. Ten minutes after the application of the histamine the relative reactions were: number 5, ++++; number 2, ++; number 3, +. After 24 minutes the reactions of scratches number 2 and 3 had dwindled to nothing; while scratch number 5 showed a +++ reaction. There was still swelling and redness in the case of the scratch (number 5) to which histamine alone was applied, after 55 minutes. Check experiments were run almost simultaneously on the right arm. The reactions in scratches number 6, 7, and 10 were carried out at the same time. Due to faulty technique scratch number 5 was extremely shallow; therefore, scratch number 11 was made and histamine applied to it 6 minutes later. As before scratches number 10 and 11 itched whereas this was not noticed when the scratches were pre-treated. Twenty-two minutes after the application of the histamine the relative reactions were: number 10, ++++; number 11, ++++; number 7, ++; number 6, ++. After 34 minutes the wheals and erythrema in scratches number 6 and 7 had practically disappeared, while scratch number 11 was still very swollen, number 10 was next in intensity. After 44 minutes the reactions in scratches number 6 and 7 had disappeared; while there were still active reactions in the cases of scratches numbers 10 and 11. The scratch treated with histamine alone, number 11, still itched a little bit at this time. The reaction in scratches number 10 and 11 persisted at least one hour four minutes, while the reaction in scratch number 5 persisted for at least two hours twenty-three minutes.

As these data show, there can be no question that sodium rhodanate and Ringer's solution definitely localize and reduce the skin reaction produced by histamine dihydrochloride.

Next, it seemed advisable to check up on the action of sodium rhodanate against the skin reaction produced by hay-fever pollens. Dr. B. F. Hauenstein, Tompkins County Pathologist, kindly performed the rest of the experiments reported upon the junior author. The patient was found to have a ++++ skin reaction to giant-ragweed-pollen extract; likewise there was +++ reaction to ragweed-pollen extract.

The upper part of both arms was washed with soap and cleaned with alcohol followed by ether. Two scratches were made about two inches apart and a 10% solution or sodium rhodanate allowed to soak into each for about 10 minutes. The excess solution was rubbed off and giant-ragweed extract was rubbed into the top scratch. Into the second scratch, which was used as a control, orchard-grass extract was rubbed. Third and fourth scratches were then made. Giant-ragweed extract was rubbed into the third scratch; the fourth scratch was treated in the same way with orchard-grass extract. Both controls (orchard-grass extract) formed wheals, the reactions being identical to all intents and purposes. Despite the wheals, the orchard-grass extract reactions were considered to be negative.

The skin reaction to the giant-ragweed extract on the untreated scratch was again ++++, the wheal being somewhat larger than the one formed when the sensitivity test was made. The striking thing is that the scratch which was pre-treated with the 10% solution of sodium rhodanate showed only a ++ reaction to the giant ragweed extract. The reaction in this case was then only one-half as great as that which occurred when sodium rhodanate was not used.

It was found that a daily dose of one gram of sodium rhodanate taken by mouth for 3 successive days did not cut down the skin reaction to giant-ragweed extract. The possible cause for this situation is that not enough sodium rhodanate was in the system of the patient.

The following solutions were used in the experiments about to be reported: A solution of histamine dihydrochloride containing 30 mg. per 100 cc., a 10% solution of sodium rhodanate, and a 10% solution of ephedrine sulphate. On the day that these experiments were performed the patient was slightly refractive to the giant-ragweed extract; no reason for this could be conjured up.

After cleaning the arm as previously described, three scratches of equal depth were made. A little of the 10% ephedrine sulphate solution was applied to the first scratch. When the area had dried the giant-ragweed-pollen extract was applied. Solid sodium rhodanate was mixed with a little of the pollen extract, and this system applied to the second scratch. The pollen extract alone was applied to the third scratch. The three reactions were compared from time to time. The first thing which was noticed was that the ephedrine and sodium rhodanate delayed markedly the onset of the reaction However, when the reaction finally took place the erythrema was more pronounced in these two cases than in the blank; this was manifested by the presence of a more intense red coloration. Larger wheals formed in the cases where ephedrine and sodium rhodanate were used than in the control, that is, the reaction produced by the pollen extract alone. Furthermore, the reaction produced by the pollen extract alone subsided quite a few minutes before the other two reactions.

Thus it has been shown that sodium rhodanate behaves in the same way that it does in anaphylaxis:[1] it both synergizes and antagonizes the reaction depending upon whether it is applied before, simultaneously with, or after the application of the reacting substance. These data tell us that ephedrine when previously applied to the site of the reaction synergizes the action of the pollen extract. Since ephedrine is a peptizing agent for protein sols, it should, like sodium rhodanate, antagonize the reaction of the pollen extract when applied beforehand. It has in fact been demonstrated[2] that the internal use of ephedrine can prevent skin reactions. This must mean that in the experiment reported above the ephedrine in the scratch was not absorbed entirely before the pollen extract was applied. The reaction then would appear to be like what one would expect from a mixture of ephedrine and the pollen extract.

The next experiment that was performed lends credence to this point of view. A mixture of the giant-ragweed-pollen extract and solid ephedrine sulphate was applied to a scratch on the arm made as before. The reaction to the mixture was slightly more intense than the reaction produced when ephedrine was applied first and the pollen extract afterwards. Also, the reaction took place rather more rapidly than before. So, it requires no stretch of the imagination to see that ephedrine acts substantially the same as sodium rhodanate in these skin reactions.

To complete the picture, ephedrine, applied locally, should stop the skin reaction produced by histamine. Since histamine dihydrochloride is in true solution the complicating factor of the slow absorption of ephedrine in the scratch and the consequent adsorption by the pollen colloids should not enter. Two scratches were made on the left arm, after properly cleaning it. The ephedrine sulphate solution was applied to one of the scratches. When this had dried, histamine solution was applied to both scratches. The histamine produced a strong reaction in the case of the untreated scratch; while the scratch that was pre-treated with ephedrine showed hardly any reaction at all. The great difference between these two reactions indicates that ephedrine is somewhat better than sodium rhodanate in its power to counteract the skin disturbance brought about by histamine. That this should be the case was not altogether unexpected in view of the fact that ephedrine sulphate is a better peptizing agent for albumin sols than is sodium rhodanate.

If we are not dealing with reversible agglomeration in these skin reactions, it is difficult to see why sodium rhodanate and ephedrine should behave exactly as the theory predicts in counteracting the skin reactions to histamine and to giant-ragweed-pollen extract. It should be borne in mind that these two compounds, sodium rhodanate and ephedrine, nullify the action of histamine when that poison is injected into the animal organism; yet sodium rhodanate tends to lower the blood pressure, and ephedrine to raise the blood pressure. This rules out blood pressure change as the cause of the antagonisms.

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[1] Bancroft and Rutzler: J. Phys. Chem., 35, 1185 (1931).

[2] Chen and Schmidt: "Ephedrine and Related Substances," 66 (1930).

Physiological, clinical, pharmacological, and colloid chemical methods all combine to support generously the conclusion that the action of histamine is to agglomerate reversibly the protein colloids of the sympathetic nervous system. Then, when the adsorptive capacity of the sympathetic nervous system for histamine is not very great, the central nervous system becomes affected, reversible agglomeration of certain of the protein colloids taking place; the result, then, is anesthesia. It does not seem to be necessary to secure any further proof that histamine acts physiologically by agglomerating protein colloids reversibly.

When circumstantial evidence is supported by direct evidence, conviction is generally inescapable.

The general conclusions of this paper are:

1. Histamine, a poison for the sympathetic nervous system, may act upon the central nervous system producing anesthesia. This is also due to reversible agglomeration of protein colloids.

2. Anesthetics antagonize histamine in herbivora, and synergize it in carnivora.

3. The isolated uterus does not respond well to histamine when that compound is added slowly to the preparation. This falls into line with the general principle that it requires much more of a compound to coagulate a sol when the compound is added slowly.

4. There is a strong resemblance between histamine shock and traumatic shock. Traumatic shock is almost surely accompanied by protein agglomeration.

5. Chronaxie experiments are cited which show that the vago-sympathetic nerve passes through a maximum chronaxie with the passage of time after the injection of histamine. It is shown that reversible agglomeration is responsible for this maximum chronaxie.

6. Histamine coagulates horse serum and *Spirosteum teres*, as it should.

7. Swelling experiments show that the superior cervical ganglia (sympathetic nervous tissue) of rabbits are peptized by sodium rhodanate and agglomerated by histamine dihydrochloride.

8. The agglomeration of the protein colloids of the superior cervical ganglia of rabbits by histamine has been shown to be reversible.

9. The agglomeration of the colloids of the superior cervical ganglia by histamine is not immediately apparent when there is fatty matter present.

10. Analogy to the swelling of the cerebral cortex of the rabbit by chloroform and sodium rhodanate suggests that in the above case the weight of the ganglion is increased by the solution of histamine in the fatty matter.

11. Chloroform, dissolving in the lipoids present in the cerebral cortex, causes an increase in weight which is definitely not due to the peptization of the proteins.

12. Sodium rhodanate causes true peptization of the protein colloids of the cerebral cortex.

13. These data suggest that it may be possible to differentiate animal tissues by swelling experiments with the proper peptizing and agglomerating agents.

14. Cocaine, an agglomerating agent, causes reversible agglomeration of the superior cervical ganglia as shown by the fact that it paralyzes them, and the irritability is restored by washing with sodium chloride solution.

15. *In vivo* both ephedrine and sodium rhodanate antagonize histamine, as one would expect from the fact that they are both good peptizing agents for proteins.

16. The skin reactions to histamine and giant-ragweed-pollen extract are stopped by pre-treatment with sodium rhodanate.

17. Ephedrine likewise counteracts the skin reaction to histamine. The peptizing agent is so slowly absorbed by the skin that it gets mixed with the pollen extract and synergizes it.

18. Ephedrine, taken internally, reduces the skin sensitivity tests.

19. When sodium rhodanate is mixed with giant-ragweed-pollen extract it synergizes the skin reaction. This is analogous to the action of sodium rhodanate in anaphylaxis; when it is administered before the antigen it protects the rabbit from shock. But, when it is mixed with the antigen the shock is very much greater.

20. Sodium rhodanate stops the itching in the skin reaction to histamine.

21. Reversible agglomeration of protein colloids is probably responsible for the skin reactions, since histamine, calcium chloride, lactic acid, and morphine, all agglomerating agents, cause skin reactions.

22. All of these proofs point clearly toward reversible agglomeration of protein sols as the mode of action of histamine in the animal organism.

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CHEMICAL ACTION IN THE GLOW DISCHARGE. VIII
THE EFFECT OF THE CATHODE MATERIAL

BY P. D. KUECK AND A. KEITH BREWER*

The various reactions discussed in the previous article of this series[1] have been studied in discharge tubes fitted with aluminum electrodes although iron was substituted in a few instances. Since the method employed in calculating M/N involves the cathode fall of potential, it seemed advisable to determine the effect of this potential on the reactivity.

According to the present theories of the glow discharge, electrons ejected from the cathode are accelerated by the potential gradient through the Crookes dark space, so that upon entering the negative glow they have energies corresponding to the cathode fall of pontential.

The normal cathode fall of potential is obtained in the discharge when the voltage drop is independent of the gas pressure and the current passing. It is dependent, however, on the nature of the gas and on the work function of the surface. The abnormal cathode fall of potential varies with both the gas pressure and the current; it is found only when the surface is completely covered with the glow. As an approximation the normal cathode fall of potential is about 100 times the work function of the surface expressed in volts.

The number of ions formed by an electron is very nearly a direct function of its velocity for the range of voltages found in the discharge. Thus, all other things being equal, the rate of ion production and hence the rate of chemical action in the discharge, should be proportional to the normal cathode fall of potential. The object of the present research was to determine if this relationship held between normal cathode fall and rate of reaction, as well as to gain some idea as to what other factors influenced the reactivity.

The effect of changing the cathode material on the rate of reaction involves several complications. The surface often tends to become oxidized or reduced in the discharge. This not only changes the normal cathode fall but it changes the gas mixture in which the reaction is being studied. In certain reactions studied the cathode surface became covered with some product of the reaction, the accumulation of which materially changed the work function. Catalytic reactions on the surface of the cathode often take place along with the regular discharge reaction due to the fact that the electrodes always become heated in the discharge. And finally some cathode materials sputter badly; it is for this reason that aluminum is almost universally used for cathodes.

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[1] J. Phys. Chem., 33, 883 (1929); 34, 153, 554, 1280, 2343 (1930); 35, 1281, 1293 (1931).

Apparatus and Method

The discharge tube was similar to that used in the previous experiments, and is illustrated in Fig. 1 of paper II.[1] The method of procedure was identical to that described in the articles of this series.

The electrode separation was of the order of 1 cm., so that the total potential drop across the tube was equal to the sum of the cathode and anode fall of potential. The total potential drop across the discharge tube was taken as the cathode fall of potential, without correcting for the anode fall of potential, since it is small compared to that of the cathode. The minimum potential drop across the discharge tube was used for the normal cathode fall of potential.

Results

The results obtained with the different electrode materials showed that invariably the rate of reaction and voltage shifted for each metal during the course of several runs; every cathode appeared to undergo a "working-in" process after which it became fairly constant. While two different cathodes of the same material never gave exactly the same voltage and rates, they checked each other as closely as is ever found in phenomena involving the work function. In the figures the values marked 1 are for the original machined surface, while 2 is the final almost steady state value.

The normal cathode fall of potential in most instances can be located to within 10 volts. Since the time-pressure curves from which the rates were calculated were all straight lines, the experimental error in the number of molecules formed per electron is never more than a few percent.

The values obtained in the synthesis of ammonia are illustrated in Fig. 1, where the normal cathode fall of potential for the different metals is plotted against the rate as expressed by the number of ammonia molecules synthesized per electron of current in the outer circuit.

The cathode materials listed are of a widely varying nature and are affected differently by the nitrogen and hydrogen. The calcium, aluminum and magnesium are normally covered with an oxide coating which is not reduced by hydrogen; the same is true for any oxide that may be on the tungsten or antimony. Again, there is the possibility of nitride formation on several of the metals. Magnesium, calcium, and aluminum definitely form nitrides; also a film of nitride may form on tungsten and possibly on iron and nickel.

The line drawn through the points represents a proportionality between normal cathode fall of potential and rate. While this line is for a weighted average of the points, the scattering is quite wide in some instances. For example, platinum, antimony, zinc, and tungsten lie outside the range of the normal scattering to be expected from surface fluctuations or experimental error.

The cathode potential-rate curve obtained for the synthesis of water is illustrated in Fig. 2.

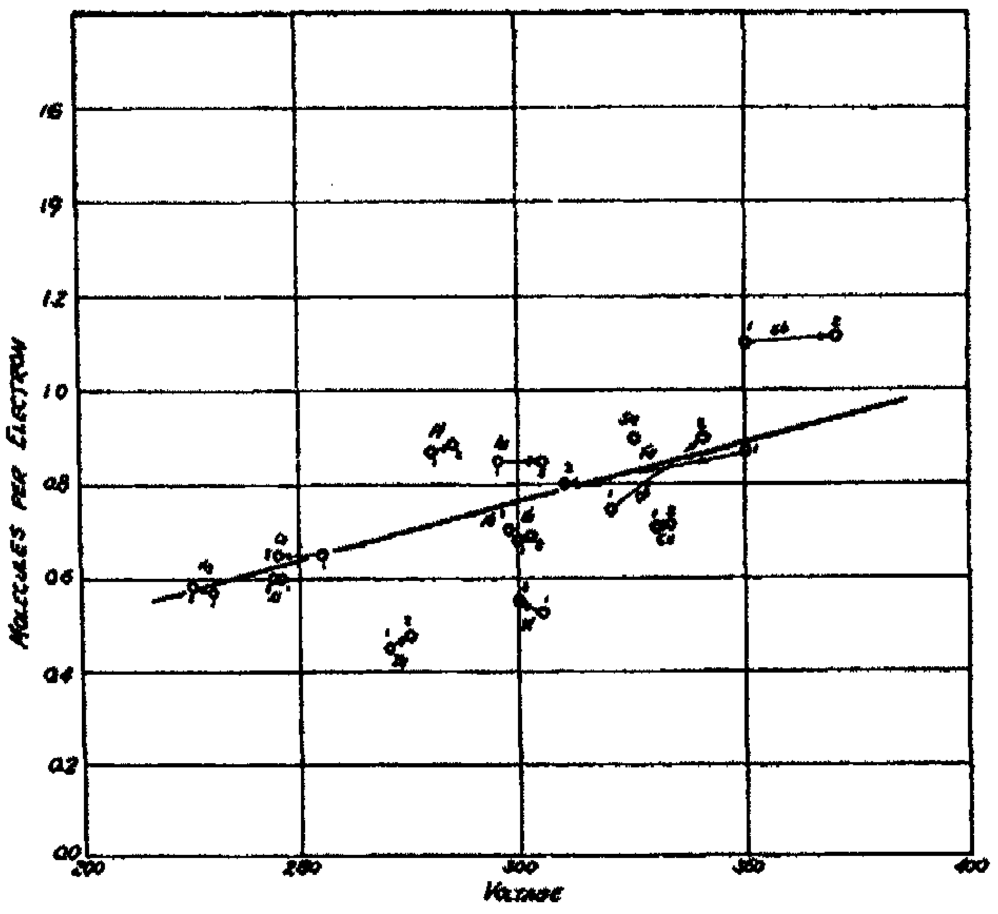

Fig. 1
Effect of the Electrode Material on the Synthesis of Ammonia

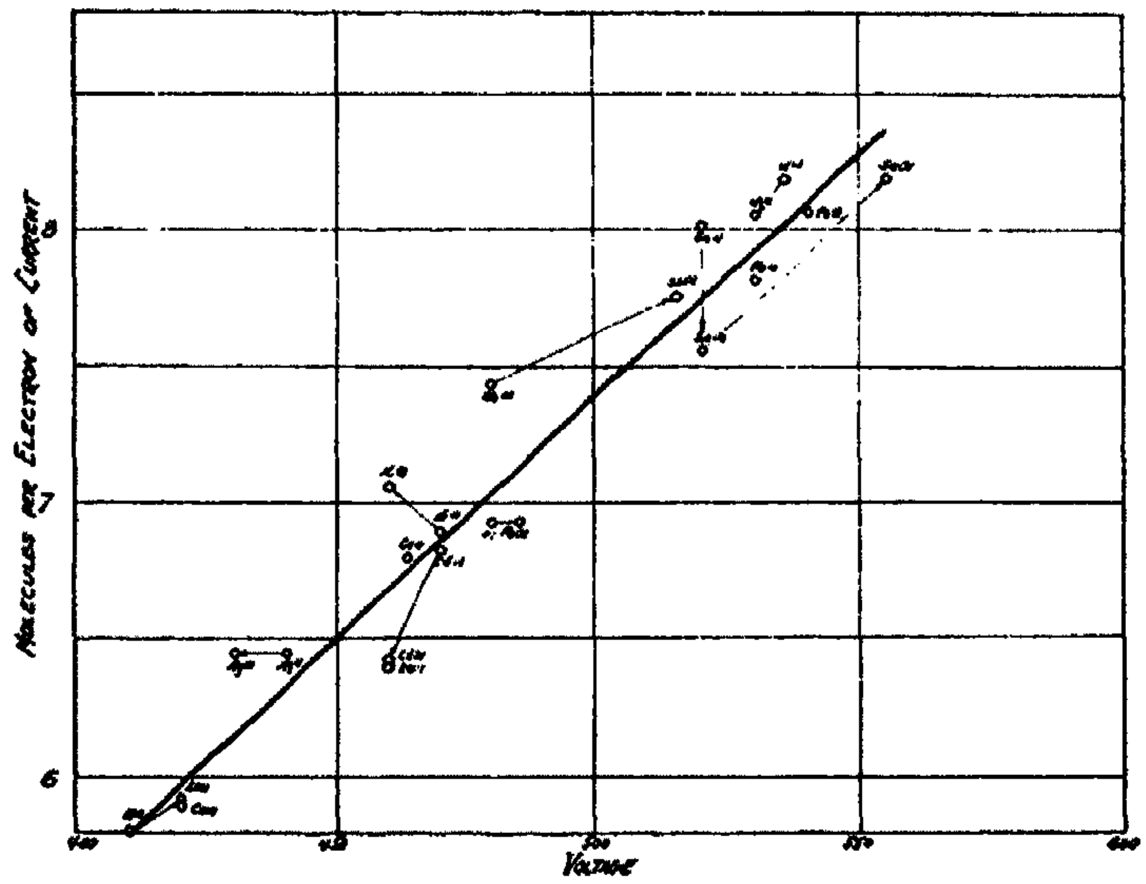

Fig. 2
Effect of the Electrode Material on the Synthesis of Water

The line drawn through the point again represents a proportionality between voltage and rate. It will be seen that the observed points follow the line somewhat more closely than in Fig. 1.

Unfortunately, curves could not be obtained for all the reactions studied in this series. In the oxidation of nitrogen, ozone was formed along with the nitrogen dioxide at the pressure and current density where the normal cathode fall was obtained. In the oxidation of methane both the voltage and rate for all electrode materials approached constant values during the working-in process. This was due to the deposition of a film of resinous material over the cathode which left the final surface the same in every instance.

The effect of the anode material on the reactivity was determined in a manner similar to that just described, except that the anode rather than the cathode, was changed. No detectable change in the rate of reaction was observed irrespective of the composition of the anode.

The Yield

The yields in terms of volts per electron of current for various cathode materials are shown in Tables I and II. The values given are for steady state conditions. The columns represent, respectively, the normal cathode fall of potential, the number of molecules synthesized per electron of current, volts per molecule per electron of current, and the deviation from the average.

TABLE I

The Synthesis of Ammonia

Metal	Volts	M/e	V/M/e	Deviation
Mg	225	.58	388	− 5.7%
Al	244	.60	407	− 1.0
Ca	250	.65	385	− 6.5
Zn	275	.48	572	+39.0
Pt	285	.87	328	−20.4
Ni*	297	.70	425	+ 3.2
Ni	302	.69	437	+ 6.1
W	300	.55	547	+32.7
Au	305	.85	359	−12.9
Fe	310	.80	388	− 5.7
Cu	332	.72	460	+11.6
Sn	330	.90	367	−10.9
Cd	340	.90	378	− 8.2
Sb	370	1.11	333	−19.1
		Average	412	

* Special impregnated nickel used in the manufacture of spark plugs.

TABLE II

The Synthesis of Water

Metal	Volts	M/e	V/M/e	Deviation
Al	420	5.9	71.3	+4.1%
Ca	420	5.85	71.8	+4.7
Mg	430	6.45	66.7	−2.6
Zn	460	6.4	71.4	+4.2
Cd	460	6.45	68.3	− .3
Ni	460	7.05	65.2	−4.7
Fe	480	6.93	69.1	+ .8
Sb	520	7.75	67.2	−1.9
W	530	8.10	65.5	−4.4
Pb	540	8.12	66.5	−4.4
Sn	560	8.20	68.3	− .3
		Average	68.55	

The values obtained for the synthesis of water are very constant, the power consumption per molecule synthesized never varying 5% from the average. In the case of ammonia, however, the deviations are much greater. Zinc and tungsten give abnormally poor yields, while platinum and antimony are especially efficient; the iron and aluminum cathodes used in the general study of the ammonia reaction give values which are very close to the average.

The deviations recorded in Table II are somewhat greater than the experimental error; nickel, for instance, is definitely more efficient than is zinc. In Table I the deviations are far beyond the experimental error, zinc being only a little more than half as efficient as platinum. It is interesting to note that in both reactions zinc shows the lowest efficiency of any of the metals.

Discussion of Results

It is evident from the results presented in Figs. 1 and 2 that the rate of reaction, in general, increases linearly with the normal cathode fall of potential. Also, the reactivities for various cathodes line up as well as can be expected, with what is known about their relative work functions, i.e., calcium, magnesium, and aluminum, are low, nickel and iron are intermediate, and antimony is high.

In spite of the fact that the results as a whole are very definite, individual variations are quite large. During the working-in process the rate and voltage for a majority of the metals varied in the expected manner; however, there are instances like nickel in Fig. 2 where a lowering of the cathode fall is accompanied by an increase in reactivity. Likewise two metals with the same voltage characteristics may give quite different rates as will be seen in Fig. 2 for zinc and nickel. The order of reactivity from reaction to reaction also shows variations; for instance, the position of tungsten in Figs. 1 and 2 is quite different. This is due to the change in the work function of the metals in the presence of the different gases.

The gradual changes in voltage occasioned by the change in pressure have no effect on the rate of reaction. This is in direct contrast to the change in voltage due to a change in the normal cathode fall of potential due to different cathodes, which is always accompanied by a change in rate. Thus, in the synthesis of ammonia with a nickel cathode, the fall of potential increased from 305 to 380 volts, in going from 9.0 to 4.0 mm. pressure, while the rate remained constant. A change in the normal cathode fall of potential by this amount would have resulted in a 28% increase in rate. This is also illustrated for the synthesis of water in Fig. 1 of paper V,[1] where it will be seen at low pressures that the voltage practically doubles while the rate of reaction remains constant. A doubling of the normal cathode fall of potential would have doubled the rate.

The proportionality between cathode fall and rate and the deviations from this proportionality are both to be expected on the basis of the usually accepted theory of the glow discharge. It is generally felt that the current in the discharge is distributed between electron and positive ion carriers. The electrons are liberated from the cathode by the impinging positive ions and by metastable molecules, while the positive ions and metastables are formed by these electrons after they have been accelerated through the cathode potential drop. Over the range of voltages found in the discharge the number of ions formed per electron is very nearly proportional to the energy of the electron. The emission of secondary electrons from metal surfaces, however, not only varies from metal to metal, but may vary over several fold for a given metal, depending on the condition of the surface. Therefore, the number of electrons emitted per positive ion or per meta-stable molecule depends on the nature and condition of the surface, hence the ratio of positive to negative carriers changes from surface to surface.

It seems probable that the cathode material may affect the rate of reaction in still another manner. The ions formed in the discharge are divided into two parts, those carrying current, and those neutralized on the walls and in the gas phase. The reactivity of the latter type is necessarily independent of the cathode. Most of the ions carrying current, however, make the necessary number of collisions with neutral molecules to form reactive clusters before striking the cathode. It seems possible, therefore, that the ion clusters neutralized on the cathode might dissociate either into the original gas molecules or into the reaction product depending on the stability of the reaction product and the catalytic activity of the cathode surface.

The deviations from the average observed in the synthesis of water are surprisingly small in view of the variation in the ratio of positive to negative carriers to be expected for different cathode materials. This is doubtless due to a comparatively constant physical condition of the surface in every case. Also, it seems probable that the positive ions carrying current may contribute to the reaction in this particular case, since water is relatively stable in the discharge and since only a few collisions are necessary for the reaction to go to completion around an H_2^+ ion in a $2H_2$-O_2 mixture.

The comparatively wide deviations given in Table I for ammonia are not surprising since the various surfaces respond differently to the action of nitrogen and hydrogen in the discharge. Thus the ratio of positive to negative carriers may vary over an appreciable range. At the same time it seems probable that the nature of the cathode surface might have a pronounced catalytic effect on the dissociation of the clusters around the positive ions which are contributing to the current, since ammonia, in contrast to water, is very easily decomposed in the discharge or on hot surfaces.

Summary

The rate of synthesis of water and of ammonia in the negative glow is, in general, directly proportional to the normal cathode falls of potential for the various metals used as cathodes. The change in the cathode potential drop due solely to a change in pressure has no effect on the rate of reaction.

Deviations from this proportionality exhibited by the various cathode materials in the synthesis of water are small, always being less than 5%. In the synthesis of ammonia, however, the deviations are materially larger.

The anode material has no effect on the rate of reaction.

The proportionality between the normal cathode fall and the rate is interpreted as being due to an increase in positive ion production with increased electron acceleration. It is suggested that the deviations from surface to surface are due to changes in the ratio of electron to positive ion current carriers, and to variations in the ability of the ions that carry current to contribute to the reaction.

THE ACTION OF HYDROGEN SULPHIDE ON CHROMATES
PART II. HYDROGEN CHROMATE

BY H. B. DUNNICLIFF AND G. S. KOTWANI

Dunnicliff and Soni[1] showed that the final products of the action of hydrogen sulphide on potassium chromate are sulphur, potassium thiosulphate, potassium polysulphide (probably the pentasulphide) and chromium hydroxide. Preliminary experiments on the action of hydrogen sulphide on an aqueous solution of chromic acid indicated that the green precipitate includes a complex compound of chromium containing a co-ordinated sulphate because an insoluble chromium compound containing both sulphate and hydroxyl or water groups was found in the final precipitate. The present paper gives a detailed account of the action of hydrogen sulphide on chromic acid.

A 5% solution of chromic acid of tested purity was used throughout.

When a slow current of hydrogen sulphide, purified by passing over iodine and then through successive scrubbers containing sodium sulphide and water, was passed for about 1½ hours, the bright orange colour changed quickly to a dull purple and then after about 25 minutes, to a distinct brown. A rise in temperature of about 7°C. was observed. After about 15-20 minutes more, a brown solid separated. This brown solid, called in the sequel the "intermediate product" settles down if the passage of hydrogen sulphide is stopped at this stage. If, however, the current of hydrogen sulphide is continued, the colour of the brown solid passes through various shades and ultimately gives a whitish-green precipitate after about 1½ hours from the start. The time varies with the rate of passage of the gas.

The precipitate contains chromium hydroxide, $Cr(OH)_3$, sulphate (SO_4) and sulphur. Sulphur dioxide is evolved when the whitish-green precipitate is treated with hydrochloric acid, indicating the possible presence of a salt of one or more of the thionic acids (thiosulphate, trithionate or dithionate). The final filtrate contains no acid or basic radicals (except the $[HS]'$ or $[S]''$ of hydrogen sulphide solution).

In the early stages of this investigation, an attempt was made to ascertain (a) the proportion of sulphate, sulphur and hydroxide in this precipitate and (b) if the available oxygen could be accounted for in the products of oxidation of the hydrogen sulphide as sulphur and sulphate, vide Table I.

When these experiments were carried out it was imagined that the amount of the compound which gave sulphur dioxide with hydrochloric acid was very small. This was found to be incorrect and these results had ultimately to be discarded. They are included in the paper as they suggested that a definite reaction was being investigated and some of the figures have been used in a

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[1] J. Phys. Chem., 33, 81 (1929).

TABLE I

The Action of Hydrogen Sulphide on a 5% solution of Chromic Acid

		Grams per 100 grams of chromic acid		
i.	Experiment No.	1	2	3
ii.	Sulphur	9.37	9.60	9.38
iii.	$\frac{\text{CrO}_3 \text{ (Mols)}}{\text{S (atoms)}}$	3.40 : 1	3.33 : 1	3.41 : 1
iv.	Sulphate	13.80	13.52	13.30
v.	Sulphur contained in the above sulphate	4.598	4.508	4.480
vi.	Total sulphur (ii + v)	13.96	14.11	13.86
vii.	$\frac{\text{CrO}_3 \text{ (Mols)}}{\text{S (atoms)}}$	9.2 : 4	9.1 : 4	9.2 : 4
viii.	Chromium present. (theory requires 52.25 grams)	52.25	52.20	52.15

later part of the paper and the inconsistencies observed suggested lines of attack which are described in the sequel.

In order to determine the mechanism of the reaction, it was decided to investigate the products at three stages.

Stage I—When hydrogen sulphide was added in just insufficient quantity to produce any precipitate.

Stage II—When hydrogen sulphide was added until the brown intermediate precipitate was formed.

Stage III—When hydrogen sulphide was bubbled through the solution until the precipitation was complete.

Stage I—Hydrogen sulphide was added in insufficient quantity to produce a precipitate.

Constant amounts (20 c.c.) of 5% chromic acid solution were treated with equal quantities of saturated hydrogen sulphide solution diluted to different degrees with water, 10 c.c., 20 c.c., 30 c.c., to study the effect of concentration. No precipitate, not even sulphur, was formed in any experiment but the colour of the solution changed from orange through dark purple to dark brown.

When chromium sulphate or chromium thiosulphate solution was added to chromic acid solution, a similar colour was produced. Thiosulphates are oxidised by chromic acid.

No colour change was observed when sodium dithionate or tetrathionate solution was added to chromic acid and sulphate ions were absent.

The dark brown solution (Stage I) obtained by the action of hydrogen sulphide on chromic acid contained sulphate, possibly colloidal chromium hydroxide, chromium present partly as a co-ordinated compound, colloidal sulphur and unused chromic acid.

The methods of analysis were as follows:—

Sulphate:—(a) by adding hydrochloric acid and precipitating with barium chloride, (b) by treating the solution with 0.3N caustic soda to separate hydroxide and then determining the sulphate in the filtrate.

The co-ordinated group is broken up by the alkali treatment, quantitatively precipitating the chromium as hydroxide and making all the sulphate available for precipitation as barium sulphate.

Experiment	$BaSO_4$ by (a)	$BaSO_4$ by (b)
I.	0.0804	0.1666
II.	0.2255	0.4475

These results were obtained with solutions which had stood for some time.

The 'sulphate' determined by (a) is half that determined by (b). This shows that half of the sulphate is present as sulphate ion and half as a co-ordinated group in a complex chromium compound.

Determinations of sulphate by methods (a) and (b) v.s., after varying intervals of time, showed that chromium sulphate formed by the action of hydrogen sulphide on chromic acid (Stage I) is produced originally in the solution as an ionised sulphate which gradually becomes co-ordinated on standing, the reaction being complete when the ionic and coordinated sulphate are equal in amount (vide Table II).

Table II

20 cc. of 5% chromic acid solution were used in the experiments.

Time of contact of solutions	Quantity of hydrogen sulphide used	$BaSO_4$ Method (a) "ionic" $[SO_4]$	$BaSO_4$ Method (b) Total $[SO_4]$
hours	c. c.	gram.	gram.
0.10	20	0.216	0.238
0.33	30	0.277	0.343
24.00	20	0.144	0.298

Unused chromic acid was estimated by titration against standard ferrous ammonium sulphate.

Chromium present as hydroxide or co-ordinated sulphate was determined by precipitation with ammonium hydroxide.

Table III gives the results obtained.

From these results it is observed that:—

(a) For the same amount of hydrogen sulphide, the amount of chromic acid decomposed diminishes with the concentrations. (Expts. 1 to 6, column iv).

(b) For the same amount of hydrogen sulphide, the amount of sulphate formed diminishes with increasing dilution of the chromic acid (column v a).

(c) The amount of sulphate formed increases with the amount of hydrogen sulphide used for a constant quantity of chromic acid.

TABLE III

Composition of the Solution just before Precipitation of the Intermediate Product

20 c.cs. of 5% chromic acid solution (i.e., 1 gram CrO_3) were used for each experiment

i No.	ii Quantity of water	iii Volume of H_2S used (saturated solution)	iv Free Chromic acid	v Chromic acid required to form sulphate		vi Total Chromic acid (Cols. iv + vb).	vii Cr_2O_3	viii Chromic acid calculated from Cr_2O_3 col. vii	ix Total CrO_3 (col. iv col. viii)
				*(a) 'SO_4' (actual)	**(b) 'CrO_3' (calculated)				
	c.cs.	c.cs.	grms.	grms.	grms.	grms.	grms.	grms.	grms.
1.	0	20	0.632	0.137	0.374	1.006			
2.	0	20	0.624	0.140	0.390	1.014			
3.	10	20	0.678	0.126	0.349	1.027			
4.	10	20	0.663	0.129	0.358	1.021			
5.	20	20	0.711	0.097	0.271	0.982			
6.	20	20	0.708	0.098	0.272	0.980			
7.	0	30	0.553	0.174	0.481	1.034			
8.	10	30	0.562	0.171	0.472	1.034			
9.	20	30	0.576	0.166	0.458	1.034	0.354	0.465	1.041
10.	20	30	0.573	0.156	0.435	1.008	0.361	0.470	1.043

* The solution was acidified with hydrochloric acid and precipitated at once. As the sulphate is all ionic at first vide p. 3216 this results in the complete precipitation of the $[SO_4]$ present.

** Using relationship shown in equation 2, p. 3226.

(d) The chromium present as chromic acid plus the chromium estimated as hydroxide (v.s.) accounts, within experimental error, for the amount of chromium originally present in the solution (Expts. 9 and 10).

(e) The amount of chromic acid decomposed is increased with increasing quantities of hydrogen sulphide (cf. Expts. 1-6 with Expts. 7-10).

(f) Within a reasonable approximation, experiments in which the same amount of chromic acid and hydrogen sulphide were used yielded similar results. (Expts. 1 and 2; 3 and 4; 5 and 6; 9 and 10). This suggests that the reaction takes a definite line of action and is not unduly sensitive to external conditions.

Stage II. Hydrogen sulphide is added as gas, or as a saturated solution until a brown precipitate is formed. The solution is also brown.

Examination of the solid:—It is insoluble in both cold and hot water, but is attacked by dilute hydrochloric acid leaving a residue of sulphur.

Sulphur dioxide has not been detected when the precipitate is treated with acid. This is important since the *final* precipitate always yields much sulphur dioxide with dilute hydrochloric acid. The solid was examined for $[SO_4]$, $[CrO_4]$, chromium, sulphur and hydroxide (indirect). When treated with 0.3N caustic potash, a green solid remains which contains neither sulphate nor chromate.

Sulphate in the brown precipitate was determined by method (a) and (b), p. 3216.

Table IV shows that the co-ordinated sulphate in the precipitate is equal to the amount of ionic sulphate present.

TABLE IV

Determination of the state of combination of the sulphate groups in the precipitate and filtrate of the intermediate stage (from 20 c.c. of 5% chromic acid)

i Method Precipitate	ii Barium sulphate grm.	iii Method Filtrate	iv Barium sulphate grm.
Dissolved in HCl and determined sulphate in the filtrate	0.1025	Treated with HCl and precipitated the sulphate with barium chloride	0.3350
Extracted with KOH and determined sulphate in the filtrate	0.2083	Treated with KOH and determined sulphate in the filtrate	0.3550

The figures show (column iv) that, in the filtrate from the intermediate precipitate, the sulphate is all in the ionic form.

This was confirmed (Table V) by examining two more filtrates immediately after filtration.

TABLE V

The barium sulphate found was:

Method	Expt. I grams	Expt. II grams
(a) Determination of $[SO_4]$ direct in the presence of hydrochloric acid	0.1050	0.1300
(b) Precipitation with ammonium hydroxide and determination of $[SO_4]$ in the filtrate	0.1043	0.1350

The following determinations were carried out at the intermediate stage:—

1. The brown precipitate was directly extracted with 0.3N potassium hydroxide. Chromate and sulphate (Table VI, cols. iv and vii) were determined in the solution.

2. The residual green solid was dissolved in dilute hydrochloric acid and the chromium precipitated as hydroxide (Table VI, col. v).

3. Chromate, chromium and sulphate were also determined in the filtrate (Table VII, cols. iv, v, and vii).

The above results show that the action takes place moderately slowly and that continued suspension of the solid in the solution leads to a diminution of the chromic acid.

If the solution obtained just before precipitate formation is allowed to stand, the brown precipitate slowly forms. The solution contains chromic acid, chromium sulphate (unco-ordinated), chromium hydroxide and sulphur in the colloidal state. Hence it appears that the addition of hydrogen sulphide accelerates an action by which the co-ordinated chromium sulphate containing hydroxy groups and water molecules is formed and also induces the coagulation of the excess of chromium hydroxide and sulphur.

Attempts to synthesise the brown Intermediate Precipitate:—

1. When the chromium sulphate is exposed to chromic acid solution, a brown precipitate is formed. This precipitate, though similar in appearance to that produced in the action of hydrogen sulphide on chromic acid, has not the same constitution *because its suspension in water, when treated with hydrogen sulphide gives a green residue which contains no thiosulphate.*

2. A further possibility—and one that appears at first sight more probable—is that the co-ordinated sulphato-chromium-aquo-sulphate (vide p. 3235) is precipitated and the chromic acid combines simultaneously with the colloidal chromium hydroxide and separates as an insoluble chromium chromate.

TABLE VI

Examination of the Precipitate of the Intermediate Stage

20 c.c. of chromic acid solution were used and 75 c.c. saturated hydrogen sulphide solution

i No.	ii Time of exposure to H_2S Hours	iii Weight of CrO_3 present grms.	iv CrO_3 grm.	v Chromium as ion estimated as Cr_2O_3 gram (Cr_2O_3)	vi CrO_3 corresponding to Cr_2O_3 in col. v gram	vii Weight of $[SO_4]$ present gram	viii Total chromic acid accounted for (sum of cols. iv and vi) gram
A.	Filtered immediately after addition	1.000	0.666	0.389	0.512	0.104	0.578
B.	24	1.000	0.088	0.630	0.829	0.218	0.918
C.	48	1.000	0.077	0.715	0.921	0.200	0.998
D.	After about	0.981	0.079	0.471	0.622	0.164	0.701*
E.	half an hour	0.981	0.077	0.472	0.620	0.159	0.697*

TABLE VII

Examination of the Filtrate of the Intermediate Stage

The letters of the experiments correspond with those in Table VI, the filtrates being taken from the precipitates there reported

A.	Filtered immediately after precipitation	1.000	0.035	0.295	0.388	0.142	0.423
B.	24	1.000	0.016	0.061	0.079	0.044	0.095
C.	48	1.000	0.008	0.000	0.000	0.046	0.008
D.	After about	0.981	0.037	0.185	0.243	0.098	0.280*
E.	half an hour	0.981	0.034	0.182	0.239	0.108	0.273*

* Experiments D and E were carried out taking particular care to have exactly similar conditions in all operations. They show that the reaction proceeds in a systematic manner.

Total of columns vii in Tables VI and VII	Experiment	A.	B.	C.	D.	E.	
	Grams	1.001	1.013	1.006	0.981	0.970	Theory = 1.00 gram

This possibility was investigated as follows:—

The chromium hydroxide precipitated from chromium sulphate was treated with 5% chromic acid solution. The brown substance which formed was filtered off. Analysis of the filtrate showed that a considerable quantity of the chromic acid had been taken up by the precipitate. The washed precipitate was extracted with potassium hydroxide and chromic acid and chromium hydroxide were determined.

TABLE VIII

Cr_2O_3 grm.	CrO_4 grm.	Molecular ratio $Cr_2O_3:CrO_4$	Approximate formula
0.1237	0.0369	2.56 : 1	$Cr_2O_{3.8}$
0.1182	0.0358	2.52 : 1	$Cr_2O_{3.8}$
0.1075	0.0448	1.83 : 1	$CrO_{2.0}$
0.1000	0.0448	1.71 : 1	$CrO_{2.1}$

The formula of the solid substance (col. iv), approximates to CrO_2[2] or it is possibly another so-called chromium chromate $2Cr_2O_3$, CrO_3 = Cr_5O_9, if it exists. A similar compound is said to be produced when a chromium salt is mixed with a chromate (loc. cit), but attempts to prepare it were unsuccessful. It is possible that this compound CrO_2 (or Cr_5O_9) is the cause of the brown colour of the intermediate precipitate, but reduction of the brown substance so produced by hydrogen sulphide results in the formation of a green substance which contains sulphate and sulphur but no thiosulphate or thionic acid giving sulphur dioxide on acid treatment.

The action of hydrogen sulphide on the synthetic brown substance was studied quantitatively. The final precipitate gave the following results:—

	Expt. I gram	Expt. II gram
Chromium oxide	0.2325	0.2323
Barium sulphate (direct)	0.0285	0.0275
Barium sulphate after alkali treatment	0.0275	0.0265
Thiosulphate	Absent	Absent

From these results it is clear that the brown compound formed by the action of hydrogen sulphide on chromic acid is not the same as the brown compound produced by the action of chromic acid on chromic sulphate though similar in appearance.

(3) The same process (vide Para 2) was tried in the presence of precipitated sulphur, but the resultant brown substance gave no thiosulphate on exhaustive treatment with hydrogen sulphide.

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[2] Mans: Pogg. Ann., 61, 219 (1844); Bensch: 55, 98 (1842).

(4) The final precipitate from the action of hydrogen sulphide on potassium chromate solution (i.e. $Cr(OH)_3$ and sulphur) when treated with chromic acid gives a brown product. When this brown substance is washed and then suspended in water and treated with hydrogen sulphide it yields a whitish green solid *which contains thiosulphate.*

This brown synthetic product appears therefore to be similar to the substance obtained by action of hydrogen sulphide on chromic acid solution. The essential difference between (3) and (4) is that in (4) the chromium hydroxide and sulphur were precipitated simultaneously; in (3) they were produced separately and mixed.

(5) If the intermediate brown substance formed in the treatment of potassium dichromate with hydrogen sulphide is separated and washed and its suspension in water treated with hydrogen sulphide, the resultant green substance contains sulphate, thiosulphate and hydroxide just as the final precipitate from hydrogen sulphide and chromic acid.

Hence it appears that the brown intermediate compound or mixture is formed by the action of chromic acid on a mixture of chromium hydroxide and sulphur coagulated from the colloidal state in the presence of each other.

It has been shown in Stage I (Table III) that the co-ordinated sulphate slowly forms in solution but that the concentration conditions are such that no precipitate separates. Since only ionic sulphate is found in the filtrate of the intermediate stage, it is clear that the co-ordinated sulphate is the portion which separates as a precipitate. It has not been found possible to determine whether

(a) this precipitate on formation is an insoluble "basic" sulphate in which part of the $[SO_4]$ is co-ordinated and which adsorbs or combines with the CrO_3 from the solution, or

(b) whether the removal of the CrO_3 from solution simultaneously with the development of the brown precipitate is due to the formation of a sulphatochromium compound in which part of the sulphate group is replaced by $[CrO_4]$ (compare Senderens: J. Chem. Soc., Abst. ii, 470, 1893).

The observations on the action of chromic acid on a mixture of chromium hydroxide and precipitated sulphur combined with the work of J. B. Senderens[3] on the action of potassium bichromate on sulphur in which thiosulphate is formed, suggest the manner in which part at any rate of the thiosulphate in the final green precipitate is produced. The results (Table IX) also show that the total of the sulphate present in the brown precipitate (Table VI, col. vii) and in the filtrate (Table VII, col. vii) is constant.

The average weight of sulphate found in the precipitate of the final stage from 1 gram of chromic acid was 0.252 gram (vide Table XVI, col. v, p. 26). The close approximation of this value to that in Table IX (0.257 gram) indicates that little or no more sulphate is formed after the brown precipitate separates.

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[3] Bull., (3), 7, 511; J. Chem. Soc. Abst., ii, 205 (1893).

TABLE IX

Intermediate Stage

(from 1 gram chromic acid)

Total sulphate present in precipitate and filtrate

Experiment	A	B	C	D	E
Table VI, col. vii.	0.104	0.218	0.200	0.164	0.159 gram
Table Vii, col. vii.	0.142	0.044	0.046	0.098	0.108 "
Total	0.246	0.262	0.246	0.264	0.267 "

Mean = 0.257 gram [SO_4]

The sulphate present in the precipitate is in two states of combination. The results detailed in the foot-note to Table VI and VII shows that all the chromic acid is accounted for.

The ratio [SO_4]:[CrO_4]:[Cr] (as equivalent) in the solid substance in experiments A to E (v.s.) is as follows:—

TABLE X

	A	B	C	D	E
[SO_4]	1.63	2.55	2.69	2.17	2.16
[CrO_4]	1	1	1	1	1
Cr	5.21	6.23	8.09	5.24	5.25

The lack of uniformity is not surprising as the reaction was stopped at different points representing intermediate stages of a continuous reaction.

In reactions carried out under exactly similar conditions (Table X, D and E) the ratio [SO_4]:[CrO_4]:Cr is the same within experimental error. This confirms one in the belief that the reaction proceeds slowly in an orderly way, and that its mechanism may be determinable.

The investigation is complicated by the fact that the reaction mixture contains several pairs of compounds which are able to react with each other, e.g. (i) chromic acid can react with chromium hydroxide (vide pp. ii et seq); (ii) chromium hydroxide can react with chromium sulphate and so on.

Action of Chromium Sulphate on Chromium Hydroxide:—

The chromium sulphate used contained only 84% of the [SO_4] required by theory for $Cr_2(SO_4)_3$. Of the sulphate present, 52% was directly precipitable by barium chloride in acid solution (HCl). All the sulphate was rendered precipitable by a preliminary alkali treatment as described above.

Chromium hydroxide was precipitated from 20 c.cs. of chromium sulphate solution, washed, and left in contact with 20 c.cs. of the same chromium sulphate solution for 24 hours. The mixture was filtered and the substance on the filter paper was washed sulphate free.

The *filtrate* showed loss of sulphate.

$BaSO_4$ precipitated by $BaCl_2$ = 0.0884 gram

$[SO_4]$ precipitated in solution after chromium was precipitated by NH_4OH and shown as $BaSO_4$ = 0.4680 "

The solid phase contained

(1). $[SO_4]$ as $BaSO_4$ obtained by extraction with hydrochloric acid and precipitation with $BaCl_2$ = 0.0353 "

(2). $[SO_4]$ as $BaSO_4$ by extraction with NH_4OH and estimation of $[SO_4]$ in the filtrate = 0.0709 "

This shows that the sulphate in the solid phase is in two states of combination and is equally divided between them.

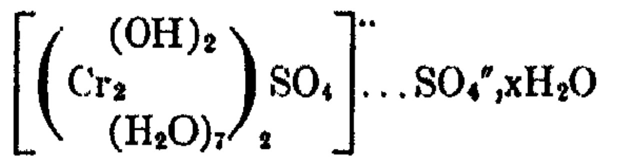
The analyses of several solid substances produced in this way are given in Table XI.

TABLE XI

Complex Chromium Sulphate produced by the Action of Chromium Sulphate on Chromium Hydroxide

Cr_2O_3 gram	$[SO_4]$ (Total) gram	Cr_2O_3 (Mols)	$[SO_4]$ (Mols)
0.1512	0.0445	2.15 :	1
0.1490	0.0437	2.16 :	1
0.1395	0.0438	2.01 :	1
0.0990	0.0292	2.14 :	1

To eliminate as far as possible, the difficulties of realising quantitative action between a solid and a substance in solution in order to produce a solid compound, small quantities had to be used. The results indicate that the formula of the solid may be expressed as:



$$\left[\left(\mathrm{Cr_2}\begin{matrix}(\mathrm{OH})_2\\ (\mathrm{H_2O})_7\end{matrix}\right)_2 \mathrm{SO_4}\right]^{\cdot\cdot}\ldots \mathrm{SO_4}'',x\mathrm{H_2O}$$

NOTE:—In the preliminary experiments (rejected) the final precipitate dried out of contact with air at laboratory temperature contained water and chromium oxide in the ratio 6.6 : 1 (mean of three determinations).

The brown precipitate appears either (a) to contain some such compound or a derivative in which $[CrO_4]$ replaces some of the hydroxy groups or (b) to be a mixture of the compound with Cr_5O_9 or (CrO_2) formed by the action of chromations or dichromations with excess of chromium hydroxide.

It will be observed that in each molecule of the above compound, four atoms of chromium and two sulphate radicles are present. The amount of chromium sesquioxide corresponding with the amount of $[SO_4]$ shown in column vii of Table VI has been calculated on this basis by multiplying the figures by 304/192. These are shown in the upper line of Table XII. The values for Cr_2O_3 in column v of Table VI are shown above. Actual values are multiplied by 10^3 in each case.

TABLE XII

Experiment No.	A	B	C	D	E
Cr_2O_3 calculated from Table VI, col. vii	165	345	316	260	252
Cr_2O_3 found by direct estimation Table VI, col v)	389	630	715	471	472

From this it appears that the brown precipitate may be composed of sulphur and approximately equal quantities of the complex sulphate and chromium hydroxide and that the latter has adsorbed or combined with a certain amount of chromic acid.

The experimental evidence shows that since sulphate appears in the early stages to the complete exclusion of thiosulphate, which, however, is certainly formed in the final stage, two different reactions take place in succession; one during the early stages of reduction in which thiosulphate is not formed, or if formed is decomposed, and a second reaction in the later stages of the reduction in which thiosulphate is formed. The distinction between the two conditions is that the first reaction takes place in a slightly acid medium and the last in a wet, solid neutral phase. This is quite sufficient to account for the relative stability of the thiosulphate in the solid phase.

It must be conjectured, therefore, that when chromic acid as part of a solid substance is reduced in the presence of sulphur and chromium hydroxide, a basic or co-ordinated thiosulphate is formed which is insoluble. The limiting condition occurs when no more chromic acid exists in the liquid phase and when all the chromic acid that is left has been taken up by the precipitate. Thiosulphate does not form until the hydrogen ion concentration is negligible.

Stage III. Hydrogen Sulphide is passed into the solution until precipitation is complete.

The filtrate contains no sulphate or thiosulphate nor any sulphur acid except hydrogen sulphide.

The green solid is insoluble in water and contains chromium sulphate, thiosulphate, hydroxide and sulphur. This when treated with hot dilute hydrochloric acid gave sulphur dioxide and a green solution containing free sulphur which was collected in a Gooch crucible, dried and weighed. Chromium and sulphate were determined in the filtrate (vide Table XIII, p. 3226). The values given are calculated as follows. Example No. 1 is used as illustration.

Assuming the reaction

$2CrO_3 + 3H_2S = Cr_2O_3 + 3H_2O + 3S$ .... (1)

48 grams of sulphur ≡ 100 grams CrO_3

or 9.12 grams of sulphur ≡ 19.00 grams CrO_3

Also, on the assumption that hydrogen sulphide is oxidised to sulphate by chromic acid,

$8CrO_3 + 3H_2S = Cr_2(SO_4)_3 + 3H_2O + 3Cr_2O_3$ .... (2)

100 grams CrO_3 ≡ 36 grams $[SO_4]$

∴ 9.55 grams SO_4 = 26.52 grams CrO_3

The total chromic acid thus accounted for = 19.00 + 26.52 = 45.52 grams.

100 grams of chromic acid yield 76.01 grams. Cr_2O_3

∴ 76.228 grams Cr_2O_3 ≡ 1.300 grams CrO_3.

TABLE XIII

Composition of final precipitate produced when a 5% solution (50 c.cs) of Chromic Acid is treated (slowly) with hydrogen sulphide gas at laboratory temperature

Results are shown for 100 grams of chromic acid

i	iia	iib	iiia	iiib
	Sulphur		Sulphate	
No.	Actual weight	In terms of chromic acid (vide equation (1))	(SO_4) actual	In terms of CrO_3 (vide equation (2))
	grams	grams	grams	grams
1.	9.12	19.00	9.55	26.52
2.	9.33	19.25	9.50	26.37
3.	8.87	18.50	9.52	26.43
4.	8.80	18.55	9.63	26.74
5.	8.80	18.55	9.42	26.30

i	iv	va	vb
		Chromium Sesquioxide (Cr_2O_3)	
No.	Chromic acid accounted for as S and (SO_4) = (col. iib + col. iiib.).	By experiment	Calculated as CrO_3
	grams.	grams.	grams.
1.	45.52	76.228	100.3
2.	45.62	76.304	100.4
3.	44.93	76.380	100.5
4.	45.43	76.226	100.3
5.	44.83	76.132	100.2

Theory = 100.0

Column vb, Table XIII, shows that all of the chromium is precipitated but that sulphur and sulphate formed account for only 45% of the chromic acid available (ibid, col. iv).

Carbon bisulphide failed to remove any sulphur from the dried precipitate. In the preliminary stages it was incorrectly assumed that all the sulphur (Table XIII, col. iia) was possibly obtainable from thiosulphate decomposed by treatment with hot dilute hydrochloric acid. Calculating the sulphur as thiosulphate and equivalent chromic acid as described below, the values in Table XIV were obtained.

The following reactions involving the formation and decomposition of thiosulphate are assumed:

$$8CrO_3 = 4Cr_2O_3 + 12\ O \quad . \quad . \quad (3)$$
$$6H_2S + 12O = 3H_2S_2O_3 + 3H_2O \quad . \quad . \quad (4)$$
$$3H_2S_2O_3\ (HCl) = 3H_2O + 3SO_2 + 3S \quad (5),$$

then, 3 × 32 grams of free sulphur would be obtained by the use of 800 grams CrO_3 or 12 grams of sulphur ≡ 100 grams CrO_3

∴ 9.12 grams of sulphur (Table XIV, col iia) ≡ 75.93 grams CrO_3

If the precipitate contains free sulphur as well as sulphate and thiosulphate, the second method cannot be correct. To obtain evidence on this, the precipitate was extracted with cold 0.3N caustic potash, which, under the conditions of the experiment, does not give thiosulphate with free sulphur. This eliminates sulphate and thiosulphate. The residue contained free sulphur. Hence the second method of calculation is untenable. The green solid from 50 cc. of 5% chromic acid was treated with 0.3N potassium hydroxide and the slightly yellow filtrate and washings made up to 250 cc. An aliquot portion of this was treated with dilute hydrochloric acid to decompose thiosulphate and boiled to coagulate the sulphur which separates in the reaction.

TABLE XIV

Calculation of available chromic acid in terms of sulphuric and thiosulphuric acids.

i	iia	iib	iiia	iiib
	Sulphur		Sulphate	
No.	Actual weight obtained, assumed from thiosulphate.	In terms of chromic acid (vide equation (1))	Sulphate actual	Sulphate in terms of chromic acid (vide equation (2))
	grams.	grams.	grams.	grams.
1.	9.12	75.93	9.55	26.52
2.	9.33	76.70	9.50	26.37
3.	8.87	73.91	9.52	26.43
4.	8.97	74.75	9.63	26.74
5.	8.80	73.30	9.42	26.30

i	iv	
No.	Chromic acid accounted for (col. iib and col. iiib) as sulphur from thiosulphate) and sulphate	
	grams.	
1.	102.52	(Theory = 100.0 gms.).
2.	103.07	
3.	100.34	
4.	101.49	
5.	99.60	

The clear filtrate was used for sulphate determination. The value of sulphate obtained by this method in two experiments carried out side by side under identical conditions was nearly three times the value obtained by the direct hydrochloric acid method (not twice, as so frequently found in other experiments).

Sulphate by KOH method	24.72	24.75	for 100 grams
Sulphate by HCl method	9.50	9.55	of CrO_3

It was shown that this increase in value of the sulphate determined by the hydroxide method was not due to the decomposition of thiosulphate (or dithionate) by the potassium hydroxide.

Three other possibilities exist:

(1) Partial decomposition (hydrolysis) of thiosulphate* with the formation of sulphate.

(2) Hydrolysis of trithionate if it is formed as an intermediate stage in the reaction.

TABLE XV

Sulphate	As grams of $BaSO_3$	
	i	ii
(a) Total present in Chromium Sulphate used	0.8280	0.8280
(b) Remaining (coordinated) in solution after 10 days	0.2325	0.2200
(c) Obtainable from chromium sulphate (a-b)	0.5955	0.6080
(d) $BaSO_4$ actually obtained	0.8041	0.8193
(e) $BaSO_4$ derived from decomposition of barium thiosulphate (d-c)	0.2086	0.2113

Hence after 10 days, about one third of the chromium thiosulphate had hydrolysed giving sulphate $[S_2O_3]'' + H_2O = H_2S + [SO_4]''$

(3) Intramolecular change.

The first was examined experimentally, and it was found that while chromium thiosulphate is hydrolysed in solution, there is no evidence of its hydrolysis under the conditions described.

(2) and (3) will be discussed in the theoretical portion of the paper (p. 3235).

Direct Estimation of Thiosulphate, Sulphate and Sulphur present in the Final Precipitate:—

The precipitate from 50 c.c. of 5% chromic acid was extracted with 75 c.c. of 0.3N potassium hydroxide at a a temperature not exceeding 25°C. and the filtrate was made up to 250 c.c. by washing, etc.

In an aliquot portion of this solution, thiosulphate was determined by two different methods.

---

* Chromium thiosulphate was made by the double decomposition of the sulphate with barium thiosulphate (Plimpton: J. Chem. Soc., 67, 314 (1895)). 48% of the sulphate in the original chromium sulphate was co-ordinated, but the removal of the sulphations from the solution as barium sulphate caused more co-ordinated sulphate to become progressively ionised.

Method No 1. The solution was treated with a suspension of zinc carbonate and glycerine to remove traces of sulphide, and filtered. After acidifying the filtrate with acetic acid, it was titrated against N/98.4 iodine.[4] Sulphide was shown to be absent by the authors' (K. and W.) method.

In one experiment, the $[S_2O_3]$ present from 50 c.c. of 5% chromic acid solution was found to be 0.1532 gram. CrO_3 required to form 0.1532 gram of $[S_2O_3]$ (equations (3) and (4) $= 0.1532 \times 800/3 \times 112 = 0.3625$ gram (from 50 c.c.).

$\therefore$ out of 100 grams CrO_3, $0.3625 \times 40 = 14.50$ grams are used in the production of thiosulphate.

Sulphate:—

Another portion was acidified with hydrochloric acid, heated to boiling to coagulate sulphur, and filtered. The filtrate was used for sulphate determination.

Sulphur was determined by the direct decomposition of the precipitate from a known volume of solution. The sulphur was weighed in a Gooch crucible. It contained both free sulphur and sulphur set free from thiosulphate.

The results of these analyses are embodied in Table XVI. The methods of calculation are detailed on pp. 3226 and 3227, and supplemented with those given below.

Combining equations (3), (4) and (5)

$$8CrO_3 + 6H_2S = 4Cr_2O_3 + \underset{\substack{\downarrow \\ HCl \\ \downarrow \\ (3H_2O\ +\ 3SO_2)\ +\ 3S \ldots\ldots (5)}}{3H_2S_2O_3} + 3H_2O \ldots\ldots (6)$$

Hence, 100 grams CrO_3 yield 12 grams of sulphur.

Table XVI, col. v shows that 5.96 gms. of $[S_2O_3]$ are formed. This corresponds with 14.17 grams of chromic acid (equation (6)).

The sulphur yielded by this thiosulphate on acid treatment is 1.70 grams (equation (5)).

Hence the weight of free sulphur in the precipitate from 100 grams CrO_3 is $(9.00 - 1.70) = 7.30$ grams, the chromic acid equivalent of which is 15.21 grams (equation (1)).

Actual sulphate was 25.22 grams and the chromic acid equivalent to this

$= 70.6$ grams (equation (2)).

100 grams of CrO_3 is therefore accounted for as follows:—

	grams
Expended in Thiosulphate formation =	14.17
Expended in Sulphur formation =	15.21
Expended in Sulphate formation =	70.06
Total....................	99.44

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[4] A. Kurtenacher and R. Wollak: Z. anorg. Chem., **161**, 201 (1927).

Table XVI

Final Green Precipitate

Determination of Sulphate, Thiosulphate and Sulphur

Method No. 1

Values are shown as grams per 100 grams of chromic acid

	(i)		(ii)	(iii)	(iv)	(v)	
						Mean Exptl. values	Calculated values
1.	Experiment		1 grams	2 grams	3 grams		
2.	Thiosulphate Method No. 1	(a) actual weight	5.88	6.09	5.91	5.96	
		(b) chromic acid (equation (6))	14.02	14.50	14.09		14.17
3.	Sulphur deposited from thiosulphate calc. from 2(a)		1.683	1.740	1.691		1.70
4.	Total sulphur (average value)		9.00	9.00	9.00	9.00	
5.	Sulphur in the free state in the green precipitate	(a) actual weight (No. 4—No. 3)	7.317	7.260	7.309		7.30
		(b) in terms of chromic acid (equation(1))	15.24	15.12	15.23		15.21
6.	Sulphate SO_4	(a) actual weight	25.13	25.25	25.28	25.22	
		(b) in terms of chromic acid (equation(2))	69.80	70.09	70.32		70.06
7.	Total chromic acid accounted for (Theory = 100 grams)		99.06	99.71	99.61		99.44
8.	Chromium oxide actually determined (Theory = 76.0 grams)		76.24	76.44	76.36	76.35	

TABLE XVII

Final Green Precipitate

Method No. 2

Decomposition of the final precipitate produced from a 5% solution of Chromic Acid (50 c.c.) when treated with hydrochloric acid and the SO_2 evolved is absorbed by bromine and forms H_2SO_4

Results in the table are shown as grams per 100 grams of chromic acid

i		ii	iii	iv	v	
(1) Thiosulphate Method No. 2	(a) actual weight of $BaSO_4$	9.65	9.06	9.88	9.53	—
	(b) in terms of CrO_3 (equation 6)	11.04	10.37	11.30	—	10.90
(2). Sulphur separated from thiosulphate		1.325	1.244	1.356	—	1.308
(3). Total sulphur (actual weight)		9.000	8.964	8.684	8.883	—
(4). Free sulphur	(a) i.e., (3)-(4)	7.675	7.720	7.328	—	7.675
	(b) in terms of CrO_3 (equation 1)	15.99	16.10	15.41	—	15.77
(5). Sulphate	(a) direct, actual weight SO_4	24.43	25.12	25.03	24.86	—
	(b) in terms of CrO_3 (equation)	67.90	69.80	69.54	—	69.10
(6). Total chromic acid accounted for (Theory 100 grams) = (1b + 4b + 5b)		94.93	96.27	96.25	—	95.77

The conclusion that no sulphate is formed by the decomposition of thiosulphate is also confirmed by the fact that the total (average) sulphate in the final precipitate (25.2 grams) from 100 grams of chromic acid is equal to the total sulphate formed in the intermediate stage (25.7 grams) (vide Table IX).

Method No. 2. The thiosulphate in the green precipitate was also determined by treating the precipitate with hydrochloric acid and blowing off the sulphur dioxide with a current of carbon dioxide gas into bromine water. This oxidises the sulphur dioxide to sulphuric acid. Bromine was removed by boiling and the sulphate determined. The values for thiosulphate by the method are a little lower than those obtained by the first method. (Control against A.R. sodium thiosulphate gave 98.5% of theory).

Sulphate and sulphur were also estimated in the bluish-green solution, and the sulphate determined direct is about 2/3 of the total sulphate. For results, see Table XVII.

In the determination of thiosulphate in the final green precipitate by the decomposition of the product by hydrochloric acid, the calculations, referred to the mean values of experiments 1, 2 and 3 are based on equations (5) and (6) v.s.

(1) Since 3 × 233 grams $BaSO_4 \equiv$ 800 grams CrO_3 $\therefore$ 9.53 grams $BaSO_4$ (col. v, a) $\equiv$ 10.90 grams CrO_3 (col. v, b).

(2) 3 × 32 grams of sulphur $\equiv$ 800 grams CrO_3 $\therefore$ 10.90 grams CrO_3 = 1.31 grams of sulphur; Hence the sulphur existing in the precipitate as such = 8.882 − 1.308 = 7.574 grams.

(3) The chromic acid spent in oxidising hydrogen sulphide to sulphur −

$$\frac{7.574 \times 200}{96} = 15.78 \text{ grams.}$$

Mean value for sulphate found from 100 grams CrO_3 = 24.86 grams (col. v, a).

This corresponds to 69.10 grams CrO_3 (col. vb).

Hence the chromic acid is accounted for as follows:

Expended in sulphate formation	=	69.10 grams.
Expended in thiosulphate formation	=	10.90 grams.
Expended in sulphur formation	=	15.78 grams.
Total	=	95.78 grams.

The sulphate and sulphur values compare favourably with the results summarised in col. v of Table XVI but the thiosulphate values are low. This is not unexpected in view of the evidence[5] showing that the decomposition of thiosulphate by acids is accompanied by side reactions.

The ability to account for all the chromic acid in terms of sulphur, sulphate and thiosulphate suggests that the correct ultimate products have been found.

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[5] Bassett and Durrant: J. Chem. Soc., 1927, 1416-17.

To check this, all the sulphur products were converted into sulphate by boiling the final precipitate with bromine water under reflux until no solid was left and the sulphate determined in the solution.

The quantity of [SO_4] theoretically producible from 100 grams CrO_3 assuming half of the oxygen to be "available" = 36.0 grams [SO_4].

Experimental values found = (i) 36.11, (ii) 35.98, (iii) 36.47 grams (SO_4].

The concurrence confirms the conclusions arrived at.

It is interesting to note that the analyses in Table XVI work out to the following equation involving the loss of only 5% (i.e. 3 atoms) of available oxygen in the chromic acid used.

$$
\begin{aligned}
2(5H_2CrO_4 + 3H_2S) = {} & Cr_2(S_2O_3)_3 + 5Cr_2(SO_4)_3 \\
& 48Cr(OH)_3 + 15\,S + 24H_2O
\end{aligned}
$$

(The co-ordination formulae have been omitted for simplicity).

Summary and Discussion

The course of the action of hydrogen sulphide on 5% chromic acid solution has been studied in three stages.

Stage I. Up to the point at which a brown (intermediate) precipitate just commences to form.

The solution contains colloidal chromium hydroxide, colloidal sulphur, chromium in the ionic state, undecomposed chromic acid and sulphate. The sulphate is at first all in the ionic form and precipitable by barium chloride. After standing for some time, half of the sulphate becomes "co-ordinated." The whole of the reduced chromic acid is accounted for as sulphate and chromium is present as salt of hydroxide.

Stage II. A brown precipitate called the "Intermediate" precipitate is formed which contains

(1) a co-ordinated sulphato-chromium sulphate.

(2) In approximately equivalent quantity, chromium hydroxide which is partly converted into

(3) A compound having the formula Cr_5O_9 or CrO_2 by the action of unused chromic acid.

(4) Free sulphur.

The filtrate contains sulphate all of which is ionic, chromium hydroxide, unreduced chromic acid and colloidal sulphur.

Stage III. The final green precipitate contains

(1) one or more co-ordinated chromium sulphates.

(2) chromium thiosulphate, probably co-ordinated.

(3) free sulphur.

(4) chromium hydroxide.

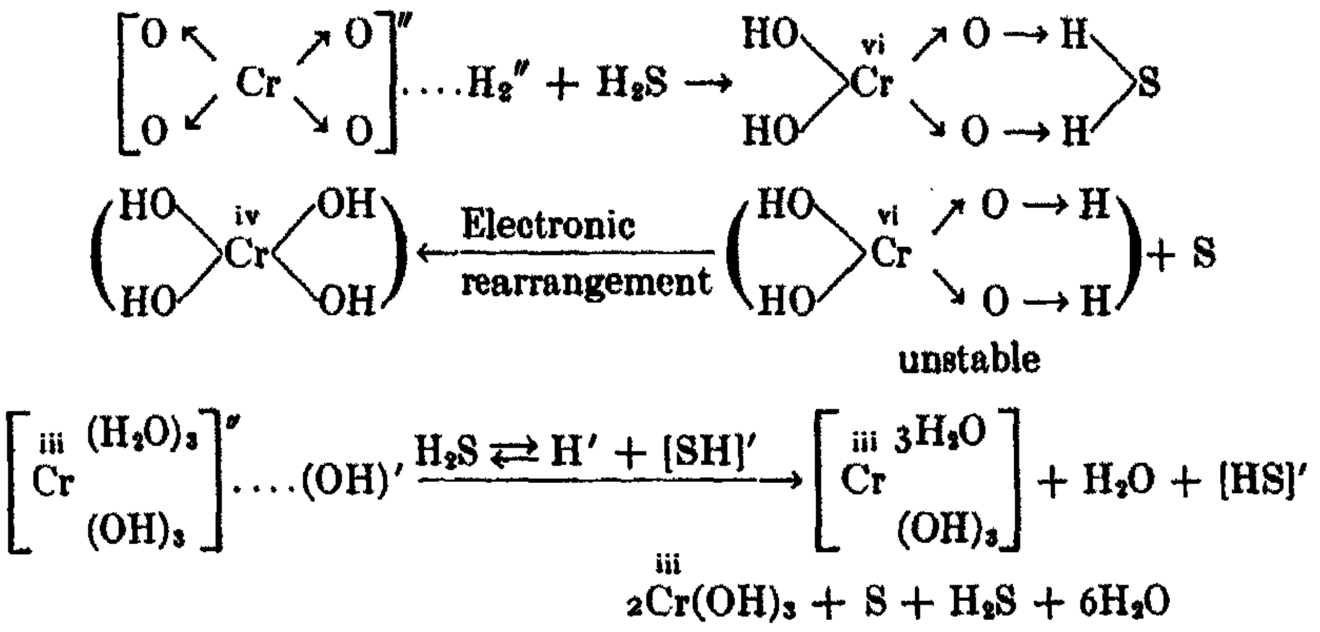
The sulphate in the "co-ordinated" state in the final precipitate is greater than that in the intermediate precipitate and, with respect to the "ionic" sulphate, its amount approaches the ratio 2:1.

Since the total sulphate in the final stage equals the sum of the sulphate in the precipitate and solution in the intermediate stage, no sulphate is formed by the action of hydrogen sulphide on the brown precipitate nor by the hydrolysis of the chromium thiosulphate complex. Hence the increase in the proportion of co-ordinated sulphate to ionic sulphate is probably due to intramolecular rearrangement.

The whole of the oxidising power of the chromic acid has been accounted for in Stages II and III of the reaction in terms of the products given above.

Interpretation of the Results

Assuming that chromic acid contains some H_2CrO_4, the production of sulphur and chromium hydroxide is accounted for as proposed by Dunnicliff and Soni (loc. cit).



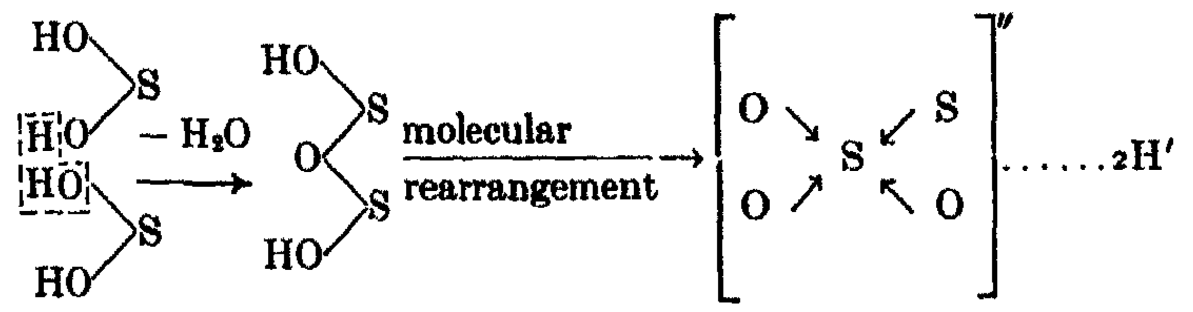
Theoretically, the sulphate can be accounted for either direct via sulphoxylic acid (H_2SO_2), the first hydrolysis product of sulphur, or via thiosulphate or trithionate.

Thus:[6]

$$2H_2O + 2S = H_2S + H_2SO_2$$

The sulphoxylic acid would be readily oxidised to sulphate by the chromic acid.

The possibility that sulphate may be formed via thiosulphate depends on the assumption that, two molecules of sulphoxylic acid might lose one molecule of water giving thiosulphuric acid.



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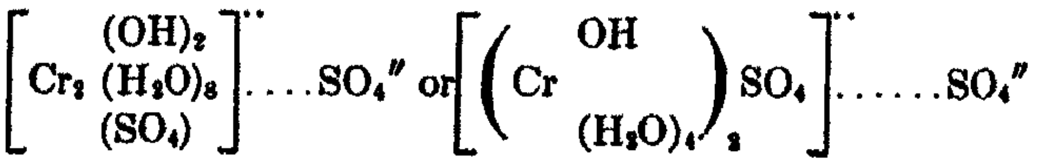
[6] Bassett and Durrant: J. Chem. Soc., 1927, 1401.

though Bassett and Durrant[6] could adduce no evidence of this decomposition and it would not be favoured by an acid medium. If formed, this thiosulphuric acid would be oxidised to sulphuric acid by the chromic acid present.

The formation of trithionate would be difficult to account for and its transformation to thiosulphate requires a neutral medium.

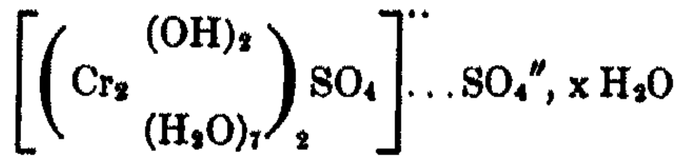
Hence the authors favour the direct oxidation of sulphoxylic as the method of formation of sulphate.

The sulphate first formed is all precipitable and the interaction between the chromium hydroxide and formation of the co-ordination compound is comparatively slow and succeeded by coagulation. The fact that the "co-ordinated" sulphate and ionic sulphate are equal in amount in the "intermediate" precipitate may be indicated by the formula.



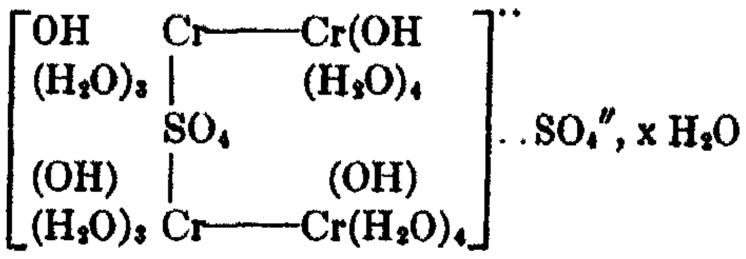
$$\left[\mathrm{Cr_2}\begin{array}{c}(\mathrm{OH})_2\\(\mathrm{H_2O})_8\\(\mathrm{SO_4})\end{array}\right]^{\cdot\cdot}\ldots\mathrm{SO_4}'' \text{ or } \left[\left(\mathrm{Cr}\begin{array}{c}\mathrm{OH}\\ \\(\mathrm{H_2O})_4\end{array}\right)_2\mathrm{SO_4}\right]^{\cdot\cdot}\ldots\ldots\mathrm{SO_4}''$$

i.e. sulphato-dihydroxo-octaquo-dichromium sulphate. Synthetic experiments indicate that the formula is probably more complex and has the composition



$$\left[\left(\mathrm{Cr_2}\begin{array}{c}(\mathrm{OH})_2\\ \\(\mathrm{H_2O})_7\end{array}\right)_2\mathrm{SO_4}\right]^{\cdot\cdot}\ldots\mathrm{SO_4}'', \mathrm{x\,H_2O}$$

or



$$\left[\begin{array}{lll}\mathrm{OH} & \mathrm{Cr} & \!\!\!-\!\!\!-\!\!\!-\mathrm{Cr(OH}\\(\mathrm{H_2O})_3 & | & (\mathrm{H_2O})_4\\ & \mathrm{SO_4} & \\(\mathrm{OH}) & | & (\mathrm{OH})\\(\mathrm{H_2O})_3 & \mathrm{Cr} & \!\!\!-\!\!\!-\!\!\!-\mathrm{Cr(H_2O)_4}\end{array}\right]^{\cdot\cdot}\ldots\mathrm{SO_4}'', \mathrm{x\,H_2O}$$

This precipitate undergoes further changes which result in the co-ordination of more $[SO_4]$ at the expense of the ionic $[SO_4]$.

The Formation of Thiosulphate in the Precipitate:—

Again assuming that sulphoxylic acid is the first sulphur oxy-acid formed, the appearance of thiosulphate in the precipitate may develop in two ways. The hydrolysis of trithionate (if it could be formed) is ruled out since under neutral conditions it yields chiefly sulphate and thiosulphate:[7]

$$H_2S_3O_6 + H_2O = H_2SO_4 + H_2S_2O_3$$

This would involve an increase in the sulphate content of the final product.

This is contrary to experimental evidence (p. 3222) which shows that the amount of sulphate in the final precipitate is equal to the amount at the intermediate stage.

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[7] Kurtenacker and Kaufmann: Z. anorg. Chem., 148, 43 (1925); Foerster: 144, 337 (1925)

The development of thiosulphate via the dehydration of two molecules of sulphoxylic acid (vide p. 3234) is also improbable.

The authors are of opinion that the thiosulphate is synthesised in the precipitate as follows:—

Sulphur by the action of water yields sulphoxylic acid. This is oxidised by the CrO_2 or Cr_5O_9 in the precipitate to sulphurous acid which in the presence of co-precipitated sulphur and chromium hydroxide gives chromium thiosulphate. Under the conditions of the reaction this compound becomes partly (or wholly) co-ordinated and forms a complex insoluble compound with the excess chromium hydroxide.

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A STUDY OF THE PREPARATION AND CERTAIN PROPERTIES OF COLLOIDAL HYDROUS BERYLLIUM OXIDE SOLS*

BY WILLARD H. MADSON AND FRANCIS C. KRAUSKOPF

Introduction

One of the most interesting compounds of beryllium is the hydroxide. It is easily prepared by precipitation from solutions by various alkaline reagents.

J. M. van Bemmelen[1] distinguished two forms of beryllium hydroxide. The granular alpha-hydroxide prepared by precipitation from alkaline solution of the oxide, and the gelatinous beta-hydroxide precipitated by ammonia from a solution of beryllium sulfate. After considerable research on the two forms, van Bemmelen concluded that the alpha-hydroxide was a definite compound, $Be(OH)_2$, but that the beta-hydroxide was of indefinite composition and behaved like gelatinous aluminum and ferric hydroxide. "It may therefore be regarded as colloidal beryllium oxide for there is little to show that the water is other than adsorbed or mechanically held"[2] The various hydrated beryllium hydroxides which A. Atterberg[3] claims to have prepared may be regarded as different stages in the desiccation of the gelatinous or beta-hydroxide.

The properties of beryllium hydroxide vary greatly with the mode of preparation. One equivalent of concentrated solutions of normal salts can dissolve from one to five equivalents of the hydroxide depending on the salt used. The solubility of the hydroxide and its sensitiveness to reagents are greatly diminished if it has been dried by warming, or boiled for a long time in water. When the hydroxide is first precipitated by strong alkalies, it is very voluminous, easily adsorbs carbon dioxide and is easily soluble in potassium hydroxide, potassium carbonate, ammonium carbonate or in acids. On standing it slowly changes to the more stable form, which is granular and much less active. These same differences of properties of the two forms of the hydroxide were also observed by Haber and van Oordt.[3a]

It is a well-known fact that beryllium hydroxide must be washed with water containing an electrolyte to prevent the loss of colloidal beryllium hydroxide through the filter paper. Concerning colloidal beryllium hydroxide Weiser[4] states, "While colloidal solutions of hydrous beryllium oxide have not

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* Contribution from the Laboratory of General Chemistry, University of Wisconsin.

* An abstract from a thesis presented by Willard H. Madson, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Wisconsin.

[1] J. prakt. Chem., 66, 227 (1882); Z. anorg. Chem., 18, 126 (1898).

[2] Mellor: " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. V (1923).

[3] Atterberg: Kongl. Svenska Vet. Akad. Hand., 12, 1 (1873).

[3a] Haber and van Oordt: Z. anorg. Chem., 38, 377-398 (1904).

[4] Weiser: "The Hydrous Oxides," p. 163 (1926).

been described in detail Bohm and Niclassen[5] prepared a clear concentrated sol by peptizing a freshly made gelatinous oxide with a small amount of 0.05 M HCl. Since the gelatinous oxide runs through the filter paper when an attempt is made to wash out adsorbed salts there is little doubt that a pure sol could be prepared by thorough washing of the hydrous gel using the centrifuge or supercentrifuge."

It was therefore the purpose of this investigation to prepare pure hydrous beryllium oxide sols and to study certa'n of their properties.

Preparation of Colloidal Hydrous Beryllium Oxide

Attempts were made to prepare colloidal beryllium oxide by many of the well-known methods for the preparation of hydrous colloidal oxides, such as peptizing the precipitated hydroxide (beta) by various reagents, hydrolysis of salts under different conditions, etc. But in every case, however the conditions were varied, the solutions were perfectly clear (after standing a short time) and gave no colloidal tests, such as the Tyndall effect, cataphoresis or flocculation by electrolytes.

Sols prepared by the method described by the authors[6] (developed during this investigation) contained some colloidal hydrous aluminum oxide. Therefore the beryllium salt was purified by conversion of the commercial carbonate (C.P) to the basic acetate and recrystallization several times from hot glacial acetic acid solutions. The basic acetate was converted to the chloride (for use in the preparation of sols) by boiling a small amount of the salt with a large excess of approximately six normal hydrochloric acid until a syrupy mass was formed. It was also found that in the preparation of the sols, a substitution of six inch porcelain casseroles for the pyrex beakers, greatly increased the concentration of the sols produced by the above method.

Various methods were tried in an attempt to produce more concentrated sols. Syrupy beryllium chloride was slowly heated to a white paste and then poured into boiling water. A very concentrated sol was thus produced but after equilibrium of settling had been established, the sol was no more concentrated than sols prepared by the casserole method. Sols were made by substituting various concentrations of sodium hydroxide solutions for the boiling water. Dilute solutions of the alkali acted like electrolytes, slowly coagulating the sols, while the more concentrated solutions dissolved the hydrous oxide presumably forming a soluble beryllate. Dilute solutions of HCl were substituted for the water but this did not increase the stability or concentration of the sols, although stable sols were produced. The more concentrated solutions of the acid dissolved the hydrous oxide.

It appeared that the heating of the salt and the formation of the "basic chloride" before the addition of the water was most important in determining the character of the sols. A study was made to determine the temperature that would give the best results. Samples of syrupy beryllium chloride were

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[5] Bohm and Niclassen: Z. anorg. Chem., 132, 5 (1924).

[6] Madson and Krauskopf: J. Chem. Educ., 6, 334 (1929).

heated (by means of an oil bath) as follows: (1) at 167°-170°C. for five hours; (2) at 142°-150°C. for seventeen hours, and (3) at 118°-128°C. for seventy-two hours and after heating added to boiling water. Analyses of the sols thus produced (after they had been dialyzed for 4 days) showed no weighable beryllium oxide. Therefore the chloride must be quickly decomposed in order to produce the "oxychloride" apparently necessary for the preparation of a stable sol.

Twenty-four liters of colloidal hydrous beryllium oxide were prepared, February 15, 1930, using the following method: Pure basic beryllium acetate was converted to a syrupy chloride as previously described. Fifteen ml. portions of this syrup (containing about 5 g. of $BeCl_2$) were heated in six inch casseroles, using a small flame of an adjustable burner. When the material was nearly dry, that is when only a few syrupy bubbles were forming, the flame was turned up to full height and when the redness of the flame could be seen through the bottom of the casserole, one liter of boiling water was added. The sol thus formed was boiled for about a minute and then allowed to cool in the air in three-liter flasks. About thirty liters were prepared in this manner. After twenty-four hours the colloidal "solutions" were siphoned into a 24-liter pyrex Florence flask, leaving the beryllium oxide that had been heated too hot to form in colloidal suspension on the bottom of each of the three-liter flasks. The sol was designated as sol No. 24 L. The increased temperature just before the addition of the water produced colloidal systems which were from two to three times as concentrated as those prepared without increasing the temperature. Four months later this sol had a pH value of 5.61 measured by means of a glass electrode.

Sol No. 24 L was analyzed at various times by the following method: one hundred ml. portions of the sol were evaporated in a platinum crucible by means of an electric hot plate and afterward heated to constant weight by means of a Meeker burner, and weighed as beryllium oxide. Table I gives the results of the analyses.

TABLE I

Analyses of Sol No. 24 L

Date of analysis	3-1-'30	7-10-'30	7-16-'30	2-4-'31
mg. BeO per l.	193	186	185	178

Three sols were prepared by evaporating the beryllium chloride syrup nearly to dryness in a quartz evaporating dish, then turning the flame up and quickly heating the dish and its contents to redness and immediately plunging it into a liter of boiling water. Very concentrated sols were thus produced but equilibrium of settling has not been established and therefore it is impossible to tell whether or not the sols will be more concentrated than the others.

Purification of the Sols

The sols were dialyzed in the dialyzer described by Sorum.[7] The collodion bags were prepared from Mallinckrodt's U.S.P. collodion. The perfectly clean 250 ml. Erlenmeyer flasks were partly filled with collodion. After a small amount had been poured out the rest was slowly allowed to flow out while the flask was completely rotated twice. The time of emptying was approximately fifteen seconds. The flask was then allowed to drain for thirty seconds, and then a moderate current of air passed into the flask for forty-five seconds. Afterward the flask was immediately filled with distilled water. One minute later the collodion bag was removed, the neck inserted and the collodion allowed to dry on the neck thus holding the bag. Before using, the bags were thoroughly washed with distilled water. They were never used more than three times, usually only once or twice.

About two liters of distilled water were allowed to flow through each of the twelve batteries of the dialyzer each hour. With the exception of sol No. 17d (12), all sols were dialyzed at room temperature a few hours before they were heated to about 80°C. Usually the sols were partly cooled before being removed. Small amounts of distilled water were added at various times to replace water lost by evaporation. All sols were kept in well-stoppered pyrex flasks. Utmost care was always exercised to prevent any contamination of the sols. Table II summarizes the purification of the sols used in this investigation. The stock sol No. 24 L was the source of all sols mentioned in the table.

Table II

Summary of the Purification of the Sols

Sol No.	Total No. hrs. dial.	Hrs. dial. hot	mg. BeO per l. after dial.	Temp. C.
11d	108	87	63	70–80
12d	101	99	57	70–80
15d	143	130	53	75–80
16d	168	162	51	75–80
17d(12)	12	12	86	75–80
17d(24)	24	19	77	75–80
17d(48)	48	44	72	75–80
17d(72)	72	68	65	75–80
18d	97	88	64	75–80

In general dialyzed sols gave the following tests for chlorides when tested with acidified silver nitrate: dialyzed less than 50 hours, distinct test for chlorides; dialyzed 50-100 hours, faint test for chlorides; dialyzed more than 100 hours, no test for chlorides. Sols No. 18d, No. 17d(12), and No. 17d(72) showed absolutely no precipitation during eight months. The other dialyzed sols had formed a very slight precipitate after they had stood for two weeks or

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[7] Sorum: J. Am. Chem. Soc., 50, 1263 (1928).

more. This slight precipitate may have been caused by slight contamination during the removal of samples for the determination of flocculation values. Some of the undialyzed sols have shown no precipitation in more than two years.

Flocculation Values

I. *Theoretical.*

Hydrous beryllium oxide sols belong to the class of sols usually known as lyophobic or suspensoid colloidal systems. The stability of the sols is due to the three factors: (1) the Brownian movement, (2) attraction between the dispersed particle and the dispersion medium, and (3) the electric charge of the particle. The last factor is the most important in this case.

It is generally conceded that the charge of a colloidal particle is due to the diffuse Helmholtz electric double layer. If this charge is destroyed the stability of the sol is decreased and the sol, if a suspensoid, coagulates. It was first thought that it was necessary to completely neutralize the charge of a suspensoid in order to cause coagulation. This complete neutralization was called the iso-electric point. Later investigations of Powis[8] have indicated that a lowering of the potential of the interface to a certain characteristic value, which he calls the "critical potential," is sufficient to produce flocculation.

Flocculation depends upon the probability of collision and upon the probability of adhesion. Murray[9] outlines four conditions for comparable work in the coagulation of colloids by electrolytes: (1) uniform size of colloidal particles, (2) uniform concentration of the colloids, (3) quick and uniform mixings of colloid and electrolyte, and (4) uniform treatment after mixing. Thus flocculation values vary with the method used in their determination. However, the values give a relative indication of the stability of the various sols.

II. *Experimental determination of flocculation values.*

a—Standard solutions.

All solutions were carefully prepared, using calibrated weights and calibrated volumetric flasks. The solutions were kept in pyrex flasks. The preparation of the solutions is given in some detail because the flocculation values vary with the impurity of the solution. Concentrations are expressed in mols per liter of solution.

Potassium Chloride: molar. Mallinckrodt's reagent quality dried at 110°C.

Potassium Acetate, .303 molar; Potassium Mono-chlor Acetate, .404 molar; Potassium Di-chlor Acetate, .404 molar; Potassium Trichlor Acetate, .404 molar. The acetates were prepared by using a definite amount of standard KOH solution and neutralizing it with the respective acids using phenolphthalein indicator. (The potassium hydroxide solution was prepared from a saturated solution of C.P. KOH and standardized with a standard sulfuric acid solution.)

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[8] Powis: Z. physik. Chem., 89, 186 (1915).

[9] Murray: Chem. News, 123, 277 (1921).

Potassium Chromate, molar/20. The C.P. salt was recrystallized from water solution and dried at 120°C.

Magnesium Sulfate, molar/25. Mallinckrodt's reagent quality $MgSO_4.7H_2O$, undried.

Potassium Sulfate, molar/25. The C.P. salt was recrystallized several times from water and dried at 110°C.

Sodium Sulfate, molar/25. Mallinckrodt's (dried) reagent quality, dried at 110°C.

Tertiary Potassium Phosphate, (K_3PO_4), molar/25: Mallinckrodt's C.P. salt dried at 110°C.

Primary Potassium Phosphate (KH_2PO_4) molar/25: Mallinckrodt's C.P. salt was recrystallized several times from water solution and dried at 110°C.

Secondary Potassium Phosphate ($K_2HPO_4.3H_2O$), molar/25: Large transparent colorless crystals of Mallinckrodt's reagent quality potassium phosphate, dibasic; not dried.

Tertiary Potassium Arsenate, (K_3AsO_4), molar/25: Mallinckrodt's potassium arsenate was recrystallized three times from water and dried at 105°C.

Potassium Ferricyanide, ($K_3Fe(CN)_6$) molar/25: Mallinckrodt's reagent quality salt was not dried for previous experiments showed that drying did not change the flocculation power. Solutions were made using carbon dioxide free water and were always prepared just before using for their flocculation power changed slightly with age.

Potassium Ferrocyanide, ($K_4Fe(CN)_6.3H_2O$), molar/50: Mallinckrodt's reagent quality potassium ferrocyanide was used. The salt was not dried for previous experiments showed that more uniform results were obtained without drying. The solutions were made with carbon dioxide free water and kept in "blackened" pyrex flasks. The flocculation power of ferrocyanide solutions kept in this manner remained practically constant for two weeks.

b—Method and apparatus used in the determination of flocculation values.

Test tubes: the five-inch pyrex test tubes were so thoroughly cleaned that the solutions would not stick to the sides of the tube. Utmost care had to be taken to have them absolutely clean or varying results were obtained. The test tubes were stoppered (when used) with carefully cleaned rubber stoppers,

All pipets and the micro burets were calibrated before using. The preparation of the solutions has been previously described.

Procedure—The concentration of electrolyte, such that one to two ml. of the electrolyte added to two ml. of sol in a total volume of 5 ml. would cause complete flocculation within 24 hours, was first determined. Then this concentration of electrolyte was placed in a calibrated micro buret which was graduated to 1/20 ml. Water was placed in the other micro buret which was graduated to 1/10 ml. Then various concentrations of the electrolyte were placed in test tubes by adding from 0.1 to 3.0 ml. of the electrolyte and making up the total volume added to 3.0 ml. by adding the required amount of water from the other buret. Usually a rough run was first made by varying the electrolyte in each tube from 0.2 to 0.5 ml. To each of these solutions was added a ml. of the sol and the tubes stoppered. After the sol was added each tube was shaken five times. The sol was always added from a calibrated two ml. pipet and allowed to flow down the side of the test tube, never allowed to drop directly into the solution. The solutions were allowed to stand for twenty-four hours and the approximate flocculation value determined in this manner.

After the approximate flocculation value was determined, solutions were made by varying the concentration of the electrolyte in the successive tubes by 0.1 ml. Usually duplicates of each of eight concentrations were used in each run. The lowest concentration of electrolyte which caused complete flocculation was usually easily determined. Often the sol in one tube of a series would be partly flocculated and in the next completely flocculated as was the case with all the others in which the electrolyte was more concentrated. Occasionally there would be two tubes of partial flocculation but never more than two if the concentrations were varied by only 0.1 ml. of added electrolyte. It was practically impossible to determine what concentration produced complete flocculation if the data were taken by artificial light. Therefore all observations were made by daylight.

In this work, flocculation value has been defined as the number of millimoles of electrolyte per liter necessary to completely precipitate the sol within 24 hours. The concentration is computed for the total volume of sol plus added electrolyte.

c—Experimental results of the determination of flocculation values.

Tables III, IV, V, and VI, give the flocculation values of sixteen different electrolytes, using different sols. All sols were not used in each determination but comparisons were made which showed that the values of all sols were in agreement.

At first the technique required to obtain reproducible results was somewhat difficult, but after this was developed the flocculation values were easily checked. No results were omitted which were obtained after such satisfactory technique had been developed for each electrolyte. Satisfactory results of the flocculation value of potassium chloride were very difficult to obtain. The technique was quickly developed for all the other electrolytes.

Flocculation values of some electrolytes, such as potassium dichromate, could not be determined because the comparatively deep color of the solution made it impossible to visibly tell when flocculation was complete. The flocculation value of but one univalent inorganic anion (Cl^-) was determined because of the large value and therefore comparatively inaccurate results. Other univalent anions, such as nitrate, bromide, and iodide, were tried insofar as to be sure that their flocculation values were also comparatively large.

TABLE III

Effect of Change of Valence of Inorganic Anions on Flocculation Value of Electrolytes

Electrolyte	Sol. No.	mg.BeO per l.	Hours dialyzed	Flocculation value
Potassium chloride	16d	52	168	240
				240
	17d(72)	65	72	220
				220
	17d(12)	86	12	220
				220
Potassium chromate	16d	52	168	0.22
				0.20
				0.20
	15d	53	143	0.24
				0.24
				0.24
	11d	63	108	0.24
				0.20
	12d	57	101	0.24
				0.24
	17d(72)	65	72	0.22
				0.22
	17d(48)	72	48	0.24
				0.22
	17d(24)	77	24	0.22
				0.22
	17d(12)	86	12	0.26
				0.26
	24 L	185	0	1.20
				1.20
				1.20
Tertiary potassium arsenate	16d	52	168	0.048
				0.048
				0.044
				0.044
	15d	53	143	0.040
				0.042
	18d	64	97	0.042
				0.042
Potassium ferricyanide	16d	52	168	0.026
				0.024
				0.024
				0.024
				0.026
				0.026

TABLE III (continued)

Electrolyte	Sol No.	mg. BeO per l.	Hours dialyzed	Flocculation value
	18d	64	97	0.024
				0.024
Potassium ferrocyanide	16d	52	168	0.008
				0.010
				0.008
				0.008
				0.010
				0.010
				0.009
				0.011
	15d	53	143	0.008
	18d	64	97	0.010
				0.010
				0.010
				0.012
				0.012
				0.013
				0.013
				0.013

TABLE IV

Flocculation Values of the Potassium Acetates

Electrolyte	Sol No.	mg. BeO per l.	Hours dialyzed	Flocculation value
Potassium monochloracetate	18d	64	97	145
				145
				137
				145
				145
Potassium dichloracetate	18d	64	97	81
				81
Potassium trichloracetate	18d	64	97	73
				73
				73
				73
Potassium acetate	18d	64	97	67
				61
				57
				57
				57
				57

Table V

Flocculation Values of Various Sulfates

Electrolyte	Sol No.	mg. BeO per l	Hours dialyzed	Flocculation value
Magnesium sulfate	16d	52	168	0.22
				0.22
	15d	53	143	0.22
				0.22
	12d	57	101	0.22
				0.22
Ammonium sulfate	16d	52	168	0.22
				0.22
	15d	53	143	0.22
				0.22
	12d	57	101	0.20
				0.20
Potassium sulfate	16d	52	168	0.20
				0.20
	15d	53	143	0.20
				0.20
	12d	57	101	0.22
				0.22
				0.20
				0.20
	17d(72)	65	72	0.22
				0.20
	17d(48)	72	48	0.22
				0.22
	17d(24)	77	24	0.22
				0.22
	17d(12)	86	12	0.22
				0.22
	24L	185	0	0.26
				0.26
Sodium sulfate	16d	52	168	0.20
				0.20
	15d	53	143	0.20
				0.20
	12d	57	101	0.20
				0.20
				0.20
				0.20

TABLE VI

Flocculation Values of the Potassium Ortho Phosphates

Electrolyte	Sol No.	mg.BeO per l.	Hours dialyzed	Flocculation value
Tertiary potassium phosphate	18d	64	97	0.048
				0.048
Primary potassium phosphate	16d	52	168	0.044
				0.044
				0.044
	15d	53	143	0.044
				0.044
				0.048
	12d	57	101	0.048
				0.048
	18d	64	97	0.044
				0.044
	17d(72)	65	72	0.048
				0.044
	17d(48)	72	48	0.048
				0.048
	17d(24)	77	24	0.048
				0.048
	17d(12)	86	12	0.048
				0.048
	24L	185	0	0.84
				0.84
				0.80
Secondary potassium phosphate	16d	52	168	0.032
				0.032
				0.034
				0.034
	15d	53	143	0.032
				0.032
				0.032
				0.032
	18d	64	97	0.035
				0.035
				0.036
				0.036
	17d(72)	65	72	0.034
				0.034

There are several points to be given consideration concerning these flocculation values. First, all results for each electrolyte agree very closely with each other with the possible exception of those for potassium ferrocyanide. With the ferrocyanide one must take into account the fact that the solutions used were extremely dilute, and also that they change in the presence of light. Although this fluctuation was practically eliminated by using freshly prepared solutions and keeping them in the dark, it was impossible to get as good results with such unstable solutions. However the results of ferrocyanide ion show the order of magnitude of the flocculation value and considering all the variables they are in very good agreement.

Second, the flocculation values are reproducible over a long period of time. This is especially shown with secondary potassium phosphate where more than two months elapsed between the first and last determinations. Also the last determinations were made with entirely new standard phosphate solutions. All values agreed with those previously determined irrespective of the time interval, though no determinations were made over a time interval of more than seventy-one days.

Third, the flocculation values are of the same order of magnitude as those for ferric oxide.[10] The values for ferric oxide are uniformly lower than those for beryllium oxide, especially for potassium chloride. The sols of ferric oxide are more concentrated than the beryllium oxide sols; this may account, in part for the variation.

Table VII is a condensed summary of the flocculation values of hydrous beryllium oxide sols as given in the four preceding tables. This summary contains data for dialyzed sols only.

TABLE VII

Summary of the Flocculation Values of Colloidal Beryllium Oxide

Electrolyte	Floc. value	No. dif. sols	No. values averaged
KCl	227	3	6
$CH_2ClCOOK$	143	1	5
$CHCl_2COOK$	81	1	2
CCl_3COOK	73	1	4
CH_3COOK	59	1	6
K_2CrO_4	0.229	8	18
$MgSO_4$	0.220	3	6
$(NH_4)_2SO_4$	0.213	3	6
K_2SO_4	0.211	7	16
Na_2SO_4	0.200	3	8
K_3PO_4	0.048	1	2
KH_2PO_4	0.046	8	20
K_3AsO_4	0.044	3	8
$K_2HPO_4.3H_2O$	0.033	4	14
$K_3Fe(CN)_6$	0.0248	2	8
$K_4Fe(CN)_6$	0.0103	5	17

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[10] Hazel and Sorum: J. Am. Chem. Soc., 53, 49-54 (1931).

The Influence of the Length of Time of Dialysis on Certain Properties of Hydrous Beryllium Oxide Sols

a—Flocculation values.

It is a well known fact that the properties of lyophobic and lyophillic colloidal systems are very dependent upon the purity of the system. Therefore dialysis markedly changes the properties of the sols. Often many colloidal systems are completely destroyed by dialysis, sometimes in a very few hours. After a certain purity is obtained further dialysis does not change the properties to any noticeable degree. The time necessary to obtain this degree of purity is dependent upon the type of sol used, upon the impurities and stabilizing materials present, and upon the method of dialysis.

A study was made of the variation of flocculation values of certain electrolytes, for colloidal hydrous beryllium oxide sols, with the length of time of dialysis. The flocculation values of the four electrolytes, potassium chloride potassium chromate, potassium sulfate and primary potassium phosphate, were determined for the undialyzed sol No. 24 L and for other sols which had been dialyzed from twelve to one hundred sixty hours. The experimental results are given in Table VIII.

TABLE VIII

Flocculation Values for Beryllium Hydroxide Sols
Variation with Time of Dialysis

Sol No.	Hours dialyzed	Electrolytes			
		KCl	K_2CrO_4	K_2SO_4	KH_2PO_4
24 L	0	>600	1.20	0.26	0.830
17d(12)	12	220	0.26	0.22	0.048
17d(24)	24	—	0.22	0.22	0.048
17d(48)	48	—	0.23	0.22	0.048
17d(72)	72	220	0.22	0.21	0.046
18d	97	—	—	—	0.048
12d	101	—	0.24	0.21	0.048
11d	108	—	0.22	—	—
15d	143	—	0.24	0.20	0.045
16d	168	240	0.21	0.20	0.044

The data show that the flocculation values for the electrolytes decrease rapidly at first, become practically constant after twelve hours of dialysis with the exception of those for potassium chromate and even these become constant after twenty-four hours.

b—Concentration of the sols.

The previous experiment led to a study of the change of concentration of the hydrous beryllium oxide sols with the time of dialysis. Table IX and Fig. 1 give the results of such a study.

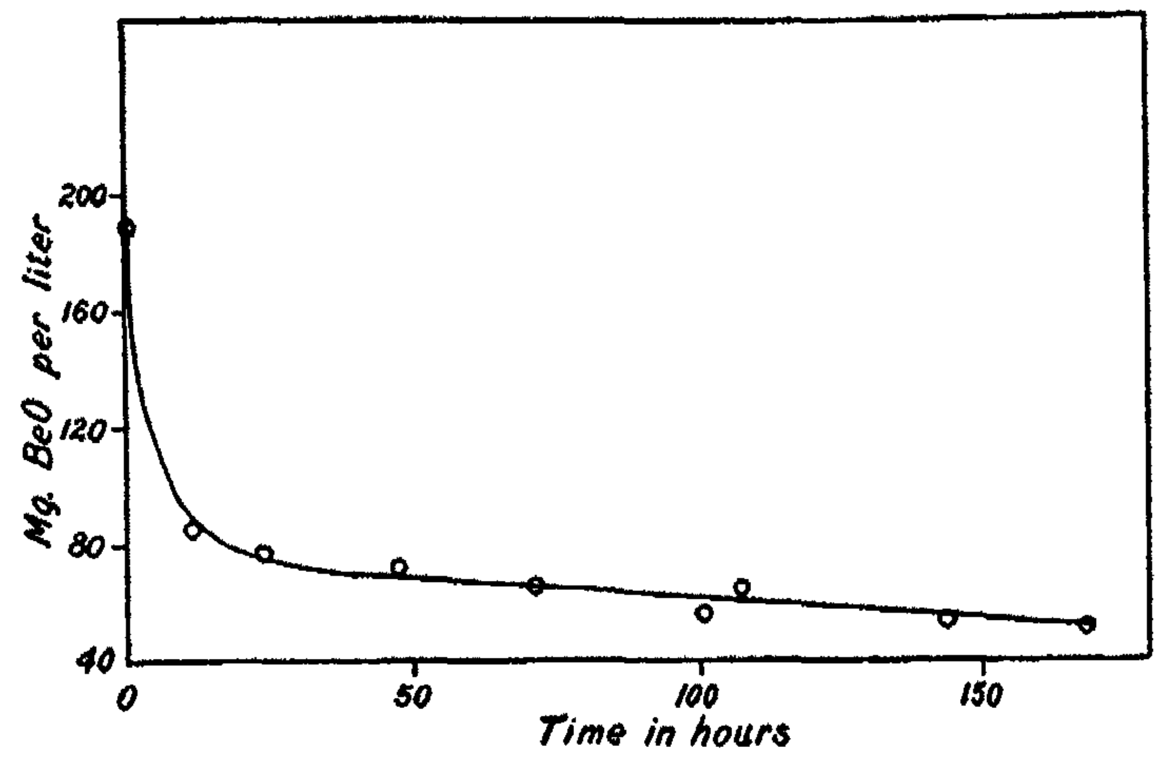

Fig. 1

Variation of Concentration with the Length of Time of Dialysis

Table IX

Variation of the Concentration of Beryllium Oxide with Time of Dialysis

Sol No.	Hours dialyzed	mg. BeO per l.
24 L	0	185
17d(12)	12	86
17d(24)	24	77
17d(48)	48	72
17d(72)	72	65
12d	101	57
11d	108	63
15d	143	53
16d	168	52

The data show that there is a rapid decrease of beryllium content during the first few hours of dialysis. After fifty hours there is a rather constant decrease as shown by the straight line part of the graph (Fig. 1). It is impossible to duplicate exactly the pore size of the membranes by the method used in the preparation of the sacs. This may account for the slight variations in the decrease of beryllium content.

The large decrease of BeO content during the first hours of dialysis was expected. The concentrations of the various sols were determined by evaporating a definite amount of the sol in a platinum dish, heating to redness and constant weight and weighing as beryllium oxide. Thus any soluble beryllium salt in the undialyzed or partly dialyzed sols was determined as the oxide and not as its proper salt, and no account was taken of its solubility. Any soluble beryllium salt diffuses through the membrane very quickly. Thus the data show a large apparent decrease of colloidal beryllium hydroxide which is probably not the case but is largely a loss of soluble beryllium salts and a rather constant decrease of colloidal hydrous beryllium oxide.

c—The hydrogen ion concentration of colloidal hydrous beryllium oxide systems.

The colloidal systems of hydrous beryllium oxide as prepared were apparently the result of the hydrolysis of some basic salt or salts of beryllium. Therefore the undialyzed sols should contain some free acid and consequently have a pH value less than seven. This value should increase with dialysis. A study was made of the influence of dialysis on the hydrogen ion concentration of the sols.

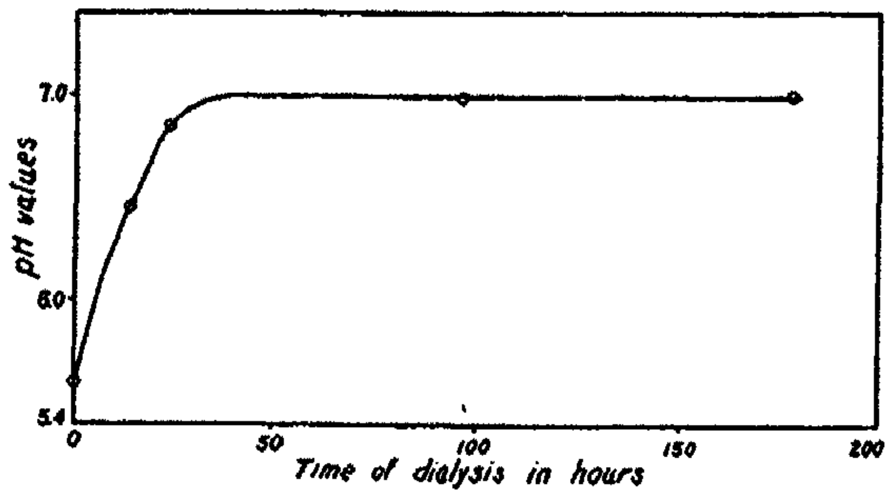

FIG. 2

The Influence of the Length of Time of Dialysis on the Hydrogen Ion Concentration of Colloidal Hydrous Beryllium Oxide Sols.

The hydrogen ion concentration of five sols were determined by means of the glass electrode and apparatus described by Hazel and Sorum.[11]

Table X and Fig. 2 give the experimental data obtained.

TABLE X

The Influence of the Time of Dialysis on the Hydrogen Ion Concentration of Colloidal Hydrous Beryllium Oxide Systems

Sol No.	Hours dialyzed	pH
24 L	0	5.61
17d(12)	12	6.46
17d(24)	24	6.86
18d	97	6.98
16d	168	7.00

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[11] Hazel and Sorum: J. Am. Chem Soc., 53, 49 (1931).

The Lyotropic Series and Hydrous Beryllium Oxide.

The behavior of colloidal systems with added electrolytes shows certain trends some of which are illustrated by well known rules, i.e., Traube's rule, the Schulze-Hardy rule, the Burton-Bishop rule etc. One of the most general of such phenomena is the lyotropic series. The series vary for different colloidal systems expecially if the sols are of different classes. However they usually follow a general order.

The following lyotropic series were obtained from the flocculation values for hydrous beryllium oxide sols as given in Table VII. Anions (increasing flocculation values): ferrocyanide, ferricyanide, secondary phosphate, tertiary arsenate, primary phosphate, tertiary phosphate, sulfate, chromate, acetate, trichlor acetate, di-chlor acetate, mono-chlor acetate and chloride. Cations (increasing flocculation values): Sodium, potassium, ammonium and magnesium.

These series follow the general order of lyotropic series and agree especially well with the series for ferric oxide sols,[12] the only reversal being the sulfate and chromate.

Hydrous Beryllium Oxide Sols and the Irregular Series.

Many colloidal systems, both lyophobic and lyophillic, exhibit the property of being either positively or negatively charged depending on the method of preparation or upon the dispersion medium and its impurities. Concerning the phenomenon of irregular series Kruyt[13] states "it will always occur when the potential-lowering effect of the cation is far in excess of the potential-raising effect of the anion. This may be due to a high valence of the ion or to a high degree of adsorbability. Polyvalent cations give, therefore, irregular series when they are combined with monovalent anions. But monovalent organic cations act in the same way."

Von Kohei Hakozaki,[14] has shown that positive colloidal iron oxide can be recharged negatively by the addition of potassium ferrocyanide. This suggested that the charge of hydrous beryllium oxide sols might be reversed by the addition of various amounts of ferrocyanide.

Table XI gives the various concentrations of potassium ferrocyanide added to sol No. 15d. In every case from molar 0.012 to molar 0.000008 ferrocyanide, there was complete flocculation within twenty-four hours, while with the more dilute solutions there was no flocculation. Thus it was impossible to change the charge of the sol by the above method using the stated concentrations. If there had been a change of the charge there would have been a region of no flocculation somewhere above 0.000008 molar potassium ferrocyanide.

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[12] Weiser and Middleton: J. Phys. Chem., 24, 641 (1920); Pauli and Wittenberger: Kolloid-Z., 50, 228 (1930).

[13] Kruyt: "Colloids," p. 90, trans. by van Klooster (1930).

[14] Von Kohei Hakozaki: Kolloid-Z., 39, 319 (1926).

TABLE XI

Coagulation of Sol No. 15d by Potassium Ferrocyanide
(2 ml. of sol added to 3 ml. of electrolyte soln.)

Conc. of $K_4Fe(CN)_6$	Observations	Conc. of $K_4Fe(CN)_6$	Observations	Conc. of $K_4Fe(CN)_6$	Observations
0.012	*	0.00096	*	0.000080	*
0.0104	*	0.00080	*	0.000080	*
0.0088	*	0.00064	*	0.000056	*
0.0072	*	0.00060	*	0.000054	*
0.0056	*	0.00054	*	0.000048	*
0.0040	*	0.00048	*	0.000044	*
0.0032	*	0.00044	*	0.000040	*
0.0024	*	0.00040	*	0.000036	*
0.00208	*	0.00036	*	0.000032	*
0.00192	*	0.00032	*	0.000028	*
0.00176	*	0.00028	*	0.000024	*
0.00160	*	0.00024	*	0.000020	*
0.00144	*	0.00020	*	0.000016	*
0.00128	*	0.00016	*	0.000012	*
0.00112	*	0.00012	*	0.000008	*

* Complete flocculation in 24 hours. Concentrations, mols per liter of total volume. concentrations less than 0.000008 molar did not cause flocculation in 24 hours.

Discussion

The previous descriptions of the various sols show that their properties are, in general, independent of the preparation except for the heat treatment just before the addition of the water. Many details of preparation (other than those already described) were varied in order to find out if the properties of the sols were changed thereby. Some sols were cooled immediately after preparation, others were allowed to cool at room temperature; some were dialyzed immediately after preparation, even before they had cooled, while others were dialyzed after several days, weeks, or months; still others were siphoned from various depths of an eight liter aspirator bottle of sol (after the sol had stood in the bottle for one month); but in no case were appreciable variations of the properties observed.

Some of the sols were very milky white in appearance when they were first formed, afterward they gradually became less opaque because of the settling of the larger particles. Occasionally a stratification would form and the heavy layer settle slightly and then in about a week either rise again or be destroyed in some unknown manner. This phenomenon was observed when the sols were kept perfectly still and special care taken not to destroy the stratification. In a few cases the stratification would form and the heavy layer slowly and continually settle until the entire sol had the bluish white appearance of the upper layer. This continual settling of the heavy layer was observed only when the sols were very milky in appearance and apparently rather concentrated. Usually there was no stratification of any kind.

Several dialyzed sols were carefully frozen solid and allowed to melt at room temperature. In every case complete coagulation was caused by a single freezing and melting of the dialyzed sol. In no case was coagulation caused by freezing undialyzed sols even though some were frozen and allowed to melt several times. It was thus shown that dialysis decreased the stability of the sols.

The decrease of the stability of the sols with dialysis was also illustrated by boiling. Undialyzed sols were not coagulated by continuous boiling (refluxing) for as long as one week. Boiling dialyzed sols caused them to slowly coagulate, the speed of this coagulation being dependent on the length of time of boiling. Also dialyzed sols changed appearance upon being boiled; the color changed from bluish white, nearly transparent, to definitely opaque milky white. This color change was not perceptible when undialyzed sols were boiled. With many sols there was no settling when centrifuged at 1200 r.p.m. for an hour while a few sols were slightly coagulated by this treatment. These properties indicate that the sols were very stable and had the characteristics of lyophobic colloidal systems.

Since the sols were prepared from beryllium chloride and water, it might seem that they were the result of simple hydrolysis of the salt with the formation of colloidal beryllium hydroxide and hydrochloric acid; and thus also the stability be attributed to an excess of beryllium chloride similar to certain theoretical explanations of the stability of colloidal hydrous aluminum and ferric oxide systems.

The amount of chloride present in the sols decreased with continued dialysis from an easily detected amount after 12 hours of dialysis to no detectible amount (using acidified silver nitrate) after 140 hours. The flocculation values of electrolytes, and therefore the stability of the sols, remained constant during the same length of time of dialysis. Apparently, then, the sols are not the results of the simple hydrolysis mentioned above and their stability is not entirely due to the excess of beryllium chloride.

The method of formation of the sols suggested that they may not be $Be(OH)_2$ but some lower hydrate. Therefore the following experiment was carried out.

Sols No. 28 and No. 29 were prepared from the stock sol 24 L by dialyzing for 100 hours. One month later no precipitate had formed in either sol and at that time each sol was coagulated by the addition of 100 ml. of M/500 primary potassium phosphate. The supernatant liquid was decanted off and each of the precipitates separated from most of the water by centrifuging. Each coagulum was then dried for one month, at room temperature, in sulfuric acid desiccators through which carbon dioxide free air was allowed to slowly pass. After one month each residue had become constant as was indicated by repeated weighings. The amount of phosphate present in each coagulum was calculated from the loss of phosphate in the supernatant liquid from each sol. The experimental data in Table XII show the loss of weight of hydrous beryllium oxide in each coagulum upon heating, (all weights given in grams).

TABLE XII

Analysis of Coagulum

	Sol. No. 28		Sol No. 29	
wgt. of KH_2PO_4 added	0.02723		0.02723	
" " " left in soln.	0.01593		0.01551	
" " " adsorbed		0.01130		0.01171
" " coagulum dried at room temperature	0.1229		0.0866	
" " KH_2PO_4 in coagulum	0.0113		0.0117	
" " $Be(OH)_2$ " "		0.1116		0.0749
" " coagulum after heating	0.1021		0.0709	
loss of wgt. by heating coagulum	0.0208		0.0157	
" " " by heating ads. KH_2PO_4	0.0016*		0.0016*	
" " " by heating "$Be(OH)_2$"		0.0192		0.0141
experimental		17.20%		18.83%
theoretical		41.87%		41.87%

* Due to change from KH_2PO_4 to KPO_3.

The data indicate that hydrous beryllium oxide sols are not colloidal beryllium hydroxide but a hydrous oxide in which there is less than one molecule of water for two molecules of beryllium oxide. This small amount of hydration is also indicated by the fact that solutions of ethyl alcohol of concentrations varying from 25% to 80% will not coagulate the sols within twenty-four hours, while even 90% ethyl alcohol will coagulate but a few. It appears that the sols are not the result of simple hydrolysis but a complicated combination of decomposition and then hydrolysis (or partial hydrolysis) of the resulting product or products. Thus the stability of the sols may be due to: (1) some minute amount of beryllium chloride or oxy-chloride, (2) some minute amount of basic beryllium acetate, (3) the character of hydrolysis, (4) the slight hydration of the oxide, and (5) the amphoteric nature of the oxide.

The slight hydration of the oxide tends to decrease the stability of the sol rather than stabilize it. This also explains, in part, why it was impossible to make more concentrated sols, for it is more difficult to make anhydrous oxide sols than those which are highly hydrated. Since the method of preparation used to make the chloride does not eliminate all acetate, the acetate must be considered in the stability factors although it was present in so small amounts that it could not be detected by the ordinary methods.

The properties of highly purified colloidal hydrous beryllium oxide sols are very similar to those of highly purified hydrous ferric oxide sols with one exception, that of the Burton-Bishop rule. An attempt was made to determine the influence of the variation of the concentration of the sols on the flocculation values. Since all beryllium oxide sols that were prepared were comparatively very dilute, no convincing experimental data were obtained, for the amount of change of flocculation value decreases with the dilution of the original sol. It is quite probable that the Burton-Bishop rule might hold for beryllium oxide sols if a stable sol of sufficient concentration could be prepared.

In general the flocculation values of the sixteen anions studied were of the order expected. The flocculation values of the various phosphates and acetates need explanation.

Table VI gives the flocculation values of the primary, secondary, and tertiary potassium phosphates as 0.045, 0.035, and 0.048 respectively. According to the present theories of flocculation, coagulation is caused by the decrease of the charge of the colloidal particle to a certain minimum called the critical potential. The flocculation is due also primarily to the ions of a charge opposite to that carried by the colloidal particle. Thus the flocculation of colloidal hydrous beryllium oxide sols must be due primarily to the negative ions, for the sols are positively charged. Therefore some explanation must be given for the fact that primary and tertiary potassium phosphates have higher flocculation values than does secondary potassium phosphate.

The ionization constants for phosphoric acid[*] have been given as 9.4×10^{-3}, 1.4×10^{-7}, and 2.7×10^{-12} for the first, second and third hydrogens respectively. Therefore the three phosphate solutions will effectively ionize as follows:

KH_2PO_4

$$KH_2PO_4 \rightleftarrows K^+ + H_2PO_4^-$$
$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{--}$$
$$HPO_4^{--} \rightleftarrows H^+ + PO_4^{---}$$
$$HOH \rightleftarrows H^+ + OH^-$$

K_2HPO_4

$$K_2HPO_4 \rightleftarrows 2K^+ + HPO_4^{--}$$
$$HPO_4^{--} \rightleftarrows H^+ + PO_4^{---}$$
$$HPO_4^{--} + H^+ \rightleftarrows H_2PO_4^-$$
$$HOH \rightleftarrows H^+ + OH^-$$

K_3PO_4

$$K_3PO_4 \rightleftarrows 3K^+ + PO_4^{---}$$
$$HOH \rightleftarrows H^+ + OH^-$$
$$PO_4^{---} + H^+ \rightleftarrows HPO_4^{--}$$
$$HPO_4^{--} + H^+ \rightleftarrows H_2PO_4^-$$

Each solution contains the same ions and the only variations are in the number of ions and their proportions. Experiments have shown that the pH values for phosphate solutions of the concentrations used, increase from 3-5 for the primary to about 8 for the secondary. Therefore the flocculation values can not be explained on any simple adsorption of hydroxyl or hydrogen ions, for if that were the case, there would be a regular change of the floccu-

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[*] Britton: "Hydrogen Ions," p. 135 (1929).

lation values, either increase or decrease, from the primary, through the secondary to the tertiary phosphates. The flocculation values show that this is not the case.

Also it is well known that the flocculation power of ions increases enormously from the monovalent, to the bivalent, to the trivalent, etc. Therefore PO^{---} ion should have a much greater flocculating power than either HPO_4^{--} or $H_2PO_4^-$, with the last having the least flocculating power of the three ions. Ionization constants show that, for phosphate solutions of the same molar concentrations, the tertiary phosphate solution has the greatest number of PO_4^{---} ions. Therefore the tertiary phosphate might be expected to have the greatest flocculation power. Again data show that this is not the case.

Simple ionization and adsorption alone do not explain the differences of flocculation values of these phosphates.

Beryllium oxide and hydroxide are thought to be amphoteric and thus their properties are changed as the pH of the solutions changes. Therefore the solubility of the hydroxide (or oxide) changes with the pH of the solution, and there must be a minimum solubility at some definite pH value, which may be called the "minimum solubility pH." As the pH of the solutions changes from approximately 3-5 with the primary phosphates to about 9 with the tertiary, phosphate, this pH of minimum solubility of the hydroxide is passed. It is also reasonable to assume that the properties of the colloidal oxide or hydroxide also change with the amphoteric nature of the compounds, thus having a minimum stability of the sols at or near the transition pH for the change from basic to acidic properties of the oxide. Then also it is easily seen why the secondary phosphate, which has an intermediate pH value to the other two phosphates, should have a higher flocculating power than either the primary or tertiary phosphates. The secondary phosphate solution has a pH value nearer the pH of minimum stability of the sol and the sol is more easily coagulated under those conditions, which gives the secondary phosphate lower flocculation value. The other two phosphate solutions have pH values farther away from this pH of minimum stability and therefore the sol is more stable and the salts have higher flocculation values. However more work should be done to definitely prove that this and other sols of amphoteric oxides have a decreased stability at some rather definite pH value of the system.

Table VII shows that the flocculation power of the acetates decrease in the order, CH_3COO^-, CCl_3COO^-, $CHCl_2COO^-$, and CH_2ClCOO^-. The flocculation value of the potassium salts of the acetates are 59, 73, 81, and 143, respectively.

Neither the order of the increasing degree of dissociation of the acids, the order of the increasing molar conductances of the salt, nor the order of the increasing ionic mobilities of the acetate ions, follows this order of increasing flocculation values. Also there is not sufficient variation in the conductance and in the ionic mobilities to account for the large variation of the flocculation values.

Thus the flocculation values are dependent upon the three properties, ionization, adsorbability and the size of the ions. The acetate has the greatest flocculation power for it is highly adsorbed due to its organic nature. The other three acetates are all organic but their degree of ionization increases with increase of chlorine content. Thus of the three chloride substituted acetates the flocculation power decreases in the following order: tri-chloracetate, di-chloracetate and mono-chloracetate.

Summary

1. A new method for the preparation of hydrous beryllium oxide sols has been developed. and a study made of the effect of changing the conditions of preparation.

2. A detailed study has been made of certain properties of highly purified colloidal hydrous beryllium oxide systems.

3. The flocculation values of sixteen different electrolytes for hydrous beryllium oxide have been determined by the classical method.

4. The nature of the coagulum of hydrous beryllium oxide sols has been determined.

5. A study has been made of the influence of the length of time of dialysis of hydrous beryllium oxide sols on:-
   a) flocculation values of various electrolytes
   b) the concentration of the sols
   c) the hydrogen ion concentration of the sols.

6. Theoretical explanations have been given for:—
   a) the variations of the flocculation values of the phosphates and of the acetates.
   b) the change of concentration of the sols with the length of time of dialysis.
   c) the change of flocculation values of electrolytes with the length of time of dialysis.
   d) the stability of hydrous beryllium oxide sols prepared by the method developed in this investigation.

Madison, Wisconsin
June, 1931.

THE SOLUBILITY RELATIONS OF THE ISOMERIC DIHYDROXYBENZENES[*]

BY W. H. WALKER, A. R. COLLETT AND C. L. LAZZELL

In previous communications to this Journal, Collett and Lazzell have reported a series of measurements of solubility for several systems of disubstituted benzene derivatives, namely the nitranilines,[1] the aminobenzoic acids,[2] and the nitrobenzoic acids.[3] A survey of the literature revealed that no systematic investigation of the solubilities of the dihydroxybenzenes in a series of solvents has ever been reported. Most of the data obtained by previous investigators has been collected by Seidell.[4] Lang[5] has obtained complete data for the solubilities of these isomers in acetone. The present investigation was undertaken with the primary object of obtaining data for another system of disubstituted benzene derivatives which could be used in our study of the solubility relations of systems of this type. Incidentally these solubility measurements are of value, since the dihydroxybenzenes are of considerable commercial importance.

In this paper are presented solubility measurements, from about 25°C to the respective melting temperature of the solute, for the three dihydroxybenzenes in benzene, carbon tetrachloride, water, acetone and absolute ethyl alcohol. Chloroform and ether were also used as solvents but it was found impossible to secure reliable data for quinol in chloroform and for resorcinol in ether. A few of the values recorded in Seidell and the International Critical Tables have been incorporated with the data presented herein, so as to secure greater ranges of temperature for purposes of interpolation. Each of the values so used has been properly identified in the tables which are included in the body of this report.

Materials

In the preliminary attempts to purify the isomers it was observed that the products of crystallization were susceptible to the influence of sunlight and air. Crystals, which were obtained in transparent condition, soon became discolored upon exposure to air and sunlight, especially in the case of quinol. Because of this fact all further purification of the isomers was carried out in a dark room and the purified materials were dried and kept in an atmosphere of hydrogen over calcium chloride or sulfuric acid. On observing these precau-

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[*] Presented before the Division of Physical and Inorganic Chemistry at the Cincinnati Meeting of the American Chemical Society, September, 1930.

[1] Collett and Johnston: J. Phys. Chem., 30, 70-82 (1926).

[2] Lazzell and Johnston: J. Phys. Chem., 32, 1331-41 (1928).

[3] Collett and Lazzell: J. Phys. Chem., 34, 1838-47 (1930).

[4] A. Seidell: "Solubility of Inorganic and Organic Compounds" 2nd Ed.: Vol I, pages 323, 575 and 580, Vol. II, pages 1234, 1383 and 1389.

[5] International Critical Tables, Vol. IV, page 111.

tions the discoloration of the purified material was avoided. This action of air and sunlight may account for the wide divergence in the melting points which have been recorded in the literature for these compounds. Two solvents, water and alcohol, were employed in the purification of the solutes by repeated crystallization; the process being carried out until no further change in the melting point was observed. All melting points were secured by the capillary tube method using thermometers certified by the Bureau of Standards and corrected for stem emergence.

Catechol: The best grade of catechol secured from the Eastman Kodak Company melted at 103-104° C; the purified product melted at 104.4-104.6° C. International Critical Tables give 105° C.

Resorcinol: Merck's U. S. P. resorcinol was purified and yielded a product melting at 109.4° C. International Critical Tables give 110° C.

Quinol: J. T. Baker's C. P. quinol was purified and yielded fine glistening needle shaped crystals, whose melting point was 172.9° C. International Critical Tables give 170.5° C.

Andrews, Lynn and Johnston,[1] purifying these isomers by sublimation in an atmosphere of carbon dioxide, obtained the following melting temperatures by means of time-temperature cooling curves using thermocouples: catechol, 104.3° C; resorcinol, 109.6-109.7° C; and quinol, 172.3° C. The melting points obtained by Andrews, Lynn and Johnston would naturally be expected to be somewhat lower than those obtained by the capillary tube method owing to the error of super heating which is inherent in this method.

Acetone: C. P. acetone was dried over calcium chloride and twice distilled using a Glinsky column; the fraction used boiled between 55.9-60.0° C at 747 mm.

Ethyl Alcohol: 95% ethyl alcohol was refluxed with lime, distilled, dried with sodium and redistilled twice; the major fraction boiled at 78.4° C under 760 mm pressure.

Benzene: Thiophene free Kahlbaum benzene was dried over sodium and distilled; redistillation yielded a major fraction boiling between 80.3-80.4° C at 760 mm.

Chloroform: Merck C. P. chloroform, dried over calcium chloride, was twice distilled and the final fraction was secured at 60.3-60.4° C and 737 mm.

Carbon tetrachloride: C. P. carbon tetrachloride, dried over calcium chloride was twice distilled using a Glinsky column; the major fraction boiled at 75.1-75.2° C at 740 mm.

Ether: U. S. P. material was washed three times with distilled water, dried over calcium chloride and twice distilled. The fraction boiling at 34.7-34.9° C at 760 mm was used.

Method

The experimental data on solubility presented in this article were chiefly obtained by the synthetic method. This consists essentially of subjecting known quantities of solute and solvent, which are sealed in small glass bulbs,

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[1] J. Am. Chem. Soc., 48, 1282 (1926).

to a very gradual rise in temperature and recording the point at which the last crystal goes into solution as the saturation temperature. Details of the method used in obtaining these solubility measurements may be found in a previous paper.[1] A sketch of the apparatus employed is shown in Fig. 1. One important modification in the procedure was made necessary by the fact that if air was allowed to remain in the small glass bulbs, oxidation of the solute apparently took place, especially at the higher temperatures. This difficulty was avoided by sweeping out the air with dry hydrogen just before the bulb was sealed.

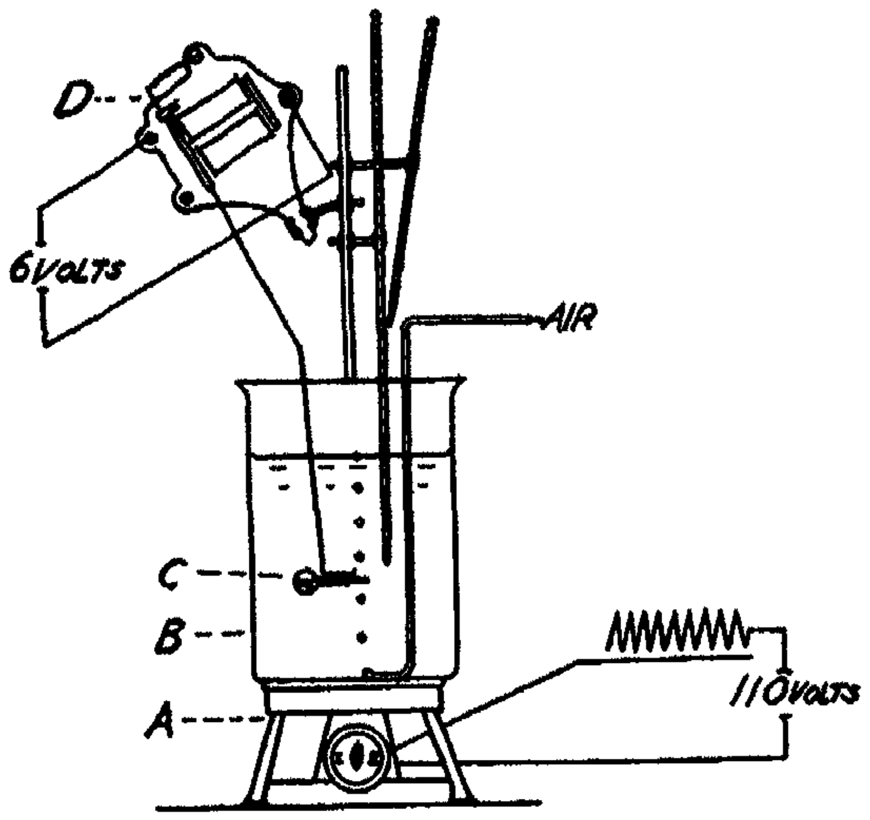

Fig. 1

A—Electric Hotplate—3 heats
B—4 liter Pyrex Beaker
C—Sample Bulb
D—Faraday six-inch bell with gong removed

Several determinations of solubility for these isomers at 25° C were made by an analytical procedure. The values so obtained are indicated in the table of results. The procedure was as follows: duplicate samples of the given solute were placed in 250 c.c. ground glass stoppered bottles with the chosen solvent; care being taken to have an excess of solute present. These bottles were then suspended in a thermostat at 25 ± 0.1° C and kept there for 24 hours with frequent shaking. The solute was then allowed to settle for an hour and samples of the solution (50 to 100 c.c.) secured by means of pipettes equipped with filter plugs; transferred to tared glass stoppered Erlenmeyer flasks and immediately weighed. The solvent was then removed by evaporation at room temperature under reduced pressure (about 20-30 mm) and the amount of solute present obtained by again weighing the flasks. The results presented in the tables are in all cases the mean of at least two measurements.

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[1] Collett and Lazzell: J. Phys. Chem., 34, 1839 (1930).

Experimental Results

The experimental measurements of solubility which were obtained for the three dihydroxybenzenes are listed in Tables I-III; C being the molal percentage of each isomer ($C = 100 N$, where N is the mol fraction of the dihydroxybenzene) and t, the temperature in degrees centigrade. A few values taken from Seidell (loc. cit.) are indicated by * and a few taken from the International Critical Tables by †. Values which were obtained by the analytical method previously described may be identified by ‡ which follows them. All other data given below were obtained by the synthetic method. Thermometers used were calibrated by comparison with thermometers certified by the United States Bureau of Standards.

TABLE I

Experimental Values of the Solubility of Ortho-dihydroxybenzene (Catechol) in Terms of Mol Percentage

Benzene		Chloroform		Carbon tetrachloride	
C	t	C	t	C	t
100.00	104.5	100.00	104.5	100.00	104.5
83.59	97.0	85.29	98.0	85.97	98.3
74.85	93.3	71.98	92.0	72.31	94.6
61.32	88.9	59.12	86.6	59.08	92.6
48.52	85.1	46.21	82.3	45.74	91.5
34.81	82.0	35.93	79.0	36.36	91.1
20.03	77.2	21.37	73.7	19.45	90.5
11.05	70.6	10.69	65.8	10.47	88.5
5.29	59.6	5.49	55.3	4.35	83.5
0.862‡	25.0	2.322‡	25.0	0.156‡	25.0

Acetone		Water		Alcohol	
C	t	C	t	C	t
100.00	104.5	100.00	104.5	100.00	104.5
82.21	91.0	47.11	66.2	96.05	101.7
70.78	77.4	37.23	57.1	69.84	81.5
58.66	53.2	37.10	56.7	59.10	67.9
55.1 †	42.2	23.01	41.2	45.45	43.1
49.5 †	18.0	6.88*	20.0		

Ether	
C	t
100.00	104.5
84.53	95.0
73.37	85.6
56.13	60.5
41.03	9.8

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* A. Seidell: "Solubilities of Inorganic and Organic Compounds," Vol. I and II, Second Edition.

† International Critical Tables, Vol. IV, page 111.

‡ Analytical data.

TABLE II

Experimental Values of the Solubility of Meta-dihydroxybenzene (Resorcinol) in Terms of Mol Percentage

Benzene		Chloroform		Carbon tetrachloride	
C	t	C	t	C	t
100.00	109.4	100.00	109.4	100.00	109.4
85.17	101.7	85.19	102.3	85.31	104.1
68.56	97.3	Two liquid layers		Two liquid layers	
Two liquid layers		5.68	90.0	0.84	100.7
9.34	93.4	5.15	89.4	0.65	95.4
5.16	87.4	0.521‡	25.0	0.231‡	25.0
2.95	79.3	Triple point 94.8°C.		Triple point 103.7°C.	
2.02	72.6				
1.14	61.1				
0.244‡	25.0				
Triple point 95.9°C.					

Acetone		Water		Alcohol	
C	t	C	t	C	t
100.00	109.4	100.00	109.4	100.00	109.4
85.49	98.3	72.15	88.5	81.92	95.8
67.93	75.1	63.28	80.5	67.85	83.8
59.12	51.8	53.95	70.7	53.13	60.1
49.5 †	12.0	48.62	64.4	39.34*	20.0
		37.80	50.4	37.2 *	10.4
		36.76	49.3		
		33.18	44.5		
		26.35	33.61		

* A. Seidell: "Solubilities of Inorganic and Organic Compounds," Vol. I and II, Second Edition.

† International Critical Tables, Vol. IV, page 111.

‡ Analytical data.

TABLE III

Experimental Values of the Solubility of Para-dihydroxybenzene (Quinol: Hydroquinone) in Terms of Mol Percentage

Acetone		Benzene		Water	
C	t	C	t	C	t
100.00	172.9	100.00	172.9	100.00	172.9
82.84	160.3	81.68	163.8	65.18	147.2
71.55	148.4	75.06	161.0	60.35	141.8
58.78	131.3	68.03	158.8	52.95	136.0
46.45	105.3	Two liquid layers		49.11	131.7
40.61	90.2	13.21	154.1	39.24	120.3
38.37	82.4	5.70	143.2	35.29	114.6
35.17	69.5	5.21	141.2	13.55	81.9
34.11	66.5	0.0364‡	25.0	10.25	75.3
29.54	58.8	Triple point 157.1°C.		1.19*	25.0
25.98	54.8			1.16*	20.0
21.25	45.6				

TABLE III (continued)

Ether		Carbon tetrachloride		Alcohol	
C	t	C	t	C	t
100.00	172.9	100.00	172.9	100.00	172.9
57.78	145.0	86.73	167.2	93.85	167.9
46.06	133.2	Two liquid layers		67.61	146.0
35.24	117.3	1.89	154.0	57.05	134.5
21.62	89.9	1.42	147.3	44.33	115.1
		0.85	137.3	34.71	91.2
		0.69	132.4	22.18	43.0
		0.0081‡	25.0		

Triple point 163.2°C.

* Seidell: "Solubilities of Inorganic and Organic Compounds," Vol. I and II, Second Edition.

† International Critical Tables, Vol. IV, page 111.

‡ Analytical data.

The results presented in the above tables have been plotted on a large scale in terms of C versus t and from these curves values of solubility have been obtained at ten degree intervals of temperature. Table IV was constructed from these values. In a few cases extrapolations were made beyond the experimental data but where this was done the values have been enclosed in parentheses. From the integrated form of the ideal solubility equations have been calculated the values listed under the column headed "Ideal." These calculations were based on a changing value for ΔH, the molal heat of fusion, with temperature. The dependence of ΔH on temperature has been expressed by the following equations which were obtained by Andrews, Lynn and Johnston[1] from calorimetric measurements.

Dihydroxybenzenes

Ortho $\Delta H = 3563 + 23.49t - 0.053t^2$ calories

Meta $\Delta H = 3172 + 23.25t - 0.061t^2$ calories

Para $\Delta H = 3167 + 23.00t - 0.022t^2$ calories

When these expressions are converted to functions of the absolute temperature they yield the following:

Ortho $\Delta H = -6800 + 52.43T - 0.053T^2$

Meta $\Delta H = -7724 + 56.57T - 0.061T^2$

Para $\Delta H = -4752 + 25.01T - 0.022T^2$

The insertion of these expressions for ΔH in the unintegrated form of the ideal solubility equation $\frac{d\ln N}{dT} = \frac{\Delta H}{RT^2}$ and its subsequent integration between the limits T_A and T gives

$$\log N_A = K_1\left(\frac{T_A - T}{T}\right) + K_2 \log \frac{T_A}{T} + K_3 (T_A - T)$$

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[1] J. Am. Chem. Soc., 48, 1281 (1926). Details of the method of calculation may be found in J. Phys. Chem., 29, 1041 (1925).

TABLE IV

Solubility of the Dihydroxybenzenes in Various Solvents as interpolated at a Series of Temperatures, expressed in Terms of Mol Percentage

Temp.	Ideal	$(CH_3)_2CO$	C_2H_5OH	C_6H_6	H_2O	CCl_4	$(C_2H_5)_2O$	$CHCl_3$
				Ortho (m. p. 104.5)				
20.0	11.80	50.08	(36.40)	0.60	6.88	0.10		2.10
30.0	17.70	52.20	(39.80)	1.15	14.10	0.35		2.70
40.0	24.35	54.48	43.95	1.80	21.95	0.60	(46.95)	3.30
50.0	31.62	57.58	48.92	3.02	30.78	0.95	(51.10)	4.32
60.0	39.70	61.55	54.37	5.35	40.25	1.18	55.86	7.38
70.0	48.71	66.42	60.38	10.60	51.65	1.75	61.55	14.70
80.0	59.75	72.65	68.20	29.55	64.69	3.15	68.50	39.20
90.0	73.44	81.35	80.09	64.30	78.70	15.80	77.85	67.18
100.0	91.35	93.00	93.55	90.32	93.20	89.42	92.40	89.45
104.5	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
				Meta (m. p. 109.4)				
20.0	17.95	51.55	39.34	(0.15)	18.65			
30.0	22.16	53.94	41.91	0.40	24.25	0.07		0.63
40.0	26.74	56.20	44.79	0.60	30.44	0.17		0.84
50.0	32.77	58.63	48.40	0.75	37.49	0.27		1.06
60.0	40.47	61.38	53.10	1.00	45.00	0.38		1.27
70.0	48.64	65.25	58.34	1.76	53.45	0.47		1.48
80.0	57.99	71.21	64.69	3.17	63.01	0.58		1.70
90.0	69.40	79.60	74.65	6.40	73.83	0.69		5.64
100.0	83.02	89.35	87.38	79.80	86.09	0.80		78.50
109.4	100.00	100.00	100.00	100.00	100.00	100.00		100.00

TABLE IV (Continued)

Para (m. p. 172.9)

Temp.	Ideal	$(CH_3)_2CO$	C_2H_5OH	C_6H_6	H_2O	CCl_4	$(C_2H_5)_2O$	$CHCl_3$
20.0	5.35	(11.30)	(17.25)	(0.02)	1.16			
30.0	6.76	(15.00)	(19.40)	(0.04)	1.35	0.01		
40.0	8.24	18.95	21.58	(0.20)	2.10	0.07		
50.0	10.25	23.45	23.89	(0.50)	3.35	0.14		
60.0	12.60	30.90	26.08	0.62	5.45	0.20	(8.39)	
70.0	15.54	35.22	28.57	0.80	8.42	0.27	(12.70)	
80.0	19.00	37.60	31.16	0.90	12.61	0.33	17.07	
90.0	23.01	40.58	34.25	1.00	18.29	0.40	21.66	
100.0	27.70	44.30	37.70	1.18	24.50	0.47	26.30	
110.0	33.32	48.35	41.83	1.41	31.07	0.54	31.28	
120.0	39.70	52.75	47.00	2.00	38.50	0.60	36.85	
130.0	47.90	58.18	53.60	3.08	47.30	0.68	43.51	
140.0	58.10	64.90	61.75	4.96	57.01	0.95	52.60	
150.0	69.39	72.71	71.56	8.10	68.28	1.60	63.63	
160.0	81.19	82.30	82.79	72.30	80.74	2.20	76.90	
172.9	100.00	100.00	100.00	100.00	100.00	100.00	100.00	

where N_A is the mol fraction of solute, T_A the melting temperature of the solute, and T any absolute temperature at which the solubility is desired. In the above expression all the constants have been grouped as K_1 K_2 and K_3, and below are listed the values calculated for each isomer.

	T_A	K_1	K_2	K_3
Ortho	377.5	3.931	−26.38	0.01156
Meta	382.4	4.408	−28.42	0.01332
Para	445.9	2.324	−17.60	0.00480

Discussion of Results

It will be noted that no data are given in the above tables for quinol in chloroform. Attempts were made to secure such data but it was noticed that successive determinations of the saturation temperatures of bulbs containing low concentrations of quinol gave lower and lower results. In higher mol concentrations of quinol the solute darkened with melting and two liquid layers were produced. In a particular instance one of the bulbs exploded with considerable violence. These phenomena indicated that there was a probable reaction between solute and solvent with ultimate decomposition. In order to further investigate this probable reaction between quinol and chloroform, a quantity of each of these substances was placed in an autoclave and heated to 125° C for several hours. A cursory examination of the reaction mixture revealed that only carbonaceous material remained and that considerable quantities of hydrogen chloride had been formed.

It will also be noted that no data are given for resorcinol in ether. When bulbs containing 3 to 45 mol per cent of resorcinol were made it was found that the saturation temperature was below 30° C. However on standing, a light brown solid precipitated and in the case of a bulb containing 5 mol per cent no apparent solution of this precipitate was noticed even at twenty degrees above the original saturation temperature. A bulb containing 55 mol per cent of resorcinol gave a saturation temperature of 69° on the first trial; 67° on the second and 65.5° on a third trial. Mol concentrations of resorcinol higher that 55 per cent formed solutions so viscous that proper agitation of the crystals in the bulb was impossible. Thus no reliable data could be obtained. This anomalous behavior of resorcinol in ether may be due to compound formation and seems worthy of further investigation.

Fig. 2 is a plot of the data obtained in this investigation. By referring to the curves for the ortho compound it will be noted that the solvents employed form curves of two general types; those showing only simple curvature, such as acetone, falling in one group and those showing double curvature, such as CCl_4, falling in another. The solvents in the first group are mainly polar liquids, while those of the second group are non-polar. It is interesting to note the position of the various curves with respect to the ideal curve. Those for alcohol, acetone and ether fall below the ideal; that for water almost coincides with the ideal, and those for chloroform, benzene and carbon tetrachloride are at a considerable distance above the ideal. Intersection of the alcohol and ether curves occurs at 69 mol per cent and of the ideal and water curve at 37 mol per cent.

Inspection of the curves obtained for the meta isomer show the same grouping of solvents, as was noted in the case of the ortho compound; the polar liquids, such as acetone, possessing high solvent power and the non-polar liquids low solvent power. In fact the non-polar group of solvents possesses such low solvent power that the solute melts to form a second liquid layer before solution takes place. No attempt was made in the cases of chloroform, carbon tetrachloride and benzene to determine the critical solution temperature and no particular efforts were made to secure accurate values for the triple point. Only one pair of curves intersect, namely that for chloroform

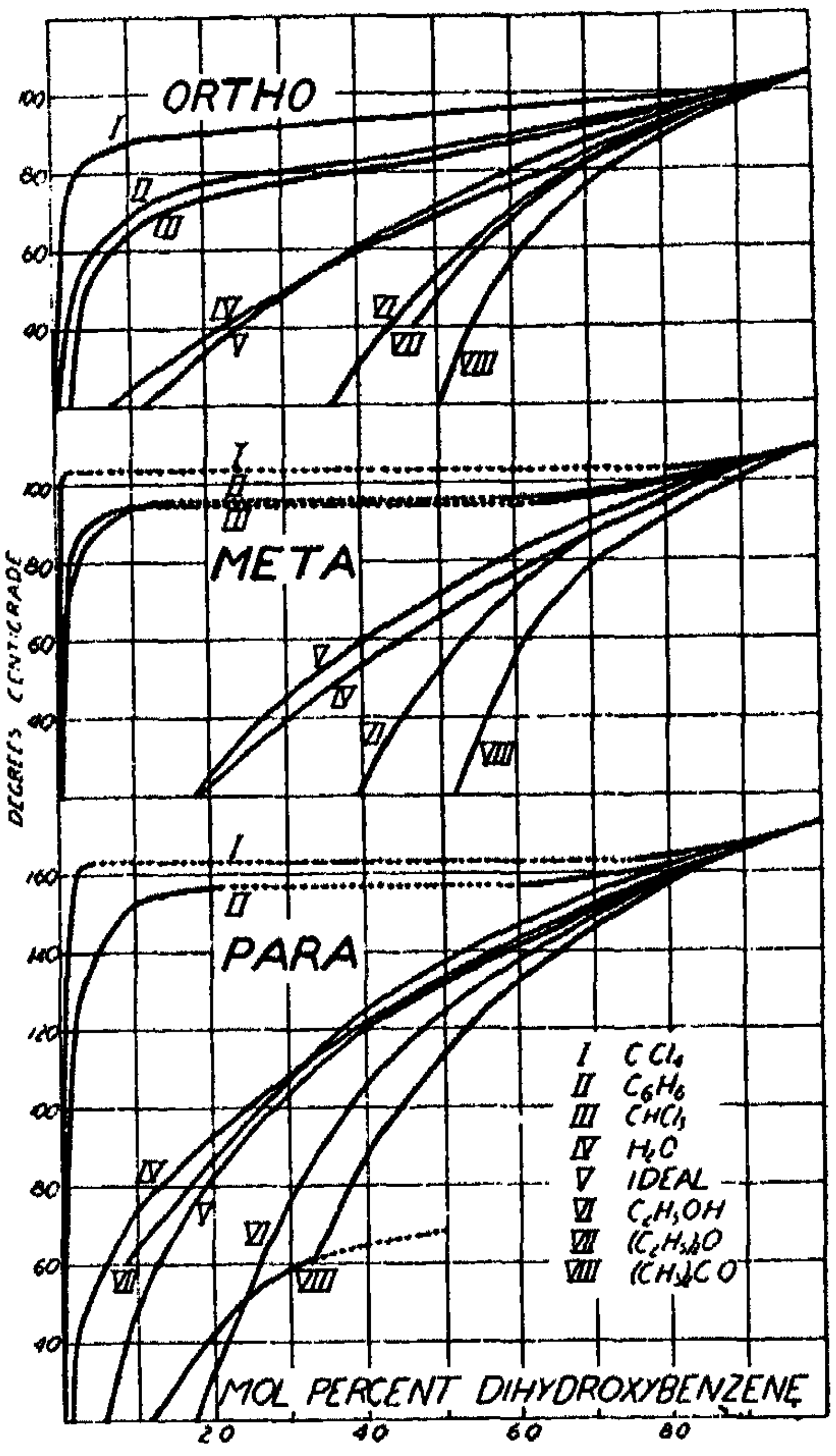

FIG. 2

and benzene. For resorcinol the curves for the polar solvents all lie below the ideal and non-polar all lie above.

Referring to the curves for para dihydroxybenzene it will be observed that again the polar liquids are the best solvents; the non-polar group forming two liquid layers as in the case of resorcinol. As before the critical solution temperature was not determined and only the approximate value of the triple point recorded. Two intersections will be noted, water and ether at 32 mol per cent and acetone and alcohol at 24 mol per cent. This last intersection is discussed more fully in a succeeding paragraph since it is produced by compound formation. In this instance the acetone and alcohol curves lie below, the water and ether slightly above, and the chloroform and benzene curves far above the ideal curve.

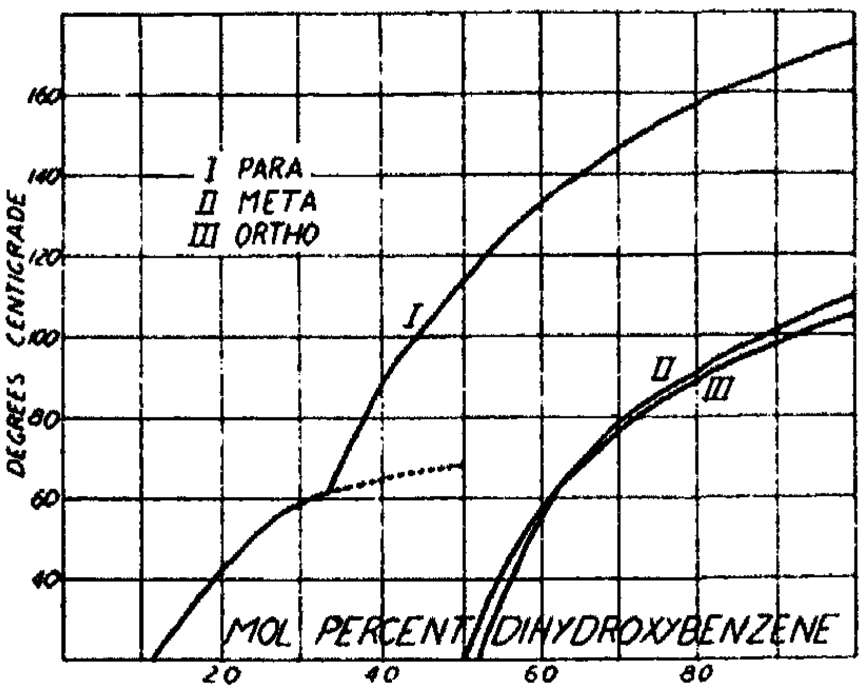

Fig. 3

A graph of the solubilities of the three isomers in acetone is shown in Fig. 3. This figure is of interest for two reasons: first because of the crossing of the solubility curves for catechol and resorcinol at about 63 mol per cent, signifying that resorcinol is the more soluble below 64° C even though its melting temperature is higher than that of catechol; and second because of the abrupt change of slope in the curve for quinol. This break in the curve occurs at 62° and 33 mol per cent and indicates compound formation between quinol and acetone. When the curve for the compound is extended as shown by the dotted line, in Fig. 3, a maximum is reached at about 50 mol per cent which indicates an unstable compound of 1 mol of acetone to one of quinol with a melting point of 68 to 69° C. Lang[1] had previously worked on the solubility of the isomers in acetone and our results show good agreement with his in the cases of catechol and resorcinol. Our data for quinol, however, do not agree at all since he reports the formation of a compound of 1 mol of acetone and 1 mol of quinol which has a melting temperature of 148° C. Since the original data

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[1] International Critical Tables, Vol. IV, page 111.

of Lang is found in his thesis (Zurich) and appears not to have been published elsewhere it has not been available for comparison with the data as published in the International Critical Tables. This compound formed by 1 mol of acetone and 1 mol of quinol was previously reported by S. Habermann[1] who noted its very unstable character when exposed to air.

The solubility curves for the three isomers in ethyl alcohol all show the same type of curvature. The values given by Speyers[2] for resorcinol in alcohol deviate considerable at temperatures above 40° from those recorded in this article. Water, of all those investigated, is the solvent which most nearly forms ideal solutions with the dihydroxybenzenes; the curve for quinol lying just above the ideal, that for resorcinol below and that for catechol crossing the ideal curve. Comparison of our data with that of Speyers (loc. cit.) for resorcinol and water again shows deviations which increase with increasing temperatures. Apparently there seems to be some factor in the method employed by Speyers which causes inaccuracies in the results obtained at the higher temperature. This error in the method used by Speyers has also been observed and discussed by other workers,[3] who were unable to check data given by Speyers. Ether forms solubility curves of the same general type with catechol and quinol and may be considered a very good solvent for these compounds. As previously explained no reliable data could be obtained for resorcinol in ether. Chloroform was not found to be very satisfactory as a solvent since it possesses low solvent power for the dihydroxybenzenes. The curve for catechol shows a reverse curvature which indicates that the region of two liquid layers is not far distant. Resorcinol in chloroform has a region of two liquid layers between 12-62.5 mol per cent. Quinol also reached this region of two liquid layers with chloroform but as stated at the beginning of this discussion a reaction apparently takes place with decomposition of the solute. Benzene is a very poor solvent for quinol and resorcinol since in these two cases a region of two liquid layers exists, for the former between 5 and 75 mol per cent and for the latter between 16 and 60 mol per cent. Although there is only a difference of five degrees between the melting point of catechol and resorcinol yet that is sufficient to remove the catechol and benzene from the region of two liquid layers. The curve does however show the double curvature characteristic of the near approach to that field. The only data available in the literature for comparison was that of Rothmund.[4] The agreement is not very close except in the case of the triple point determination and a few determinations at lower temperatures. By far the most unsatisfactory solvent for the dihydroxybenzenes is carbon tetrachloride which forms two liquid layers with quinol and resorcinol over the greater range of concentrations. In case of catechol no region of two liquid layers was observed but it will be noted that the greater portion of the curve lies about parallel to the concentration axis, indicating a very close approach to the four phase region.

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[1] Monatsheft., 5, 329 (1884) through Abstracts J. Chem. Soc., 48, 53 (1885).

[2] Seidell: loc. cit.

[3] H. Lee Ward: J. Phys. Chem., 30, 1317 (1926); Sunier: J. Phys. Chem., 34, 2582 (1930).

[4] Z. physik. Chem., 26, 475 (1898).

Comparison of this system of isomers with the nitro benzoic acids (loc. cit.) shows considerable variation with respect to the solvent power of the various liquids over a range of temperature. Owing to the frequent crossings of the curves for this system it is impossible to assign a definite order of solubility for the solvents, as was done for the nitro benzoic acids, since this may vary for the same isomer depending on the particular temperatures selected. A consideration of the completed results of this investigation yields further evidence in support of the statement made in a previous communication[1] that the validity of certain rules of solubility which are current may be seriously questioned.

A study of the curves in Fig. 1 for the isomers in benzene reveals that if a mixture containing all three of the isomers were subjected to repeated crystallization from this solvent it would be possible to obtain pure catechol. Details of the method used to calculate the number of crystallization necessary for complete separation may be found in a previous article.[2]

Summary

The solubility curves of the three dihydroxybenzenes were determined from approximately 25°C to the respective melting temperature, in carbon tetrachloride, benzene, ethyl alcohol, water, acetone, chloroform and ether. Reliable data for resorcinol in ether, and quinol in chloroform could not be obtained. The synthetic method was employed except in a few determinations at 25°C which were secured by an analytical method. Evidence supporting the existence of an unstable molecular compound of one mol of quinol to one of acetone has been obtained.

A brief discussion of the results and a comparison with previous data are given.

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[1] Collett and Lazzell: J. Phys. Chem. 34, 1846 (1930).

[2] Collett and Johnston: J. Phys. Chem., 30, 70 (1926).

CATALYTIC OXIDATION OF ETHYL ALCOHOL

BY ALLAN R. DAY

In previous work[1] quantitative data were obtained on the behavior of the rare earth oxides as catalysts for vapor phase oxidation as compared with copper oxide as a catalyst. The effect of addition of various amounts of a rare earth oxide (Sm_2O_3) to copper oxide was also studied. In order to obtain more positive information as to the role which the rare earth oxide plays, it was decided to study the effect of samarium oxide on the catalytic properties of metallic silver in the oxidation of ethyl alcohol.

Experimental

The apparatus used was essentially the same as in the previous work. The only exception being that the steam jacket which was used as a preheater was replaced by a pyrex coil enclosed in an asbestos box and maintained at a uniform temperature by means of a small burner. The burner was regulated so that the mixture of air and alcohol left the coil at a temperature of 105°C ± 1°. Preliminary work showed that the temperature of this gaseous mixture was an important factor. Up to 145°C. the yield of aldehyde was not affected but above that temperature an appreciable drop in yield was noted, even when the catalyst temperature would otherwise have been low. It is obvious that unless the catalyst temperature can be kept constant two variables are bound to enter into work of this kind, namely, catalyst temperature and space-velocity. The catalyst temperature might be kept constant either by regulating the temperature of the incoming gases or by cooling the catalyst chamber where otherwise the catalyst temperature would be too high. As stated above, however, when the inlet gases were heated above 145°C. an appreciable drop in yield of aldehyde was noted even when otherwise the catalyst temperature would have been low. As a result of this preliminary work a temperature of 105°C. was adopted and used throughout the investigation.

A satisfactory method for cooling the catalyst tube, thereby regulating the catalyst temperature, has not been found. Such a method would indeed have to be flexible in order to keep the catalyst temperature constant while other factors such as thermostat temperature and air rate are being varied.

A further attempt was made to keep the catalyst temperature constant by supplying external heat to the tube by means of a bath or furnace, but here again difficulties were encountered. The yields of aldehyde decreased, the yields of acetic acid increased and at the same time the total amount of alcohol accounted for, as aldehyde, acetic acid and unchanged alcohol, decreased.

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[1] Lowdermilk and Day: J. Am. Chem. Soc., 52, 3535 (1930).

Since these efforts to eliminate one of the variables were unsatisfactory, usually leading to decreased yields of the desired product (acetaldehyde) they were abandoned and the following process adopted.

The oxidation process was carried out by passing measured quantities of dry air through the vaporizer, containing the ethyl alcohol, maintained at constant temperature by means of a thermostat. The alcohol-air mixture passed through the preheater and then into the catalytic chamber, the catalyst having been previously heated to about 350°C. by means of a small burner. The heat of reaction was sufficient to maintain the reaction after it had once started. The catalyst temperatures were measured by means of a quartz thermometer, the bulb of which was buried in the catalyst. The same amount of catalyst was used for all of the runs. In each case the catalyst chamber (length 15 mm., diameter 17 mm.) was filled with the impregnated 12 mesh pumice. The length of each run was carefully timed by means of a stop-watch. The products of the reaction were collected in several absorption flasks which were part of the cooling system. The flasks were then emptied and rinsed and the resulting solution diluted to a definite volume. Aliquots of this solution were taken for analysis.

The following types of catalysts were employed:

A. 2.7928 g. of silver (equivalent to 3 g. of Ag_2O) deposited on 9 cc. of 12 mesh pumice.

B. 2.7858 g. of silver (equivalent to 2.9925 g. of Ag_2O) and 0.0075 g. of samarium oxide deposited on 9 cc. of 12 mesh pumice.

C. 2.7788 g. of silver (equivalent to 2.985 g. of Ag_2O) and 0.015 g. of samarium oxide deposited on 9 cc. of 12 mesh pumice.

D. 2.7648 g. of silver (equivalent to 2.97 g. of Ag_2O) and 0.03 g. of samarium oxide deposited on 9 cc. of 12 mesh pumice.

E. 2.6532 g. of silver (equivalent to 2.85 g. of Ag_2O) and 0.15 g. of samarium oxide deposited on 9 cc. of 12 mesh pumice.

These catalysts were prepared in the same manner as the catalysts used in the previous work. Duplicate catalyst preparations, for each type of catalyst (A, B, C, D and E) were used in order to determine whether the variations in yield might be due to variations in catalyst preparation. It was found that duplicate catalyst preparations gave excellent check results and consequently the small but constant variations recorded in Table I can scarcely be attributed to the use of various catalyst preparations.

The ethyl alcohol (95 percent) which was used for the experiments was free from aldehyde in most cases. In some few cases the alcohol gave a slight test with Schiff's reagent.

Determination of Acetaldehyde.—The aldehyde was determined by Ripper's method. This method gave good check results, usually varying at the maximum about 0.3% for two or more analyses of the same aldehyde solution.

Determination of Acetic Acid.—To a definite amount of standard NaOH solution was added a little barium chloride solution and a few drops of phenol-

TABLE I

Catalyst	Air rate L/M	Bath T°C.	Catalyst T°C.	C_2H_5OH-O_2 ratio moles C_2H_5OH/moles O_2	Moles of C_2H_5OH passed over catalyst	Moles of CH_3CHO formed	Yields of CH_3CHO %	Material yields of CH_3CHO %	Moles of CH_3COOH formed	Moles of C_2H_5OH recovered	% Loss of C_2H_5OH
A	1.08	45	478	1/0.883	1.06	0.591	55.7	78.3	0.063	0.306	9
	1.08	45	482	1/0.891	1.002	0.563	56.2	77.5	0.062	0.276	10.7
	0.83	45	437	1/0.881	0.963	0.584	60.6	79.0	0.043	0.224	12.8
	0.83	45	434	1/0.890	1.065	0.640	60.1	78.8	0.044	0.253	12
	0.60	45	369	1/0.895	0.947	0.633	66.7	80.0	0.034	0.156	13.1
	0.60	45	371	1/0.899	1.010	0.678	67.1	80.7	0.040	0.170	12.1
	0.83	47	439	1/0.761	1.028	0.659	64.1	80.1	0.050	0.206	10.9
	0.83	47	444	1/0.766	0.997	0.643	64.4	79.9	0.053	0.193	10.8
	0.60	47	370	1/0.762	1.067	0.756	70.8	81.6	0.044	0.141	11.8
	0.60	47	371	1/0.768	1.058	0.745	70.4	81.5	0.048	0.144	11.4
	0.83	50	438	1/0.620	0.958	0.661	68.9	82.4	0.049	0.156	9.6
	0.83	50	442	1/0.614	0.984	0.681	69.2	81.9	0.053	0.153	9.8
	0.60	50	373	1/0.626	0.939	0.698	74.3	84.2	0.049	0.111	8.6
	0.60	50	367	1/0.630	1.083	0.810	74.7	85.1	0.051	0.131	9.1
	0.83	53	424	1/0.529	0.928	0.688	74.1	88.3	0.050	0.149	4.4
	0.83	53	429	1/0.521	0.994	0.734	73.8	88.9	0.056	0.169	4.0
	0.60	53	367	1/0.513	0.907	0.709	78.1	89.5	0.046	0.115	4.0
	0.60	53	373	1/0.525	1.088	0.844	77.5	89.9	0.062	0.150	2.9
	0.94	54	471	1/0.495	0.924	0.663	71.7	88.8	0.051	0.178	3.4
	0.94	54	469	1/0.503	0.973	0.694	71.3	88.1	0.060	0.186	3.3
	0.77	54	428	1/0.492	1.073	0.794	74.0	90.7	0.053	0.197	2.7
	0.77	54	422	1/0.501	1.007	0.750	74.5	90.1	0.046	0.175	3.5
	0.60	54	369	1/0.501	0.896	0.703	78.4	91.6	0.043	0.129	2.4
	0.60	54	376	1/0.509	0.953	0.742	77.8	91.1	0.052	0.139	2.1

TABLE I (Continued)

Catalyst	Air rate L/M	Bath T°C.	Catalyst T°C.	C_2H_5OH–O_2 ratio moles C_2H_5OH/moles O_2	Moles of C_2H_5OH passed over catalyst	Moles of CH_3CHO formed	Yields of CH_3CHO %	Material yields of CH_3CHO %	Moles of CH_3COOH formed	Moles of C_2H_5OH recovered	% Loss of C_2H_5OH
B	0.75	50	477	1/0.616	1.029	0.742	72.1	81.1	0.057	0.114	11.2
	0.75	50	473	1/0.624	0.905	0.657	72.6	81.6	0.048	0.100	11.4
	0.45	50	372	1/0.636	0.926	0.711	76.7	85.3	0.036	0.093	9.2
	0.45	50	372	1/0.633	0.994	0.766	77.1	84.7	0.043	0.090	9.5
	0.83	54	478	1/0.496	1.029	0.775	75.3	82.0	0.057	0.085	10.8
	0.83	54	483	1/0.496	0.995	0.753	75.6	81.4	0.057	0.070	10.5
	0.65	54	446	1/0.503	0.954	0.742	77.7	88.5	0.054	0.116	4.4
	0.65	54	444	1/0.507	0.998	0.779	78.0	88.9	0.053	0.122	4.4
	0.45	54	367	1/0.513	1.007	0.805	79.9	91.6	0.042	0.130	2.9
	0.45	54	369	1/0.511	1.078	0.858	79.5	92.6	0.039	0.152	2.6
C	0.83	50	474	1/0.620	0.905	0.630	69.5	80.2	0.048	0.120	11.8
	0.83	50	479	1/0.618	0.951	0.657	69.1	81.0	0.052	0.140	10.7
	0.49	50	373	1/0.633	0.922	0.689	74.7	83.5	0.038	0.097	10.6
	0.49	50	371	1/0.626	1.051	0.791	75.2	83.9	0.038	0.109	10.7
	0.83	54	458	1/0.497	0.964	0.744	77.1	88.2	0.053	0.121	4.7
	0.83	54	462	1/0.492	0.934	0.719	76.9	88.5	0.057	0.122	3.8
	0.71	54	445	1/0.495	0.989	0.763	77.1	89.1	0.054	0.133	3.9
	0.71	54	445	1/0.503	1.024	0.795	77.6	91.8	0.060	0.158	1.1
	0.49	54	369	1/0.508	0.974	0.763	78.3	91.6	0.054	0.141	1.6
	0.49	54	372	1/0.509	1.008	0.795	78.8	92.1	0.053	0.145	1.4

TABLE I (Continued)

Catalyst	Air rate L/M	Bath T°C.	Catalyst T°C.	$C_2H_5OH-O_2$ ratio moles C_2H_5OH/moles O_2	Moles of C_2H_5OH passed over cayalyst	Moles of CH_3CHO formed	Yields of CH_3CHO %	Material yields of CH_3CHO %	Moles of CH_3COOH formed	Moles of C_2H_5OH recovered	% Loss of C_2H_5OH
D	0.77	50	468	1/0.616	0.884	0.633	71.6	81.5	0.038	0.108	11.8
	0.77	50	472	1/0.614	0.951	0.674	70.8	79.2	0.044	0.100	13.9
	0.60	50	416	1/0.621	0.983	0.732	74.3	79.6	0.035	0.064	15.4
	0.60	50	415	1/0.615	1.036	0.766	73.9	79.7	0.036	0.075	15.3
D	0.65	54	441	1/0.497	0.933	0.682	73.1	83.1	0.046	0.113	9.8
	0.65	54	444	1/0.502	0.943	0.693	73.5	86.6	0.045	0.115	9.5
	0.49	54	370	1/0.506	0.925	0.699	75.5	86.5	0.034	0.127	7.0
	0.49	54	371	1/0.503	1.036	0.781	75.3	88.1	0.033	0.150	6.9
E	0.83	50	477	1/0.613	0.974	0.689	70.7	78.5	0.033	0.097	15.9
	0.83	50	474	1/0.620	0.953	0.670	70.3	78.0	0.028	0.095	16.7
	0.49	50	368	1/0.627	1.050	0.770	73.3	79.0	0.032	0.076	16.3
	0.49	50	371	1/0.630	0.933	0.690	73.9	79.8	0.029	0.069	15.5
	0.75	54	460	1/0.493	0.957	0.706	73.7	81.5	0.034	0.091	13.1
	0.75	54	460	1/0.495	1.014	0.747	73.6	81.3	0.035	0.096	13.4
	0.49	54	372	1/0.508	0.939	0.699	74.4	87.1	0.030	0.137	7.7
	0.49	54	369	1/0.505	1.023	0.766	74.7	87.6	0.037	0.149	6.9

phthalein. The resulting solution was titrated with a portion of the condensate until the red color was discharged. This adaptation of Winkler's method gave excellent results.

Determination of Unchanged Ethyl Alcohol.—A suitable aliquot of the condensate was treated with an excess of ammoniacal silver nitrate and heated on a steam bath for 2-3 hours under a slight pressure. The resulting mixture was distilled until about two-thirds of the solution passed over. The distillate was just acidified with sulphuric acid and again distilled. This method yielded a distillate which gave no tests for aldehyde or acetic acid. The alcohol content of this solution was determined by means of a dipping refractometer. The results obtained checked fairly well, usually within 0.5-0.8%.

The results obtained for duplicate runs under various conditions are given in Table I. Space does not permit recording all the data obtained. Only the more important results are included. The process yields were based upon the total amount of alcohol used, while the material yields were based upon the actual amount of alcohol oxidized.

A minimum catalyst temperature of about 370°C. was used throughout. Below that temperature the reaction was more difficult to maintain, but apparently the reaction will take place as low as 320°-330°C., although with somewhat lower yields due to the irregularity of the reaction. At a temperature of about 370°C. glowing was often not apparent, even in a darkened room, but the reaction seemed to maintain itself uniformly.

Discussion of Results

Fig. 1 and A in Table I show the effect of various alcohol-oxygen ratios on the yields of acetaldehyde when silver was used as the catalyst (catalyst A). It will be noted that the curve for a thermostat temperature of 54°C shows the highest yields. At a bath temperature of 54°C. the ratio, moles C_2H_5OH/moles O_2, was 1/0.492 to 0.509. The theoretical ratio calculated for the same conditions is 1/0.5. It is interesting to note that with metallic silver the highest yields were obtained using the theoretical oxygen supply, while with copper (in previous work) considerably more than the theoretical oxygen supply was necessary. The yields of aldehyde were appreciably lowered by working at thermostat temperatures higher than 54°C. Lowering of the thermostat temperature also produced a marked decrease in the yields of aldehyde.

Moreau and Mignonac[1] have used silverized asbestos as a catalyst for the oxidation of ethyl alcohol to acetaldehyde. They reported a yield of acetaldehyde, using reduced silver as the catalyst, which corresponded to an 84 percent conversion of the alcohol used. They added the theoretical amount of air in two installments to the alcohol vapor, the outlet gases from the first reaction tube being cooled before adding the second installment of air and passing into the second reaction tube.

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[1] Moreau and Mignonac: Compt. rend., **170**, 258 (1920).

Simington and Adkins[1] using silver gauze and working at a bath temperature of 46°C. obtained a 43.7 percent yield of acetaldehyde. They obtained a 76 percent yield, however, when they used a catalyst composed of 90% Cu and 10% Ag.

Most of the earlier work has been carried out at lower thermostat temperatures and higher air rates, and as a result there would have been available more oxygen per gram of alcohol. The present investigation shows rather definitely that a bath temperature of 54°C. represents the optimum temperature.

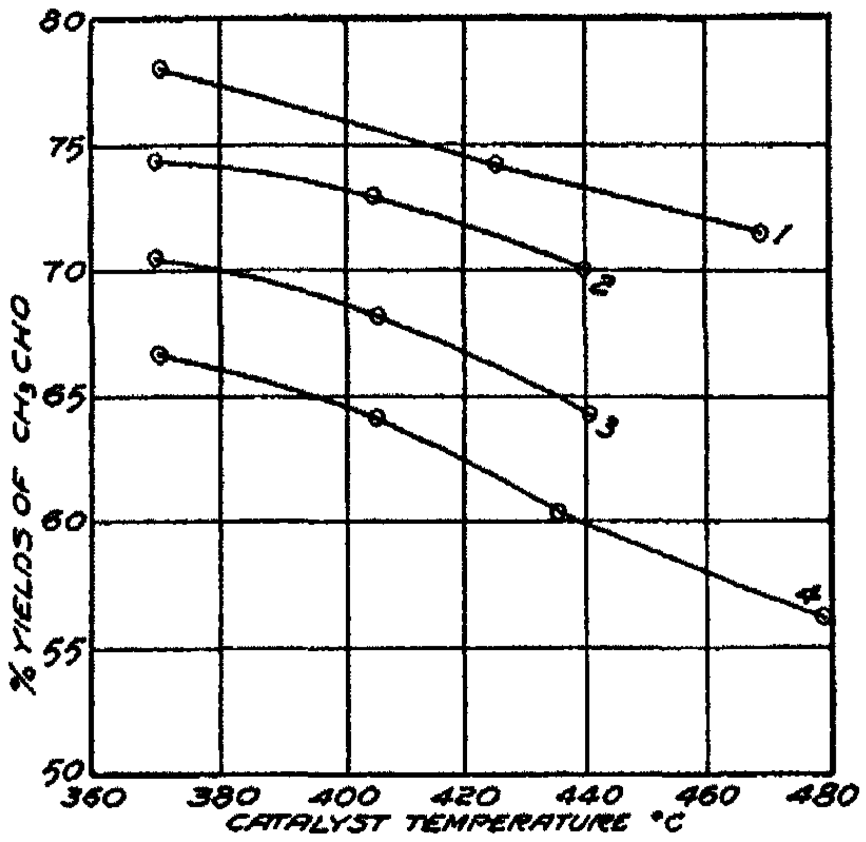

Fig. 1

(1) Bath at 54°; (2) Bath at 50°; (3) Bath at 47°; (4) Bath at 45°.

The results recorded in Table I (B and C) show that the presence of small amounts of samarium oxide (.25% and .50% respectively) with silver slightly increases the process yields of aldehyde. These results are more readily interpreted from a study of Fig. 2. It is interesting to compare the slopes of curves (1) and (2) with the slope of (3). At a temperature of about 370°C. the differences in process yields are quite small but as the catalyst temperature rises the differences become larger. This is just the opposite of what one would expect from previous experience. The material yields for the optimum conditions (catalyst temperature about 370°C.) remain about the same as with the pure silver catalyst, but as the catalyst temperature rises they fall off much more rapidly than in the case of the silver catalyst. These variations in process and material yields remained consistent throughout the work even when duplicate catalyst preparations were used. It would seem that the presence of small amounts of the rare earth oxide does increase the process yields of acetaldehyde and at the same time exerts a stabilizing influence on

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[1] Simington and Adkins: J. Am. Chem. Soc., 50, 1449 (1928).

the process yields of aldehyde as the catalyst temperature rises. The same cannot be said of the material yields for, except at the optimum conditions, they are materially decreased.

The results recorded in Table I (D and E) show that the presence of larger amounts of samarium oxide (1% and 5% respectively) causes a marked lowering of the yields of acetaldehyde. Here again, however, it will be noted that the decrease in process yields was not so rapid as in the case of the silver catalyst. It was thought at first that this rather marked lowering of process and material yields was due to further oxidation and possibly to increased decomposition of the aldehyde. Other facts, however, do not confirm this explanation. It was found, at a thermostat temperature of 54°C., that when the Sm_2O_3 content reached 5 percent, the amount of unsaturated compounds produced during the reaction became somewhat larger. This was determined by bromine absorption. No effort was made to identify the products, only the relative amounts being measured. This might indicate that when the rare earth oxide occupies a sufficient area of the contact surface it may, in small part, function as a dehydrating agent, especially if an excess of air for the oxidation of alcohol to aldehyde is not present.

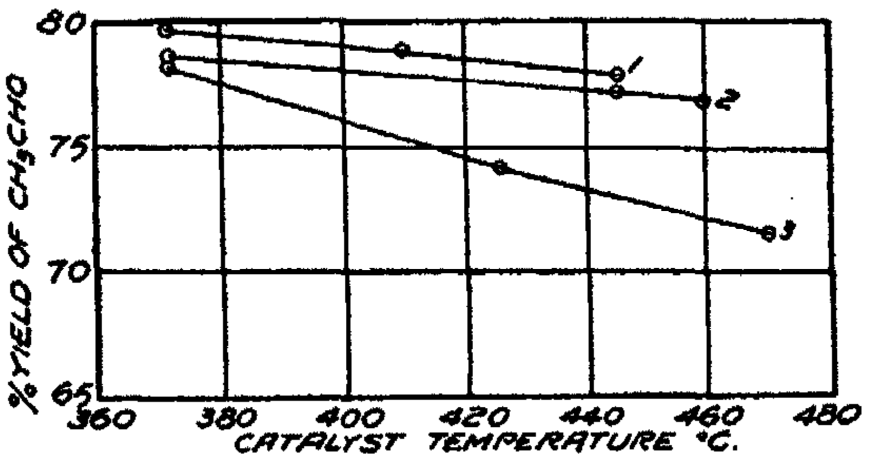

FIG. 2

(1) Catalyst, B; (2) Catalyst, C; (3) Catalyst, A. Bath at 54° C.

The exact role played by the rare earth oxides can not be based upon one set of results. Further work is needed on the higher alcohols and other compounds before any general conclusions can be made.

Summary

1. Data have been obtained showing the effect produced on the catalytic activity of silver by the addition of small amounts of samarium oxide.

2. It has been shown that the presence of small amounts of samarium oxide (at a low catalyst temperature, about 370°C.) slightly increases the yields of acetaldehyde.

3. Higher yields of acetaldehyde have been obtained by a one step vapor phase oxidation of ethyl alcohol than have been previously reported from similar methods.

KINETICS OF THE REACTION BETWEEN POTASSIUM PERSULFATE AND SODIUM THIOPHENOLATE

BY T. B. DOUGLAS

Apparently no work has been done on the kinetics of the oxidation of a mercaptan to the corresponding disulfide. In this paper are given the results of a study of the velocity of the reaction between potassium persulfate and sodium thiophenolate in alkaline solution.

The kinetics of a similar reaction, that between a persulfate and an inorganic iodide, have been investigated.[1] Although the reaction is stoichiometrically trimolecular, the results indicate that the reaction whose velocity was being measured was bimolecular, and consequently that the process took place in two steps, one slow and the other relatively fast.

Experimental Procedure

Baker's C. P. potassium persulfate was used. This salt was carefully analyzed by reaction with ferrous sulfate and back-titration with permanganate, the average value obtained being 97.6 percent purity, the contamination probably being $KHSO_4$ from decomposition. All standard solutions of the salt were prepared on the basis of this figure.

The thiophenol first used was prepared by the reduction of Eastman's benzene sulfonyl chloride, and collection of the fraction boiling 166°-169° (uncorr.). The second supply of thiophenol was prepared by the treatment of phenyl magnesium bromide with sulfur, and collection of the fraction boiling 168°-169° (uncorr.).

The standard solutions of $K_2S_2O_8$ were prepared by weighing the salt, and these solutions were used within a day after preparation to avoid the error due to slow decomposition. In preparing both reaction-solutions, only water which had previously been boiled could be used, since the sodium thiophenolate, if dissolved in ordinary water, was found to decompose at the rate of 5 percent per hour because of oxidation by dissolved oxygen. Care was taken not to agitate the solutions and thus introduce air, in the course of their preparation.

The sodium thiophenolate solutions were prepared by dissolving approximately twice the calculated amount of thiophenol in sodium hydroxide of the proper titre, removing the solution by filtration or decantation, and diluting with sodium hydroxide of the same titre just before use, in accordance with a standardization of the thiophenolate solution just performed. This was necessary because of a slow but inevitable drop of titre of the thiophenolate solution due to dissolved oxygen. A standardization of this solution im-

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[1] A. von Kiss and L. von Zombory: Rec. Trav. chim., 46, 225 (1927).

mediately after the velocity measurement gave data from which to calculate the correction on the thiophenolate concentration in the reaction-mixture, since this concentration was slowly decreasing, during the course of the slow reaction, from that calculated from oxidation by persulfates alone.

Titration of the thiophenolate solutions was performed with 0.05 N aqueous iodine after diluting the thiophenolate with water to about 0.005 N and acidifying it (no precipitation of thiophenol taking place at this dilution). An attempt to titrate the thiophenol in alkaline solution with iodine, acidify, and then back-titrate with thiosulfate showed that in alkaline solution iodine oxidizes thiophenol further than to disulfide and in no way which could be followed quantitatively.

The concentration of excess NaOH in the thiophenolate solution, definite for each series of determinations, fell between 0.005 N and 0.25 N. One determination was made on each individual reaction-mixture. A quantity of the persulfate solution and a quantity of the thiophenolate solution each containing 0.001 equivalent of reactant were set into a thermostat at 25° (±0.1°), and, after the temperature of the thermostat had been reached, the persulfate was poured into the thiophenolate, rapid mixing being effected by vigorous swirling of the flask. The reaction was arrested by pouring the mixture into a liter of water, and, after acidification and addition of starch, was titrated with iodine. A correction of 0.40 ml of 0.05 N iodine, amounting to 2 to 7 percent of the total titration-reading, was found necessary, because of the large amount of water present.

Results

The velocity constants are calculated on the basis of a bimolecular and also a trimolecular reaction. The values obtained are given in Table I.

Discussion

The data show clearly that the reaction whose velocity is being measured is bimolecular. Hence the total reaction is really composed of two reactions, one being much more rapid than the other. Attempting an atomistic picture, one conceives that by a slow reaction there is formed a very reactive intermediate product, which disappears approximately as fast as it is formed. Such a case might be expressed by the following equations:

Slow........$S_2O_8^{--} + C_6H_5S^- \rightarrow S_2O_8^{---} + C_6H_5S;$

$(2C_6H_5S \rightarrow C_6H_5S.SC_6H_5;)$

Fast........$S_2O_8^{---} + C_6H_5S^- \rightarrow 2SO_4^{--} + C_6H_5S.$

As the concentration of OH^- is increased, the velocity constant becomes larger. Hence the OH^- acts catalytically. Also, the velocity constant varies with varying concentration of the reactants. The author proposes the following hypothesis as a possible explanation of the mechanism of this catalysis.

TABLE I

Reaction Velocities in Oxidation of Sodium Thiophenolate by Potassium Persulfate at 25°C

(The concentration of C_6H_5SNa indicated below is the initial one. Concentrations of the two reactants are equivalent unless otherwise stated. Calculation of the velocity constants given below is based on the *corrected* initial concentrations referred to above. These corrections are not noted here.)

Progress of Reaction percent	Time minutes	k bimolecular	k trimolecular
A. C_6H_5SNa = 0.0025 M			
a. NaOH = 0.01 M			
12	16	3.40	1450
20	28	3.55	1590
28	47	3.35	1610
49	120	3.25	1920
		Average: 3.40	
b. NaOH = 0.0113 M			
18	25	3.50	1560
c. NaOH = 0.025 M			
12	14	4.05	1750
13	14	4.25	1840
18	25	3.95	1750
21	25	4.20	1890
29	40	4.00	1910
30	40	4.25	2070
39	64	3.95	2080
51	120	3.55	2150
53	121	3.70	2290
		Average: 4.00	
B. C_6H_5SNa = 0.005 M			
a. NaOH = 0.005 M			
12	8	3.50	760
26	19	3.70	870
40	36	3.60	950
69	120	3.65	1530
		Average: 3.60	
b. NaOH = 0.01 M*			
11	7	3.60	770
23	16	3.75	860
38	32	3.85	1000
53	60	3.75	1220
69	120	3.75	1580
		Average: 3.75	
c. NaOH = 0.025 M			
13	7	4.40	950
27	16	4.60	1100
43	32	4.80	1330
58	60	4.60	1570
73	120	4.55	2160
		Average: 4.60	
d. NaOH = 0.25 M*			
14	7	4.55	980
18	12	3.95	890
31	60	1.50	370
C. C_6H_5SNa = 0.01 M			
a. NaOH = 0.01 M*			
25	8	4.15	490
41	16	4.25	570
56	30	4.30	710
71	60	4.00	880
		Average: 4.20	
b. NaOH = 0.025 M			
30	8	5.20	630
48	17	5.50	800
69	45	4.90	1030
		Average: 5.20	
D. $K_2S_2O_8$ = 0.01 M			
C_6H_5SNa = 0.01 M (approx.) NaOH = 0.09 M (approx.)			
12	2	6.75	1550
22	4	6.70	1640
42	10	6.05	1730
72	40	4.05	1840

* At 25.2°.

The reaction depends ultimately on the collision of thiophenolate ions with persulfate ions. Let us suppose that temporary combination takes place, and in a reaction so mobile as to remain in equilibrium:

(a).............. $C_6H_5S^- + S_2O_8^{--} \rightleftarrows (C_6H_5S).(S_2O_8)^{---}$,

for which:

(1).............. $\dfrac{[(C_6H_5S).(S_2O_8)^{---}]}{[C_6H_5S^-]\,[S_2O_8^{--}]} = K_1$,

this complex being so unstable that its formation does not appreciably affect $[C_6H_5S^-]$ nor $[S_2O_8^{--}]$, the concentrations of the original ions. Such a complex would very likely decompose automatically in one of two ways: (1) into the ions out of which it was formed, according to the reverse of reaction (a), or (2) in a manner involving exchange of electrons, such as:

(b)........ $(C_6H_5S).(S_2O_8)^{---} \longrightarrow C_6H_5S + S_2O_8^{---}$,

following which we must suppose a secondary reaction:

(c)........ $S_2O_8^{---} + C_6H_5S^- \longrightarrow 2SO_4^{--} + C_6H_5S$.

Let us suppose either reaction (b) or reaction (c) sufficiently slow to contribute to the measured velocity. If reaction (b) were the rapid one, thiophenolate would disappear in large amount almost immediately. Since this is contrary to experimental fact, we shall consider (b) as the slow, and (c) as the comparatively fast, reactions. (To assume both reactions slow would greatly complicate the derivations.)

In order to attempt to explain the catalytic action of OH^-, let us suppose that a complex ion is formed as follows:

(d)........ $C_6H_5S^- + OH^- \rightleftarrows (C_6H_5S).(OH)^{--}$,

in mobile equilibrium, for which:

(2)........... $\dfrac{[(C_6H_5S).(OH)^{--}]}{[C_6H_5S^-]\,[OH^-]} = K_2$,

assuming this complex also to be so unstable that its formation does not appreciably affect $[C_6H_5S^-]$, but to be so highly reactive that approximately all direct oxidation of thiophenolate takes place through oxidation of this complex. Reaction (c) should then be corrected to read:

(c′)........ $S_2O_8^{---} + (C_6H_5S).(OH)^{--} \longrightarrow 2\,SO_4^{--} + C_6H_5S + OH^-$.

There is a third possibility in the disappearance of the hypothetical ion $(C_6H_5S).(S_2O_8)^{---}$:

(e)........ $(C_6H_5S).(S_2O_8)^{---} + (C_6H_5S).(OH)^{--} \longrightarrow$
$2\,C_6H_5S + 2SO_4^{--} + OH^-$.

The measured reaction velocity, thus assumed to be dependent on simultaneous reactions (b) and (e), will be:

$$-\frac{d[C_6H_5S^-]}{dt} = k_1[(C_6H_5S).(S_2O_8)^{---}] + k_2 \\ [(C_6H_5S).(S_2O_8)^{---}]\,[(C_6H_5S).(OH)^{--}].$$

Substituting the equivalents of $[(C_6H_5S).(S_2O_8)^{---}]$ and $[(C_6H_5S).(OH)^{--}]$ from equations (1) and (2), respectively, and factoring, we have:

$$-\frac{d[C_6H_5S^-]}{dt} = \{K_1\,k_1 + K_1\,K_2\,k_2\,[C_6H_5S^-]\,[OH^-]\} \\ \{[C_6H_5S^-]\,[S_2O_8^{--}]\}.$$

Expressed more simply:

$$-\frac{d[C_6H_5S^-]}{dt} = \{k_I + k_{II}\,[C_6H_5S^-]\,[OH^-]\} \\ \{[S_2O_8^{--}]\,[C_6H_5S^-]\}.$$

The expression $k_I + k_{II}\,[C_6H_5S^-][OH^-]$ is the modified velocity constant, and will subsequently be represented by k.

An attempt has been made to apply this modification to the data obtained. Each experimentally determined value for k is associated with the *average* concentration of total thiophenolate of the interval of concentration change of that particular determination, since, $[OH^-]$ remaining constant

TABLE II

Comparison of the Calculated and Experimental Values for the Velocity Constants of the Reaction between Persulfate and Thiophenolate at 25°C

(The *average* concentration of C_6H_5SNa, as described above, is indicated below.)

NaOH moles per liter	k (calculated)	k (found)
	C_6H_5SNa = 0.0022 M	
0.01	3.50	3.40
0.0113	3.55	3.50
0.025	3.95	4.00
	C_6H_5SNa = 0.0040 M	
0.005	3.50	3.60
0.01	3.75	3.75
0.025	4.50	4.60
	C_6H_5SNa = 0.0076 M	
0.01	4.20	4.20
0.025	5.60	5.20

during a single determination, k becomes a first-degree function of [$C_6H_5S^-$] in accordance with the foregoing hypothesis. Calculation of the different values for k_I of the modified velocity constant gives a mean value of 3.25. A value for k_I cannot easily be determined directly, because it is very difficult to dissolve thiophenol in very weakly alkaline aqueous solutions.

Table II affords a comparison between the calculated and experimental values of k. The value used for k_{II} in the calculations is the one which gives the best agreement between the calculated and experimental values for the constant. In all these calculations the activity coefficient of each ion concerned is assumed to be unity. This is intrinsically, of course, not true.

From Table I the experimental velocity constant is seen to fall off very sharply during the course of the reaction when the OH^- concentration is high. No possible explanation of this behavior is offered except to state that oxidation further than to the disulfide stage may take place, with consequent faster lowering of the persulfate concentration than anticipated.

Summary

The velocity of the reaction between potassium persulfate and sodium thiophenolate in alkaline solution has been studied, and, although the reaction is stoichiometrically trimolecular, the results indicate that the measured reaction is bimolecular.

The values obtained for the velocity constant of the simple velocity equation are found to vary in a more or less regular manner with varying hydroxide concentration or with varying concentration of the reactants. A hypothesis involving increased activation through complex ion formation has been proposed as a possible explanation of this anomaly.

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THE EFFECT OF WHEAT GERM OIL ON THE KEEPING QUALITIES OF FATS AND FOOD RATIONS*

BY P. E. ROLLER

Considerable interest has been displayed for some time concerning the rancidity of fats and oils, both edible and inedible, and concerning methods of preventing or delaying rancidity. Moureu and Dufraisse[1] have published a number of articles in which they discuss anti-oxidants. Holm, Greenbank, and Deysher[2] have shown that glycerol, resorcinol, phenol, benzylic alcohol, and dihydroxystearic acid delay the rate of adsorption of oxygen by linseed oil. Some of the other investigators who have worked on anti-oxidants are: Fisher,[3] Lund,[4] Smith and Wood,[5] Fiero,[6] Yoshio Tanaka and Mitsuo Nakamura,[7] Husa and Husa,[8] Mattill,[9] and Mattill and Crawford.[10]

Wheat germ oil has received considerable attention in the treatment of certain ailments and deficiency diseases[11,12,13,14]. Barnett Sure[15] has done considerable work on the dietary requirements of wheat germ oil for reproduction. Mattill[16] and Anderegg and Nelson[17] have suggested that perhaps vitamin E in food rations may be destroyed when oxidative changes take place in fats. Some facts which are presented confirm this assumption. Wheat germ oil was found to protect food rations for a certain period of time as well as to supply the necessary vitamins. Mattill found that the vitamin E content did not parallel the acetyl values of vegetable fats and oils. He also found that other vegetable fats and oils would not protect food rations in a similar manner as wheat germ oil did.

The present investigation was carried out to study the effect of wheat germ oil and the different constituents of the oil on the keeping qualities of fats and oils and food rations.

Laboratory Method and Apparatus

The effect of wheat germ oil on the keeping quality of fats and oils was determined by a modified form of apparatus such as was used by Moureu and Dufraisse[1] and refined later by Greenbank and Holm.[18]

In every case, about 500 cc. of fat were melted and a definite quantity removed by a warmed pipette. This furnished a uniform portion of the 500 cc. sample. To this portion a definite amount of wheat germ oil was added. From 10 cc. to 20 cc. samples of this mixture were pipetted into 250 cc. Erlenmeyer flasks which were connected to mercury manometers. Oxygen replaced the air in the flasks. The thermostat was maintained at a temperature of 70°C. During the temperature adjustment, the pressures in the system were adjusted by means of two-way stopcocks inserted in the tubes

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* Contribution from the Research Division of The S. M. A. Corporation, Cleveland, Ohio.

connecting the manometers and the flasks. The period for temperature adjustment varied from thirty minutes to two hours or two hours and thirty minutes.

It was found that the induction period for cod liver oil was generally one of the shorter induction periods for fats. Skimmed milk powder was used as the basis for all the food rations. When the cod liver oil and skimmed milk powder were thoroughly mixed together, rancidity was easily detected by the penetrating odor, very likely acrolein. Generally 50 g. of skimmed milk powder, 8 cc. of cod liver oil, and various amounts of wheat germ oil were used. The mixtures were put in pint jars in an air atmosphere at room temperature.

Results

It has been reported by Mattill[16] that vegetable oils, other than wheat germ oil, sometimes afford protective action in preventing rancidity in food rations, but wheat germ oil affords almost unfailing protection. It was of interest to find that not all samples of wheat germ oil afford protective action for fats and oils, and food rations. Typical sets of results are given for an active sample and an inactive sample of wheat germ oil. Two different flasks containing fat of the same composition were used at the same time. Manometer No. I and Manometer No. II were connected to the flasks.

TABLE I

Active wheat germ oil was added to cod liver oil

	% wheat germ oil	Induction Periods	
		Manometer No. I	Manometer No. II
Trial I	0	1 hr. 10 min.	1 hr. 5 min.
" II	0	1 " 10 "	1 " 15 "
" I	.25	1 " 35 "	1 " 35 "
" II	.25	1 " 40 "	1 " 45 "
" I	.5	1 " 35 "	1 " 35 "
" II	.5	1 " 40 "	1 " 45 "
" I	1.47	2 " 10 "	2 " 10 "
" II	1.47	2 " 10 "	2 " 10 "
" I	2.4	2 " 15 "	2 " 5 "
" II	2.4	2 " 10 "	2 " 20 "
" I	4.8	3 " 30 "	3 " 30 "
" II	4.8	3 " 25 "	3 " 25 "
" I	7	3 " 20 "	3 " 45 "
" I	9.1	4 " 15 "	4 " 20 "
" II	9.1	4 " 15 "	
" I	13	4 " 30 "	4 " 30 "
" II	13	4 " 30 "	4 " 30 "
" I	17	4 " 30 "	4 " 35 "

TABLE II

Inactive wheat germ oil was added to cod liver oil

% wheat germ oil	Induction Periods Manometer No. I	Manometer No. II
0	1 hr. 20 min.	1 hr. 15 min.
1.7	1 " 15 "	1 " 10 "
3.2	1 " 20 "	1 " 10 "
6.2	1 " 15 "	1 " 10 "
9.1	1 " 15 "	1 " 15 "
13	1 " 15 "	1 " 15 "

Wheat germ oil has been added to tallow and oleo oil with similar results. The active oil increases the induction period of the fat in each case, but the type of the induction period curve varies, depending upon the fat and the sample of wheat germ oil.

The Effect of Lecithin upon the Induction Period of Fats

The sample of the inactive wheat germ oil which was used to obtain the previous data, contained approximately 1.15% lecithin. The lecithin content for another sample of inactive oil was 2.15% and for two different samples of active oil 3.81% and 6.16%. The oil which contained 3.81% lecithin was almost as active as the active samples containing 6.16% lecithin, and the sample containing 1.15% lecithin was as inactive as the sample containing 2.15% lecithin. These results indicate that the lecithin content had very little, if any, effect on the keeping quality of fats.

It was thought that perhaps if lecithin were added to one of the inactive samples of wheat germ oil, the induction periods of fats and oils might be changed. The lecithin (the lecithin was obtained from Eastman Kodak Company, Grade P683) was dissolved in ethyl ether and then mixed with the wheat germ oil. The ether was removed by evaporation. The lecithin content of the oil which was originally 1.15%, was increased 2%. This oil was then added to the different fats and oils by the method which has been given before. No noticeable increase in the induction periods of the fats and oils was obtained, as is indicated in the following table.

TABLE III

	Induction Periods Manometer No. I	Manometer No. II	% wheat germ oil
Oleo oil	5 hr. 20 min.	5 hr. 15 min.	0
Oleo oil	5 " 0 "	5 " 20 "	9.1
Edible beef tallow	3 " 50 "	3 " 20 "	0
Edible beef tallow	3 " 55 "	3 " 50 "	9.1

The Effect of Unsaponifiable Material in Active Wheat Germ Oil upon the Induction Period of Fats

The unsaponifiable material was obtained by the method of Allen and Thompson.[19] The unsaponifiable material obtained in this manner from 10 cc. of active oil was added to 10 cc. of the inactive oil. If the active constituent of wheat germ oil is present in the unsaponifiable material, then the inactive oil to which the unsaponifiable material is added should assume an activity approximately equal to that of the active oil. One sample will illustrate the results which were obtained.

Fat	Induction period
Edible beef tallow	3 hrs. 55 min.
Edible beef tallow containing 11% of the inactive oil and unsaponifiable material	3 hrs. 55 min.

Since wheat germ oil is known to be rich in sitosterol, it seemed worth while to observe the effect of increasing the concentration of this constituent upon the protective action of wheat germ oil. Several experimental deter-

TABLE IV

	Induction Periods		Wheat germ oil and sitosterol content
	Manometer No. I	Manometer No. II	
Cod liver oil	1 hr. 30 min.	1 hr. 45 min.	None
Cod liver oil	1 " 30 "	1 " 40 "	2 cc. wheat germ oil in 20 cc. cod liver oil. .0871 g. sitosterol to 12 cc. wheat germ oil
Edible beef tallow	3 " 40 "		None.
Edible beef tallow	3 " 45 "	3 " 25 "	2 cc. wheat germ oil in 20 cc. tallow. .0871 g. sitosterol to 12 cc. wheat germ oil
Oleo oil	5 " 30 "	5 " 30 "	None.
Oleo oil	5 " 10 "	5 " 25 "	2 cc. wheat germ oil in 20 cc. Oleo oil. .0871 g. sitosterol to 12 cc. wheat germ oil
Cod liver oil	1 " 25 "	1 " 30 "	None.
Cod liver oil	1 " 25 "	1 " 30 "	2 cc. wheat germ oil in 20 cc. cod liver oil. .1912 g. sitosterol to 15 cc. wheat germ oil
Edible beef tallow	3 " 40 "		None.
Edible beef tallow	3 " 45 "	3 " 25 "	2 cc. wheat germ oil in 20 cc. tallow. .1912 g. sitosterol to 15 cc. wheat germ oil

minations were made with sitosterol (melting point 136-138°C.) which was separated from a sample of active oil. The results were the same as those which were obtained with the unsaponifiable material. Some of the results are given in Table IV.

The Effect of Glycerol on the Induction Periods of Fats

Since the acid numbers of the active oils were found to be between 11 and 13 and the acid numbers of the inactive oils between 7 and 8, it was thought that perhaps there might be a small amount of free gylcerol present which has been found to exert a protective action[7] on the oxidation of fats and oils. A small amount of the active oil was washed with water. The oil was removed by filtering on a moist filter. The wash water was concentrated and the following color tests were applied: salicylic acid, resorcinol, and β-napthol.[20] A positive test for glycerol was obtained in each case. The wash water from the inactive oil gave color reactions which were less distinct than the wash water from the active oil.

To 10 cc. of the inactive wheat germ oil .235 cc. of glycerol was added and the mixture emulsified as well as possible. In flasks No. I and No. II, 5 cc. of wheat germ oil and glycerol were added to 40 cc. of Norwegian cod liver oil. In flasks No. III and No. IV, no wheat germ oil and glycerol were added.

TABLE V

Difference in mm. of the levels of Hg. in manometers

Time	No. I	No. II	No. III	No. IV
1 hr. 10 min.	1.2	1.2	3.0	3.0
1 " 20 "	1.7	2.8	5.0	5.0
1 " 30 "	2.5	3.2	7.0	6.5
1 " 50 "	4.5	5.0	9.5	10.0
2 " 0 "	6.0	6.0	11.2	12.0

The induction period for No. I and No. II was 1 hr. 30 minutes and for No. III and No. IV, 1 hr. 5 minutes. The table shows the protective action of glycerol since the wheat germ oil alone had no effect.

The Protective Action of Wheat Germ Oil on Skimmed Milk Powder and Cod Liver Oil

The previous tests which were made on fats were also made with cod liver oil and skimmed milk powder. A typical set of results is given. In all determinations 50 g. of skimmed milk powder and 8 cc. of cod liver oil were used.

The results with skimmed milk powder are consistent with the previous data. It will be noted that sitosterol slightly shortened the induction period of the cod liver oil. The inactive wheat germ oil increased the induction period

TABLE VI

Tests began in March, 1930

	Developed Rancidity in
Skimmed milk powder-cod liver oil	10 days
" " " " " " —1 cc. glycerol	15 days
" " " " " " —2 cc. inactive wheat germ oil containing .76% sitosterol	" 8 "
" " " " " " —1 cc. inactive wheat germ oil containing 1.39% sitersterol	" 8 "
" " " " " " —2 cc. inactive wheat germ oil containing 1.39% sitosterol	" 8 "
" " " " " " —1 cc. inactive wheat germ oil	14 "
" " " " " " —2 cc. inactive wheat germ oil	15 "
" " " " " " —1 cc. active wheat germ oil	37 "
" " " " " " —2 cc. active wheat germ oil	No rancidity after 10 mo.
" " " " " " —1 cc. inactive wheat germ oil containing .87% lecithin	16 days
" " " " " " —2 cc. inactive wheat germ oil containing .87% lecithin	16 days

of the cod liver oil a few days and the addition of lecithin increased this period slightly. 2 cc. of glycerol or 2 cc. of active wheat germ oil were sufficient to prevent rancidity for long periods of time.

Summary

Wheat germ oil is not an unfailing anti-oxidant for fats, oils, and food rations. The lecithin content did not affect the properties of wheat germ oil. The activity of wheat germ oil was not in proportion to its lecithin content; nor was the activity increased by the addition of lecithin. The unsaponifiable material and sitosterol had no effect upon the activity of the oil. Although free acid was present in fairly large amounts, especially in the active oil, the activity of the oil was not in proportion to the acid numbers. The activity of wheat germ oil, then, must be due to the glycerol in the fat or the acids and glycerides which the oil contains. It has been known for some time that the OH group in organic compounds is a protective group, and the high acetyl value of the active oil was indicative of this fact. (The acetyl value of the active oils was approximately 30, while for the inactive oils, the acetyl value was approximately 15). The fatty acids obtained from wheat germ oil contain about 20% to 25% linolic acid and over 50% oleic acid and ricinoleic acid (from analysis of the oil used). It has been shown that linolic acid is easily oxidized, while oleic acid is slower, and ricinoleic acid still more slowly oxidized.[2] Therefore, it seems probable that the active oil contains the glycerides of hydroxy acids which may consist largely of ricinoleic acid.

Acknowledgment

It is a pleasure to acknowledge the valuable assistance rendered by Dr. A. F. O. Germann, Director of the Research Laboratory of The S. M. A. Corporation.

Acknowledgment is also made to Dr. Oliver Kamm, Scientific Director of the Parke, Davis & Co. Research Laboratories and to Dr. John F. Anderson, Director of Research for E. R. Squibb & Sons for supplying the different samples of oil.

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STUDIES IN ELECTROCAPILLARITY

Part IV. The Effect of Salts on the Electrocapillary Curves of Solutions containing Surface-active Substances

BY J. A. V. BUTLER AND A. WIGHTMAN

According to a theory of electrocapillary action which has been put forward by one of us,[1] the lowering of the surface tension at the interface between mercury and the solution produced by the presence of many organic substances is related to the potential difference by an equation of the form

$$\Delta\gamma = \Delta\gamma_m e^{-a(V-V_m)^2}$$

where V_m is the potential difference at which the surface tension lowering (for the given solution) has its maximum value $\Delta\gamma_m$, and $\Delta\gamma$ is the lowering at the potential difference V. The curve of $\Delta\gamma$ against V (which we shall call the adsorption curve) as determined by this equation is completely symmetrical about the potential difference V. The study of Gouy's data[2] for numerous organic substances in normal sodium sulphate solution showed that while this equation was, in most cases, in excellent agreement with the right hand (negative) branches of the adsorption curves, these were often unsymmetrical and lower on the left (positive) side. In Parts II and III of this series of papers,[3] the electrocapillary behaviour of solutions containing two surface-active substances has been examined, and it has been shown that the adsorption of one substance is in general reduced by the presence of a second surface-active substance, in some cases to the extent of the complete exclusion of the first substance. Since the sulphate ion, like most inorganic anions, itself causes a lowering of the surface tension on the positive side of the electrocapillary curve, it appeared probable that the asymmetry of the adsorption curves in normal sodium sulphate might be due to the partial displacement of the adsorbed substances at the more positive potentials by adsorbed sulphate ions. We have therefore examined the effect of varying the nature and concentration of the salt on the adsorption curves of some typical surface-active substances.

It is well known that the electrocapillary curves of most inorganic salt solutions are practically parallel at high negative potential differences, and may be made to coincide in the region from −1.2 to −1.8 volts (referred to the normal calomel electrode) by small displacements parallel to the axis of the potential difference. These displacements have been ascribed to the liquid junction potential difference between the standard electrode and the solution under examination. When taking the surface tension lowering caused by a substance as the difference between the surface tension of the salt

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[1] J. A. V. Butler: Proc. Roy. Soc., 122A, 399 (1929).

[2] Ann. Chim. Phys., 8, 291; 9, 75 (1906).

[3] J. Phys. Chem., 34, 2297, 2841 (1930).

solution and that of the solution containing the same concentration of the salt, together with the added substance, it is important to take into account any displacement due to this cause. No difficulty arises with non-ionised solutes at a moderate concentration, as the curves of the mixtures usually coincide with those of the primitive salt solutions at the extreme right (for solutions containing 4 mols per cent of alcohol a slight displacement is necessary to make them coincide at -1.8 volts). But when the added substance is also a salt, as in the case of sodium salicylate, and has a concentration which is comparable with, or greater than that of the inorganic salt, it is necessary to displace the curve of the mixture until it coincides on the extreme right with the curve of the primitive solution.

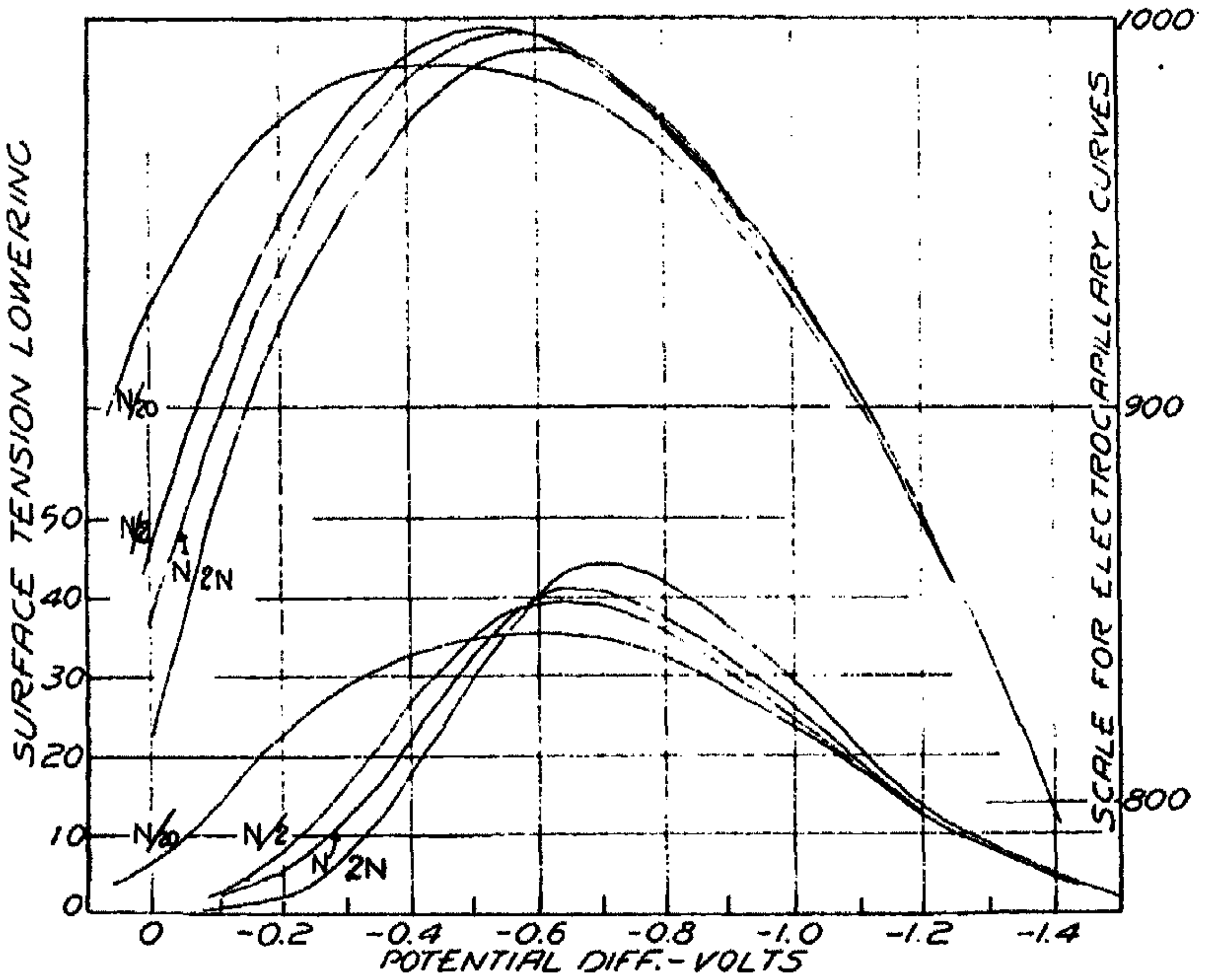

FIG. 1

Surface tension lowerings of ethyl alcohol (4M) in lithium chloride solutions. Electrocapillary curves of lithium chloride in water in the upper part of the diagram.

In order to facilitate the comparison of the behaviour of salt solutions of different concentrations, the electrocapillary curves of the salt solutions have been displaced so as to coincide with that of normal potassium chloride at -1.5 volts. In the diagrams given in this paper, the adsorption curves have also been given the same displacement. The displacements required are listed with the experimental data below.

(1) *Ethyl alcohol.* In Fig. 1 the upper part of the diagram shows the electrocapillary curves of solutions of lithium chloride in water, and the lower part, the surface tension lowerings produced by the presence of ethyl

alcohol to the extent of 4 mols per cent. It can be seen that the surface tension of the primitive solution is raised by increasing the salt concentration at potential differences greater than −0.7 volts, while below −0.4 volts it is positively adsorbed to an increasing extent as the potential of the mercury becomes more positive. The behaviour of the alcohol is closely related to that of the salt. In the region in which the salt is negatively adsorbed the surface tension lowering of the alcohol increases with the salt concentration but in the region in which the salt is positively adsorbed the surface tension lowering of the alcohol falls off rapidly as the salt concentration is increased. The adsorption curves of alcohol, which are markedly asymmetrical at the higher concentrations of the salt, thus become broader as that is decreased and are very nearly symmetrical at the smallest salt concentration.

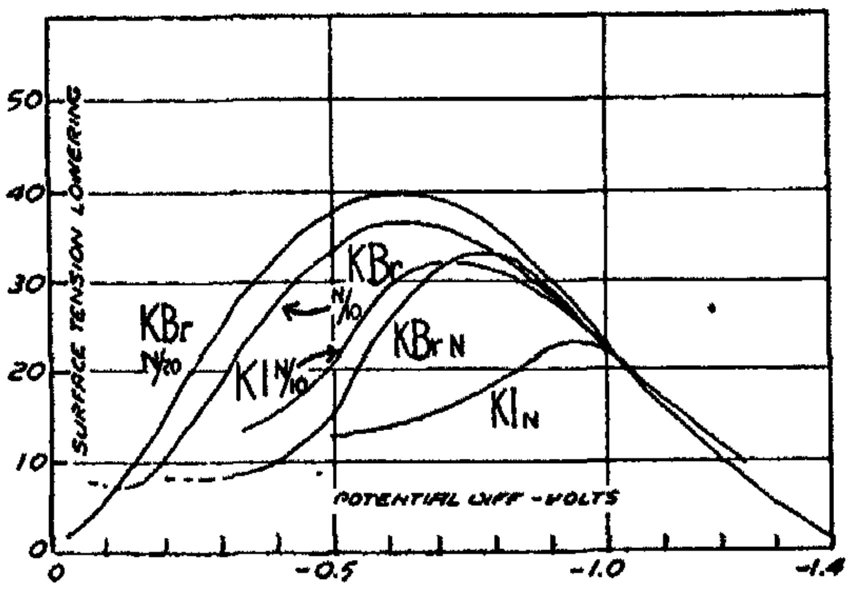

Fig. 2

Surface tension lowerings of ethyl alcohol (4M) in potassium bromide and iodide solutions.

The behaviour of alcohol in potassium bromide and iodide solutions is very similar. (See Fig. 2. The electrocapillary curves of some of the salt solutions are shown in Fig. 3). The bromide and iodide ions are much more surface-active than the chloride ion and when they are present the electrocapillary curve begins to fall at much higher values of the potential difference. As might be expected in these solutions the displacement of the alcohol by the surface active anion begins to take effect further to the right of the curves. The effect of N potassium bromide on the adsorption of alcohol is about the same as that of N/10 potassium iodide, and that of N/20 potassium bromide about the same as that of N/2 lithium chloride. Thus it appears that solutions containing chloride, bromide and iodide ions, having concentrations in the ratios 100:10:1, have approximately the same effect on the behaviour of alcohol. The electrocapillary curves of solutions containing chloride, bromide and iodide ions, in these ratios, also approximate to each other. We may therefore conclude that the effect of these ions on the behaviour of alcohol is proportional to their effect on the electrocapillary curve in the primitive solutions, and that their surface activities have relative magnitudes approximately in the ratios 1:10:100.

(2). *Phenol.* The behaviour of phenol is very similar. Fig. 3 shows the surface tension lowerings of N/10 phenol in a series of solutions containing the halogen ions, and in the upper part of the diagram the corresponding electrocapillary curves of the salt solutions. The electrocapillary curves of potassium chloride solutions are nearly identical with those of lithium chloride solutions at the same concentrations, and the behaviour of phenol in the former is very similar to that of alcohol in the latter. The adsorption curve of phenol becomes more symmetrical as the concentration of potassium chloride is decreased. The effect of the bromide and iodide ions on the behaviour of phenol, is very similar in kind and extent to their effect on alcohol.

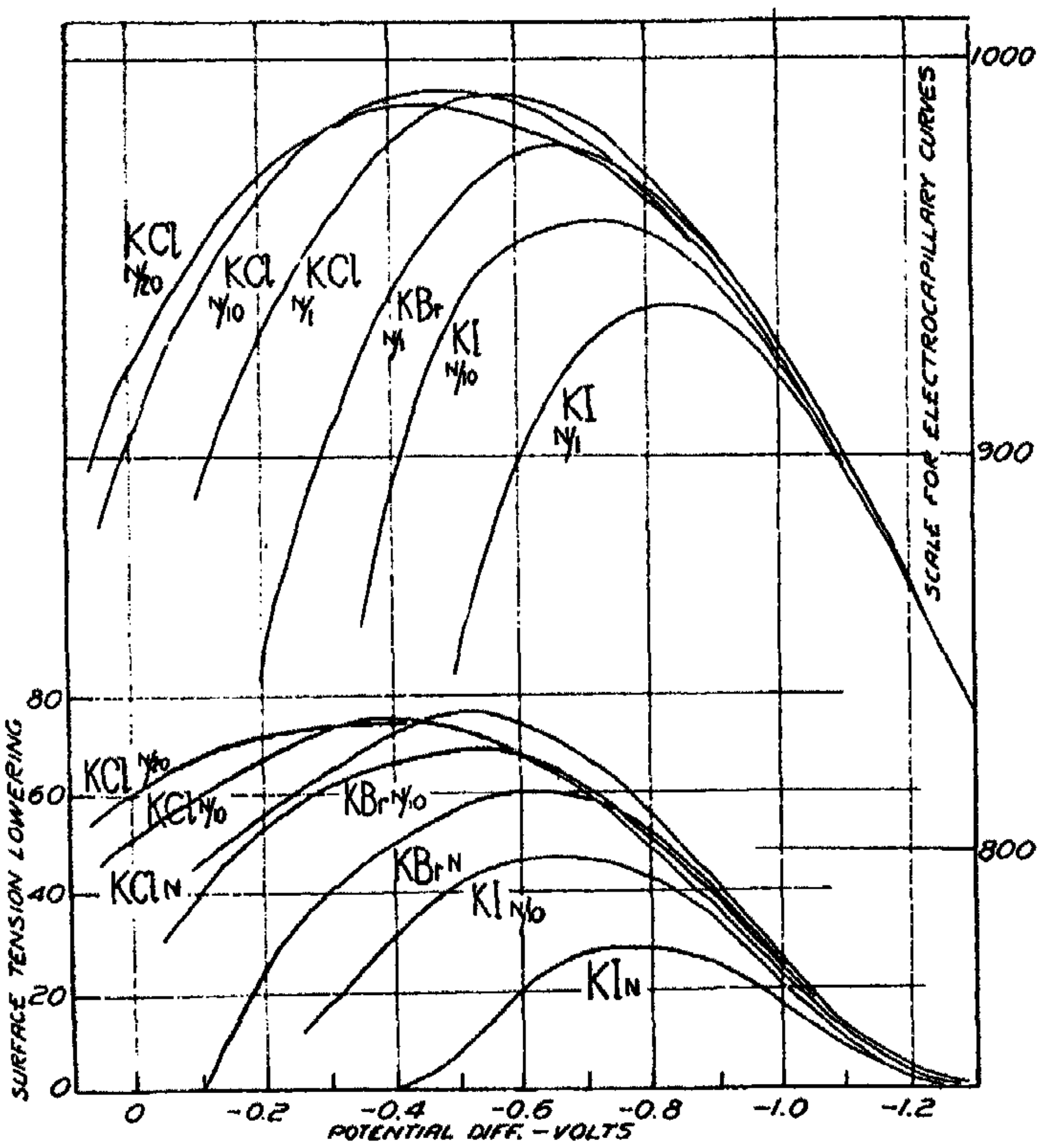

Fig. 3

Surface tension lowerings of phenol (N/10) in potassium halide solutions. Electrocapillary curves of the salt solutions in water in the upper part of the diagram.

Fig. 4 shows the behaviour of phenol in sodium sulphate and ammonium nitrate solutions. The latter salt is of interest because measurements can be extended with its solutions further in the positive direction than with any of the other salts employed. The electrocapillary curve is lowered by an increase of the concentration of this salt, at all potentials more positive than

−0.7, and the surface tension lowering of the phenol is reduced by an increase of the salt concentration over the same range. Sodium sulphate is notable in that an increase of its concentration from N/10 to N/1 raises the adsorption curve of phenol through practically the whole of the region in which measurements can be obtained.

(3) *Sodium salicylate.* In Part I of this series of papers[1] it was pointed out that strong electrolytes having surface-active positive ions (e.g. substituted ammonium salts) show a maximum adsorption when the potential difference has a high negative value (−1.3 to −1.5 volts), whereas the maximum for non-ionised substances falls within the range −0.4 to −0.7 volts. It was to be expected on theoretical grounds that the maximum of the adsorption curves of strong electrolytes having surface-active anions would occur at a similar interval towards positive values. The adsorption curves of a number of salts of organic acids were measured in N/1 sodium sulphate and it was found that their maxima occurred between −0.13 and −0.30 volts, which are not nearly so positive as was expected. It seemed probable that this anomaly was due to the reduction of the adsorption of the organic anions at the extreme left of the curves owing to the adsorption of sulphate ions, which cause a considerable lowering of the surface tension in this region.

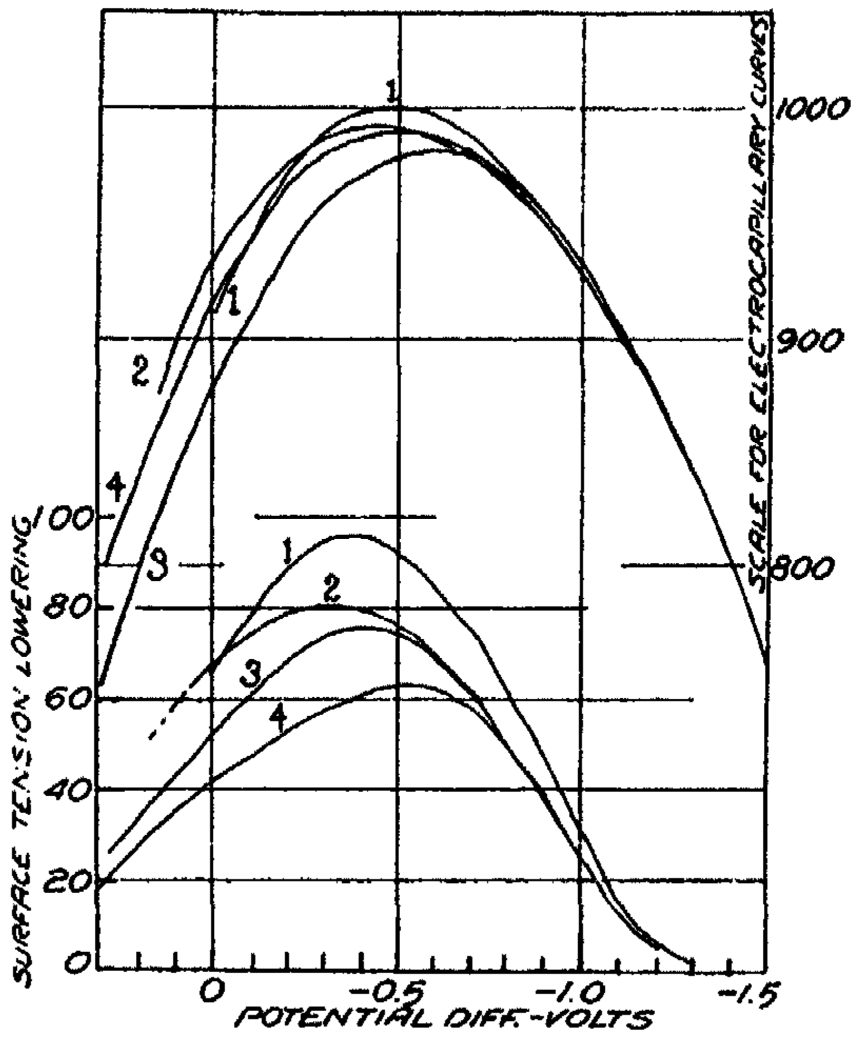

Fig. 4

Surface tension lowerings of phenol (N/10) in sodium sulphate and ammonium nitrate solutions. 1. Sodium sulphate (N); (2) sodium sulphate (N/10); (3) ammonium nitrate (N); (4) ammonium nitrate (N/10).

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[1] J. Phys. Chem., 34, 2286 (1930).

We have therefore determined the surface tension lowerings of N/10 sodium salicylate in solutions of sodium sulphate, ammonium nitrate, potassium chloride and potassium bromide, of various concentrations. The curves obtained are shown in Figs. 5 and 6. It is evident that as the concentration of the inorganic salt is increased, the maximum of the adsorption curve of the salicylate moves towards more positive values of the potential difference, and at the smallest salt concentrations is beyond the most positive values for which measurements can be obtained. Thus, when the salt concentration is sufficiently reduced we realise the behaviour which was expected on theoretical grounds.

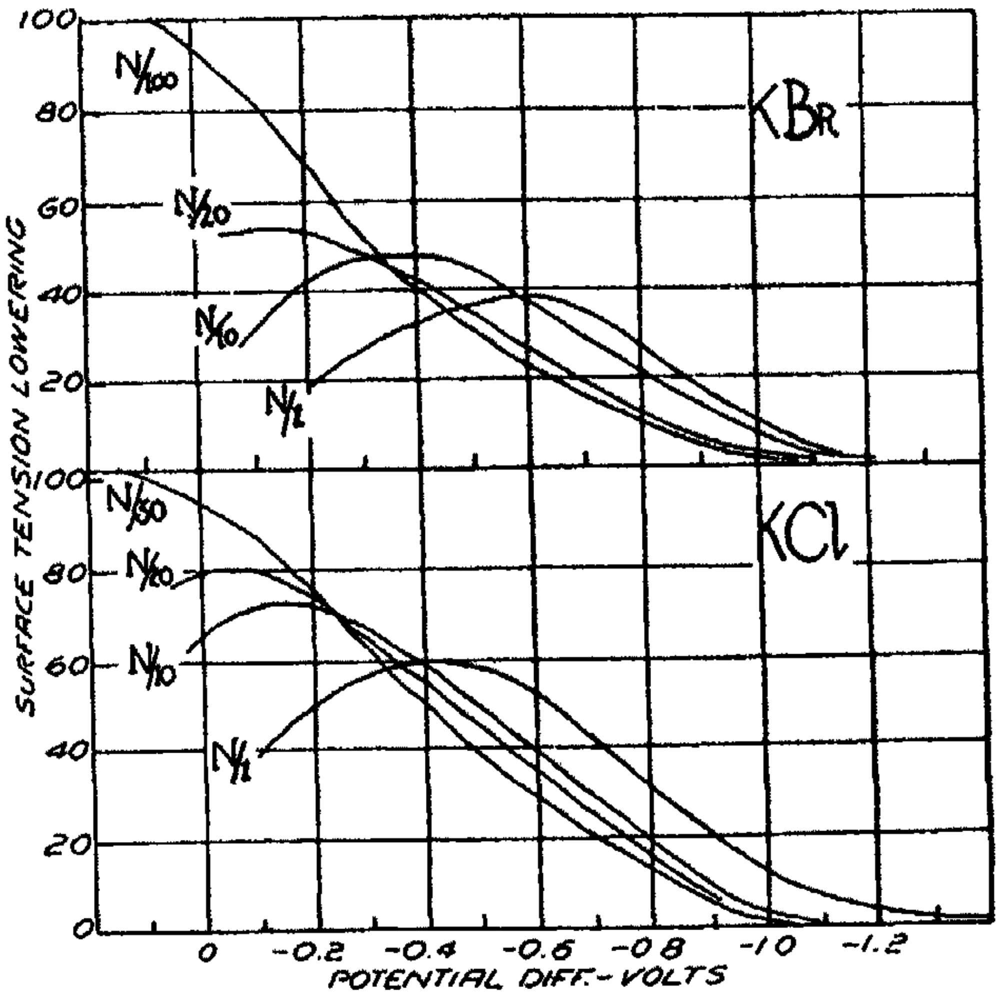

Fig. 5

Surface tension lowerings produced by sodium salicylate (N/10) in potassium chloride and potassium bromide solutions.

Experimental Data

The experimental arrangements were similar to those of the previous papers of this series. Since it was possible that small differences of surface tension would be of importance, the vessel containing the solution at the tip of the capillary was water-jacketted and kept at a constant temperature (20°).

The salts used were the best available A.R. quality. The ethyl alcohol was dried over quicklime, and distilled. The phenol was also purified by distillation, and had the mp. 40.8°.

The following tables give the surface tension lowerings produced by the presence of ethyl alcohol phenol and sodium salicylate in the inorganic salt solutions. In determining these values, the electrocapillary curve of the mixture has been displaced (if required) parallel to the axis of the potential differences, so as to make it coincide with the curve of the primitive salt solution at − 1.8 volts. The displacement required is given in the column D_1. D_2 gives the displacements required to make the electrocapillary curves of the salt solutions coincide with the curve of normal potassium chloride at (and above) − 1.5 volts.

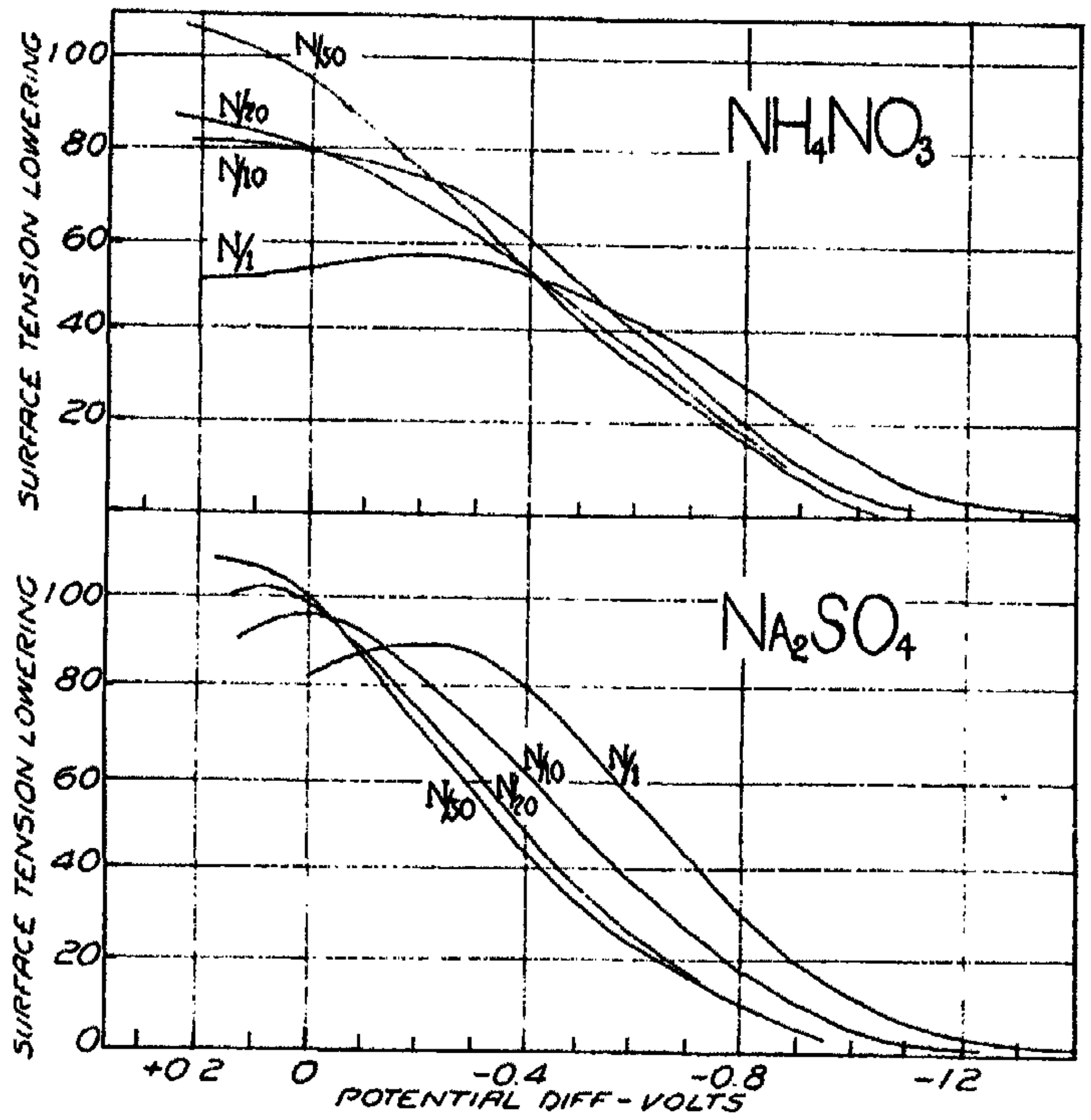

Fig. 6

Surface tension lowerings produced by sodium salicylate (N/10) in ammonium nitrate and sodium sulphate solutions.

The potential differences are given with reference to the normal calomel electrode. The surface tension lowerings are given in terms of Gouy's scale, i.e. the maximum surface tension between mercury and normal sodium sulphate at 20° is taken as 1001.7, corresponding to a maximum value of 1000 for the surface tension between mercury and water, according to Gouy's measurements.[1]

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[1] The ratio of the maximum heights of the electrocapillary curve in normal sodium sulphate and water (1001.7:1000) was determined at 18°. Our measurements are at 20°, but this difference of temperature cannot appreciably affect the ratio.

The data from which the electrocapillary curves of the solutions of salts in water have been constructed are not given here, for they would occupy a considerable space, and the general features of the curves can be seen in the diagrams. We propose, however, to publish the data for these curves in another paper, and to give a theoretical discussion of them.

TABLE I

Surface Tension Lowerings of Ethyl Alcohol (4 mols per cent) in various Salt Solutions

Potential difference	Lithium Chloride*				Potassium Bromide			Potassium Iodide	
	2M	1M	0.5M	0.05M	1N	0.1N	0.05N	1N	0.1N
−0.0	0.5	0.0	0.3	3.6	—	—	—	—	—
−0.2	2.2	5.1	6.9	17.3	8.5	8.3	6.3	—	—
−0.4	18.8	21.7	25.8	31.0	10.0	24.9	28.1	(16.6)	13.7
−0.6	41.0	40.3	39.0	34.7	25.4	35.8	38.8	12.5	28.3
−0.8	41.5	37.4	36.3	34.7	32.9	34.1	38.1	18.8	31.2
−1.0	28.6	26.1	24.7	27.0	23.6	24.8	28.1	21.5	25.9
−1.2	12.5	13.2	13.1	16.1	4.9	12.4	16.4	12.2	14.7
−1.4	6.0	5.3	5.8	6.8	—	5.9	7.8	4.7	5.9
−1.6	0.2	0.5	1.0	2.4	—	1.7	1.2	0.7	1.2
D_1	+0.01	+0.01	+0.01	+0.01	+0.005	+0.010	+0.015	—	—
D_2	−0.01	0.0	+0.01	+0.07	+0.005	+0.04	+0.065	0.0	+0.045

* In the lithium chloride solutions, which are taken from another series of measurements, the concentrations are expressed as gram molecules per 1000 grams of solvent; in the other solutions they refer to gram-equivalents per litre.

TABLE II

Surface Tension Lowerings of Phenol (N/10) in various Salt Solutions

Potential difference	Potassium Chloride			Potassium Bromide			Potassium Iodide		
	1N	0.1N	0.05N	1N	0.1N	0.05N	1N	0.1N	0.05N
0.0	—	45.7	54.0	—	—	—	—	—	—
−0.2	55.3	63.9	69.3	25.2	50.6	55.2	—	—	—
−0.4	71.8	74.1	73.5	49.1	67.1	62.0	(−1.3)	20.5	30.1
−0.6	73.7	69.8	70.8	60.5	68.6	65.6	19.7	43.2	48.6
−0.8	55.5	53.5	59.0	51.5	55.7	50.3	28.2	47.1	50.8
−1.0	26.6	28.9	35.5	25.1	30.6	30.8	17.3	26.7	32.1
−1.2	4.2	6.7	12.4	3.7	7.1	12.6	2.0	5.7	7.2
−1.4	0.0	0.5	0.0	0.2	0.0	1.5	0.3	0.0	0.0
D_1	—	—	—	—	—	—	—	—	—
D_2	—	+0.05	+0.06	+0.005	+0.04	+0.015	0.0	+0.045	+0.07

TABLE II (Continued)

Potential difference	Sodium Sulphate			Ammonium Nitrate		
	1N	0.1N	0.05N	1N	0.1N	0.05N
+0.4	—	—	—	9.4	—	—
+0.2	—	—	—	27.4	30.1	37.0
0.0	65.9	64.1	63.9	42.2	49.4	52.0
−0.2	88.5	77.1	72.3	53.1	66.1	65.7
−0.4	94.3	79.4	74.6	59.7	75.4	72.5
−0.6	83.9	72.2	71.5	59.5	70.3	70.6
−0.8	61.6	56.4	58.3	48.1	54.0	56.5
−1.0	29.5	29.1	39.5	20.7	27.1	34.2
−1.2	5.7	7.4	14.3	2.0	6.2	10.1
−1.4	0.5	0.5	1.5	1.3	0.0	1.3
D_1	—	—	—	—	—	—
D_2	+0.01	+0.055	+0.08	0.0	+0.035	+0.055

TABLE III

Surface Tension Lowerings of Sodium Salicylate (N/10) in various Salt Solutions

Potential difference	Potassium Chloride				Potassium Bromide				
	1N	0.1N	0.05N	0.02N	1N	0.1N	0.05 N	0.02N	0.01N
+0.1	—	—	—	100	—	—	—	—	—
0.0	—	62.9	76.8	94.6	—	—	—	(49.6)	98.9
−0.2	49.1	71.5	75.0	78.7	19.2	40.2	52.3	57.5	76.2
−0.4	58.9	60.7	57.0	53.6	32.5	46.6	42.5	44.4	45.6
−0.6	51.0	42.0	37.7	32.3	37.3	38.3	30.3	30.1	28.9
−0.8	30.4	23.7	18.7	16.5	25.4	23.2	13.3	15.6	13.6
−1.0	11.4	3.7	3.9	2.9	9.4	8.4	4.0	7.2	4.0
−1.2	3.0	0.2	3.0	0.0	1.3	3.0	1.9	2.0	0.0
D_1	—	−0.025	−0.030	−0.07	−0.01	−0.01	−0.01	−0.03	−0.10
D_2	—	+0.05	+0.06	+0.11	+0.005	+0.04	+0.065	+0.10	+0.17

Potential difference	Ammonium Nitrate				Sodium Sulphate			
	1N	0.1N	0.05N	0.02N	1N	0.1N	0.05N	0.02N
+0.2	50.8	81.2	86.7	106.6	—	—	—	—
+0.1	51.8	79.7	84.3	100.6	—	90.1	99.9	107.1
0.0	52.9	79.4	79.2	95.8	81.2	95.3	99.9	104.0
−0.2	56.3	74.1	72.0	77.7	88.6	84.6	78.8	81.2
−0.4	52.3	62.2	55.8	55.6	79.4	64.2	51.8	52.1
−0.6	42.6	42.4	40.2	35.7	55.7	38.9	28.8	30.1
−0.8	28.3	20.7	20.8	17.8	30.3	18.3	11.9	13.6
−1.0	10.4	4.2	7.7	2.9	12.3	5.6	3.2	3.4
−1.2	3.0	0.0	0.0	0.0	3.9	0.8	0.0	0.0
D_1	—	−0.015	−0.01	−0.05	—	−0.02	−0.04	−0.055
D_2	0.0	+0.035	+0.055	+0.08	+0.01	+0.055	+0.08	+0.135

Summary

1. The effect of varying the nature and the concentration of inorganic salts on the electrocapillary curves of solutions containing ethyl alcohol, phenol and sodium salicylate has been investigated.

2. In general the adsorption curves of ethyl alcohol and phenol become more symmetrical as the salt concentration is lowered. The surface-active bromide and iodide ions greatly reduce the adsorption of these solutes in the region in which the ions themselves are adsorbed. In solutions containing chloride, nitrate and sulphate ions, the surface tension lowering caused by the organic substances is increased by increasing the salt concentration in the region in which the salt is negatively adsorbed, and decreased in the region in which the salt is positively adsorbed.

3. The maximum of the adsorption curve of sodium salicylate moves towards positive potentials as the concentration of the inorganic salt is decreased and its magnitude increases. It has been shown that the maxima for strong electrolytes with surface-active cations occur between −1.3 and −1.5 volts, and for non-ionised substances in the region of −0.5 volts. It is now found that at very small concentrations of the inorganic salt, the maximum for a salt with a surface-active anion occurs at a potential more positive than +0.2. The behavior which was expected on theoretical grounds has thus been established.

We are indebted to the Department of Scientific and Industrial Research for a Studentship, granted to one of us (A. W.), which enabled him to take part in this work, and to Imperial Chemical Industries, Ltd., for a grant which defrayed the cost of part of the apparatus.

Chemistry Department,
University of Edinburgh,
June 18, 1931.

16 · 157

ELECTRODEPOSITION OF METALS FROM ANHYDROUS AMMONIA*

BY HAROLD SIMMONS BOOTH AND MENAHEM MERLUB-SOBEL

That the aqueous world we chance to live in is but one of the many possible, was first indicated by the epoch-making studies of Franklin on the "ammonia system;"[1] with Franklin's work the chemical equivalent of Ptolemaic geocentricism came to an end. No less demolishing of previous trends of thought—and creative of new—were the further conclusions drawn by Kraus[2] from his researches on certain electrochemical phenomena in liquid ammonia, for it is to Kraus we are indebted for the concept of the ionization of the elementary alkaline and alkaline earth metals in ammonia to yield normal metal ions and free (though generally solvated) electrons. It was this same research pyramid which yielded the concepts currently accepted regarding the nature of metallicity and the mechanism of electrical conduction in metals.

The monumental researches on the electrochemical phases of ammonia solutions, by others as well as by Kraus, have, peculiarly enough, included extremely little concerning actual electrodeposition of metals from this solvent. This fact is all the more surprising when viewed in contrast with electrodeposition studies made in the far less electrochemically understood pyridine[3] or in contrast with Röhler's[4] work in the otherwise almost unstudied formamide.

It was the purpose of this study to fill this gap.

Theoretical Considerations

As an electrolytic solvent, ammonia presents somewhat of an anomaly. Its relatively low dielectric constant (21-23) would normally be expected to allow for no great aptitude toward electrolytic conduction, yet its power in this respect is almost the equal of water. Early in their studies on this solvent Franklin and Kraus[5] concluded that dissociation is far less in ammonia than

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* Abstracted from a thesis submitted to the faculty of the Graduate School of Western Reserve University by Menahem Merlub-Sobel in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1930.

The experimental work reported upon here was done in the period of 1926-1928; previous publication was prevented, however, by the illness of the junior author. Recently, similar studies on ammonia electrodeposition were announced by Taft and Barham in the May, 1930, issue of The Journal of Physical Chemistry, representing partial duplication—but partial only—of this work.

[1] Franklin: Am. Chem. J., 47, 285-317 (1912); J. Am. Chem. Soc., 27, 820-51 (1905); Proc. Eighth Int. Cong. Applied Chem., 6, 119-30 (1912); See also Franklin: J. Am. Chem. Soc., 46, 2137-51 (1924).

[2] Kraus: J. Am. Chem. Soc., 30, 1323-44 (1908); 36, 864-77 (1914); 43, 749-70 (1921); 44, 1216-39 (1922); Trans. Am. Electrochem. Soc., 21, 119-20 (1912); Kraus and Lucasse: J. Am. Chem. Soc., 43, 2529-39 (1921).

[3] Müller et al.: Monatsheft., 44, 219-30 (1924).

[4] Röhler: Z. Elektrochemie, 16, 419-36 (1910).

[5] Franklin and Kraus: Am. Chem. J., 23, 297-8 (1900).

in water, but that its great fluidity results in so much greater ionic migration velocities as to counterbalance completely the factor of a low dielectric constant. Comparing ammonia at −33°C. with water at 18°C., the fluidity ratio is of quite significant a magnitude, 4.16: 1,[1] but even the interplay of dielectric constants and fluidities is admittedly insufficient to explain completely why some solvents prove excellent conducting media and others fail miserably in this regard.

Consideration of the theoretical cause of high ammonia conductivities is of considerable consequence even in practical electrodeposition. Whether a metal will be deposited out of solution in any solvent where hydrogen ions are a product of the ionization of the solvent must depend upon the relative values of two potentials—that given by

$$E_M = RT/nF.\ \ln P_M/p_M + n_M$$

and that of

$$E_H = RT/F.\ \ln P_{H_2}/p_{H^+} + n_H$$

where P_M represents the electrolytic solution pressure of the metal.
P_{H_2} represents the electrolytic solution pressure of hydrogen.
p_M represents the osmotic pressure of the metal ions in solution.
p_{H^+} represents the osmotic pressure of the hydrogen ions in the solution due to primary ionization of the solvent, and to any added ionogen dissociating to give H^+.
n_M represents the overvoltage of metal deposition.
n_H represents the overvoltage of hydrogen evolution.
Since the osmotic pressure of the metal ions in solution will always be a function of their concentration, deposition will be facilitated, all other factors being equal, by increased ionization rather than by a mere high conductivity resulting from low viscosities. Conversely, the tendency toward metal deposition will rise and fall with decrease and increase of the actual hydrogen ion concentration.

What the exact value of this last concentration is for pure ammonia is unknown, but it is undoubtedly very low.[2] Some estimate may be made from the data of Carvallo,[3] in which the conductivity of ammonia, after standing, is given as 5×10^{-10} at 20°C. and 3.7×10^{-11} at −80°C. By the method of Kohlrausch, and utilizing the ion conductances, at −33°C., found by Kraus and Bray[4] for the NH_4^+ and NH_2^- ions in NH_3, we may compute the approximate elementary ionization of ammonia into H^+ and NH_2^- as yielding concentrations of

$$(5 \times 10^{-10} \times 10^3)/(131 + 133) = 0.02 \times 10^{-7}$$

as compared with the 0.8×10^{-7} accepted for water at 18°C. The use of the NH_4^+ ion conductance as an H^+ value is amply justified by the fact that NH_4^+ in liquid ammonia is merely a solvated hydrogen ion, and might better be written as $H(NH_3)^+$.

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[1] Kraus: "The Properties of Electrically Conducting Systems," p. 109.

[2] Kraus: "The Properties of Electrically Conducting Systems," p. 230.

[3] Carvallo: Compt. rend., **156**, 1755-8 (1913).

[4] Kraus and Bray: J. Am. Chem. Soc., **35**, 1335 (1913).

On this basis, the hydrogen ion concentration of ammonia is approximately 1/40 that of water, which would lead to the expectation that electrodeposition of metals would prove materially easier, even though the advantage of the lower hydrogen ion concentration in ammonia is decreased in part by the simultaneously lower ionic concentration of dissolved salts, as previously discussed.

Current Status of Aqueous Electrodeposition

Metals which have been deposited by electrolysis of aqueous solutions of their compounds are quite sharply delineated from those where failure results. Those which can be deposited include all metals in Group I-B of the periodic table (Cu, Ag, Au) and all Group II-B if the uncertain beryllium and magnesium are assigned to the alkaline earths, leaving only zinc, cadmium and mercury. The same situation applies to Group III-B, gallium, indium and thallium all being amenable to electrochemical treatment, as opposed to the failure registered by all other inherently trivalent metals, including the rare earths. In the fourth group of the periodic table, germanium is somewhat in doubt, but otherwise the rule continues to hold that only the minor, or B, division can be deposited (tin and lead, in this case); the fifth group is normal to the extent that arsenic, antimony and bismuth deposit readily, while the other elements of the group are not obtainable in this manner.[1] In the whole of the sixth group, tellurium and chromium are the only metallic representatives which permit deposition, the failure of molybdenum and tungsten to respond to electrolytic operations being somewhat of an electrochemical mystery in view of the ease of deposition of the more active chromium. The seventh of the periodic table groups holds but one metal as yet subjected to any study—manganese; according to Allmand and Campbell[2] it deposits only because, fortuitously, an extremely high hydrogen overvoltage acts to prevent hydrogen being released (at least so completely as to exclude all metal deposition). Manganese, therefore, is about at the very border line for aqueous deposition. The transition, or eighth, group, with its three triads, represents elements all of which can be electrolyzed out of water solution.

On the other side of the picture are the metals not amenable to deposition practice. They include the alkalies in Group I-A, the alkaline earths of II-A, the boron-aluminum rare earth grouping of III-A, the tetravalent metalloid congeners, the high melting point metals of the fifth group, and, finally, tungsten, molybdenum and uranium in the same group that harbors the relatively easy-to-deposit chromium.

It is immediately apparent that the high e.m.f. of deposition which explains readily enough our inability to obtain metallic deposition with the alkali or alkaline earth members, or aluminum and the rare earths, is not broad enough to cover all metals of the non-electrolyzable groups. For example, tungsten and molybdenum hold approximately the same position

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[1] Personal unreported work by the junior author has negatived the claims of deposition made for tantalum.

[2] Allmand and Campbell: Trans. Faraday Soc., 19, 559-73 (1924).

in the normal aqueous series as does mercury, which is below hydrogen,[1] yet neither of these metals can be deposited from water solution; the work of Mann and Halversen[2] seems to indicate that the presence of the slightest trace of the OH grouping, even if organic, is fatal to the deposition of tungsten.[3]

A completely satisfactory explanation of these phenomena is yet to be found. On the basis of unreported work, the authors, with data admittedly inadequate at present to make their viewpoint much more than a working hypothesis at best, are of the opinion that in cases where aqueous electrodeposition fails despite a relatively low position in the electromotive series, the situation is merely a reflection of the paucity or absence of elementary or simple metallic ions.

Since even the alkali metals can be formed, in quasi-free state, by ammonia electrolysis, failure of other metals to deposit, if and when failure is evidenced in liquid ammonia, would be because of some such factor also—or, at least, because of factors similar in character to those operative in water, whatever may be their true nature.

Previous Work in Anhydrous Ammonia of Electrodeposition Interest

That ammonium nitrate absorbs ammonia at room temperatures, forming an electrolytic solvent, has been known ever since the work of Divers[4] indicated that this solvent (which we now recognize as merely a concentrated solution of nitric acid in anhydrous ammonia) electrolyzes to yield hydrogen at the cathode and one third the volume of nitrogen at the anode, if platinum and iron positive electrodes are utilized. When silver, mercury, lead, copper, zinc, or magnesium anodes are employed, however, electrolytic corrosion takes place. Nothing is indicated by Divers as to whether cathodic deposition of a metal would occur after sufficient metallic ion is electrolyzed into the solution. The work of Booth and Torrey[5] gives good reason to believe that such deposition would replace, in part at least, hydrogen evolution.

When first the systematic study of ammonia solutions began, Cady[6] showed that the passage of current through a silver, lead, mercury, copper, or barium salt solution in anhydrous ammonia resulted in the deposition of the metal on the cathode. Nothing is stated by Cady regarding the nature of the deposit obtained.

Since the alkali metals are so soluble in ammonia, it is but to be expected that electrolysis of salts of these metals would yield, cathodically, solutions of the metals, more or less concentrated as conditions permitted. Operating

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[1] Russell and Rowell: J. Chem. Soc., **130**, 1881-92 (1926).

[2] Mann and Halversen: Trans. Am. Electrochem. Soc., **45**, 493-508 (1924).

[3] Since submission of this manuscript, Colin G. Fink and Frank L. Jones: Trans. Am. Electrochem. Soc., April (1931), have succeeded in plating tungsten from aqueous alkaline solutions.

[4] Divers: Phil. Trans., **163**, 359-75 (1873): Proc. Roy. Soc., **21**, 109-11 (1873).

[5] Booth and Torrey: J. Am. Chem. Soc., **52**, 2581 (1930); J. Phys. Chem. **35**, 2465, 2492, 3111 (1931).

[6] Cady: J. Phys. Chem., **1**, 707-13 (1897).

at −70°C. Ruff[1] electrolyzed a KI solution, and obtained drops of a copper-colored material known to be but a concentrated solution of potassium in ammonia; this, as soon as permitted out of the concentrated KI phase, redissolved in the ammonia with the blue color characteristic of the alkalies.

Cottrell,[2] in his work on ammonia-acetylene reactions, has reported magnesium as slightly soluble in ammonia; on electrolysis, blue streaks developed from the cathode and an almost microscopic tree-like growth of bright metal grew out along the glass container. Quite evidently, magnesium is at the very threshold of alkalinity, if ammonia solubility is to be used as a criterion.

Like the others of the top row of the periodic system, beryllium is sui generis. Not truly an alkaline earth, as evidenced by full insolubility in ammonia, it is yet too high in the aqueous e.m.f. series[3] for electrodeposition. Booth and Torrey[4] have shown that beryllium can be deposited from anhydrous ammonia solutions of beryllium chloride and of dehydrated beryllium nitrate, their studies representing the first active effort at utilizing ammonia directly as an electrodeposition medium.

Studies on electrode potentials in liquid ammonia, of interest to electrodeposition because electrode potential values determine the electromotive series in a given solvent, have been made by Cady,[5] who found a tendency of electrodes, copper and zinc particularly, to vary in their potentials when measured against their ammonia salt solutions. Johnson and Wilsmore,[6] operating in the same field, found potential values in ammonia generally higher than in water; their tests included silver, mercury, copper, lead, nickel, cadmium, zinc, ammonium, magnesium, calcium, sodium and potassium. It is noteworthy that the potassium and sodium values are almost identical; these check quite closely with the values announced by Forbes and Norton[7] for the oxidation potentials of sodium and potassium.

In studying the true nature of oxidation, Cady and Taft[8] electrolyzed solutions of TlI and CuI in ammonia. Electrolysis of thallous iodide resulted in oxidation to Tl^{+++} ions, with simultaneous deposition of metallic thallium on the cathode. The deposited metal bridged over rapidly—a tendency of thallium no less in ammonia electrolyses than in aqueous, as we shall see later—although the use of 110 volts would obviously have made massive and coherent electrodeposition of any element impossible. The cuprous salt, on electrolysis, oxidized to yield the blue solution characteristic of cupric salts.

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[1] Ruff: Ber., 34, 2604-7 (1901).

[2] Cottrell: J. Phys. Chem., 18, 85-100 (1914).

[3] Latimer: J. Phys. Chem., 31, 1267-9 (1927), is of interest in this connection, the data being based on thermodynamic considerations rather than actual electrical measurements. See, however, Bodforss: Z. physik. Chem., 124, 66-82 (1926) and 130, 82-9 (1927), in which beryllium is placed between cadmium and zinc.

[4] Booth and Torrey: loc. cit.

[5] Cady: J. Phys. Chem., 9, 477-503 (1905).

[6] Johnson and Wilsmore: Trans. Faraday Soc., 3, 70-80 (1907).

[7] Forbes and Norton: J. Am. Chem. Soc., 48, 2278-85 (1926).

[8] Cady and Taft: J. Phys. Chem., 29, 1057-74 (1925).

In strict analogy with the viewpoint that anodes are "oxidized" electrolytically in water solution, the very apposite term "nitridation" has been synthesized to represent the analogous de-electronization process in liquid ammonia. Utilizing NH_4N_3 solutions (effectively, ammonated hydronitric acid solutions), Browne, Holmes and King[1] found that copper, silver, cadmium, lead and antimony are electrolytically corroded, with current efficiencies slightly above 100%, which the authors explained as being due to either mechanical abrasion or purely chemical corrosion, or perhaps to a tendency toward the formation of compounds containing the metal in a lower state of valence.

Closest in approach to actual electrodeposition studies in ammonia was the work on decomposition potentials and metal overvoltages, recently reported by Groening and Cady.[2] Nitrate and chloride decomposition voltages proved lower in ammonia; iodides and nitrites were higher than in water. In general, metal overvoltages were indicated as higher than in aqueous solution. It was in conjunction with overvoltage measurements that metals were deposited on to cathodic surfaces; the metals studied were silver, nickel, cadmium, mercury, lead, zinc and iron.

Scope of this Research

What little was available in the literature regarding electrodeposition in ammonia, obtained as a by-product of other work, was far from encouraging. Groening and Cady[3] declared, in explanation of some of their results, that "the metal seldom deposited in smooth form." This, despite electrode rotation, which normally aids materially toward obtaining good plating. Kraus,[4] too, summarizing his vast experience in the field, pointed out that "metals in the electropositive condition, when precipitated from liquid ammonia solution, almost invariably appear in spongy form."

The problem here, therefore, integrated itself into the question of whether ammonia cathodic electrolyses inherently did not permit of bright, smooth, adherent deposits, such as are produceable in water, or whether, by proper manipulation of current densities, solutions, and perhaps temperatures, results analogous to aqueous deposition, and on a par with it, could be obtained. The criterion of good deposition was, as always, a purely visual one: a deposit, to be considered satisfactory, had to possess, first and foremost, adherence—then compactness—and, finally, typical metallic lustre (the last two factors as opposed to the "burnt" spongy type of deposit encountered in ordinary electrodeposition when current densities are too high).

The Apparatus and its Manipulation

Since ammonia boils, at normal pressure, at about −33°C., it was most logical to attempt all electrodepositions first at this temperature, and most of the studies were therefore carried out at about the boiling point of am-

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[1] Browne, Holmes and King: J. Am. Chem. Soc., 41, 1769-76 (1919).

[2] Groening and Cady: J. Phys. Chem., 30, 1597-1615 (1926).

[3] Groening and Cady: loc. cit.

[4] Kraus: Trans. Am. Electrochem. Soc., 45, 175-86 (1924).

monia, to eliminate pressure problems. Only when complete failure at low pressures and temperatures was definitely evidenced for certain metals was a change made to a room temperature, high pressure unit.

The normal pressure arrangement is shown diagramatically in Fig. 1. The anhydrous ammonia passed directly through the steel valve into the glass inlet tube of a barium oxide drying tube. Beyond the BaO[1] tube, stopcocked connections were made to a high vacuum pump and to a supply of dry nitrogen. Another stopcock permitted closing off the operating cell from this preliminary section. Pressures were measured by a manometer set between this point and the cell proper, both being further protected by stopcocks. Ammonia passed into the cell through the first angle bend, and was liquefied by external cooling; it could be forced out at the end of the run through the outlet tube (see cell detail diagram, Fig. 2). The outlet was connected, through a stopcock and an unwired rubber connection, to a trap holding about one inch of mercury, which acted to prevent influx of air during agitation.

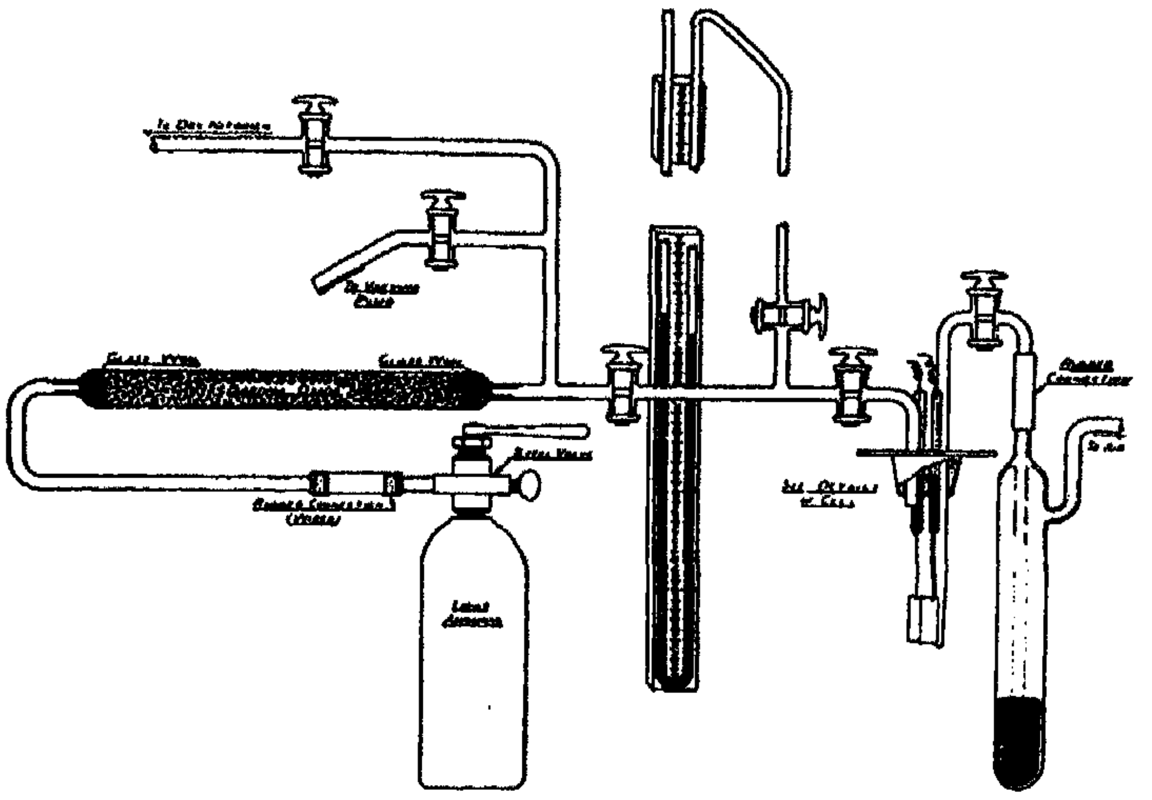

Fig. 1
Unit No. 1
Normal Pressure, Low Temperature Cell

For the cell, a large-lipped glass tube was fitted with a four-hole rubber stopper and was set through a cushioning cork ring. Rubber stopper and cork were drawn together tightly by the use of iron plates and wing nut bolts. Through the stopper came the two electric leads, while a third tube brought the ammonia in, as gas, and otherwise connected the cell to the preliminary vacuum pumping and nitrogen system; the last of the tubes was the liquid

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[1] Booth and McIntyre, in Ind. Eng. Chem., Anal. Ed. 2, 13 (1930), have shown that barium oxide is a very effective desiccant for ammonia.

ammonia withdrawal tube, reaching to the bottom of the cell. The lower half of the electrolysis cell was encircled by a Dewar flask; for preliminary condensation, liquid air or CO_2-ether was used, while the electrolysis proper was conducted with the solution surrounded by an ammonia bath, thereby assuring operation in the vicinity of −33°C.

For cell operation, a weighed amount of electrolyzing salt was added and the unit immediately assembled. After repeated evacuation and filling with nitrogen, to remove adsorbed moisture from the system, pure anhydrous synthetic ammonia, dried by metallic sodium, was drawn from the cylinder into the cell. A CO_2-ether mixture is preferable for liquefying ammonia, since it does not cause solidification. After sufficient ammonia had been liquefied, the preliminary system was cut off from the cell, leaving only the manometer connected. Agitation of the liquid in the cell, so as to obtain complete solution of the salt or, at least, saturation, was accomplished by a rapid sequence of opening and closing the stopcock controlling the liquid ammonia outlet tube in the cell. Under the few centimeters mercury pressure present, the liquid ammonia solution would rise in the tube, but after ascending about five or ten centimeters, it would reach a portion of the tube considerably warmer than the liquid ammonia, and a powerful back pressure would therefore develop by the flashing of the ammonia into vapor, and this pressure

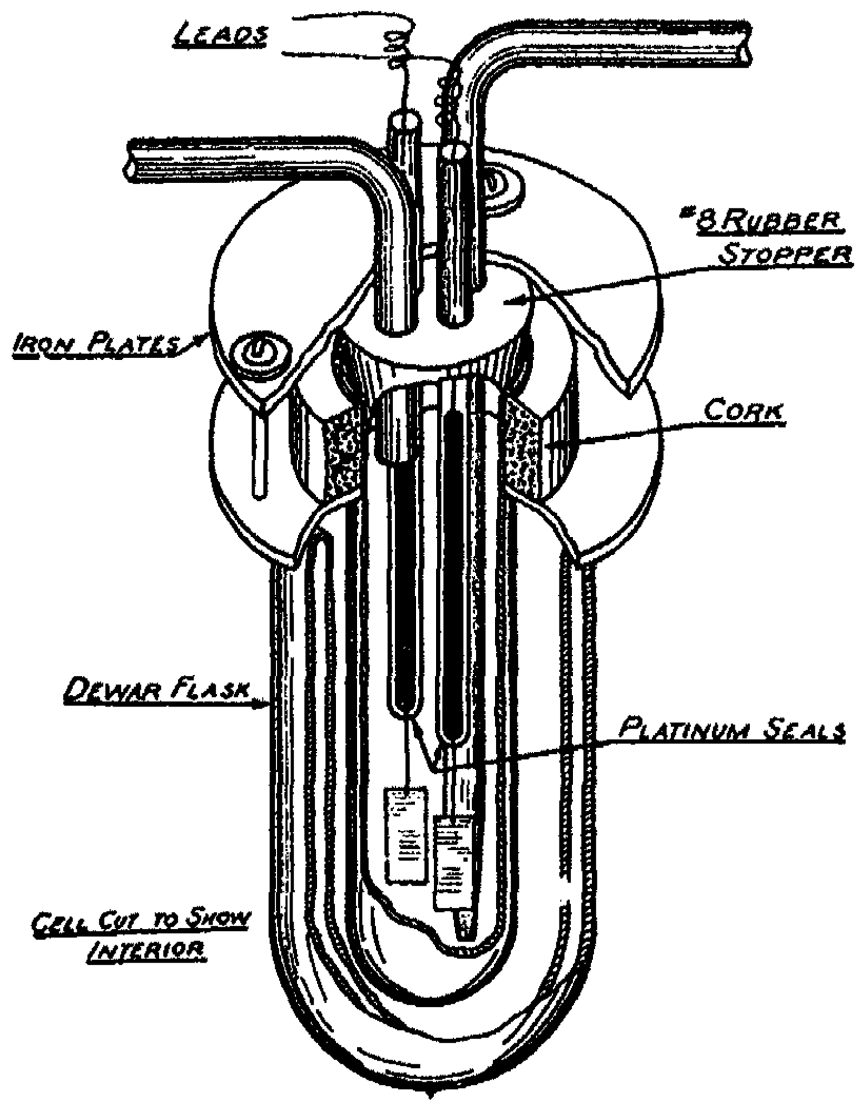

FIG. 2
Normal Low Pressure Cell

would force the liquid back with some violence, making thorough agitation of the solution possible without external appliances. The mercury trap, of course, prevented any drawing back of air or moisture into the lines.

After electrolysis had been completed, the mercury trap was replaced by a loosely stoppered Dewar flask. By opening the stopcock, the pressure in the cell, increased by the removal of the external ammonia bath, forced the contents over into the Dewar, from which point the solution was discarded. The stopcock was closed and a fresh quantity of ammonia condensed in the cell in the manner originally used, in order to wash the electrodes. When this had been drawn off as before, the system was evacuated partially, and ethyl alcohol drawn into the cell for further washing, by placing the ammonia outlet tube tip in a beaker of alcohol, and opening the stopcock. Alcohol washings were continued till the electrodes showed freedom from all salts, and then the cell was taken apart.

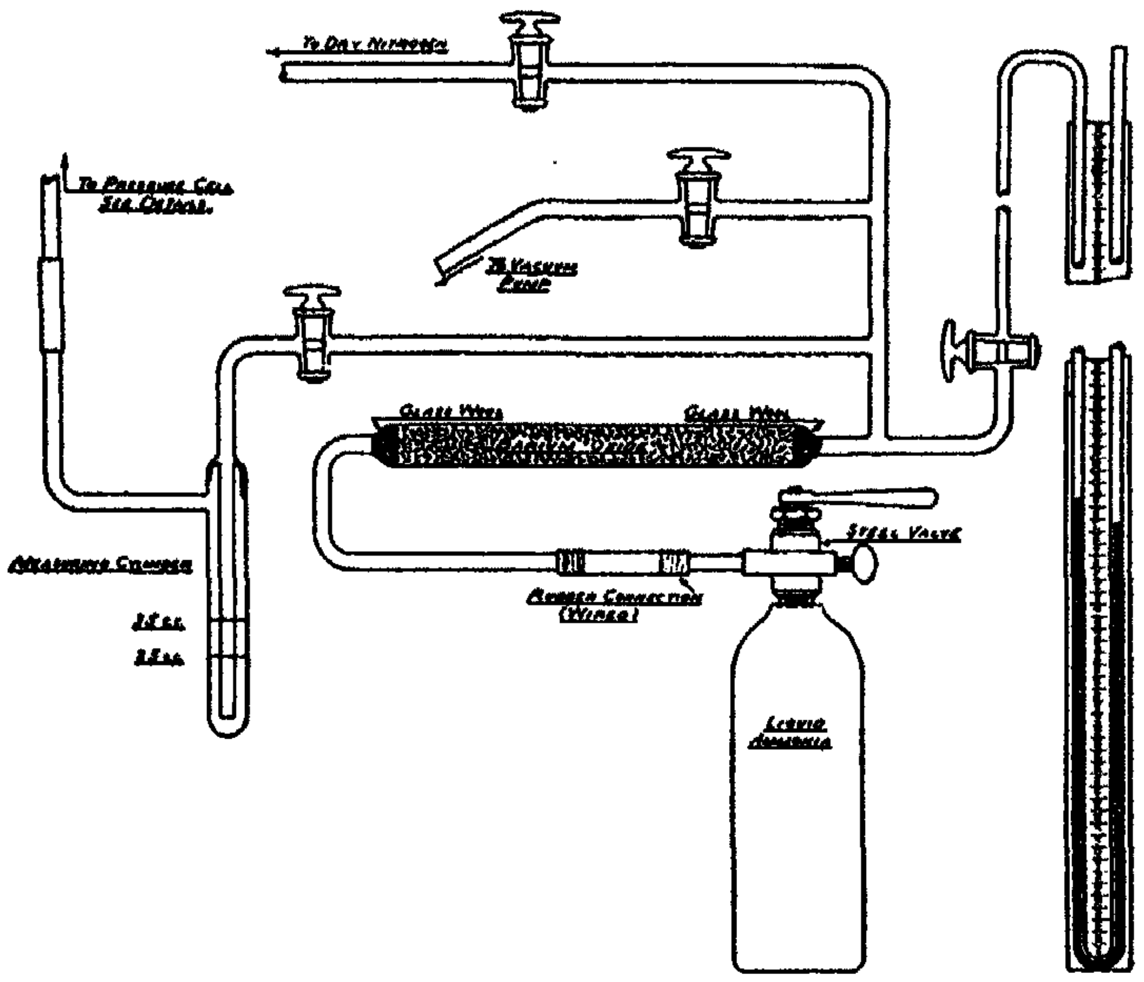

Fig. 3
Unit No. 2
High Pressure, Room Temperature Cell

After a large amount of experimentation had proven low temperature electrolysis ineffective for a number of metals, an entirely different type of cell had to be devised, to operate at room temperatures and therefore at pressures of several atmospheres. The preliminary part of this apparatus was identical with that used for low temperature work, but here the barium oxide tube was followed by a measuring tube into which the ammonia was first condensed before being revolatilized into the operating cell. The arrangement is shown in Fig. 3.

The complete high pressure unit consisted of a standard all-iron valve capable of withstanding 250 lbs. pressure, and specially packed so that it held vacuum also. A steel pipe cross connected the valve down to the cell and up to a standard ammonia pressure gauge. The remaining side of the cross was closed from the ammonia line, but was tapped to receive a supporting rod, enabling the whole unit to be clamped as desired.

Relatively little difficulty was experienced in any part of the apparatus other than in the cell itself. It was obviously impossible to utilize the steel container as anything but a pressure-resistant jacket; electrolysis in a steel tube would have involved the risk of the tube acting as an intermediate cathode, and throwing iron into the deposit as well as into the solution. A number of attempts at enameling the inside of the tube proved utter failures. The arrangement shown in Fig. 4 was finally adopted, after considerable experimentation: About an inch of mercury was placed in the jacket, and a hard glass tube about one quarter of an inch smaller in diameter forced down into it, giving the tube a cushion of mercury. Into the tube, from above, passed the two electrodes, and pressure electrolysis took place therefore inside of a glass tube completely protected from the effects of such pressure by virtue of its being completely equalized.

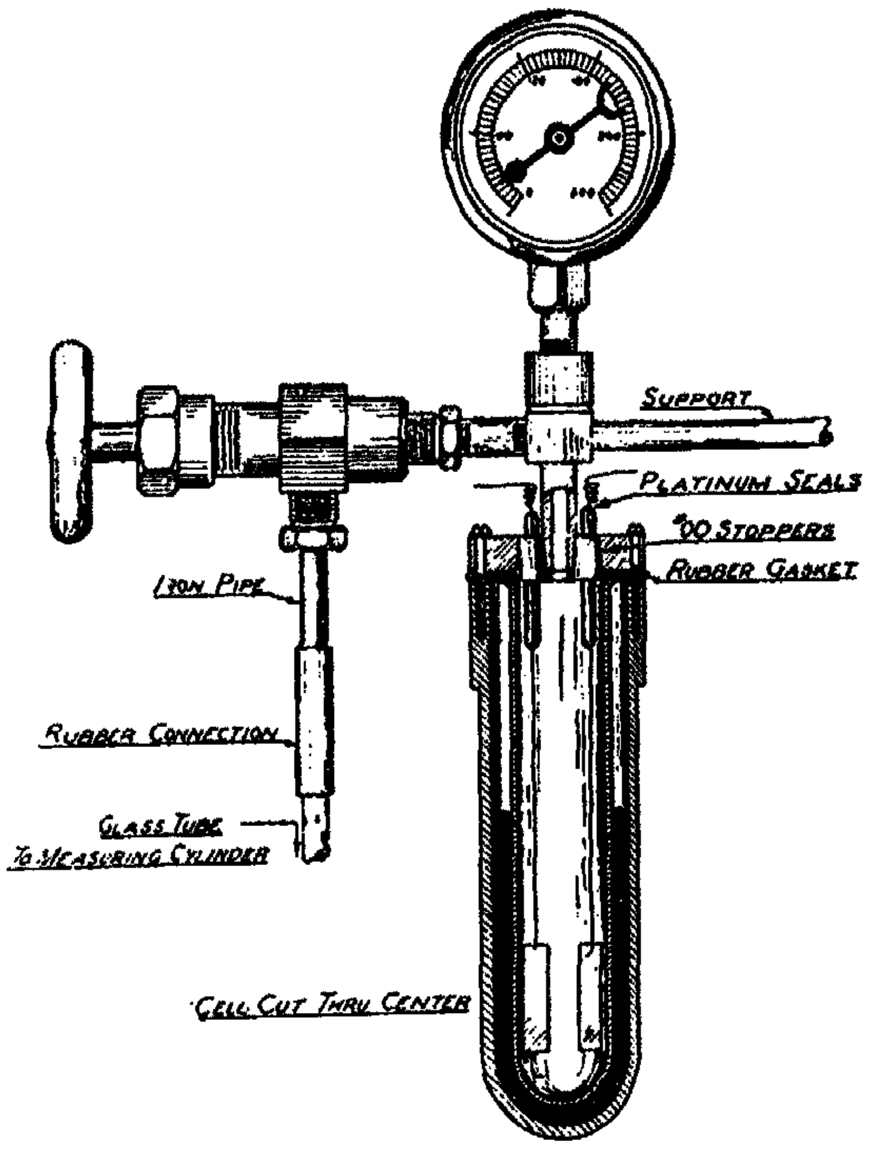

Fig. 4
High Pressure Cell

One factor did continue to give trouble for a long period. The tube carrying the platinum seals had to be set through the cell cap, and no leakage was to be permitted. Repeated efforts at using DeKhotinsky cement and its modifications, low melting alloys, and even adamant cements, all proved futile. The method finally adopted, simple enough admittedly, involved the use of tiny rubber stoppers through which the tubes passed. By setting these stoppers with taper upward, the cap being drilled accurately so as to make a perfect fit, increased pressure only served to tighten the seal.

Complete sealing between the cap and the cell was accomplished by a rubber gasket, and proved quite adequate.

Upon completion of a run in the high pressure unit, the cell was cooled to the normal boiling point of ammonia or lower, quickly taken apart, and the electrodes plunged immediately into anhydrous alcohol. Had individual runs been more fruitful of results, more elaborate washings, ammonia and otherwise, would have been called for, and the necessary devices could readily have been set into the cell to withdraw the ammonia and to wash the electrodes in situ. However, there was no occasion for this, as further reports on the individual metals will indicate.

Experimental Results

While many salts have been listed as ammonia soluble, most such determinations were made at room temperature. Solubilities at -33°C. proved significantly lower and thereby curtailed the choice of salts materially. In each case, those salts are reported upon which proved most satisfactory after preliminary tests.

Copper. Preference was given to the cuprous salts, even though none were available which did not show some amount of cupric contamination (recognizable by color of resulting solutions). This latter factor was of little importance, since electrolysis would have oxidized the cuprous ion to cupric anyway, at least to some extent, as has been indicated by the work of Cady and Taft.[1] Best results were obtained in a run involving the solution of 0.3330 grams of CuI in 30 c.c. of ammonia, with a current of approximately 10 milliamperes on a 6 square centimeter cathode face, equivalent to 167 milliamperes per square decimeter. The voltage required was 0.7 for an electrode separation of 12 mm. No hydrogen or other gas was evolved. Based on cuprous copper, anode corrosion was 81.2%, and deposition only 11.8%, while from a cupric standpoint anode loss was 162.4% of theory and the cathode gain 23.5%. High corrosions and low depositions were characteristic of all copper runs; even when current densities were too high for good plating this held true. Burnt deposits suffered further deterioration after the electrolysis was completed, irrespective of whether kept in a desiccator or in the open.

Silver. As might have been expected, silver gave an excellent deposit. A weight of 0.3085 grams of pure silver iodide dissolved extremely easily

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[1] Cady and Taft: J. Phys. Chem., 29, 1057-74 (1925).

in 40 c.c. of ammonia, and with a silver rod anode and a gold cathode, a current of 215 milliamperes per square decimeter was employed. Anode corrosion was somewhat under theory, 86.0%, deposition slightly above, 101.2%.

Gold. Both AuI and the complex cyanide made in situ by the interaction of AuI with KCN gave good plating, the former operating perfectly at 250 milliamperes per square decimeter, on a platinum cathode and a gold anode, while the latter required a lower density of current, 87 milliamperes to the square decimeter giving the best results. Voltage for the iodide was about 1.5, the cyanide requiring about 2.0 for the same electrode separation, 14 mm. For the best gold iodide run, 0.4963 grams were dissolved in 25 c.c. of ammonia; the double cyanide received 0.2294 grams of AuI and 0.1142 grams of KCN. Both depositions were perfect, and throwing power complete; the cyanide bath gave results the equal of any aqueous cyanide electrolysis. Attack of the gold anode was practically nil in all iodide electrolyses; for the cyanide bath it was 3.6%. Cathode efficiencies were quite good, hovering around the 87.6% value found for the best iodide run, while cyanide gave 82.6%.

Beryllium. The findings of Booth and Torrey, previously mentioned, were corroborated in this research; here beryllium iodide was used because of its greater solubility at low temperatures, though even this was far from adequately soluble. A weight of 1.5435 grams of salt, synthesized by reaction between iodine and beryllium metal flake, failed to dissolve to more than a small extent at first in 25 c.c. of ammonia. A cast beryllium plate, about one-eighth of an inch thick and 1 × 3 centimeters in area, was used as an anode and was set about 18 mm. from the gold cathode twice the area. As electrolysis continued, more of the salt went into solution, doubtlessly due to internal heating effects of the high currents used, varying from 12,300 to 14,200 milliamperes per square decimeter. The voltages required were from 8.2 to 27.0, the rise in internal temperature making the higher voltage range necessary. Complete metal deposition, both front and back, resulted; the metal was dark and far from the usual steely color of polished beryllium, or the gray of the unpolished, a fact hardly remarkable considering the conditions of operation.

Zinc. A dense deposit of fine, though somewhat matty, metal was obtained by the use of zinc cyanide with 0.2070 grams of the salt dissolved in 40 c.c. of ammonia and with 20 mm. electrode separation. Current was equivalent to 74 milliamperes per square decimeter; voltage averaged somewhat under 2. Deposition was good, as was also throwing power. Anode corrosion was 110.3%, cathode deposition 90.4%.

Cadmium. Plating of cadmium was tried with two soluble salts, potassium cadmium cyanide and cadmium thiocyanate. The former gave bright metal, although there was a tendency toward spottiness and burning, with 667 milliamperes per square decimeter. The thiocyanate bath, not nearly as soluble, gave warty edges, like copper from an aqueous sulphate bath, but otherwise the deposit was good, using the same current density. Anode corrosions were 101-103%, cathode depositions from 87.5-95.5%. Voltages differed remarkably, despite the fact that electrode separations were identical—20 mm.; this was, of course, a reflection of the poorer solubility of the thiocyanate. With the latter, pressures of 3.0-3.5 volts were required—the double cyanide called for only 0.8 or so.

Mercury. Our only normally liquid metal, mercury, was readily electrolyzed out of ammonia solution of 0.8182 grams of HgI_2 in 30 c.c. of ammonia. A current of 433 milliamperes per square decimeter gave a deposit of beautiful matty metal. The metal alloyed on the gold surface, certain spots being very shiny due to excess of mercury (crystals which had melted completely before alloying). Some tendency to "tree," as in the case of lead and thallium, was noticed. A platinum, and therefore insoluble, anode being employed, a relatively high voltage requirement of 1.5 was encountered, with an electrode separation of only 13 mm. Based on Hg^{++}, the ion added, deposition was 89.3%.

Thallium. In simple aqueous electrodepositions, both lead and thallium stand out because of their tendency to form spongy, tree-like growths of metal; ammonia solutions proved almost as bad in this respect. The individual crystals of the "tree" were somewhat smaller in the case of thallium than held true for lead, both iodide and nitrate giving almost identical results. Deposits were not weighed because the tiny size of the crystals made washing very difficult, even by the manipulation successful with lead. Anode corrosions were again well beyond theoretical requirements—106.6% and 117.6% for the nitrate and iodide, respectively.

Tin. Since stannic chloride did not dissolve adequately in ammonia at −33°C., although giving a good deposit, with a stannous anode corrosion of 112.8% and a stannic deposition of 60.1%, it was decided to utilize stannic iodide as an electrolyzing salt. The dried salt weighed 0.6554 grams—30 c.c. of ammonia were used—but even here solution was far from complete; the red salt merely turned white, forming an ammoniate as a milky white liquid, the precipitate settling slowly but completely. Despite this relative insolubility, the solution yielded a fine metallic deposit, back no less than front, with a current of 333 milliamperes per square decimeter—about 1.1 volts—showing a stannous anode corrosion of 95.5% and cathode deposition of 40.1% (based on Sn^{++++}, which was the ion at first present, these were 190.9% and 80.1% respectively).

Lead. Just as water solutions of ordinary, simple salts fail to give firm adherent plating of lead, irrespective of current density, so ammonia solutions failed also, though the "treeing" tendency is not as sharp. Neither the iodide nor the nitrate gave deposits of the desired characteristics, so sodium ammonoplumbite, the ammonia analogue of the ordinary, aqueous sodium plumbite,[1] made in situ by the interaction of $NaNH_2$ and PbI_2, was tried. It gave deposits apparently a bit more compact, but the fern-like growth of metal was still a characteristic. Anode corrosions for lead varied from 97.5% to 112% and cathodic deposition was 79.3% for the ammonoplumbite

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[1] See Franklin: J. Phys. Chem., 15, 509-20 (1911).

and 97.5% for the nitrate. It may be of some point to mention the fact that the lead so obtained was of extreme purity; crystals were exposed to laboratory conditions for many months without losing their lustre or assuming any of the usual lead dullness.

Arsenic. In sharp distinction to the failure of its congeners, antimony and bismuth, to deposit at all (as will be discussed later), arsenic gave a small amount of deposition, anhydrous $AsBr_3$ being used as the electrolyte. The greater part of the salt added to 30 c.c. of ammonia failed to dissolve, though it was obvious that there had been some preliminary reaction between it and the ammonia, since the precipitate took on the appearance characteristic of aqueous $Al(OH)_3$. A density of 833 milliamperes per square decimeter, requiring 2.5-2.8 volts, with a lump of sublimed arsenic as anode, gave considerable gassing at the cathode, but a thin, quite uniform deposit of dark metal did form, both front and back being covered. The deposit was definitely metallic in appearance, and dissolved very rapidly in concentrated HNO_3 (aqueous). Because of anode disintegration, no anode loss could be computed; deposition was only 5.1% of coulombmeter theory.

Chromium. Electrolysis of $Cr(CNS)_3$, using aqueously deposited chromium as anode, with a cathode current density of 16,700 milliamperes per square decimeter, required between 5 and 6 volts for operation, and gave a complete thick plate on the front of the cathode, with a somewhat scanty deposit on the back. Electrode separation was only 12 mm., yet the throwing power proved far better than for most aqueous chromium baths, though still far from good, particularly when compared with other metals. Hydrogen and metal were co-deposited continually during the electrolysis and the gas had to be blown off to prevent excess pressure in the cell (lower current densities also gave vigorous gassing at both electrodes). Based on Cr^{+++} considerations, anode corrosion was 14.4%, cathode deposition only 1.2%. Electrode attack and deposition were of the same general order of magnitude with lower current densities, too, which did not give adequate plating. Chromium, therefore, acts much the same in ammonia as in water, with a sharp tendency toward anode passivity.

Manganese. In direct contraposition to the difficulties encountered with aqueous deposition of manganese, electrolysis in ammonia gave excellent results, except for the grave tendency of the plate to peel and flake off. Manganese metal of 97.2% purity was used as an anode; iron present being 1.48% and silicon 0.23%. A current of 167 milliamperes per square decimeter was used, the low voltage of about 0.9 being explained to an extent by the small electrode separation—8 mm. As electrolyte, $Mn(CNS)_2$ was used. The salt—0.2574 grams in weight—with 30 c.c of ammonia, did not dissolve completely, but formed a cloudy suspension. The deposit was not only complete on the front, but also covered most of the back of the cathode, indicating fairly good throwing power. Some of the cathode metal peeled off on the least jarring; it was washed and weighed separately. Anode corrosion was 95.4% and cathode deposition 97.8%. The metal obtained was of high purity—crystals exposed in the laboratory for some time retained their lustre, without the usual rusting, this freedom from corrosion being a characteristic of the pure metal.[1] Iron, if at all present in the deposit, was so extremely low as to give no color with the delicate thiocyanate test.

Iron. By the use of ferrous iodide at a current rate of 116-133 milliamperes per square decimeter, perfect deposition of iron was obtained; the voltage being approximately 2.75. Throwing power was excellent. Anode corrosion, rather surprisingly, ranged only from 5.4 to 6.0%, while deposition dropped to 8.7% on the optimum current density, rising again sharply to 29.2% with higher values of current. Gassing at both electrodes serves to explain the low current efficiencies.

Nickel. As with aqueous solutions, ammonia electrolysis gives fine adherent deposits of nickel, platinum-like in brightness, with fine throwing power. $Ni(CNS)_2.4NH_3$ was used, being synthesized by the method suggested by Bohart.[2] Extremely low current densities were required to prevent the deposit from peeling; only by dropping to 50 milliamperes per square decimeter was perfect adhesion obtained. No gas was evolved in any electrolysis. In the best run, 1.1579 grams of the salt were dissolved in 40 c.c. of ammonia; electrode separation was 21 mm. and a voltage of approximately 1.25 was required. Anode corrosion was 104.5%; cathode deposition 92.3%.

Cobalt. Cobalt was deposited in an analogous manner, 0.6534 grams of $Co(CNS)_2$, not entirely nickel-free, dissolving completely in 35 c.c. of ammonia. As anode, aqueously electrodeposited cobalt was used. A square decimeter density of 100-117 milliamperes required 0.7-0.8 amperes for 14 mm. separation. The deposit was considerably darker than in the case of nickel, with the slightest tendency toward blackness at certain points. Adherence was perfect, as was also the throwing power, the back being plated equally with the front. Anode loss and cathode gain were identical and close to theoretical, 98.0%.

Palladium. By the solution of 0.2578 grams of PdI_2 in 30 c.c. of ammonia (solution was readily accomplished) and electrolysis with an insoluble platinum anode, a bright shiny deposit of palladium metal was obtained, completely covering both front and back of the cathode. The current density was about 116 milliamperes per square decimeter at 1.7 volts. Electrode separation was 13 mm. Cathode deposition proved to be only 68.7%; perhaps depletion of Pd^{++} will explain the low results, though no gassing as such was observed.

Platinum. Rather surprisingly, platinum gave considerable difficulty, in this respect ammonia being radically different from water as a solvent. With the tetraiodide as the electrolyte 167-233 milliamperes per square decimeter failed to give any deposition at all, and higher current densities—1700 milliamperes or so to the square decimeter—caused considerable burning, though even under these conditions deposition efficiencies were low. A

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[1] Royce and Kahlenberg: Trans. Am. Electrochem. Soc., 50, 281-300 (1926).

[2] G. S. Bohart: J. Phys. Chem., 19, 537-63 (1915).

thin greyish deposit was the best that could be obtained, with some burnt spots. In all electrolyses, hydrogen was evolved profusely. It is interesting to note that in aqueous deposition of bright platinum, it is necessary to cut down the Pt^{++++} concentration sharply by means of phosphates or similar ions, otherwise "platinized" types of plates will result. Here, hydrogen was inevitable with any deposition at all, yet the deposit was hardly a really good one and was not very adherent. The best run indicated a 10.0% cathode efficiency, 0.2339 grams of PtI_4 being dissolved in 25 c.c. of ammonia with anode and cathode 16 mm. apart. Current density was about 1,670 milliamperes per square decimeter, and 8-12 volts were required, rising toward the end, perhaps because of a tendency for depletion near the cathode.

This brings to an end the metals where success was attained. Deposition failure occurred, among those tried, with two metals readily deposited in water, and with four which are akin in their aqueous action to that of ammonia. The former included antimony and bismuth, while the latter were represented by aluminum, thorium, tungsten and molybdenum.

Aluminum. Electrodeposition of beryllium raised great hopes for similar success with aluminum, particularly in view of the generally accepted lower electromotive position of aluminum. Nothing of the sort materialized, however; proving, if nothing else, the danger of thinking strictly by analogy. Despite the high solubility of AlI_3 at room temperatures, such solubility proved very sharply lower at the normal boiling point of ammonia and only a small portion of the salt dissolved. With the various current densities tried, there was vigorous gassing and a blue-black film seemed to form on the cathode, but this deposit, if such it was, disappeared whenever the current was turned off. Perhaps some subiodide, subnitride, or similar compound was forming by reduction. Anode corrosions (the anodes were of Hoopes Process aluminum, 99.957% pure) varied considerably, from 86.3% to 105.9%. An ammono-alkaline solution of KNH_2, with AlI_3 added to it, also failed to yield a deposit. Anode corrosion here was 84.5%.

Thorium. Thorium occupies, to the best of our present knowledge, a position in the aqueous electromotive series about the same as that of aluminum. Its failure to deposit in ammonia may or may not be in some way related to this fact. Both the iodide and bromide were tried, though in all cases, very little of the salt dissolved. Current densities of 167 to 11,700 milliamperes per square decimeter of cathode failed to yield anything but gassing. The addition of KI to a $ThBr_4$ solution caused electrolysis to separate out the blue solution of metallic potassium, but no thorium appeared. In all routine cases, the voltages necessary rose rapidly with continuation of the electrolysis, indicating rapid depletion of the conducting ions; for the bromide, the full 110 volts were required at times.

Bismuth. In these low temperature runs, attempts were made to electroplate from the anhydrous bromide, and also from the anhydrous chloride with an effort to boost the solubility by addition of acid in the form of ammonium chloride. Only a small portion of either salt dissolved, and electrolysis yielded strong gassing at the cathode. Both types of run showed full, and over, anode attack—108.4 and 109.3%. At the anode, a bismuth plate 4 square centimeters in size, a white salt seemed to form during operation, and slowly float away. Voltages rose in both types of run, indicating decomposition of the electrolyte.

Antimony. Essentially the same situation held true for antimony. The tribromide dissolved to so small an extent that no deposition was possible.[1]

Molybdenum. The electrolyte used in the many attempts at precipitating molybdenum was the pentachloride.[2] Electrolyses were tried at various current densities, ranging from 67 to 15,200 milliamperes per square centimeter. Except for black or brown films occasionally found on the cathode, which probably represented lower-valence compounds of molybdenum, ammoniated or ammonlyzed, there was no deposition. Anode corrosions on pure molybdenum sheet were relatively low, but quite consistent, considering the range of current densities—the lowest was 23.0% based on Mo^{+++++}, the highest 36.8%. Voltage requirements were not at all excessive, even though the salt proved relatively insoluble in the solvent at −33°C.; a dark precipitate, slow in settling, always formed.

One experiment was made involving the addition of ethyl acetate to the ammonia, in the hope of increasing the $MoCl_5$ solubility. This was based on the work of Lloyd,[3] who showed that $MoCl_5$, dissolved in methyl or ethyl acetate, conducted extremely well, but definitely failed to give any hope along electrodeposition lines. As in all other runs, gassing was strong, but was rather difficult to watch here because the solution turned black, though no visible precipitate as such appeared for quite some time; when it did, it was brownish-black in color, the solution remaining black nevertheless. It proved necessary to bleed off the hydrogen quite frequently, as was true of all cases where deposition failed. There was absolutely no plating of metal, despite fairly good conduction. Anode corrosion was of the same order of magnitude as in other molybdenum runs, 30.3%.

Tungsten. Like the molybdenum it resembles so closely, tungsten failed in all electrodeposition efforts. As ionogen, WBr_5 was utilized. One test was made involving the addition of KI to aid current passage; on electrolysis with 1,670 milliamperes per square decimeter, only hydrogen was formed, but on raising the current, the blue of metallic alkali dissolved in ammonia appeared. Even with as high a current density as 100,000 milliamperes per square decimeter, there was no deposition on the cathode. Quite definitely, potassium separates while tungsten does not.

High Pressure Cell

Since failure with the six metals just listed had been complicated by the adverse factor of low salt solubility, it was hoped that the higher solubility brought by electrolyzing at room temperatures would result in deposition.

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[1] For antimony salts insolubility, see Franklin: Z. anorg. Chem., 46, 33 (1905).

[2] Bergstrom: J. Am. Chem. Soc., 47, 2317-23 (1925).

[3] Lloyd: J. Phys. Chem., 17, 592-5 (1913).

This seemed particularly logical since the aluminum, molybdenum, and tungsten halides used were known to be very soluble at the higher temperature ranges.

Beryllium. Though the deposition of beryllium had proved quite feasible at lower temperatures, it was decided to try a run in the high pressure cell as a check on the cell itself. This time the far more available $BeCl_2$ was used as ionogen; 6.9915 grams were used to 25 c.c. of ammonia. Voltage requirements rose rapidly, indicating a depletion of ions, or coating of the electrodes with carbon halides always found in beryllium chlorides made by the carbon tetrachloride method; within about half an hour of operation, the total internal resistance of the cell rose from about 9 to about 84 ohms. Despite this difficulty, a very adherent, even if fully black, deposit of metal was obtained. Cathode efficiency was only 5.7%, as opposed to an anode attack of 64.8%.

Aluminum. Greatest effort was directed toward the electrodeposition of aluminum, the analogue of which, beryllium, had proven so tractable. Currents tried were from 3,300 to 33,300 milliamperes per square decimeter; these high currents resulted in the cell heating up, and building up pressures as high as 250 pounds, both by increased vapor pressure of the ammonia and by hydrogen evolution. Aluminum iodide was the salt used, about 3 grams to 25 c.c. of ammonia. Electrode separations here were somewhat lower than in the other cell—15 mm. was general. Anode losses ranged from 83.1% to 104.6%, not radically different from values obtained in the low temperature electrolyses.

Thorium. Continuing its electrochemical resemblance to aluminum, thorium failed to give any deposition from a bromide solution, the electrolyses involving current densities as high as 26,700 milliamperes per square decimeter of cathode. Anode corrosions were uniformly high and of the same order of magnitude, as before 128.7%-133.0%. Whatever factor is operative in the case of aluminum probably carries through here also.

Bismuth. Of the two metalloids that had failed deposition, it was deemed better to concentrate on the more metallic bismuth. Both low and high current densities failed to give any deposition whatever, the latter rising as high as 16,500 per square decimeter; rather surprisingly, only 13.4-16.0 volts were required, indicating the presence of considerable electrolyte—most likely, however, the product of ammonolysis. The salt used was $BiBr_3$, anhydrous—about 2.5 grams to 25 c.c. of ammonia. Anode corrosion in the most representative run was 80.6%.

Molybdenum. No greater success was attained in pressure electrolysis of $MoCl_5$ than had attended the lower temperature operation. With 2.3631 grams dissolved in 35 c.c. of ammonia, no deposition was obtained with 5,830 milliamperes to the square decimeter; there was only evidence of strong gassing during the run, as indicated by pressure rise. Electrolytic attack on the anode was lower than previously, being only 17.6%.

Tungsten. This metal followed molybdenum closely, yielding no deposition at all with WBr_5, despite a current of 16,700 milliamperes per square decimeter on the cathode; the cathode remained clean and bright. The anode, a rod of swaged tungsten 4 × 4 millimeters in size, showed a loss of the same order of magnitude as the molybdenum above, viz, 15.5%.

Summary

Many metals can be deposited cathodically from anhydrous ammonia solutions of their salts in compact, adherent form.

Of the commoner metals which can be deposited from water solution, only bismuth and antimony indicate complete failure to deposit cathodically from ammonia.

Of the commoner metals not deposited from aqueous electrolytes, beryllium is the only one found successful in ammonia (other than the alkalies and alkaline earths, as long previously known).

An electrolysis cell has been designed for high pressure electrodeposition studies.

High pressure, room temperature electrolyses do not give electrodeposition in ammonia in the case of those metals failing at the normal boiling point of the solvent.

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AN X-RAY STUDY OF THE ALLOYS OF SILVER WITH BISMUTH, ANTIMONY AND ARSENIC. PART II

BY S. J. BRODERICK AND W. F. EHRET

The Silver-Arsenic System

The earliest systematic investigation of the silver-arsenic system was carried out by Friedrich and Leroux.[1] Using both the thermal and microscopical methods of analysis, Heike and Leroux[2] completed the work of the former men and established the diagram shown in Fig. 1. Their analysis revealed a solid solution region (α) between 95 and 100%* silver. The eutectic came at 540°C. and 82% silver. It consisted of arsenic and β mixed crystals (7.5% As) and upon cooling below 374° the β phase was transformed into the eutectoid of arsenic and α.

Preparation of Alloys

The vapor pressure of solid arsenic reaches one atmosphere at about 615°. At temperatures above this the metal sublimes rapidly without melting if kept in an open vessel. Consequently this series of alloys could not be prepared in open crucibles. Instead, transparent quartz tubes were used. By means of an oxygen-gas flame the tubes were sealed at one end and drawn out to a rather small bore at a point two or three inches from the closed end. Weighed pellets of silver and portions of powdered arsenic were introduced, connection was made to a vacuum pump and the tubes were sealed off. Evacuating eliminated the possibility of oxide formation. The melts were made in an electric muffle furnace at the temperature at which fusion took place. It was found advisable to keep the temperature as low as possible in effecting fusion because arsenic develops a considerable vapor pressure at temperatures above its melting point. The vapor pressure of pure arsenic is 36 atmospheres at the melting point, 814°. In order to insure a thorough mixing, the tubes were inverted after the first fusion and the alloys remelted. The method of chemical analysis and the X-ray apparatus were the same as mentioned in Part I of this paper.[3] Quenched specimens were obtained in the usual manner, i.e., filings were first sealed in evacuated quartz tubes, then annealed, and finally quenched in cold water. This practice rapidly brings the alloy to a state of equilibrium at the elevated temperature and the quenching is quick and uniform. Annealing temperatures were controlled by means of a calibrated thermocouple.

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[1] Friedrich and Leroux: Metallurgie, 3, 192 (1906).

[2] Heike and Leroux: Z. anorg. Chem., 92, 119 (1915).

* The percentage compositions are weight percents unless otherwise mentioned.

[3] Broderick and Ehret: J. Phys. Chem., 35, 2627 (1931).

Experimental Results

In this system, only the range from 20-100% silver was studied because of the difficulty of preparing alloys with high arsenic content. Plate 1 shows a series of photograms of the silver-arsenic alloys. On the photogram of the 20% silver alloy one can easily see the superimposed patterns of the two phases, arsenic and alpha. These two phases coexist at ordinary temperatures up to a composition of 95% silver which marks the limit of the solid solution range of arsenic in silver. This limit could not be determined with any degree of accuracy by plotting percentage composition against the size of the silver lattice (as was done in the silver-bismuth system) because the increase in the silver lattice parameter is so slight. The microscope is more accurate in fixing this point which has been found to be close to 5% arsenic. The increase in the silver lattice is from 4.076 to 4.080 Å. Since this difference is only slightly greater than the experimental error it might easily be ascribed to the latter if it were not for the fact that the photogram for the 94.2% silver alloy was taken simultaneously with that of pure silver and it is easily seen that a shift in the diffraction lines has occurred. These patterns were taken on the same film under identical conditions of exposure, development, and drying. It is therefore concluded that arsenic expands the silver lattice slightly. When less arsenic is dissolved in the silver (97.9% Ag, Plate 1) the shift in the silver

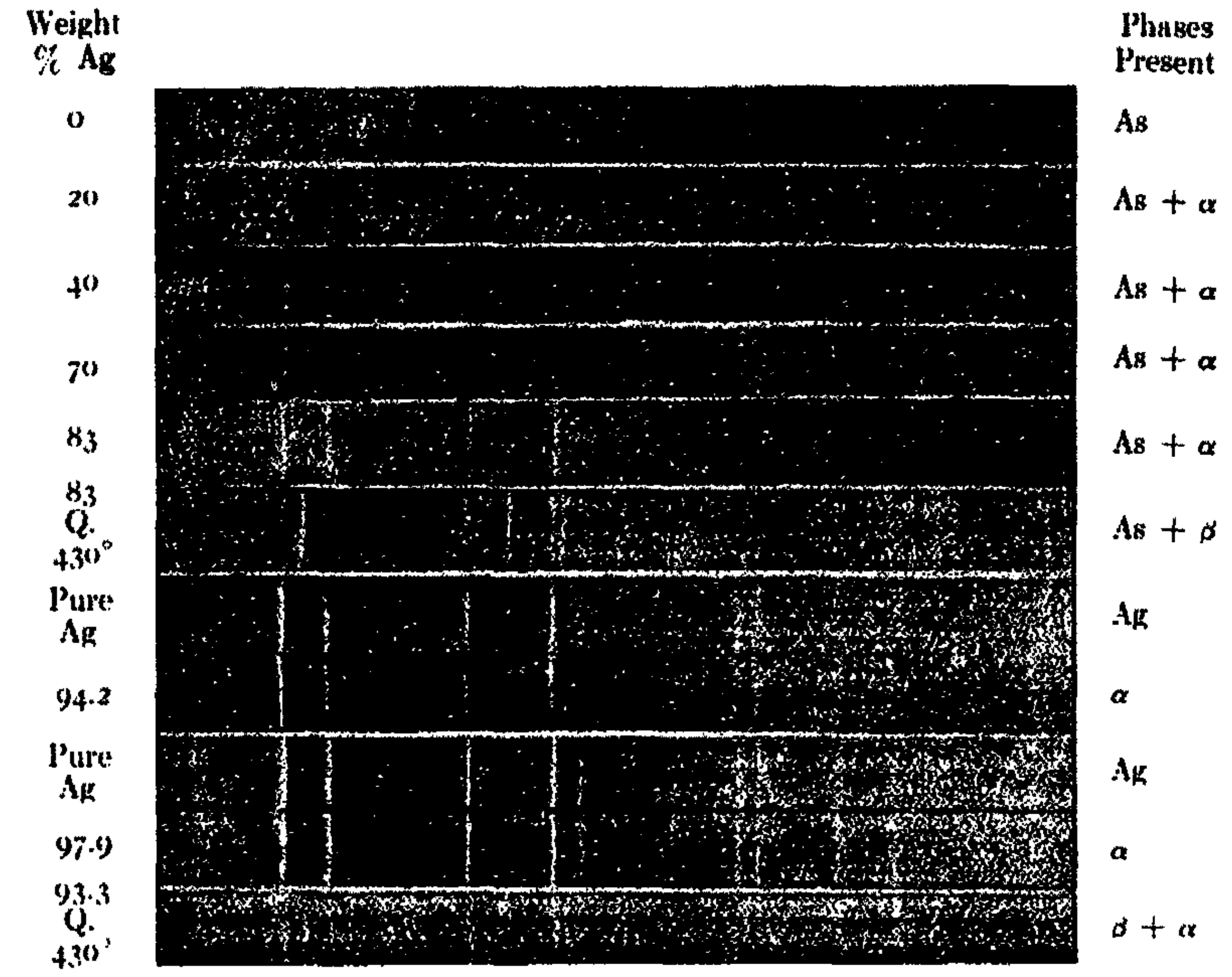

Plate I

Powder Photograms of the System Ag-As.
Mo-K Radiation

lattice can no longer be detected. The agreement between the measured density of the 5% arsenic alloy (10.25 gms. per cc.) and that calculated (10.26) indicates that the solid solution is one that is formed by simple substitution. From the fact that none of the photograms reveal a diffraction pattern for arsenic that differs from that of pure arsenic, it is concluded that the solubility of silver in arsenic is very low or nil.

Beta Phase: Microscopical investigation of quenched specimens by Heike and Leroux[1] indicated the existence of this solid phase at temperatures above 374°. Their diagram shows the phase at the composition 92.5% silver. The authors have also found this phase under the microscope in specimens quenched from 475°. An examination of the photograms of alloy specimens that had been quenched from 430° or 480° and that lay in the range 80-95% silver, revealed the diffraction pattern of the β phase. From the fact that no changes in the lattice constants of the phase were noted it is inferred that the phase has either a very narrow homogeneity range or it is homogeneous over a range of a few percent and no change in lattice accompanies the change in composition. The composition of the phase is probably close to that found microscopically (92.5% Ag) since the photogram of the 89% silver alloy contained faint indications of the strongest diffraction lines of arsenic and the 93.2% alloy was decidedly two-phased, $\alpha + \beta$. These two percentages therefore lie on opposite sides of the homogeneity interval of the β phase. Rapid quenching from 390°, which, according to Fig. 1, should result in the appearance of the diffraction pattern of this phase, gave no indication of it. This points to the conclusion that the β phase is not stable at temperatures as low

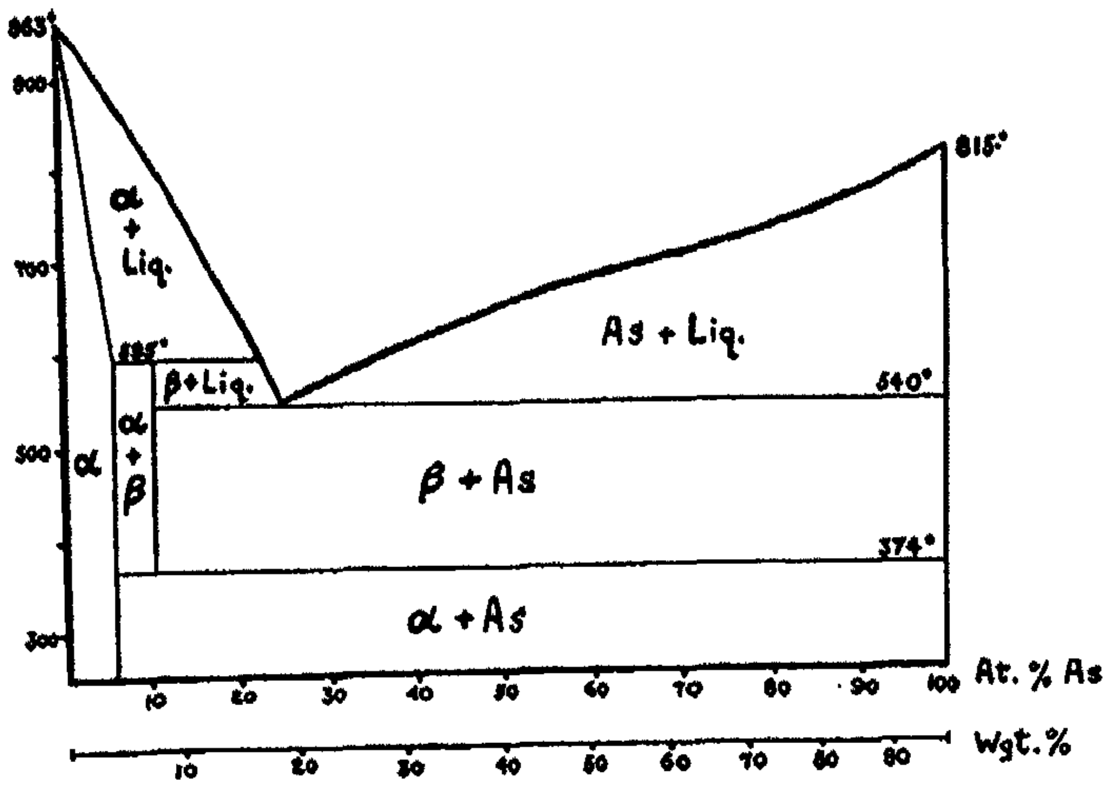

FIG. 1

Equilibrium Diagram of the System Ag-As according to Heike and Leroux.

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[1] Heike and Leroux: loc. cit.

as 390°. Since Heike and Leroux observed pronounced temperature halts at 374° for many of their alloys, it will require further experiments to settle this apparent disagreement between the thermal and X-ray analysis concerning the lower limit of stability of the β phase.

TABLE I

89% Ag.-11% As. Quenched from 480°C. Beta Phase

Indices	K Radiation of Mo.	Intensity	Spacing of Planes Observed	$\sin^2\Theta$ Observed	$\sin^2\Theta$ Calculated
100	α	M	2.500Å	0.0202	0.0201
001 (2)	α	W	2.360	0.0226	0.0226
101	α	S	2.220	0.0260	0.0258
102	α	W	1.720	0.0426	0.0427
110	α	M	1.445	0.0604	0.0603
103	α	S	1.336	0.0711	0.0710
112	α_1	M	1.238	0.0818	0.0818
112	α_2	M	1.229	0.0839	0.0840
201	α_1	M	1.213	0.0852	0.0848
201	α_2	M	1.204	0.0874	0.0873
001 (4)	α_1	V.V.W.	1.183	0.0895	0.0895
001 (4)	α_2	V.V.W.	1.174	0.0920	0.0912
101 (2)	α_1	W	1.110	0.1017	0.1017
101 (2)	α_2	W	1.101	0.1045	0.1044
104	α_1	W	1.069	0.1097	0.1094
104	α_2	W	1.063	0.1121	0.1116
103 (2)	α_1	W	0.982	0.1299	0.1296
103 (2)	α_2	W	0.976	0.1330	0.1330
211	α_1	M	0.931	0.1446	0.1442
211	α_2	M	0.926	0.1478	0.1485
114	α_1	M	0.916	0.1494	0.1490
114	α_2	M	0.911	0.1527	0.1524
105	α_1	M	0.886	0.1596	0.1598
105	α_2	M	0.881	0.1633	0.1630
213	α_1	M	0.814	0.1891	0.1890
213	α_2	M	0.809	0.1936	0.1941
001 (6)	α_1	W	0.789	0.2013	0.2016
001 (6)	α_2	W	0.785	0.2057	0.2052
205	α_1	V.W.	0.755	0.2198	0.2190
205	α_2	V.W.	0.751	0.2247	0.2242
101 (3)	α_1	V.W.	0.741	0.2282	0.2286
101 (3)	α_2	V.W.	0.737	0.2333	0.2339

$a_1 = 2.891$ Å. (Side of elementary parallelopiped)
$a_3 = 4.722$ Å. (Height of elementary parallelopiped)
$a_3/a_1 = 1.633$ = Axial ratio.

The structure of the β phase has been determined from measurements of the photogram of the 80% silver alloy quenched from 480°. Both from the position and the intensity of the diffraction lines it belongs to the hexagonal close-packed system with two atoms per elementary parallelopiped. The spacing of the planes together with the calculated and observed $\sin^2 \theta$ values are given in Table I. The size of the unit cell is found from the quadratic formulae already given in connection with the epsilon phase in the silver-antimony system (Part I). Silver and arsenic atoms are distributed at random in the lattice.

The constants A and B for the quadratic equations are calculated upon the basis of an average wave length of 0.710 Å. and also for a wave length of 0.708 Å. ($K\alpha_1$) and 0.712 Å. ($K\alpha_2$). These are given in Table II.

TABLE II

Mo-K Radiation	Wave Length	A	B
α_1	0.708 Å.	0.0198	0.0056
α_2	0.712	0.0204	0.0057
α	0.710	0.0201	0.00565

Additional support for the choice of structure is found from a comparison of the calculated and experimental values of the density. The density calculated from the structure is 9.94 gms. per cc., in good agreement with the experimental value of 9.98.

Discussion of the Ag-As, Ag-Sb, and Ag-Bi Systems and their Relation to other Alloys

A survey of the three systems examined shows that they contain several analogous structures. In all three cases there is a limited amount of solid solution in silver (α phases) and silver is practically insoluble in the other metals. In the Ag-Sb and Ag-As systems a hexagonal close-packed structure is found at 89.5 atomic % silver. This phase has a considerable homogeneity range in the former system (84-90 atomic % silver) whereas in the latter case this range is very narrow and the phase is stable only at elevated temperatures. The rhombic ϵ' phase in the Ag-Sb system does not find its counterpart in the other two systems. Ag-Bi, with the exception of the end members, shows little structural relationship to the other two systems, a state of affairs that has also been found in the series Cu-As,[1] Cu-Sb,[2] and Cu-Bi[3]. The latter system shows little resemblance to the other two whereas it resembles Ag-Bi markedly. A possible means of explaining this difference of the Bi alloys and also the general simplicity of the equilibrium diagrams of the binary alloys of Bi, lies in the fact that Bi possesses a larger atomic volume and

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[1] Katoh: Z. Kristallographie, **76**, 228 (1930).

[2] Westgren, Hägg and Eriksson: Z. physik. Chem., **B4**, 453 (1929).

[3] Ehret and Fine: Phil. Mag., **10**, 551 (1930).

smaller nuclear density[1] than all other metals with the exception of the very light alkalies and alkaline earths.

It has often been demonstrated that a knowledge of atomic volumes and radii is of considerable help in explaining the changes that take place in structural constants when solid solutions are formed. It has been pointed out that the atomic volume is practically constant for an element in all its compounds and solid solutions. Although the authors are of the opinion that the size of atoms is only of secondary importance as a determining factor in the structure of intermetallic phases, it will be of interest to examine the effect of introducing As, Sb, and Bi atoms respectively into the silver lattice. Table III presents values for the volumes occupied by the atoms in the pure metals. Table IV shows a regular decrease in solubility of added metals as their atomic volumes increase. The unusually large increase in the Ag lattice, produced by Sb, is difficult to explain. The additivity rule, in its widest sense, is apparently not applicable here, since the effective atomic radius and volume of Bi are certainly larger than those of Sb.

TABLE III

Volume occupied by Atoms

	Ag	As	Sb	Bi
Calculated from volume and no. of atoms per unit cell	16.9 Å^3	23.5 Å^3	30.2 Å^3	35.3 Å^3
Calculated from density and atomic weight	16.9	21.6	29.9	35.2
Bernal's value (loc. cit.)	16.9	—	23.6	34.0

TABLE IV

Expansion of Lattice in Solid Solutions

	As	Sb	Bi
Approx. solubility in Ag under ordinary conditions. In atomic %	7.0	5.0	3.0
Linear increase in Ag lattice in forming satd. solid soln. In Å	0.004	0.033	0.011
Linear increase per atomic percent added metal	0.0006	0.006	0.004

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[1] Bernal: Trans. Faraday Soc., 25, 367 (1929).

As the result of their broad experience with crystal structures as they exist in metallic systems, Westgren and his co-workers have announced two generalizations which have some bearing upon the systems under consideration here. Their first rule may be stated as follows: In binary metallic systems, structurally analogous phases recur when the composition is such that the ratio of valency electrons to atoms has reached a certain value. It seems quite certain that this ratio is of primary importance as a factor determining the structure of intermetallic phases. Thus it has been noticed that a close-packed hexagonal structure is found in many systems when the composition is such that the above ratio is 7:4.[1] This holds true in the systems Ag-Sb and Cu-Sb in which the ϵ phases occur very close to the compositions corresponding with a 7 to 4 valency-atom ratio. The hexagonal close-packed β phase (92.5% Ag) in the Ag-As system occurs at a composition considerably removed from the one expected,—$Ag_{13}As_3$, 86% Ag, 7:4 ratio. Likewise, Katoh[2] found a hexagonal (not close-packed) phase in the Cu-As system at 28.6% As when a close-packed one might have been expected at or near 21.5%.* These discrepancies might conceivably be attributed to the nature of the arsenic atom whose non-metallic properties are well known. Binary combinations containing a metal and arsenic are probably more akin to heteropolar unions than to metallic systems.

The second generalization concerns the space occupied by individual atoms in intermetallic phases. In practically all cases, alloy phases are formed with a contraction in volume per atom[3]. That there is contraction in the systems Ag-Sb and Cu-Sb has already been reported[1]. The authors have found a similar contraction in the Ag-As alloys as may be seen from Table V. It has been assumed that there is linear variation of volume per atom with composition in order to obtain the values in the column headed: Volume per atom, calculated.

TABLE V

The Volume per Atom in the Ag-As System

Atomic percent Arsenic	Phase	Volume per atom (observed)	Volume per atom (calculated)	% contraction
0.0	Ag	16.9 Å³	16.9 Å³	—
7.0	Saturated α	17.0	17.4	2.3
10.5	β	17.1	17.7	3.4
100.0	As	23.5	23.5	—

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[1] Westgren and Phragmén: Trans. Faraday Soc., 25, 379 (1929).

[2] Katoh: loc. cit.

[3] Westgren and Almin: Z. physik. Chem., B5, 14 (1929).

* Katoh does not mention quenching alloys in the region 21% As from higher temperatures. It is possible that a hexagonal close-packed structure exists at elevated temperatures.

Summary

The X-ray crystal structure examination of the Ag-As system supports the thermal diagram of Heike and Leroux in the main.

The solubility of arsenic in silver is close to 5 weight percent. Within this phase the lattice parameter is increased from 4.076 Å for pure silver to 4.080 Å. for the saturated phase. The solubility of silver in arsenic is practically nil. A β phase (ca. 7.5% As) appears at higher temperatures. Its structure is hexagonal close-packed with an axial ratio of 1.633. The side of the elementary parallelopiped constituting the unit cell is 2.891 Å. and the height 4.722 Å. The homogeneity range of the phase is very narrow.

The crystal structures found in the Ag-As, Ag-Sb, Ag-Bi, and related systems are discussed from the following viewpoints: (I) structure analogies, (II) atomic sizes, (III) valency-atom ratios, (IV) contraction upon forming intermetallic phases.

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REACTIONS IN THE BRUSH DISCHARGE*

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PART I

The Decomposition of Acetone

M. L. Maquenne working with organic vapors in the silent electric discharge found a decided similarity between the products formed by the discharge and the products formed by the pyrolysis of the same compounds. His first work on this subject[1] was with formic acid. He worked with a discharge tube similar to one introduced by Berthelot.[2] He reduced the pressure in the tube by means of a water pump so that there would be a more uniform discharge. He showed that the volume of hydrogen formed was always very nearly equal to the volume of carbon dioxide formed. This was true also for the gases which Berthelot found were produced by the pyrolysis of formic acid. This, he said, made evident a decided similarity between the two types of decomposition. In both cases the reactions were:

$$HCOOH = CO_2 + H_2$$
$$HCOOH = CO + H_2O$$

In a second paper on silent electric discharges[3] he describes work done with the same apparatus. He says that all substances studied *except benzene* (i.e. formic acid, methyl alcohol, ethyl alcohol, acetic acid, acetone, and methyl formate) decomposed rapidly. Quoting from his article: "Tous les corps étudiés, sauf la benzine qui résiste aux tensions électriques employées (15 millimètres d'étincelle avec condensateur), se décomposent rapidement dans un tube à effluves en oxyde de carbone, acid carbonique, hydrogène et carbures: les gaz sont les mêmes qu'on obtient par la chaleur au rouge sombre, et souvent leurs proportions relatives sont extrêmement voisines."

Because of the importance of Maquenne's conclusions it seemed wise to scrutinize carefully his gas analyses. He did not describe them in detail, but he did say that he had to resort to atmolysis in order to separate the hydrogen from the methane and ethane. He analysed for carbon monoxide by absorption in cuprous chloride solution. In some of his analyses he absorbed carbon monoxide and acetylene together in cuprous chloride. The cuprous chloride method for the determination of carbon monoxide is not now considered to be reliable. Concerning his work on ethyl alcohol he says that the gas had the odor of aldehyde and acetylene, and he continues in the same sentence to say that the gas was washed with water before proceeding with the analysis. If

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* For an excellent description of electric discharges, see Warner and Kunz, "Corona Discharge," Univ. of Ill. Bull. 114.

[1] Bull, (2) 39, 306 (1883).

[2] Ann. Chim. Phys., (5) 12, 463 (1877).

[3] Maquenne: Bull., (2) 40, 60-65 (1883).

he really wanted to know what was present in the gas it is hard to see what good he expected to accomplish by washing it with water; perhaps he thought it would remove the aldehyde. It is this sort of treatment that causes one to question the value of his analyses.

In summarizing his expectations concerning the behavior of acetone in the discharge he says: "La facilité avec laquelle l'oxyde de carbone se produit dans toutes les décompositions précédentes [decomposition of ethyl alcohol, methyl alcohol, acetic acid, and formic acid] nous a fait penser que l'acétone puorrait se dédoubler, par l'effluve, en oxyde de carbone et éthane; l'expérience a complètement vérifié cette prévision." The gases obtained from acetone in the silent electric discharge were as follows:

Pressure in the discharge tube	low	low	50 mm.	100 mm.
Carbon dioxide	1.1	0.6	1.1	0.6
Carbon monoxide	37.5	36.3	40.0	42.1
Ethylene	4.3	4.4	3.5	2.9
Ethane	32.4	33.7	29.7	30.0
Hydrogen	24.7	25.0	25.7	24.4

Acetone decomposed by heat was changed to gas of the following composition:

Temperature	dull red	above dull red
Carbon dioxide	1.2	0.6
Carbon monoxide	39.5	36.0
Ethylene	7.0	3.3
Ethane	22.4	21.8
Hydrogen	29.9	38.3

These figures are strikingly similar to the ones in the preceding table. From these data Maquenne concluded that the reactions occurring in the silent electric discharge are comparable with those due to high temperature.

Alexander v. Hemptinne[1] working with acetone vapor in an electric discharge decided that acetone was decomposed by it primarily into carbon monoxide and ethane because these were the principal constituents of the gas. This was obviously the main primary reaction but it was probably not the only one. He suggested that methane was probably produced by a secondary reaction. He did not go any deeper into the intricacies of the reactions.

G. Poma and A. Nesti[2] working with acetone in a discharge tube of the ozonizer type found that it was decomposed by a 42-cycle current into a gas mixture containing

1.6%	carbon dioxide
5.0	acetylene and ethylene
38.1	carbon monoxide
55.3	methane and ethane

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[1] Z. physik. Chem., 25, 292 (1898).

[2] Gazz., 51 II, 87-88 (1921).

The potential difference across the tube was from 5,000 to 10,000 volts. From the gas analysis they concluded that the main reaction was

$$CH_3\text{-}CO\text{-}CH_3 = CO + C_2H_6$$

This was about the only conclusion that could be drawn, because the acetylene and ethylene were not determined separately and the methane and ethane also were grouped together. Their analysis was not complete enough to enable them to draw any further conclusions about the reactions that produced the gas. Their examination of the exposed acetone revealed the presence of a γ-diketone which they said might be acetonyl acetone. The residue that was left after the acetone was evaporated was fractionally distilled. This fractionation demonstrated to them in striking fashion the complexity of the residue. Translating from their article, "a fractional distillation quickly demonstrated the remarkable complexity of the liquid mixture remaining from the proceeding distillation. The thermometer mounted without interruption, showing no tendency to hesitate at any temperature, until the product finished by decomposing and becoming resinous."

Because Maquenne had shown that silent electric discharges and pyrolysis produce similar products, it seemed advisable to look up work done on the pyrolysis of acetone before experimental work was started with the brush discharge.

Barbier and Roux[1] found that gases produced by the pyrolysis of acetone consisted of carbon monoxyde, methane, ethylene, and hydrogen. They were unable to find ethane in the mixture. They explained this by saying that under the conditions under which they were working ethane was known to decompose into ethylene and hydrogen. In the light of later work[2] it seems probable that ethane was never formed.

Schmidlin and Bergman[3] in 1910 reported ketene as a product of the pyrolysis of acetone. Since that time much work has been done on the reaction.

Peytral[4] passed acetone vapor through a short platinum tube heated to 1150°C. She concluded from her analyses of the gaseous products that the main primary reaction was the formation of ketene, thus:

$$CH_3COCH_3 = CH_4 + CH_2CO$$

She thought that this reaction was followed by a secondary reaction in which some of the ketene was broken up into ethylene and carbon monoxide. The ethylene thus formed was decomposed to some extent into acetylene and hydrogen. She did not list ethane as a product. This is in accordance with the observations of Barbier and Roux,[5] but not in accordance with the data cited by Maquenne.[6]

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[1] Bull., (2) 46, 268 (1886).

[2] Peytral: Bull., (4) 31, 122 (1922).

[3] Ber., 43, 2821 (1910).

[4] Bull., (4) 31, 122 (1922).

[5] Bull., (2) 46, 268 (1886).

[6] Bull., (2) 40, 60-65 (1883).

The most favorable conditions for the production of ketene by pyrolysis have been worked out by Hurd[1] and his associates. These conditions give consistent yields of ketene that range from thirty-five to forty-five percent based on unrecovered acetone.

Considering the extent to which this reaction takes place under favorable conditions when acetone is pyrolyzed, it seemed worth while to look for ketene in the products formed when acetone is decomposed by a brush discharge. It is not surprising that it was not listed as a product by Poma and Nesti[2] in their work on electric discharges through acetone vapor. In the apparatus used by them, if ketene had been formed, it would probably have been dissolved by the acetone in their reflux condensers and carried back to the flask of boiling acetone. The ketene would then have boiled rapidly out of the solution and would have been exposed again to the discharge. The process would have repeated until it was decomposed.

Ketene is very soluble in acetone. Schmidlin and Bergman[3] report that twenty-three percent of the total yield of ketene was dissolved in the condensed acetone. The apparatus that gives the best yields of undissolved ketene[4] was designed so that it would separate the ketene from the condensed acetone as quickly as possible. The solubility of ketene in acetone was used to advantage in the present research. The apparatus that was used was designed so that the gas that was being collected would have to pass through the condensed acetone. Thus most of the ketene was retained by it.

It seemed probable that ultra-violet light emitted by the discharge might play an important part in the decomposition of acetone. Berthelot and Gaudechon[5] have shown that acetone is rapidly decomposed by a 110-volt quartz mercury lamp into a gas containing 49% carbon monoxide, 5% methane and 46% ethane. The predominating reaction in their work was:

$$CH_3COCH_3 = CO + C_2H_6$$

Apparatus

The apparatus used in this work on acetone is shown in Fig. 1. It consists of a flask, A, in which acetone is vaporized; the discharge tube, B; a heater, C, for the discharge tube; a pneumatic trough, H; a water-jacketed tube, FG, for collecting the gas; a leveling bulb, M, which is used to run mercury into FG; and a source of high frequency current.

The discharge tube was simply two concentric glass tubes, R and S, with an aluminum foil electrode, D, around the outside tube and a two millimeter copper wire electrode inside the inside tube. All the important dimensions except the diameter of the small tube are given on the drawing. This small inner tube had an outer diameter of four millimeters and an inside diameter of slightly more than two millimeters.

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[1] "Organic Syntheses," 39 (1925).

[2] Gazz., 51 II, 87-88 (1921).

[3] Ber., 43, 2821 (1910).

[4] Hurd: "Organic Syntheses," 39 (1925).

[5] Compt. rend., 151, 478-481 (1910).

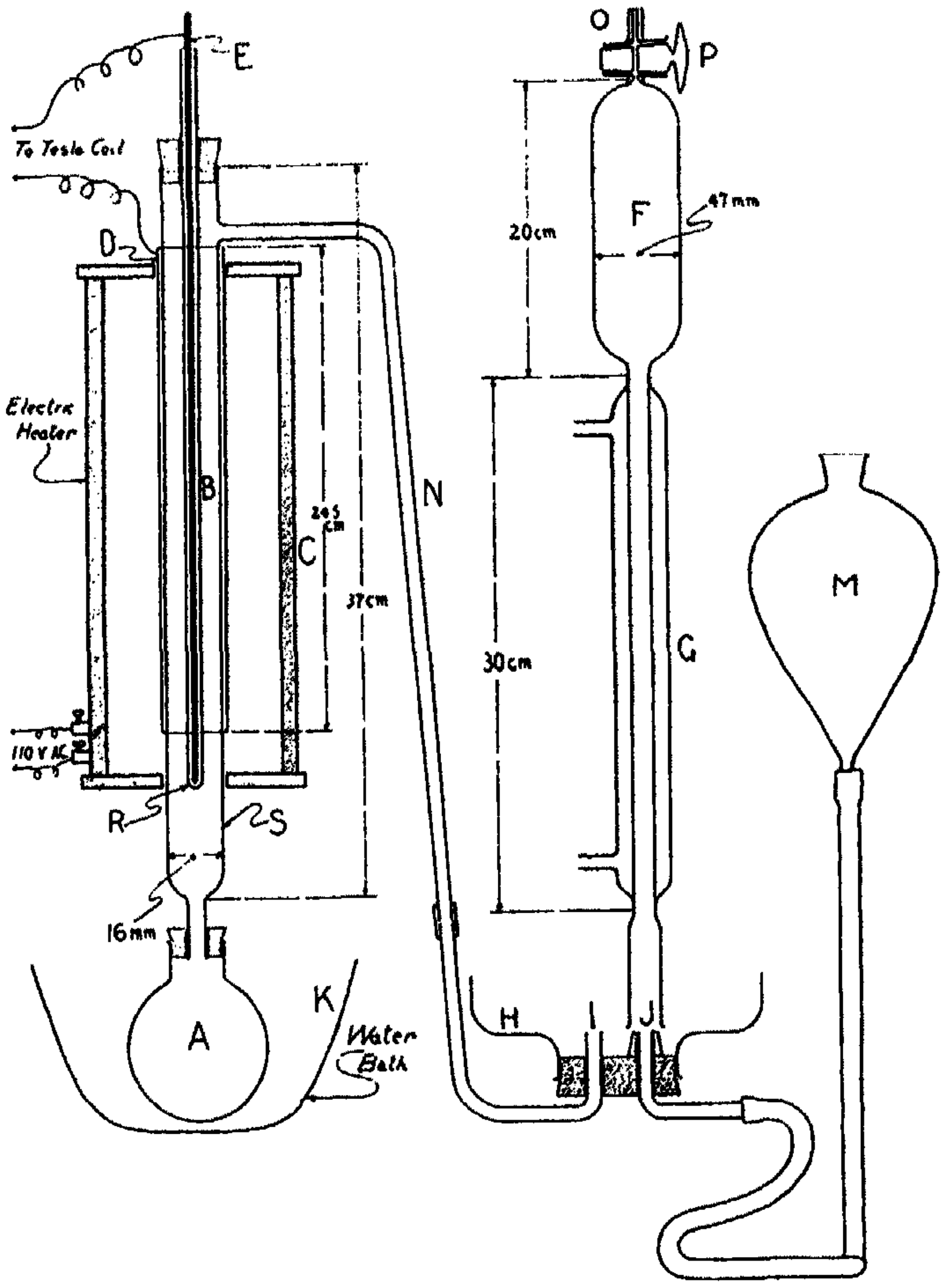

Fig. 1

The High-Frequency Alternating-Current Apparatus

When a charged condenser discharges through a circuit of low resistance the current that flows has a very high frequency. This principle was utilized in the production of the high-frequency current. Three Leyden jars charged by means of a sixty thousand volt transformer were allowed to discharge through a closed circuit of low resistance. The high-frequency current that was thus generated was made available for laboratory use by including the primary of an air-core transformer in the closed circuit. The secondary of the transformer was connected to the discharge tube. The circuit used in this work was very similar to the old-fashioned wireless spark-transmitter hook-up. The main difference was that the wires that ordinarily would lead to an antenna and ground were connected instead to the two electrodes of the discharge tube. The circuit is shown in Fig. 2. Morecroft[1] discusses such circuits in a very enlightening way. He says, concerning the function of spark gaps in these circuits: "In order that the condenser may be charged to the high potentials required for large energy storage, and to permit its discharge in a suitable closed circuit of low resistance, that circuit must contain an element whose resistance decreases instantaneously when the condenser discharges and remains at a very low value during the period of discharge. This requirement is fulfilled by the ordinary spark gap, the resistance of the gap being very high before breakdown occurs, but decreasing to a very small value when the gap has broken down under the increasing potential impressed across its terminals. The spark gap and spark are thus essential to transmitters generating high-frequency oscillations by means of condenser discharges."

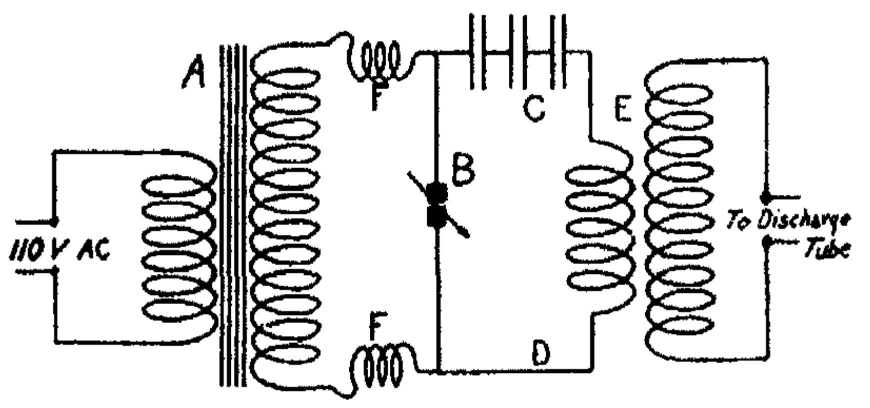

Fig. 2

The parts of the high-frequency current generator and their functions may be summarized as follows: *A* is a 3 KVA transformer capable of transforming 110 volts to 60,000 volts. It was used to charge the three Leyden jar condensers, C. The spark gap, B, automatically closed the condenser circuit when a high enough potential had been reached. While sparks were passing across the gap the condensers were discharging and therefore a high-frequency current was passing in the circuit, BCD. The air-core transformer, E, transferred the high-frequency current from the closed circuit to the electrodes of the reaction tube. The primary of the air-core transformer consisted of six turns of heavy copper wire. The secondary was made up of sixty-five turns of annunciator wire. Both the primary and the secondary were supported by a wooden frame. The choke coils, F, were mounted directly on the terminals of the transformer. They were placed in the circuit so that the high frequency current could not pass back into the transformer.

A Description of the Discharge

Warner and Kunz[2] say that "electrical discharges in gases at pressures near that of the atmosphere may be divided into five classes. These are:

1. "The dark discharge, where a small current passes through gas without making itself visible.

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[1] "Principles of Radio Communication," 330, 357 (1927).

[2] Univ. Illinois Bull., 16, No. 114 (1919).

2. "The glow discharge, where a larger current passes and the gas in the immediate neighborhood of the electrodes becomes faintly luminous.

3. "The brush discharge, such as that from points where the glow is irregular and extends into the gas some distance from the electrodes.

4. "The spark discharge, which is a transient phenomenon bridging the whole distance between the electrodes, accompanied by a bright light and a comparatively large current.

5. "The arc, in which a large current passes between the electrodes in the gas and the ionized vapors of the electrodes producing a continuous light.

"Any one of the first forms of discharge may be converted into one of the latter forms by an increase in the potential between the electrodes, depending upon the nature and pressure of the gas and the spacing, size, capacity, and shape of the electrodes."

This classification is obviously an arbitrary one. The discharge used in the work on acetone was, according to this classification, more a brush discharge than anything else. The discharge was made up largely of streamers. A large number of fine sparks also were passing. When the potential was raised gradually it was difficult to tell just when the sparks started to pass. At high potentials the tube seemed to bristle with these very fine hair-like sparks. Whether or not the sparks were passing, the predominating discharge seemed to be due to streamers.

Experimental Part

Acetone was placed in the flask, A. The temperature of the water bath around A could be kept uniform at any desired temperature. Thus with a uniform application of heat the acetone vapor would pass through the discharge tube at a more uniform rate. When the work was started it was not known whether or not the rate of flow of vapor through the tube would affect the results. Therefore the water bath was used as an aid in obtaining reproducible conditions and also to prevent superheating. Later it was found that this precaution was unnecessary.

The acetone vapor passed up through the heated discharge tube and was expelled under mercury at I. After all air had been swept out of the tube the mouth of the mercury filled bulb, FG, was placed over I. The high-frequency current was then turned on and a stop-watch was started. As the acetone vapor and gas passed up through the water-jacketed tube, G, the acetone was condensed and the gas collected over the liquid acetone. When F was filled with liquid acetone and gas, the discharge was turned off and the time read on the stop-watch.

It was necessary to correct the results of the gas analyses for gases dissolved in the condensed acetone and also to remove the acetone vapor from the gas sample before the analysis was started. Solubilities of the gases in acetone were found in Seidell: "Solubilities of Organic and Inorganic Substances." Due to the fact that acetylene is extremely soluble in acetone it was not considered necessary to analyse for it in the gas. At 25° C and one atmosphere, one liter of acetone dissolves 15.231 grams of acetylene. Analysis of the condensed acetone showed that there was only a small amount of acetylene present. This justified leaving it out of the gas analysis. The acetone vapor was removed from the gas samples by passing it through a coil of glass tubing immersed in a bath made from solid carbon dioxide and ether. Since the temperature of this bath was never below −78°, none of the constituents of the gas except the acetone were condensed. All other constituents except ketene boiled at temperatures below −78°C. The percentage of ketene was so low in the samples that its very low partial pressure would prevent it from condensing at −78°C.

The condensed acetone had to be analyzed for two constituents, acetylene and ketene. The total volume of the acetone condensed was measured. A known portion of this was used for each.

The analysis for acetylene was made as follows: About a half gram of copper sulphate was dissolved in 25 cc of hot water. Ammonium hydroxide was added until the solution was dark blue. Hydrazine sulphate was then added to the warm copper solution until it became pale blue. The acetone that was to be analyzed for acetylene was added. Cuprous acetylide was precipitated as a red powder. This was filtered off by suction and washed with dilute ammonia and finally with water. The precipitate was dissolved on the paper with hot 6 N hydrochloric acid. The paper was washed with dilute ammonia. About 2 cc of nitric acid and 5 cc of concentrated sulphuric acid were added. The solution was then evaporated until sulphur trioxide fumes were given off. This treatment converted all cupous ions to cupric. The copper was then titrated with thiocyanate using a method described in Scott's "Standard Methods of Chemical Analysis," third edition. The thiocyanate solution was standarized in cc's of acetylene under standard conditions.

Ketene was determined by a method similar to one used by Schmidlin and Bergman.[1] Water was added to the portion of the acetone that was to be analysed for ketene. The solution was then heated to boiling and the acetic acid was titrated with standard sodium hydroxide using phenolphthalein as indicator. The alkali was standardized in cubic centimeters of ketene at standard conditions.

The gas was analysed in a Hempel apparatus using the following methods of determination:

Gas	Method of determination
Ketene	Absorption in potassium hydroxide
Ethylene	Absorption in fuming sulphuric acid
Oxygen	Absorption in alkaline pyrogallol
Hydrogen	Combustion with copper oxide at 270°C
Carbon monoxide	Combustion with copper oxide at 270°C followed by absorption of carbon dioxide in potassium hydroxide.
Paraffins	Combustion with oxygen in a Dennis combustion pipette.

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[1] Ber., 43, 2823 (1910).

TABLE I

	1	2	3	4	5	6	7	8	9
Time of run (min and sec)	6-28	7-00	7-00	12-46	14-26	11-36	11-00	8-00	7-00
Temp. discharge tube ±5°	285.	285.	285.	285.	285.	285.	285.	285.	285.
cc of gas formed	221.8	206.0	202.0	170.0	192.0	196.6	189.8	209.5	169.4
cc of acetone condensed	18.9	31.6	21.5	65.0	43.4	30.3	50.2	48.8	76.8
Summary of gas analyses.—Air-free.—Corrected for Dissolved Gases									
Ketene	11.8	6.9	4.7	6.2	6.7	4.9	5.2	5.8	6.3
Ethylene	7.5	9.1	8.2	8.5	9.3	5.3	7.0	9.9	8.9
Acetylene	trace	trace	trace	trace	trace	trace	0.8	0.9	1.1
Hydrogen	13.9	14.6	14.1	11.4	12.6	12.1	14.0	15.5	16.6
Carbon monoxide	34.2	34.9	38.4	37.8	36.3	35.8	38.6	35.3	35.5
Ethane	20.1	23.0	21.6	23.7	23.4	25.5	26.0	25.6	19.1
Methane	12.4	11.4	13.2	12.5	11.6	16.4	8.6	6.9	12.5

	10	11	12	13	14	15
Time of run (min and sec)	3-18	2-43	2-55	2-52	2-6	2-57
Temp. discharge tube ±5°	110.	110.	110.	110.	285.	285.
cc of gas formed	153.0	129.0	189.0	187.6	129.4	178.1
cc of acetone condensed	122.0	80.2	17.5	16.3	70.8	87.0
Summary of gas analyses.—Air-free.—Corrected for Dissolved Gases.						
Ketene	5.7	4.5	3.1	0.4	4.5	3.8
Ethylene	14.0	10.9	11.0	11.2	13.8	9.1
Acetylene	0.9	1.6	0.7	0.7	1.5	2.2
Hydrogen	18.0	19.2	19.4	19.6	21.0	23.0
Carbon monoxide	34.7	33.5	37.8	38.0	32.9	36.4
Ethane	9.0	11.7	18.7	15.2	11.4	10.0
Methane	17.8	18.5	9.5	15.0	14.9	15.4

The data obtained from fifteen runs are given in Table I. The information obtainable from analytical data concerning the happenings in a discharge tube is fragmentary. It must be pieced together in order to give it meaning. After it all has been fitted into its proper place, a story more or less complete, should result. The completeness of the data determines the completeness of the reconstructed story. If every carbon, hydrogen, and oxygen atom originally present in the decomposed acetone vapor is accounted for by the analysis the whole story can probably be reconstructed.

The limitations of the data obtained in this work may be seen from the percents of carbon, hydrogen, and oxygen in the gas. These values, which are tabulated below, were calculated from the gas analyses. The percentage composition of acetone is given for reference.

	Carbon	Hydrogen	Oxygen
Acetone	62.02%	10.42%	27.56%
Analysis No. 1	60.3	10.2	29.5
2	61.5	11.0	27.5
3	60.6	10.6	28.8
4	61.2	10.5	28.3
5	61.4	10.7	27.9
6	60.3	10.8	28.9
7	61.3	10.7	28.0
8	62.2	10.9	26.9
9	60.7	10.7	28.6
10	60.4	10.5	29.1
11	60.5	11.2	28.3
12	60.4	10.7	28.9
13	60.3	11.1	28.6
14	61.3	11.1	27.6
15	58.8	10.4	30.8

It is evident that the composition of the gas is very nearly the same as the composition of the acetone. Therefore when a molecule of acetone is broken up into gaseous products it is changed completely to gas. Condensations with elimination of a gas do not occur to any great extent.

With these facts in mind one can proceed with confidence to the actual solution of the problem.

In the light of previous work on the decomposition of acetone by electric discharges, and the work on decomposition by pyrolysis it seems probable that some of the following reactions would be the ones that take place:

1. $CH_3COCH_3 = 1\ CO + 1\ C_2H_6$
2. $CH_3COCH_3 = 1\ CH_2{:}C{:}O + 1\ CH_4$
3. $CH_3COCH_3 = 1\ CH_2{:}C{:}O + \frac{1}{2}C_2H_6 + \frac{1}{2}\ H_2$

There may be other reactions in which acetone is changed entirely to liquid or solid products. Such reactions were not looked for or investigated in any way. The only observation related to that subject made during this research was that a small amount of a brown solid material (a few milligrams) collected on the electrodes during a long series of runs.

In all of the reactions listed above, one volume of acetone vapor decomposes to give two volumes of gas. The volume of acetone vapor decomposed to form the sample of gas is equal to the volume of CO plus the volume of ketene since these constituents contain all the $=CO$ groups originally present in the acetone. The sums of these volumes are tabulated below:

Analysis Number	Volume of CO plus ketene	Analysis Number	Volume of CO plus ketene
1	46.0cc	9	41.8cc
2	41.8	10	40.4
3	43.1	11	38.0
4	44.0	12	40.9
5	43.0	13	38.4
6	40.7	14	37.4
7	43.8	15	40.2
8	41.1		

If the reactions listed above were the only ones taking place, the sum of the volumes of carbon monoxide and ketene should be fifty in each analysis because the analyses are calculated for a 100 cc air-free sample. The volumes range from 38 to 46. Since these values are equal to the volume of acetone decomposed, the corresponding volume of gas formed according to the above reactions would range from 76 to 92. In each case it should be 100.

The first secondary reaction that suggests itself is the decomposition of ketene. Under ordinary conditions ketene is very reactive.

4. $2CH_2CO = CH_2 + CO$

This reaction may be written without the intermediate formation of ketene.

5. $2\,CH_3COCH_3 = CH_2CH_2 + 2CO + 2\,CH_4$
1 volume 2½ volumes

The volume of acetone decomposing according to this last equation is equal to two times the volume of the ethylene. If the formation of ethylene and carbon monoxide from ketene is the only secondary reaction the following relation should be true:

$2\tfrac{1}{2}\,(2 \times \text{vol. } CH_2CH_2) + 2\,(\text{acetone decomposed} - 2 \times \text{vol. of ethylene}) = 100$

The calculated values are tabulated below:

Analysis No.	Calculated value	Analysis No.	Calculated value
1	99.5	9	92.5
2	92.7	10	94.8
3	94.4	11	88.7
4	96.5	12	92.8
5	95.3	13	88.0
6	86.7	14	88.6
7	94.5	15	89.5
8	92.1		

These values range from 86.7 to 99.5. This brings out in striking fashion the fact that all of the reactions have not been accounted for.

If the predicted reactions were correct the sum, volume of ketene + 2 × the volume of ethylene, should equal the amount of ketene originally formed, because when two ketenes decompose one ethylene is formed. The amount of ketene formed should also be equal to the sum of the volume of methane and twice the volume of hydrogen, because according to the predictions methane and hydrogen are formed only during the formation of ketene. These two sets of values are tabulated below for comparison:

Analysis No.	Ketene + $2(C_2H_4)$	$CH_4 + 2H_2$
1	26.8	40.2
2	25.1	40.6
3	21.1	41.1
4	23.2	35.3
5	25.3	36.8
6	15.5	40.6
7	19.2	36.6
8	25.6	37.8
9	24.1	45.7
10	33.7	53.8
11	26.3	56.9
12	25.1	48.3
13	23.2	54.2
14	32.1	56.9
15	22.0	61.0

The entire lack of similarity between these columns of figures makes it evident that the assumed secondary reaction is not adequate to explain the gas analysis data. It indicates where the trouble lies. Methane and hydrogen are too high.

The obvious source of the excess hydrogen is from the ethane. The reactions that might occur to produce it are:

6. $CH_3CH_3 = CH \vdots CH + 2\,H_2$
7. $CH_3CH_3 = CH_2{:}CH_2 + H_2$
8. $CH_3CH_3 = CH_4 + C + H_2$

The method of interpretation up to this point has been to assume that the speculative reactions are correct and then test them out with the data. Continuing in this way we see that since acetylene is produced only in reaction number six, it may be considered as a measure of that reaction. The ethane originally formed in reaction one can be calculated by adding the ethane decomposed in reactions six, seven, and eight to the undecomposed ethane. The volume of ethane thus calculated should of course be equal to the volume of carbon monoxide. The ethane decomposed is equal to the volume of hydrogen minus that of the acetylene.

Analysis No.	Ethane undecom.	Ethane decom.	Total	Carbon monoxide
1	20.1	13.9	34.0	34.2
2	23.0	14.6	37.6	34.9
3	21.6	14.1	35.7	38.4
4	23.7	11.4	35.1	37.8
5	23.4	12.6	36.0	36.3
6	25.5	12.1	37.6	35.8
7	26.0	13.2	39.2	38.6
8	25.6	14.6	40.2	35.3
9	19.1	15.5	34.6	35.5
10	9.0	17.1	26.1	34.7
11	11.7	17.6	29.3	33.5
12	18.7	18.7	37.4	37.8
13	15.2	18.9	34.1	38.0
14	11.4	19.5	30.9	32.9
15	10.0	20.9	30.9	36.4

In most of the analyses the total ethane agrees with the carbon monoxide as well as could be expected. In numbers 1, 5, 7, and 12 the agreement is remarkably good. In 8, 10, and 15 the difference is rather large. When the carbon monoxide is larger, it could be explained by saying that some ketene decomposes to produce it. In this case we would expect the ethylene to be somewhat higher than the average. This is, in general, true. The change in ethylene content, however, would not be so marked because one volume of ethylene is formed for each two volumes of carbon monoxide. When the ethane is larger than the carbon monoxide, it could be explained by saying that some ethane has decomposed into carbon and hydrogen. This would cause the ethane to appear larger because the volume of ethane decomposed is calculated from the hydrogen present. It is hardly worth while to push such speculation any farther because of the limitations already pointed out on page 3339.

Conclusions

1. As a general rule, when gaseous products are formed from an acetone molecule, the *whole molecule* is changed to gaseous products. Condensation with liberation of gases does not occur to any great extent.

2. The principal reaction occurring to produce gas is:

$$CH_3COCH_3 = CH_3CH_3 + CO$$

Ethane is produced only in this reaction. A review of the literature has shown that this reaction does not occur during the pyrolysis of acetone. It can not, therefore, be attributed to heat effects in the region of localized discharges. Berthelot and Gaudechon have shown that acetone is rapidly decomposed according to the above equation by ultra-violet light. In our work some or all of the decomposition into carbon monoxide and ethane must have been caused by the light emitted by the discharge.

3. Ketene is produced, just as in the pyrolysis of acetone, by the following reaction:

$$CH_3COCH_3 = CH_2C{:}O + CH_4$$

Most of the ketene formed remains undecomposed. The percentage of it, however, is small. In most of the runs it was about five percent of the gas formed. Conditions are important in the production of ketene by pyrolysis. It is not surprising, therefore, that the yield of ketene was small in this work for no attempt was made to obtain optimum conditions.

4. The hydrogen, ethylene, and acetylene present in the gas come largely from the decomposition of ethane:

$$CH_3CH_3 = CH \vdots CH + 2H_2$$
$$CH_3CH_3 = CH_2{:}CH_2 + H_2$$
$$CH_3CH_3 = CH_4 + C + H_2$$

PART II

The Decomposition of Benzene

Mignonac and Saint-Aunay[1] working with benzene in the silent electric discharge found that it was changed into gas and condensation products The composition of the gas was found to be:

Hydrogen	52.0%	Ethylene	7.2%
Acetylene	32.8	Ethane	7.2

They concluded that the discharge caused the following changes:

1. Depolymerization of benzene into acetylene.
2. Formation of condensation products with the elimination of hydrogen.

A large part of the condensation product was found to be diphenyl. They also isolated a hydrocarbon that had a composition corresponding to dihydrodiphenyl. They explain the formation of these two compounds thus: In the formation of diphenyl an activated molecule and an unactivated one come together and hydrogen is eliminated. Dihydrodiphenyl is formed in the same way but without the elimination of hydrogen. Dihydrodiphenyl is thought to be an intermediate in the formation of the diphenyl.

Studies of the pyrolysis of benzene have shown that diphenyl and hydrogen are the principal products.[2] Considerable amounts of meta and para diphenyl benzenes also have been isolated but no ortho could be detected.

Bates and Taylor[3] working with photosensitization have shown that benzene is decomposed by mercury atoms excited by ultra-violet light. The gaseous products were passed through a trap surrounded by liquid air. The gas that came through was analyzed and found to contain 40% hydrocarbons and 60% hydrogen. A "heavy tarry" deposit formed on the walls of the reaction tube. A strong odor of diphenyl was present.

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[1] Bull., (4) 47, 523 (1930).

[2] Hurd. "The Pyrolysis of Carbon Compounds," 93-5.

[3] J. Am. Chem. Soc., 49, 2438 (1927).

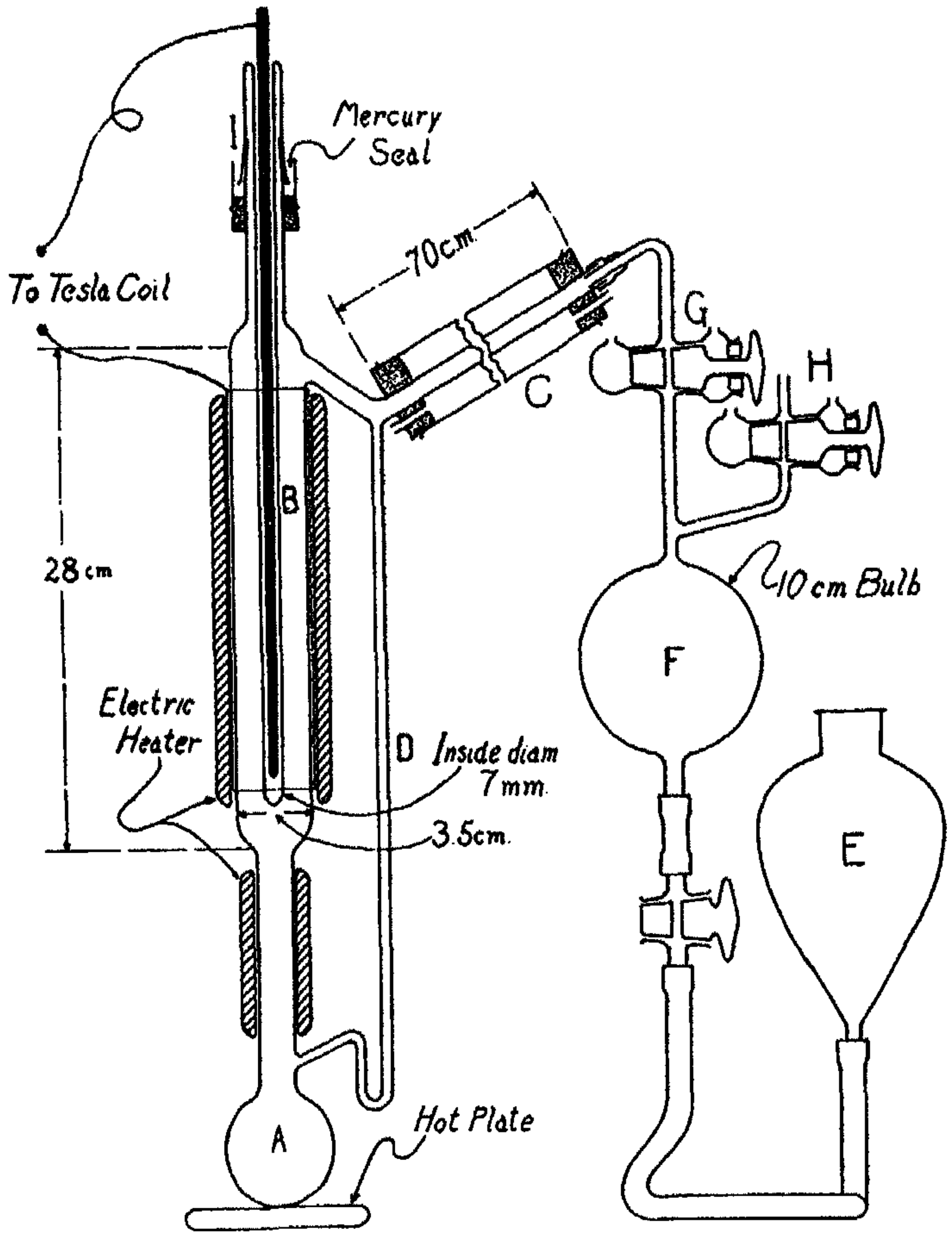

FIG. 3

When work was started on benzene it was found that, just as Maquenne[1] had pointed out in 1883, benzene gave off gaseous products more slowly than acetone. At first the same apparatus was used and a much higher potential was applied between the electrodes of the discharge tube. It was found that the discharge was much more localized under the high potential. The tubes punctured quickly.

An apparatus that was satisfactory was finally designed. Instead of running it at a potential that would eventually puncture the glass it was designed to run at a lower potential for a longer period. It is shown in Fig. 3. The benzene was boiled in the flask, A. The vapor passed up through the heated discharge tube, B, and displaced the air. It was condensed in the water-cooled condenser, C, and was returned to the flask by means of the small

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[1] Bull., (2) **40**, 60-65 (1883).

tube, D. All air except a small amount in the condenser was easily and quickly displaced by the benzene vapor. After the air had been displaced, the leveling bulb, E, was placed so that the pressure in the apparatus was about half an atmosphere with the bulb, F, filled with mercury. This slightly reduced pressure seemed to make it easier for the discharge to pass. It also kept the ground joint, I, pressed tightly down on the apparatus. Suction was then applied to H which was closed when the bulb, F, was filled with mercury. The bore of the stopcock, H, was then mercury-sealed by pouring a little mercury into the tube. The current from a Tesla coil was then turned on.

The discharge used in this work on benzene was similar to the discharge used with acetone. The main difference was that there were not so many of the fine sparks.

The gas that was formed was kept from passing back into the discharge tube by benzene vapor which was continually rising up through the tube from the boiling benzene. Polymerized products condensed with the benzene, and were washed down into the flask. The tendency for them to pass again through the discharge chamber was small because their vapor pressures were low at the boiling point of benzene.

The apparatus gave satisfactory results with the benzene because: (1) the products were swept out of the tube rapidly; (2) the products were not reexposed to the discharge, thus minimizing the tendency for secondary reactions to take place; (3) the apparatus could be kept in use for several hours; (4) it was easy to manipulate.

When a sample of benzene was exposed to the discharge a deposit collected on the walls of the discharge chamber. This deposit was heaviest on the inside electrode where the current density was greatest. The color varied from yellow to almost black. At low potential, the deposit was brownish yellow. This material which formed only in small amounts, was dry and brittle. Some of it would peel off the electrodes and some of it could be removed only by scraping. Solvents were ineffective in cleaning the electrodes.

The gas which formed during the exposure of a sample was collected in the bulb, F. It had an odor very similar to that of acetylene generated from calcium carbide.

The benzene in the flask, A, gradually turned brownish red during the exposure. When this benzene solution was evaporated a brown viscous residue remained. It had an odor which was not at all similar to the odor of the gas.

This is a superficial description of the phenomena.

Reconstructing the Story from Analytical Data

The reconstruction of the story of the "adventures of benzene molecules in a brush discharge" from analytical data depended of course on the accuracy and completeness of the data. The gas analyses presented no unsurmountable difficulties. The technique and patience required for good gas analyses are very well discussed by Martin Shepherd.[1] The gas analyses were carried

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[1] Bur. Standards J. Research, 6, 121 (1931.)

out in a modified Orsat apparatus. Analysis for acetylene was made on a separate sample of gas. Copper acetylide was precipitated and the acetylene was found by titration of the copper in the same way that it was done in the work on acetone.

Analysis of the solid products was a puzzling problem. The benzene was evaporated from the solid products that had accumulated in it. An attempt was then made to break up the chocolate-brown residue into fractions. Solvents were first tried. The following solvents were used: benzene, ether, carbon tetrachloride, chloroform, petroleum ether, glacial acetic acid, 85% formic acid, acetone, carbon disulphide, ethyl alcohol, methyl alcohol, and ethyl acetate. The residue would dissolve to some extent in all of these, but chloroform was very much the best solvent. It was surprising to find that it was a much better solvent than carbon tetrachloride. This fact was shown by evaporating a chloroform solution of the residue until it was thick and syrupy and then adding a drop of carbon tetrachloride. A *light brown* precipitate was formed. This precipitate was filtered off and dissolved in chloroform. When the chloroform was evaporated a *dark brown* residue was left. This residue had the same appearance as the original. Repeated attempts to make a separation by extraction with solvents failed. No crystals could be obtained from solutions containing large amounts of the brown material. The first conclusion that was drawn from this was that probably no crystalline products were present.

Fractional distillation up to 180°C at 20 mm., however, yielded a crystalline distillate that was white with a very slight yellowish tinge. Above 180°C the distillate was decidedly yellow. Distillation was not carried on above 250°C because cracking was obviously taking place. The distillate darkened after standing for a week or two. Diphenyl was isolated from the lower fractions by recrystalization from ether. A small amount of a product which melted at 205°C was also isolated. This was assumed to be p-diphenyl benzene. There was not enough of it to identify it by other means. A short time after this, similar work on benzene was published by Austin and Black.[1] They found p-diphenyl benzene in the products formed from benzene vapor which was exposed to the Tesla discharge.

Almost at the same time that diphenyl was isolated from the residue by distillation and crystalization, crystals were discovered in a test tube that contained some of this resinous product. The test tube had lain on its side undisturbed for about three months. The resin had run along the bottom side of the test tube and the crystals had formed along the top side. The crystals were plates so thin that they could hardly be seen edgewise. A sample of these crystals large enough for a melting point was obtained with some difficulty. It melted at 67°-69°C, the melting point of diphenyl.

This suggested that perhaps a quantitative estimation of diphenyl in a sample of resin could be made by subliming out the diphenyl. Two methods of sublimation were tried. The resin was placed in a bulb connected to a wide water cooled condenser. The bulb was heated over an electric light

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[1] J. Am. Chem. Soc., 52, 4552 (1930).

bulb for several days but no sublimate formed in the condenser. Thinking that the temperature was not high enough, I tried heating the resin in a bulb connected to a long air-cooled condenser. The heat was applied by means of an electric hot plate. The material simply refluxed and no sublimate formed. After these experiments it was evident that even though crystals had been discovered in the test tube, the time required to produce them would make the method of purification by sublimation useless at this time.

The method that eventually succeeded was steam distillation. The resin was steam-distilled as long as any material would distill. The non-volatile residue was collected. The light yellow distillate was redistilled by steam. This time the distillate was perfectly white but melted twelve degrees below the melting point of diphenyl. A reddish brown residue remained from this distillation. It appeared just like the first to which it was added.

The perfectly white distillate was re-steam-distilled and again a considerable amount of a brown residue remained and a white distillate formed. It was decided to continue the distillations until a white distillate and no residue resulted. Melting points of some of the distillates were taken. Each time the melting point came up nearer that of diphenyl. Finally after twenty-six steam distillations, a pure white distillate resulted and no residue remained. The melting point was the melting point of diphenyl. The distillate was identified as diphenyl by a mixed melting point. These results were disappointing from one point of view. It was desirable not only to get out pure diphenyl but also to get it out easily and completely enough that it could be weighed and called a quantitative estimation. Procedure requiring twenty-six steam distillations certainly could not be called quantitative. The most extreme care could not prevent loss of material during such a long process.

Ether was used to dissolve the diphenyl out of the condenser, etc. All beakers used in the work were kept meticulously clean. Whenever a sample of distillate was transferred from a beaker, the beaker was washed inside and out with ether. This was absolutely necessary because of the tendency for diphenyl to "crawl" over the edge of the beaker from the ether solution.

The analysis of the first sample exposed to the discharge showed the following results:

Benzene vapor	13.7%
Acetylene	28.8
Ethylene	9.65
Oxygen	0.3
Nitrogen	2.15
Hydrogen	41.5
Paraffins	3.9
	100.0
Total gas	164. cc.
Room temperature	26.5
Barometer	741. mm.
Time of run	5. hours
Diphenyl isolated	0.5873 gm.

The diphenyl was dried in a desiccator over calcium chloride before it was weighed. Its melting-point was 66°-68°. Pure diphenyl melted at 67°-68°C. The mixed melting point was 67°-69°C. The above weight of diphenyl corresponds to 96.3 cc. of hydrogen at 741 mm. and 26.5°C, since diphenyl must have been formed according to the following equation:

$$2\ C_6H_6 = C_6H_5.C_6H_5 + H_2$$

The hydrogen actually in the sample, 67.2 cc, was less than the hydrogen that should have been there due to the formation of diphenyl. A secondary reaction using up some of the hydrogen must have taken place. In the original benzene molecule there was one hydrogen atom for each carbon atom. Hydrogen must have been used up to form the 9.65% ethylene and the 3.9% paraffins. Supposing that the paraffin gas was all ethane we see that 27.6 cc of hydrogen was used to produce these compounds in which the ratio of carbon to hydrogen is 1:2 and 1:3 instead of 1:1 as in the original benzene molecule. The calculated volume of hydrogen added to the volume found in the gas gives 94.8 cc.

This volume was so near the volume calculated from the diphenyl (96.3) that it seemed too good to be true. If these values could be checked in other runs it would mean that all hydrogen, paraffins, ethylenes, and diphenyl had been accounted for. Acetylene would of course be formed by the depolymerization of benzene. The brown resinous product could be accounted for by the polymerization of acetylene. This could then be checked by combustion analysis. This beautiful air castle did not survive the next two analyses; but the data obtained from them were more interesting than those from the first.

When all the information that had been collected concerning the resinous product was rescrutinized for the purpose of speeding up the quantitative estimation of diphenyl it was found that in several instances light colored products changed to darker ones after standing for some time. Thus, the perfectly white distillate from the vacuum distillation turned brown after standing for several weeks. Even before a systematic examination of the resinous product was started, it was noticed that if benzene was left in the discharge apparatus for several days after a run it would change from an amber to a darker brown. There was one other bit of information concerning this color change. A brown residue was formed from a perfectly white material during a steam distillation. With this evidence the following conclusions were drawn: (1) Some material in the diphenyl was slowly changing to a colored form that would not steam distill. The form that would steam distill was colorless. (2) Heat (as in a steam distillation) accelerated this change from colorless to dark brown.

The following procedure was adopted for the purification of diphenyl: Steam distill once and collect the crystalline distillate, remove the water from it, and let it reflux on a hot plate all night. Repeat this process till there is no color change during the refluxing. It was gratifying to find that a perfectly white distillate would turn dark brown after a few minutes refluxing on a hot plate. After six alternate distillations and refluxings and a final distillation pure diphenyl was obtained. During the last period of refluxing there was no color change and *crystals of diphenyl formed inside the neck of the flask.* It should be pointed out that the apparatus used to carry out these refluxings was the same as was used in the first attempts to obtain pure diphenyl by sublimation from the resin. Thus we see that crystals of diphenyl did form in this apparatus but it was after the diphenyl had been purified.

The results from the analysis of the second sample are as follows:

Benzene vapor	12.8%
Acetylene	24.4
Ethylene	10.3
Oxygen	0.6
Nitrogen	2.4
Hydrogen	44.2
Paraffins	5.3
	100.0

Total gas	174.1 cc.
Room temperature	24.5°C
Barometer	740. mm.
Time of run	4. hours
Diphenyl isolated	0.8421 gm.
H_2 corresponding to diphenyl	127.5 cc.
Volume of H_2 in sample	76.8 cc.

Thus we see that the volume of hydrogen actually in the sample was less than the volume that should have been there. This result is similar to that from the first sample. If corrections are made for hydrogen used to produce ethylene and ethane, the calculated volume of hydrogen is 113.1 cc. This brought to light a very remarkable fact. The hydrogen that should have been present calculated from the weight of pure diphenyl actually isolated was 14.4 cc more than could be accounted for in the gas. This was such an unexpected result that it seemed advisable to check it by another complete run.

The third run was made at a much lower potential. It was supposed that lower potential would decrease the yield of diphenyl. It should, it seemed, decrease the tendency for the localization of the discharge. This in turn would decrease the tendency for localized energy dissipation and localized high temperatures. Since diphenyl is formed by the pyrolysis of benzene, a rise in temperature above the ordinary temperature of the discharge tube should favor the formation of diphenyl. Therefore it seemed that low potential should produce less diphenyl than high. In the first run 33 cc of gas were produced per hour; in the second 43.5 cc; and in the third 6.7 cc. Measurements of voltage were not made, but it is evident from the rates of gas formation that the voltage in the third run was much lower than in the previous runs. The results for the third run were as follows:

Benzene vapor	12.2%
Acetylene	38.4
Ethylene	14.7
Oxygen	0.2
Nitrogen	0.7
Hydrogen	28.1
Paraffins	5.7
	100.0

Total gas	128.9 cc.
Room temperature	23.0°C
Barometer	746.0 mm.
Time of run	19.0 hrs.
Diphenyl	1.2865 gm.
H_2 corresponding to diphenyl	206. cc.
H_2 in the sample	36.3 cc.

These data show in a very striking way that hydrogen produced during the formation of diphenyl had been used up in a secondary reaction. The volume of hydrogen used to produce ethane and ethylene from acetylene brings the volume of hydrogen that can be accounted for up to 69.9. There are 136.1 cc that can not be accounted for in the gas.

The material that was left after the steam distillations in these runs was all put together, because quantitative work on it was not planned at that time. The resin from the steam distillation of the third sample, however, was weighed before it was added to the other. There was 2.744 grams. Before making this weighing the last traces of solvents were removed by placing it while hot into a vacuum desiccator.

A combustion analysis was made on the combined resin from the three samples. Careful practice runs were made on commercial sucrose, before analysis of the resin was attempted. The results were as follows:

	Sucrose		Resin	
	1	2	1	2
Carbon	41.1%	41.2%	88.54%	90.55%
Hydrogen	6.3	6.0	5.03	5.07
Oxygen	52.6	52.8		

Some difficulty was experienced in getting the samples of resin to burn slowly and evenly. This fact shows up more plainly in the percentages, of course, than it does in the calculated C to H ratios. This ratio was 6:41 for the first sample of resin and 6:40 for the second.

It will be noticed from the combustion analyses that the hydrogen and carbon do not add up to 100% of the sample. Austin and Black[1] working

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[1] J. Am. Chem. Soc., 52, 4554 (1930).

with a similar product from benzene found 73.38% carbon and 4.77% hydrogen. Quoting from their article, "It will be seen that there remains to be accounted for from 15 to 20% of these compounds. Qualitative tests for nitrogen made with a method, which under ordinary conditions detects nitrogen in a sample containing 0.1% NH_4Cl, gave completely negative results; hence it has been assumed that the remaining portion is oxygen which is the only other element likely to be present under the circumstances.

"The difference between our powders and those of Harkins and Gans[1] is, however, easily accounted for, since they took great precautions to dry their vapors and in our work at least a trace of water vapor was undoubtedly present. Indeed on making a careful study of our plates we find a faint band at about λ3064 which is the position of the so called water vapor bands."

The work of Harkins and Gans was done on benzene vapor at 0.1 mm pressure using an electrodeless discharge. The walls of their tube became coated with a reddish brown deposit which on analysis proved to be $(CH)_n$.

The presence of a high percentage of oxygen in the reddish brown deposit obtained by Austin and Black[2] can not be satisfactorily explained by the presence of a *trace* of water vapor. It seems more probable that such a large percentage of oxygen would come from a source that could supply a large amount of oxygen. Handling the material in air would open up the possibility of absorption of oxygen from the air.

It seems that the presence of oxygen in the polymerized product indicates unsaturation; unsatisfied valences in the hydrocarbon take up oxygen from the air. In the very stable benzene molecule there is one hydrogen for every carbon. Any rearrangement of its structure would doubtless bring out the "latent unsaturation" of the molecule. Perhaps this "latent unsaturation" could be satisfied by oxygen from the air. The work of Harkins and Gans[3] is not published in sufficient detail to enable one to judge whether or not it is in agreement with these ideas.

The combustion analyses of the resin formed in our tube did not tell what became of the hydrogen that was used up by secondary reactions. Furthermore they showed that the resin itself was deficient in hydrogen. When benzene changed into the resin, $(C_6H_4)_n$, 831 cc of hydrogen must have been eliminated. The total amount of hydrogen that can not now be accounted for is 967 cc.

The hydrogen could have been used to produce liquid products. Cyclohexane very probably was one of the principal products. Although benzene is usually written with double bonds it does not react as members of the ethylene series do. For example it does not react readily with bromine. We say that it is *not* actively unsaturated. Cyclohexadiene which may be formed from benzene by saturating one double bond is actively unsaturated. It is probable that it would be more difficult for the first hydrogen to react with the benzene

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[1] J. Am. Chem. Soc., 52, 2578 (1930).

[2] J. Am. Chem. Soc., 52, 4554 (1930).

[3] J. Am. Chem. Soc., 52, 2578 (1930).

than it would be for others to react with the partly saturated ring. Therefore it seems probable that if the reaction once got started it would not stop until cyclohexane was formed.

The fact that so much gas could disappear in an electric discharge is not surprising when one considers the work of Harkins and Gans.[1] They say that "the spectrum indicates that benzene molecules rapidly decompose into molecules of C_2 and CH, and atoms of C^+ and H. The C_2, CH, C^+, and H seem to combine completely to form the reddish brown hydrocarbon, as evidenced by the fact that several thousand liters of benzene vapor decompose without giving enough gaseous residue to raise the pressure sufficiently to extinguish the discharge."

Conclusions.

1. The main reaction taking place is the formation of a resinous product which contains hydrogen and carbon atoms in the ratio of 6 to 4. The best solvent for the resin is chloroform.
2. The reaction next in importance is the formation of diphenyl. A small amount of p-diphenyl benzene also was isolated. These products are known to be formed also by the pyrolysis of benzene. Bates and Taylor have shown that diphenyl may be formed by a process sensitized by ultra-violet light. Conditions in the last run were made so as to minimize the tendency for localized discharges and the consequent localized heat effects, yet the largest yield of diphenyl was in this run. It seems probable, therefore, that some of the reaction forming diphenyl and hydrogen may have been brought about by the ultra-violet light.
3. Hydrogen, that should have been produced at the time of the formation of diphenyl and the resin, did not appear in the gas. It must have been used up in some secondary reactions.
4. The electric discharge caused gas to form much more rapidly from acetone than from benzene.

Acknowledgment.

These investigations were suggested and completed under the personal direction of Professor Wilder D. Bancroft. The author wishes to express here his gratitude for the help and encouragement received from him throughout the course of the work. He wishes also to extend sincere thanks to Professor Ralph W. Hufferd of Depauw University for valuable help and suggestions.

Cornell University.

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[1] J. Am. Chem. Soc., 52, 2578 (1930).

15-267

A GREASE-LESS VALVE

BY JOHN L. WILSON

In the study of certain reactions at low pressure (less than 1 mm mercury) it was desirable to have a convenient, grease-free means of introducing small amounts of gases into the reaction system. For this purpose a simple mercury valve was devised which not only enabled one to introduce gases from the storage vessels to the reaction system without contact with stopcock grease but also made it possible to estimate roughly the amount of gas introduced. The first of these valves made has been in use for over two years and has required no attention whatever. The valve is suitable for the transfer from the storage to the reaction system of small amounts of any gas or liquid which does not foul mercury, and may be of use in many fields of research.

The valve, sketched in Fig. 1, consists of a U-trap A, a return tube for mercury B, and a leveling bulb system C with a bubble catcher D. J leads to the storage vessel and K to the reaction system. Pyrex glass was used throughout and the dimensions are indicated on the sketch.

The operation of the valve is as follows: To transfer gas from the storage vessel to the reaction system carefully lower the mercury level in A until it is just below E and then immediately raise the level again. By this procedure a bubble of gas is introduced into the right arm of A. If the bubble is large it will travel up the arm, pushing the mercury over into the bulb G, and enter the reaction system. Smaller bubbles may be made to rise by gently tapping A or by raising and lowering the level-bulb C. When the level-bulb C is raised rapidly mercury from A enters the bulb G before G is completely filled from B. G is then emptied through B by lowering C. The bubble in the right arm of A will now be higher than before and two or three such operations will effect the introduction of the gas into the reaction system.

After a little practice it is very easy to introduce just enough gas to give the desired pressure. The amount of gas introduced can be estimated quite accurately from the length of the bubble as it rises in A.

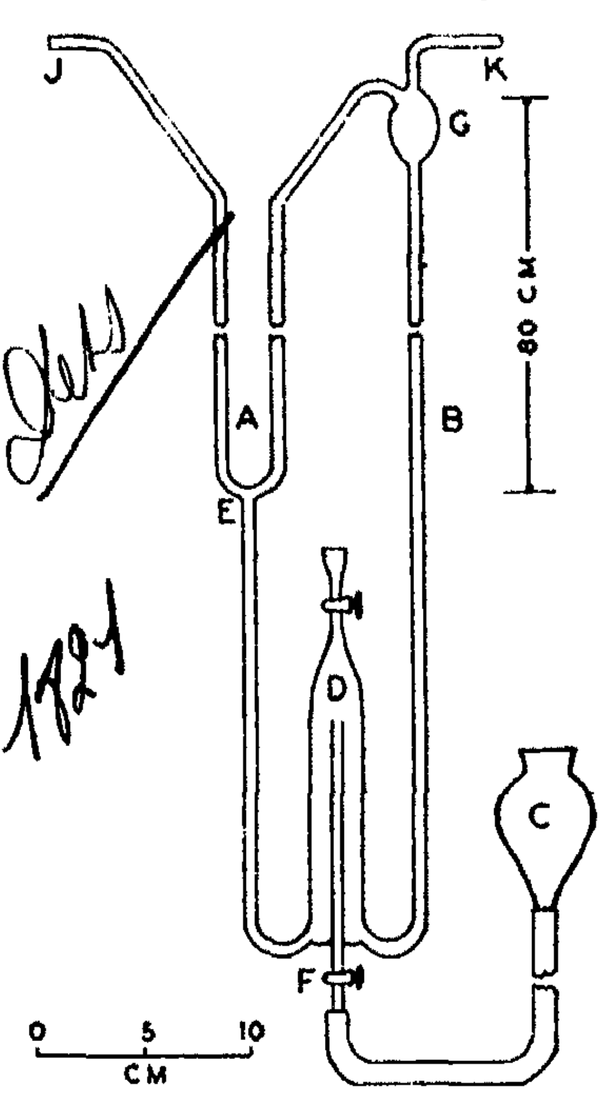

Fig. 1

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May, 1931.

THE ELECTROCAPILLARY CURVES OF MIXTURES OF THE NORMAL ALCOHOLS WITH WATER AND THE ADSORPTION OF THE ALCOHOL MOLECULES AT THE MERCURY SURFACE

BY CHARLES OCKRENT

Few complete series of the surface tensions for the whole range of concentrations of binary mixtures have been obtained, either at the air-solution interface or the mercury-solution interface. Rideal and Schofield,[1] from the data of Bircumshaw[2] on the surface tensions of ethyl alcohol water mixtures, have derived by the application of the Gibbs adsorption equation, an adsorption curve for alcohol over the whole range of concentrations and the same authors have derived a rather similar adsorption curve for pyridine in aqueous solutions at potential differences corresponding to the maximum of the electrocapillary curve from the data of Gouy.[3] In these cases the values found for the areas of the alcohol and pyridine molecules at the maximum adsorption agree quite well with those found from measurements on insoluble films. Frumkin[4] determined the electrocapillary curves of a few concentrations of ethyl alcohol in water, but there appears to be no complete series of electrocapillary curves from which similar results could be obtained at the water-charged mercury interface. It appeared desirable therefore to investigate the complete range of electrocapillary curves for mixtures of the completely miscible normal alcohols, methyl, ethyl and propyl with water and also for a number of concentrations of the less miscible butyl alcohol-water system.

Experimental

The experimental arrangements were identical with those employed by Butler and Ockrent.[5] The standard electrode, to which potential differences are referred, was as before the normal calomel electrode, the measurements being taken at room temperature.

Purification of the alcohols. Methyl alcohol was first analysed for acetone by an iodoform estimation and the acetone removed by conversion to iodoform, the small amount of iodoform formed was then hydrolysed by boiling and the alcohol solution then twice fractionally distilled and finally refluxed for two days with aluminium amalgam and then fractionated. The alcohol distilled at 64.6°.

Ethyl alcohol was purified in the manner described by Butler and Robertson[6] the alcohol boiling at 78.3°.

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[1] Proc. Roy. Soc., **109A**, 57 (1925).
[2] J. Chem. Soc., **121**, 887 (1922).
[3] Ann. Chim. Phys., **8**, 130 (1906).
[4] Z. physik. Chem., **103**, 43 (1923).
[5] J. Phys. Chem., **34**, 2286 (1930).
[6] Proc. Roy. Soc., **125A**, 694 (1930).

An analysis of the propyl alcohol showed the presence of about 2.75% of unsaturated material (probably allyl alcohol). Slight excess of bromine was added until the mixture remained brown for some time (propyl alcohol is attacked slowly by bromine) and after standing over night the mixture was fractionated, the fraction distilling between 96° and 99° being collected. This was then refluxed over freshly burned quicklime for 4 days and after standing for 48 hours was fractionated. The first portion was rejected and the fraction boiling at 97.4° and 758 mm. was collected. The boiling point given in the literature varies from 97.1 to 97.4°.

Butyl alcohol was refluxed over quicklime for several days and then fractionated. The first portions were rejected and a distillate boiling at 117.1° and 738 mm. was obtained. The boiling point given in the literature is 117.7°.

The salts employed for making the solutions conducting were A. R. ammonium nitrate and a sample of lithium chloride obtained from Merck. Analysis gave chlorine = 83.4% (LiCl, Cl = 83.6%). The LiCl was kept in a vacuum desiccator over phosphorus pentoxide.

Results

(a) *Methyl Alcohol-Water.* The electrocapillary curves of the following solutions, all of which contain 1 mol NH_4NO_3 per litre of solution were obtained. The figures refer to the molar fractions of the respective components.

	Molar Fractions	
	H_2O	CH_3OH
1.	1	0
2.	0.95	0.05
3.	0.85	0.15
4.	0.75	0.25
5.	0.50	0.50
6.	0.25	0.75
7.	0.15	0.85
8.	0.05	0.95
9.	0	1

The electrocapillary measurements are given in cms. of mercury in Table II.

(b) *Ethyl Alcohol-Water.* The electrocapillary curves of the following solutions, all of which contain 0.2 mol NH_4NO_3 per litre of solution were obtained.

	Molar Fractions	
	H_2O	C_2H_5OH
1.	1	0
2.	0.95	0.05
3.	0.85	0.15
4.	0.75	0.25
5.	0.50	0.50
6.	0.25	0.75
7.	0.05	0.95
8.	0	1

The electrocapillary measurements are given in Table III.

(c) *Propyl Alcohol-Water.* In this case two series of curves with different salt concentrations were obtained. The salt used was LiCl as this is one of the few salts which is appreciably soluble in propyl alcohol.

0.2 M LiCl

	Molar Fractions H_2O	C_3H_7OH
1.	1	0
2.	0.9975	0.0025
3.	0.9950	0.005
4.	0.99	0.01
5.	0.98	0.02
6.	0.95	0.05
7.	0.85	0.15
8.	0.75	0.25
9.	0.50	0.50
10.	0.25	0.75
11.	0.15	0.85
12.	0.05	0.95
13.	0	1

0.02 M LiCl

	Molar Fractions H_2O	C_3H_7OH
1.	1	0
2.	0.99	0.01
3.	0.98	0.02
4.	0.95	0.05
5.	0.85	0.15
6.	0.75	0.25
7.	0.50	0.50
8.	0.15	0.85

For the stronger solutions of propyl alcohol and propyl alcohol itself, satisfactory curves could not be obtained with 0.02M LiCl, probably on account of the low conductivity. The electrocapillary measurements are given in Tables IV and V.

(d) *Butyl Alcohol-Water.* The electrocapillary curves obtained in this system are limited by the limited miscibility of the components. The following solutions all 0.1 M with respect to LiCl were measured.

	Molar Fractions H_2O	C_4H_9OH
1.	1	0
2.	0.9975	0.0025
3.	0.99	0.01
4.	0.15	0.85
5.	0.05	0.95
6.	0	1

The electrocapillary measurements are given in Table VI. In all the tables only alternate electrocapillary measurements are given.

Adsorption of the Alcohols.

According to Gibbs the adsorption of a surface active solute from a dilute solution is given by the equation

$$\Gamma = -\frac{c}{RT}\cdot\frac{d\sigma}{dc}\quad\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

which may be written

$$\Gamma = -\frac{1}{RT}\cdot\frac{d\sigma}{d\ln c}$$

where Γ is the surface deficiency or excess i.e. the amount adsorbed and σ and c is the surface tension and concentration of the solution respectively. To convert to solutions which do not obey ideal laws we may employ the thermodynamic concentration or "activity" whence

$$\Gamma = -\frac{1}{RT}\cdot\frac{d\sigma}{d\ln\alpha}\quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

so that Γ is proportional to $d\sigma/d\ln\alpha$.

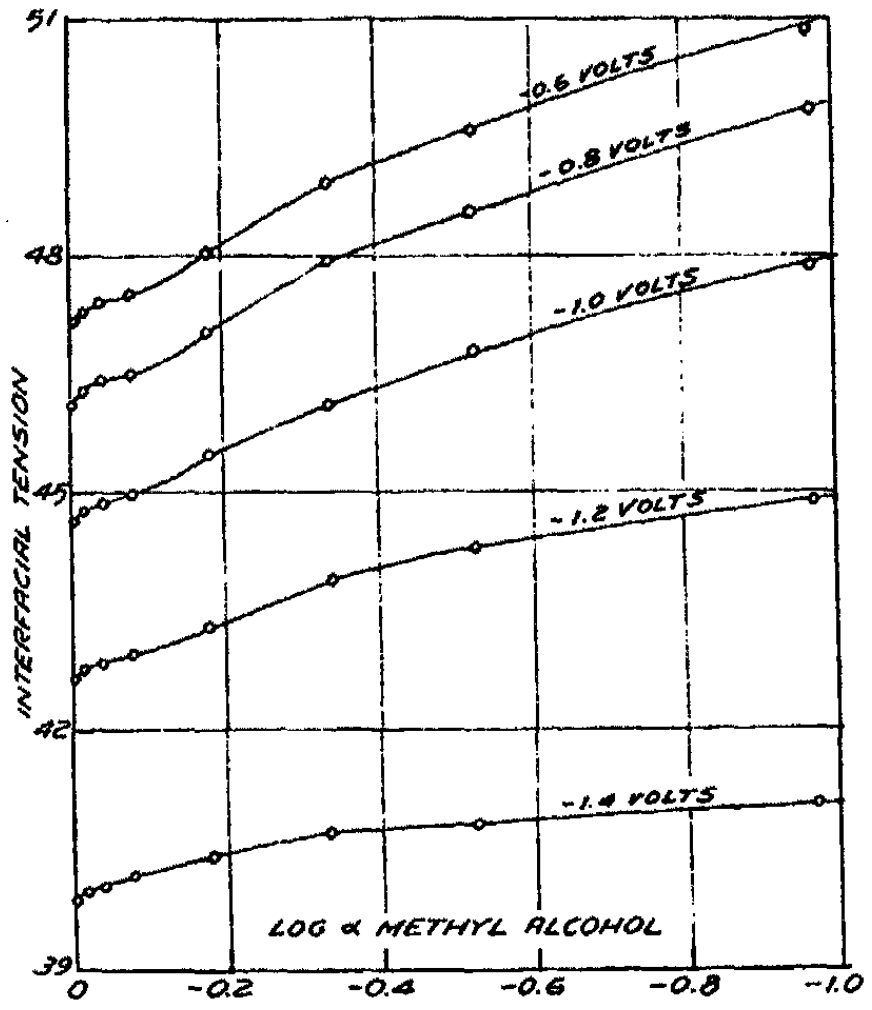

FIG. 1

In Fig. 1 the curves obtained by plotting the interfacial tensions of the methyl alcohol-water series against $\log_{10}\alpha$(alc.) are shown for some potential differences. The activity values are obtained by intrapolation to 17° from the data of the partial pressures given in Landolt-Börnstein Physikalisch-Chemische Tabellen Vol. II, 1399. The σ $\log_{10}\alpha$ curves are almost linear up to quite large alcohol concentrations, i.e. between molar fractions 0.05 and 0.25. The absolute values of the interfacial tensions may be obtained in the manner described by Butler and Ockrent.[1] The maximum height of the electrocapillary curve of M/2 sodium sulphate, which is used as reference for the capillary, is 52.20 cms. of mercury, this corresponds to 1001.7 on Gouy's

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[1] J. Phys. Chem., 34, 2841 (1930).

scale (maximum for water = 1000); Gouy's value for the maximum interfacial tension between mercury and water is 426.7 dynes/cm., so that in the apparatus employed here 1 cm. of mercury corresponds to 8.185 dynes/cm. The maximum value of the slopes $d\sigma/d\log_{10}\alpha$ occurs at about −0.7 volts and is equal to −2.91 which multiplied by the factor 8.185 gives −23.9 in absolute units; from equation (2) $\Gamma = -d\sigma/2.303RTd\log_{10}\alpha$ inserting the values of

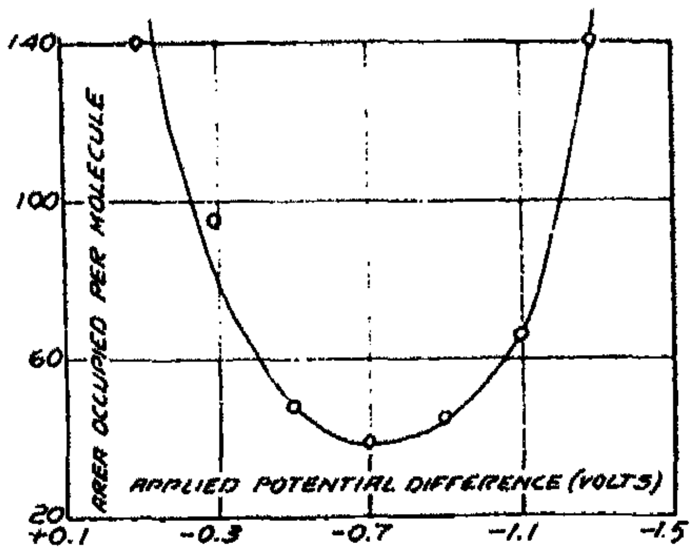

FIG. 2
Methyl Alcohol

$d\sigma/d\log_{10}\alpha = 23.9$, $R = 83.2 \times 10^6$ and $T = 290$, the amount adsorbed per square cm. of surface expressed in gram moles comes out as 4.3×10^{-10}. The number of molecules is obtained by multiplying by Avogadro's Number $N = 6.06 \times 10^{23}$, therefore $N\Gamma = 26 \times 10^{13}$ and the area occupied per molecule is $1/N\Gamma = 38 \times 10^{-16}$ sq. cms. or 38 Å². The values for all the alcohols are given in Table I.

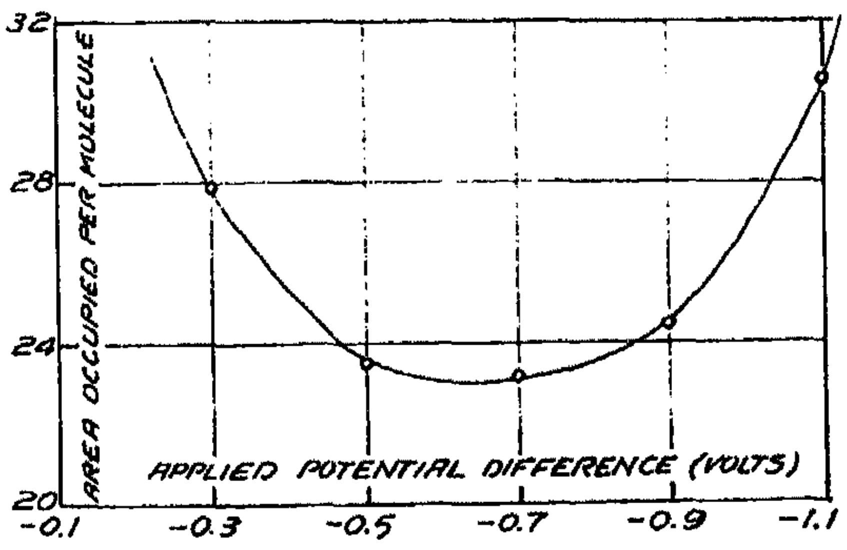

FIG. 3
Ethyl Alcohol

In Figs. 2 and 3 the areas occupied per molecule for methyl alcohol and ethyl alcohol are shown for some potential differences.

The activity values of ethyl alcohol are obtained in the same manner as for methyl alcohol, from the data in the International Critical Tables Vol. III. As propyl alcohol is much more surface active than methyl alcohol or

TABLE I

Alcohol	$d\sigma/d\log_{10}a$(max.)	Γ	$N\Gamma$	Area per mol.
Methyl	−23.9	4.3×10^{-10}	26×10^{13}	38 Å^2
Ethyl	−40.2	7.2×10^{-10}	43×10^{13}	23 Å^2

Alcohol	$d\sigma/d\log_{10}N$(max.)	Γ	$N\Gamma$	Area per mol.
Propyl (0.2M LiCl)	−28.3	5.2×10^{-10}	32×10^{13}	31 Å^2
Propyl (0.02M LiCl)	−31	5.6×10^{-10}	34×10^{13}	29 Å^2
Butyl	−30	5.4×10^{-10}	33×10^{13}	30 Å^2

ethyl alcohol, to obtain comparable values, electrocapillary measurements of weaker concentrations must be obtained, and since it is probable that activities extrapolated for solutions more dilute than 0.05 molar fraction are far from being correct, it is preferable to take the values of the slopes $d\sigma/d\log_{10}N$ (N = molar fraction), this is probably justified since at low concentrations the activity coefficients tend to unity (the slopes are taken between 0.0025 and 0.05 molar fractions). In the case of the butyl alcohol-water system only three points are available for plotting the σN curves and the value of $d\sigma/d\log_{10}N$ is obtained by taking the tangent.

Discussion

In the application of the Gibbs equation we must remember the important fact that Γ, the amount adsorbed, is not the total surface concentration but the excess or deficiency of solute in the interface over the concentration in an equal volume in the bulk of the solution. While for dilute solutions the amount adsorbed may be taken without great error as equal to the total surface concentration, for solutions which cannot be considered as dilute this cannot be done without introducing quite an appreciable error. The calculations of the areas obtained will be influenced by this consideration since a correct calculation would require the addition to the amount adsorbed ($N\Gamma$), of the concentration of solute which would be present if the adsorption was zero; arising simply from the presence of solute in the solution. This addition would result in the areas of the molecules being smaller than those calculated above. In a recent paper Harkins and Wampler[1] have taken this into consideration.

From his study of insoluble surface films on water, Langmuir[2] concluded that the films were monomolecular and that the molecules were definitely orientated with their active groups directed towards the aqueous phase. He calculated the areas of the molecules in some typical cases and for the alcohols such as myricyl alcohol he obtained an area of 27 Å^2. He further suggested that in all cases, for substances both soluble and insoluble, the Gibbs film could be regarded as monomolecular and that in the case of solutions it consisted of pure solute molecules for solutes which lowered the surface

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[1] J. Am. Chem. Soc., 53, 850 (1931).

[2] J. Am. Chem. Soc., 39, 1848 (1917).

tension of the solvent. Subsequent work on insoluble films has shown that for zero compression, the area per molecule of the normal alcohols in an insoluble film on water is 21.6 Å². The values obtained in this investigation agree fairly well with those values, especially so when we consider that they would certainly be lower if the total surface concentrations were employed to calculate the areas instead of the value of $N\Gamma$. We can conclude therefore that the alcohols at the potentials which give maximum adsorption in the surface exist as a monomolecular layer and that they are orientated in exactly the same way as at the air-water interface. This conclusion is strengthened by a comparison of the data with the results obtained by Bircumshaw[1] from surface tension measurements at the air-solution interface. Fig. 4a shows the percentage surface tension lowerings produced by ethyl alcohol at the air-solution and the mercury-solution interfaces. The lowerings are calculated as percentages of the difference of the surface tensions of water and

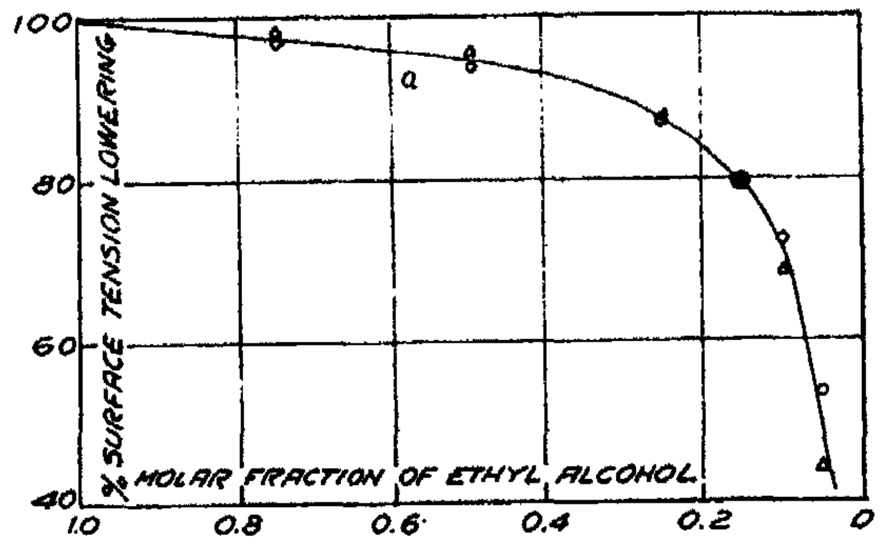

Fig. 4a

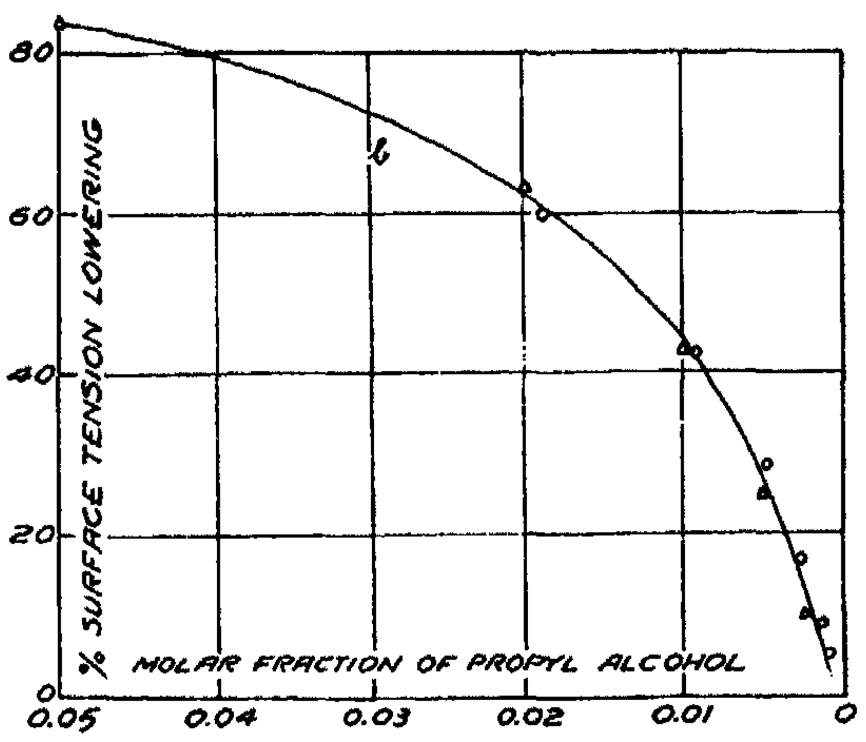

Fig. 4b

ooo air-solution interface

△ △ △ mercury-solution interface at −0.6 volts

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[1] Loc. cit.

alcohol. All the points lie on the same curve and no marked divergence appears between the two interfaces. The same applies to the lowerings produced by propyl alcohol[1] (Fig. 4b.), in this case since surface tension measurements at the air-solution interface of only a number of the weaker aqueous propyl alcohol solutions are available, only the more dilute solutions are compared.

In all the solutions investigated a salt is present as a third component and a strict application of the adsorption equation would require this to be taken into consideration. In a recent paper Butler and Wightman[2] have shown that salts, the so-called surface inactive inorganic salts, have quite considerable effects on the electrocapillary curve. The effects are not very marked on the negative side but become increasingly significant at potentials more positive than -0.4 volts. It must be admitted that this factor might be important. It is probable however that in any given series, for a given salt concentration, the effect is similar over quite large changes of concentration of the surface active solute (the alcohols for example), so that since only differences are taken into consideration in the calculations of the adsorptions this may be neglected. Further, in the case of the alcohols, the maximum adsorption occurs at about -0.6 to -0.7 volts where the effects of the "inactive" salts are not very marked. Goard and Rideal[3] obtained the σ N curves for the surface tensions of phenol in water and also in the presence of a number of different concentrations of sodium chloride, by this means the activity of the phenol could be varied. It was found that while the surface tensions are not independent of the presence of salt, yet the slopes of the σ N curves are identical. The conditions appear to be similar at the charged mercury water interface as is evidenced by the only slight differences in the value of $d\sigma/d\log_{10}N$(max.) obtained for propyl alcohol in presence of 0.02 and 0.2M LiCl.

The activity values used to obtain Γ are derived from the partial pressures of solutions containing only the components alcohol and water. The partial pressures are however influenced by the presence of a third component and differential effects may be obtained, as was shown by Shaw and Butler[4] in the case of lithium chloride in ethyl alcohol-water mixtures; those authors found however, that for concentrations of lithium chloride less than 0.5M, the changes in the partial pressures of either alcohol or water were small.

Behaviour of Water. In every case while even relatively small additions of an alcohol to water, the effect increasing as we ascend the homologous series, cause large lowerings of the interfacial tension (Figs. 5 and 6), the addition of quite considerable amounts of water to methyl alcohol only raises the interfacial tension very slightly.

The addition of 5% molar fraction of water to ethyl alcohol even appears to cause a very slight lowering while the presence of 15% molar fraction

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[1] Int. Crit. Tables, **4**, 467.

[2] J. Phys. Chem., **35**, 3293 (1931).

[3] J. Chem. Soc., **127**, 1668 (1925).

[4] Proc. Roy. Soc., **129A**, 519 (1930).

of water gives an electrocapillary curve practically identical with that of ethyl alcohol itself.

In the 0.2M LiCl series of propyl alcohol-water mixtures, the presence of 5%, 15%, 25%, 50%, 75%, and even 85% molar fractions of water causes quite measurable lowerings of the interfacial tensions of propyl alcohol at potential differences more negative than −0.6 volts and small increases at

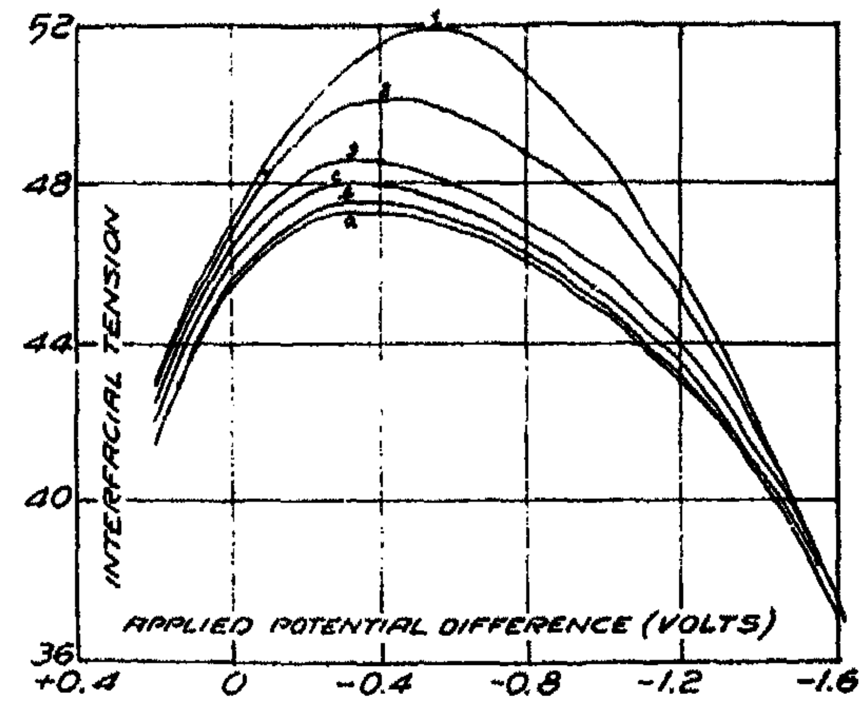

Fig. 5
Electrocapillary Curves of Ethyl Alcohol-Water Mixtures
1. Water 100% molar fraction. a. Ethyl Alcohol 100% molar fraction.
2. Water 95% molar fraction. b. Ethyl Alcohol 50% molar fraction.
3. Water 85% molar fraction. c. Ethyl Alcohol 25% molar fraction.

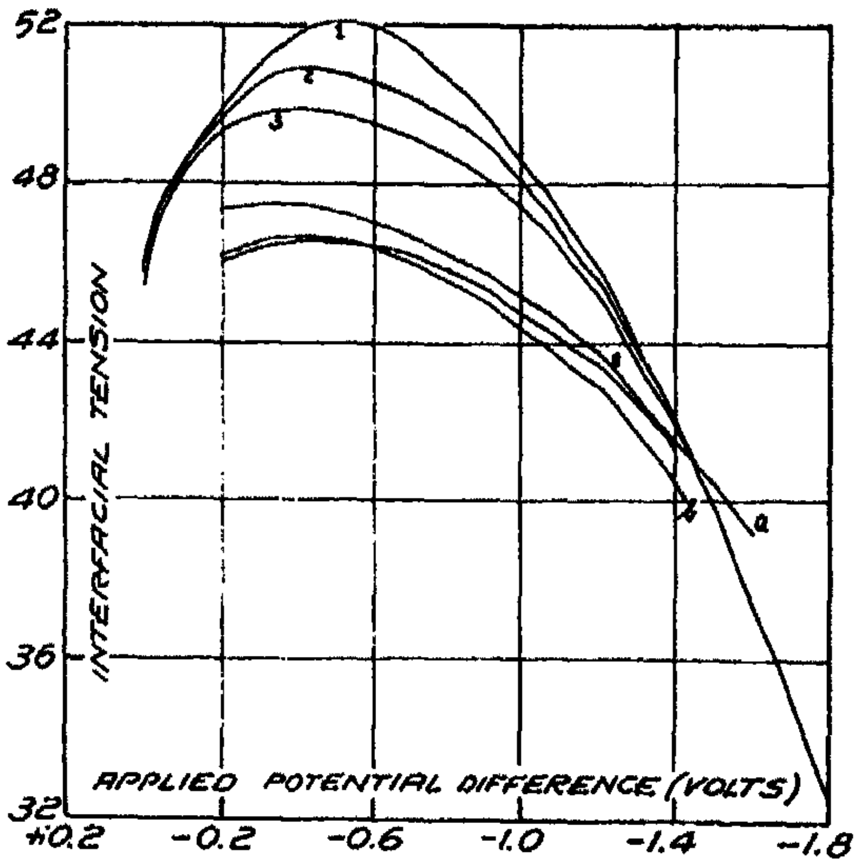

Fig. 6
Electrocapillary Curves of Propyl Alcohol-Water Mixtures
1. Water 100% molar fraction. a. Propyl Alcohol 100% molar fraction.
2. Water 99.5% molar fraction. b. Propyl Alcohol 85% molar fraction.
3. Water 99.0% molar fraction. c. Propyl Alcohol 5% molar fraction.

potential differences more positive than −0.6 volts. The same tendency is observed in the 0.02M LiCl series. It is difficult to show these effects in the figures as the curves approach each other closely.

In the butyl alcohol-water series this tendency becomes extremely well marked (Fig. 7, a, b and c), and appears to become progressively significant as the limiting miscible solution is approached.

The effects may be due to any one of the following three causes, (a) the difference in the liquid junction potential causing a displacement of the curves from the primitive (i.e. the curve of the alcohol itself), (b) a true positive adsorption of water from the alcohol solutions with increasing negative polarisation, the adsorption increasing as we ascend the homologous series of the alcohols or (c) a combination of causes (a) and (b). At high negative polarisations the electrocapillary curves of most aqueous inorganic salt solutions are nearly parallel and can be made to coincide in the region from −1.2 to −1.8 volts (referred to the normal calomel electrode), by displacements parallel to the potential difference axis. The displacements are ascribed to liquid junction potential differences between the standard electrode and the solutions investigated. They are usually small, in general not exceeding 0.07 volts and usually much less. In the case of the butyl alcohol-water system (Fig. 7, a and c), the potential difference displacement required to make the electrocapillary curve of the solution containing 85% molar fraction of butyl alcohol coincide with that of butyl alcohol at −1.5 volts is 0.35

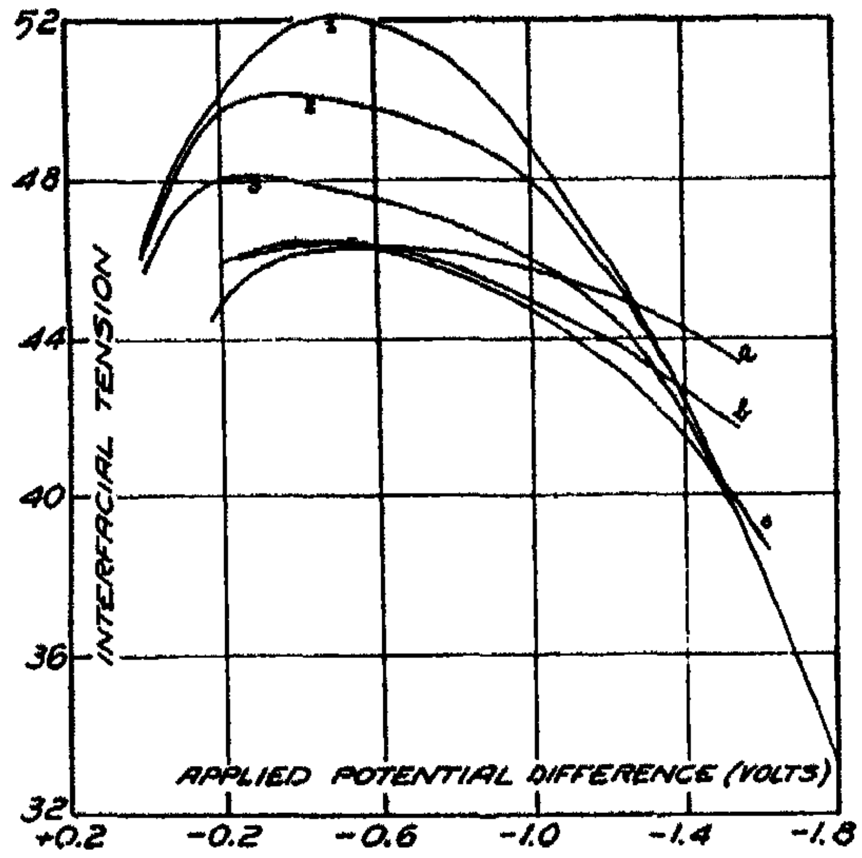

Fig. 7

Electrocapillary Curves of Butyl Alcohol-Water Mixtures.

1. Water 100% molar fraction. a. Butyl Alcohol 100% molar fraction.
2. Water 99.75% molar fraction. b. Butyl Alcohol 95% molar fraction.
3. Water 99.00% molar fraction. c. Butyl Alcohol 85% molar fraction.

volts. This displacement is certainly very big, but no data as to the liquid junction potentials of such systems is available so we cannot discuss the probability or otherwise of this effect. That water should be positively adsorbed from a solvent whose surface tension is much lower than that of itself seems at first sight surprising, but it has been shown by Davis and Swearingen[1] that water is preferentially adsorbed by silica gel from ethyl alcohol solutions. Before any definite conclusions can be drawn as to the behaviour of water in the different alcohol solutions further investigation is required.

TABLE II

Electrocapillary Curves of Methyl Alcohol-Water Mixtures

N = molar fraction of methyl alcohol V = volts

1.0 M ammonium nitrate

V	N = 1	N = 0.95	N = 0.85	N = 0.75	N = 0.50	N = 0.25	N = 0.15	N = 0.05	Water
+0.2	40.60	40.78	40.73	40.69	40.90	40.99	41.11	41.46	41.48
0.0	44.84	44.92	44.84	44.86	45.08	45.20	45.39	45.72	45.92
−0.2	46.96	47.09	47.12	47.20	47.53	47.93	48.25	48.70	48.98
−0.4	47.56	47.70	47.79	47.93	48.43	49.12	49.65	50.40	50.90
−0.6	47.19	47.31	47.46	47.52	48.07	48.93	49.58	50.77	51.45
−0.8	46.12	46.31	46.44	46.49	47.04	47.90	48.55	49.76	50.44
−1.0	44.67	44.81	44.89	45.00	45.50	46.22	46.80	47.77	48.29
−1.2	42.67	42.78	42.85	42.96	43.32	43.89	44.28	44.86	45.15
−1.4	39.88	40.02	40.04	40.17	40.41	40.68	40.80	41.06	41.16
−1.6	36.13	36.24	36.24	33.24	36.24	36.24	—	—	—

TABLE III

Electrocapillary Curves of Ethyl Alcohol-Water Mixtures

N = molar fraction of ethyl alcohol

0.2 M ammonium nitrate

V	N = 1	N = 0.95	N = 0.75	N = 0.50	N = 0.25	N = 0.15	N = 0.05	Water
+0.2	—	—	41.33	41.46	41.99	42.46	42.72	42.89
0.0	45.45	45.17	45.31	45.51	45.96	46.30	46.75	47.01
−0.2	47.01	46.83	47.07	47.27	47.80	48.32	49.36	49.96
−0.4	47.17	47.04	47.34	47.52	47.99	48.52	50.15	51.60
−0.6	46.81	46.60	46.89	47.02	47.42	47.96	49.72	51.86
−0.8	46.00	45.80	45.99	46.08	46.55	47.05	48.72	50.74
−1.0	44.74	44.61	45.75	44.86	45.26	45.74	47.28	48.61
−1.2	43.04	42.92	43.12	43.17	43.48	43.98	45.05	45.67
−1.4	40.65	40.53	40.57	40.62	41.01	41.36	41.74	41.93
−1.6	—	—	—	37.25	37.24	37.35	37.43	37.45

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[1] J. Phys. Chem., 35, 1308 (1931).

TABLE IV

Electrocapillary Curves of Propyl Alcohol-Water Mixtures

N = molar fraction of propyl alcohol

0.2 M lithium chloride

V	N = 1	N = 0.95	N = 0.85	N = 0.75	N = 0.50	N = 0.25	N = 0.15
0.0	—	—	—	—	—	—	—
−0.2	46.05	46.20	46.14	45.85	46.29	46.77	46.89
−0.4	46.57	46.56	46.63	46.65	46.75	46.93	47.00
−0.6	46.31	46.29	46.32	46.33	46.34	46.46	46.51
−0.8	45.83	45.51	45.56	45.54	45.62	45.69	45.78
−1.0	44.73	44.41	44.42	44.43	44.63	44.59	44.68
−1.2	43.39	42.95	42.95	42.82	43.12	43.14	43.27
−1.4	41.54	40.93	40.61	—	—	—	—
−1.6	39.24	38.38	—	—	—	—	—
−1.8	—	—	—	—	—	—	—

V	N = 0.05	N = 0.02	N = 0.01	N = 0.005	N = 0.0025	Water
0.0	—	45.22	45.40	45.32	45.36	45.65
−0.2	47.35	48.70	49.23	49.42	49.53	49.65
−0.4	47.43	48.78	49.82	50.83	51.39	51.73
−0.6	46.95	48.33	49.42	50.41	51.21	51.94
−0.8	46.20	47.44	48.63	49.62	50.25	50.67
−1.0	45.17	46.53	47.44	48.09	48.40	48.54
−1.2	43.71	44.85	45.25	45.54	45.63	46.71
−1.4	41.31	41.88	41.91	42.05	42.05	42.04
−1.6	—	37.61	37.60	37.64	37.60	37.58
−1.8	—	32.41	32.39	32.42	32.30	32.32

TABLE V

Electrocapillary Curves of Propyl Alcohol-Water Mixtures

N = molar fraction of propyl alcohol

0.02 M lithium chloride

V	N = 0.85	N = 0.50	N = 0.25	N = 0.15	N = 0.05	N = 0.02	N = 0.01	Water
−0.2	—	46.57	47.00	47.13	47.61	49.08	49.73	50.25
−0.4	—	46.84	47.00	47.10	47.49	49.04	50.05	51.96
−0.6	46.50	46.62	46.65	46.64	47.05	48.58	49.69	52.00
−0.8	46.26	46.01	46.00	46.00	46.34	47.86	48.92	51.00
−1.0	45.39	45.12	45.09	45.08	45.46	46.87	47.88	49.24
−1.2	—	43.64	43.84	43.78	44.18	45.41	46.03	46.63
−1.4	—	—	42.06	42.00	42.30	42.78	43.08	43.29
−1.6	—	—	—	—	39.09	39.09	39.29	39.30

Table VI

Electrocapillary Curves of Butyl Alcohol-Water Mixtures

N = molar fraction of butyl alcohol

0.1 M lithium chloride

V	N = 1	N = 0.95	N = 0.85	N = 0.01	N = 0.0025	Water
0.0	—	—	—	45.70	46.02	46.07
−0.2	44.87	45.97	45.80	48.04	49.63	49.92
−0.4	46.13	46.28	46.37	47.94	50.13	51.84
−0.6	46.26	46.27	46.19	47.56	49.73	51.94
−0.8	46.14	45.79	45.62	46.95	49.06	50.91
−1.0	45.72	44.89	44.69	46.03	47.92	48.72
−1.2	45.11	44.01	43.41	44.68	45.70	45.91
−1.4	44.26	42.65	41.60	42.12	42.33	42.32
−1.6	—	—	38.82	37.98	37.91	37.94
−1.8	—	—	—	32.84	32.82	32.80

Summary

1. The electrocapillary curves for the complete ranges of concentrations for mixtures of the normal alcohols, methyl, ethyl and propyl with water and a number of concentrations of the partially miscible butyl alcohol-water system have been obtained.

2. The areas of the alcohol molecules at the potential difference where maximum adsorption occurs have been calculated. They agree fairly well with those calculated from insoluble alcohol films on water.

3. Up to quite strong concentrations of the alcohols, the alcohols appear to form a monomolecular layer at the charged mercury surface, and are orientated in the same way as at the air-water interface.

4. In various alcohol solutions—the effect increasing as we ascend the homologous series—water appears to raise the interfacial tensions at polarisations more positive than −0.6 volts and to lower the interfacial tensions at polarisations more negative than −0.6 volts. These effects may be ascribed to large liquid junction potentials or to a positive adsorption of water at negative polarisations.

I am deeply indebted to Dr. J. A. V. Butler for many helpful suggestions. I have also to thank the Carnegie Trust for a Research Scholarship during the tenure of which this investigation was partly carried out, and Imperial Chemical Industries, Ltd. for a grant which defrayed the cost of part of the apparatus.

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July 21, 1931.

AN EXCEPTIONAL ISOTHERM AT 0° OF THE SYSTEM: PALLADIUM-HYDROGEN[*]

BY LOUIS J. GILLESPIE AND JOHN H. PERRY

The equilibrium between palladium and hydrogen appears to be well understood, as respects the region from 0° to 180° or 200° and from no hydrogen to the atomic ratio H/Pd of about 0.6 or 0.7. Pressure-composition isothermals satisfying the demands of the phase rule, for the case in which univariant systems occur, have been given by Gillespie and Hall.[1] Their conclusion that a solution of hydrogen in palladium can be in equilibrium with another phase having the composition of Pd_2H above about 80°, has recently been confirmed by the X-ray studies of Linde and Borelius[2] at 100°, 150° and 200°.

Three reservations should perhaps be made with regard to our understanding of the above-mentioned region. (1) Linde and Borelius suggest that there may be two crystalline forms of Pd_2H. (2) They suggest that the course of the isotherms of Gillespie and Hall below 80°, which led these authors to believe that below 80° Pd_2H is contaminated with an excess of dissolved hydrogen, may be due in reality to the undetected presence of the hydrogen-rich phase of Graham (obtained by electrolysis). We may add, that such a solution effect is not in evidence in the otherwise rather similar pressure-composition diagram of Valensi[3] for chromium and nitrogen, in which system the compound CrN is found in equilibrium with a solid phase containing less nitrogen. The suggestion of Linde and Borelius is logically possible; and yet there is experimental evidence pointing to the conclusion of Gillespie and Hall, and there seems to be no experimental evidence pointing against it.[4] (3) According to Wieland,[5] palladium containing analytically significant quantities of hydrogen is able to remove hydrogen from hydroquinone, producing quinone. If this were true, it would mean that all experimenters who have presented pressure-composition diagrams have been working with unstable systems, for the pressures observed by them are always measurable when appreciable quantities of hydrogen are present, and the pressure of hydrogen

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[*] Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 269.

[1] Gillespie and Hall: J. Am. Chem. Soc., **48**, 1207 (1926).

[2] Linde and Borelius: Ann. Physik, **84**, 747 (1927).

[3] Valensi: Thesis, University of Paris, Les Presses Universitaires de France, 49, Boulevard Saint-Michel, Paris V, 1929.

[4] Linde and Borelius point out that an equation $\log p = A/T + B$ satisfying the data at high temperatures also satisfies the data at the lower temperatures, suggesting that there is no discontinuity in the nature of the solid phases. But this is also in accord with the belief of Gillespie and Hall, that the hydrogen-rich phase in question is a solution of hydrogen in palladium, the composition of which approaches that of Pd_2H at high temperatures without discontinuity.

[5] Wieland: Ber., **45**, 484 (1912).

at which it could be in equilibrium with hydroquinone and quinone in a reasonable molecular ratio would be of the order of 10^{-24} atm., according to the electromotive-force measurements and calculations of Biilmann.[6] But Gillespie and Liu[7] were unable to confirm the occurence of this reaction and concluded that no valid evidence exists that palladium can dehydrogenate hydroquinone when it contains an appreciable quantity of hydrogen.

Gillespie and Hall stated that it happened twice that no change of curvature occurred in an isotherm, the isotherm rising as a continuous adsorption curve. They gave no data or curve to show the course of such a continuous curve, and indeed no such curve has been reported. The isotherm described below had been observed by us before their work, but the interpretation of it was not possible without the aid of their results.[8] It appears to belong in the palladium-hydrogen diagram, partly as a broken line indicating a metastable condition.

Experimental

The technique was similar to that of Gillespie and Hall, except that the heat treatment was not used, its benefits not having been observed. Owing to the use of a capillary-tube manometer in connection with a meter stick, the pressure at 4 mm. and less of mercury has but a small accuracy. Palladium black was prepared in two ways: palladium A, from palladosammine chloride by the method of Gutbier;[9] palladium B, by the method of Wieland.[5] In either case, the palladium black was placed in the apparatus and freed of oxygen by successively treating it with hydrogen and exhausting while hot with a mercury-vapor diffusion pump, before the addition of the measured quantities of hydrogen.

Palladium A gave at 0° an isotherm with an angle, the first ascending portion of the curve being followed by a line which for a short distance was horizontal and practically coincident with the isotherm of Gillespie and Hall.

TABLE I

Data for the Exceptional Isotherm at 0°

Cc. H_2/g. Pd	0.05	0.17	0.36	1.49	1.49	2.82	3.35
Pressure, mm.	0.3	0.4	0.9	2.9	2.1	4.2	5.0
Cc. H_2/g. Pd	4.07	4.76	5.59	6.70	7.68	8.64	9.43
Pressure, mm.	6.0	7.0	8.5	10.5	14.0	22.0	41.2
Cc. H_2/g. Pd	9.79	10.18	0.05	0.17	0.92	1.85	3.38
Pressure, mm.	58.8	89.1	0.3	0.4	1.3	2.6	4.7
Cc. H_2/g. Pd	5.06	5.94	6.66	7.75	8.55	9.34	9.94
Pressure, mm.	7.5	8.8	10.4	15.9	26.0	54.2	110.3

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[6] Biilmann: Ann. chim., [9] **15**, 109 (1921).

[7] Gillespie and Liu: J. Am. Chem. Soc., **53**, (1931).

[8] Particularly, their identical results for palladium black prepared in two ways (method of Gutbier, and method of Wieland).

[9] Gutbier: J. prakt. Chem., (2) **79**, 235 (1909).

Palladium B gave the quite different results shown in Table I. After the first series of additions of hydrogen, all the hydrogen was removed by heating and pumping and a second series of additions of hydrogen was made. In view of the great steepness of the curve at about 10 cc. per g., the two series are in good agreement.

If these results are plotted, and a smooth curve drawn without regard to the isotherm of Gillespie and Hall, the best curve from 0 to 4 mm. is close to the best corresponding curve through their data, but lies a little to the right (so that the two isotherms would intersect). But the experimental accuracy is not sufficient to establish a difference of this sort. One line is capable of representing both sets of data with an exceptional error as large as 0.8 mm. Although a better degree of consistency would be maintained in any single experiment with the technique used, it is probable that the experimental error was as large as this.[10]

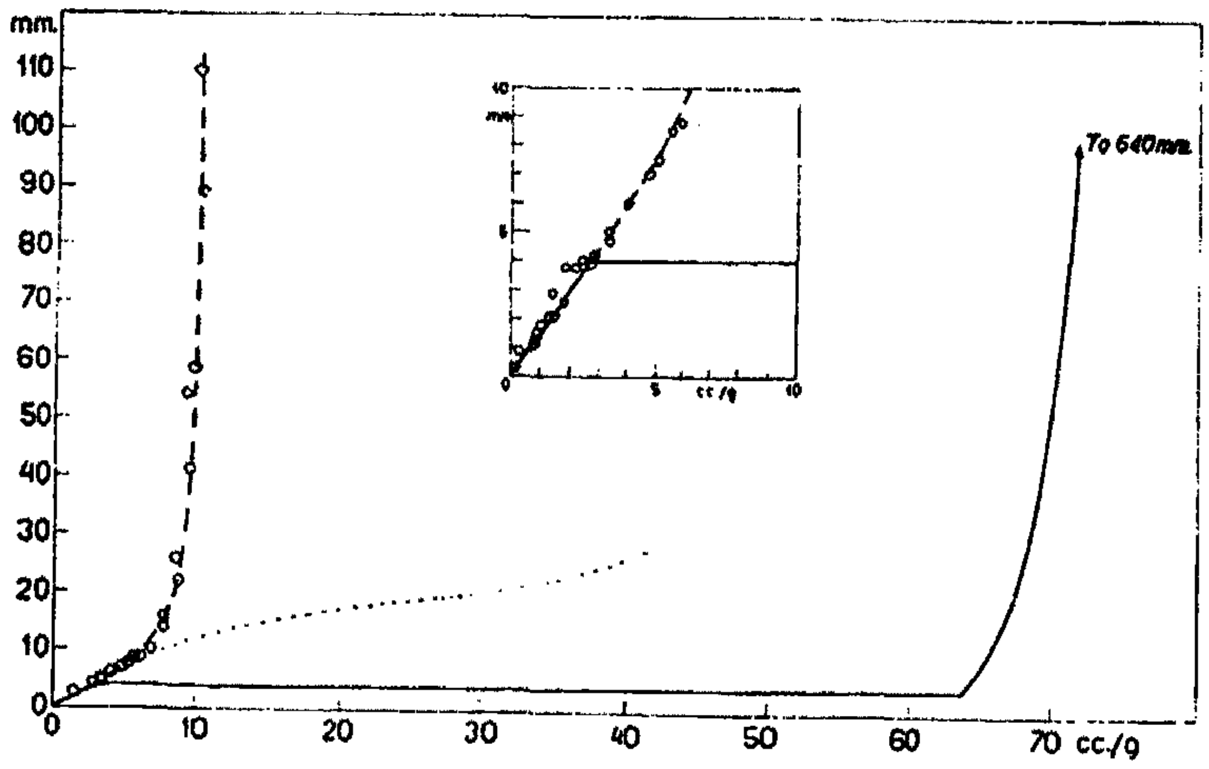

Fig. 1

The exceptional and the equilibrium isotherms for Pd and H_2 at 0°. The inset shows on an enlarged scale the observations taken near the origin.

In constructing Fig. 1, the best curve was therefore drawn for the data of Table I together with the data of Gillespie and Hall, and it is represented above 4 mm. by a broken line. It is believed that the same line should represent all data below about 4 mm., and that above this pressure the system is in a metastable condition, as indicated by the broken line. The rest of the isotherm of Gillespie and Hall is also shown for comparison, as well as a dotted line in the region between, as a basis for the following discussion.

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[10] Positive evidence that the error was of this order has been obtained by Gillespie and Ambrose from a comparison of observed and calculated heat of reaction. J. Phys. Chem., 35, 3105 (1931).

Discussion

Linde and Borelius state that under certain circumstances a (third) phase is formed, an apparent continuous extension of the hydrogen solution (easily obtained at small concentrations) up to a concentration greater than in Pd_2H. The curve for such an extension would be somewhat like the dotted line in Fig. 1. But, if we accept the broken line as the true extension of the curve into the metastable region, it is impossible that any curve such as the dotted line should be at 0° a proper extension of the curve from 0 to 4 mm., where the word "extension" is used in the same sense. At other temperatures we have no data for broken-line extensions, and from the appearance of the isotherms of Gillespie and Hall it seems probable that such extensions would lose at higher temperatures the characteristic curvature of the broken line of Fig. 1, and thus the characteristic difference between the broken and dotted line of Fig. 1 might largely be lost at higher temperatures. Yet the experiments at higher temperatures, particularly those of Lambert and Gates,[11] seem to prove clearly that isotherms resembling the dotted line, and obtained by various experimenters,[12] cannot be regarded as extensions analogous to the broken-line extension. For, Lambert and Gates obtained hysteresis loops by successive addition and subtraction of hydrogen. The occurrence of hysteresis loops clearly indicates that the solids are indifferent to a significant excess or deficit of hydrogen in the gas phase in contact with the solids. In such a case the pressure curve tells us nothing definite about the nature or composition of the solid phases.

The statement of Linde and Borelius appears therefore to need qualification as regards the composition, up to which the extension has been observed. True extensions of the curve for the weaker hydrogen solution have not been shown at temperatures other than 0°, and in this case the highest concentration reached was far from that of Pd_2H, being in fact more nearly that corresponding to 0.95 atoms of hydrogen per atom of palladium.

The characteristic shape, noted by Hoitsema, of curves in the palladium-hydrogen system such as the dotted line of Fig. 1 is evidently due to the presence of two solid phases in contact with a gas phase, the pressure of which gas can be changed considerably without provoking reasonably rapid changes in the solids.[13]

Summary

An exceptional pressure-composition isotherm has been observed at 0° for the system palladium-hydrogen, which appears to represent an extension of the first rising isotherm into a metastable region. The highest pressure observed was 110 mm. of mercury, at about 0.95 atoms of hydrogen per atom of palladium. A diagram is given showing the relation of this isotherm to the equilibrium isotherm at 0°.

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[11] Lambert and Gates: Proc. Roy. Soc., **108A**, 456 (1925).

[12] Hoitsema (and Roozeboom): Z. physik. Chem., **17**, 1 (1895); *Holt, Edgar and Firth:* **82**, 513 (1913); Lambert and Gates: *loc. cit.;* Sieverts: Z. physik. Chem., **88**, 451 (1914).

[13] The possibility, that in this system at a given temperature two solid phases might be in equilibrium with gas at more than one pressure, is excluded by the phase rule.

ENERGY DIAGRAMS OF THE HYDROGEN HALIDES IN THE GASEOUS STATE AND IN AQUEOUS SOLUTION

BY PIERRE J. VAN RYSSELBERGHE

1. Introduction

In a recent communication[1] we have presented an "energy diagram" for sodium chloride. This diagram gives the variation of the interaction energy between the sodium and chlorine constituents as a function of the distance between the two nuclei. The interaction curve for the ionic system gaseous Na^+ + gaseous Cl^- could be drawn exactly. The interaction curve for the atomic system gaseous Na + gaseous Cl (i.e. the curve corresponding to the possible formation of a homopolar molecule) was drawn in an approximate way. In aqueous solution the interaction curve for the system dissolved Na^+ + dissolved Cl^- was determined by means of the dissolution energies gaseous atom $\longrightarrow$ dissolved ion. This curve is an horizontal line except, at short internuclear distances, for a small dip corresponding to the heat of dissociation of the dissolved molecule or physical aggregate NaCl. This heat of dissociation was determined by Nernst.[2] The diagram shows that, in the gaseous state and in aqueous solution, sodium chloride is probably a polar compound, although the existence of homopolar molecules is not impossible. It would be reasonable to assume that both in the gaseous state and in aqueous solution the two types of molecules exist, or better, that a certain number of homopolar molecules are in equilibrium with polar or ionic sodium chloride.

It is advisable to reserve the term "polar molecule" to molecules having a dipole moment. It is well known that chemically such molecules may be homopolar. Molecules in which the constituents are ions held together by the interplay of the electrostatic forces and of the Born repulsive forces could then be called "ionic molecules." In ionic crystal lattices those molecules do not exist but the term is useful to designate gaseous molecules the constituents of which are ions. According to the wave mechanical theory of valence proposed by London[3] a homopolar molecule is formed from atoms when a sharing of pairs of electrons with opposite spins is possible. To this sharing corresponds an interaction energy, the "exchange" energy (Austausch-Energie) which is to be superposed to the electrostatic interaction energy of the charge clouds of the electrons. In ionic systems the interaction energy at large distances is due to the Coulomb forces between the ions. At shorter distances the interaction energy of the charge clouds has to be considered. A repulsion ensues. At a certain distance between nuclei attraction and repulsion balance each other and we say that an ionic molecule is formed.

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[1] P. Van Rysselberghe: J. Phys. Chem., 35, 1054 (1931).
[2] W. Nernst: Z. physik. Chem., 135, 237 (1928).
[3] F. London: Z. Physik, 46, 455 (1928).

In the solid state, however, the term would not be appropriate, except in the case of molecular lattices. Such lattices may correspond to compounds which in the vapor state are intermediate between the ionic and the homopolar type or simply to ionic compounds for which the wave mechanical perturbation effects of higher order (polarization effects) prevent the formation of an ionic crystal. As shown by London condensation, crystallization or van der Waals attractions depend on those higher order effects.

Hydrogen halides have been considered by Franck and his co-workers[1] and also by London as homopolar compounds. London's reasoning has been recalled in our previous communication.

It seemed interesting to us to examine more in detail the case of the hydrogen halides and to draw complete energy diagrams in which data for the dissolved systems would be included. It is well known that in solution hydrogen halides are typical ionic compounds. Incidentally we are able to deduce the heats of dissociation of the four hydrogen halides. A certain systematic discrepancy between these heats of dissociation and thermochemical data leads to a discussion about polarization effects.

2. Interaction Curves of the Gaseous Ionic Systems Hydrogen Ion + Halogen Ion

If we call Φ the interaction potential energy of the system H^+ + (halogen)$^-$, E_∞ the sum of the ionization energy of hydrogen and of the electroaffinity of the halogen, e the elementary electrical charge and r the distance between the two nuclei we have, at large distances:

$$\Phi = E_\infty - \frac{e^2}{r} \qquad (1)$$

At small distances, a repulsion term has to be added to the right-hand side of this equation.

Equation (1) represents an hyperbola. It intersects the horizontal axis ($\Phi = 0$) for a value R of r, such that

$$R = \frac{e^2}{E_\infty} = \frac{14.3}{E_\infty}\,\text{Å} \qquad (2)$$

in which E_∞ is expressed in volt-electrons.[2] If R is larger than the equilibrium distance R_0 between the nuclei (as determined, for instance, from dipole moments) the compound is ionic. If R is equal to or smaller than this distance, the compound is homopolar. This is easily seen because when R is larger than R_0, the minimum of Φ (corresponding to an equilibrium between the electrostatic attraction and the repulsion neglected in equation (1)) lies below that of the homopolar interaction curve.

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[1] J. Franck and H. Kuhn: Z. Physik, **43**, 164 (1927).

[2] F. London: Z. Physik, **44**, 455 (1927).

Table I gives the values of the electroaffinity A of the four halogen atoms, of E_∞ obtained by adding to A the ionization energy of hydrogen: 13.45 V.e., of R and R_0.

All the energy values used in this work are taken from Fredenhagen's papers[1] or from the Landolt-Börnstein tables. The values of R_0 are taken from London's paper where an analogous table could be found.[2]

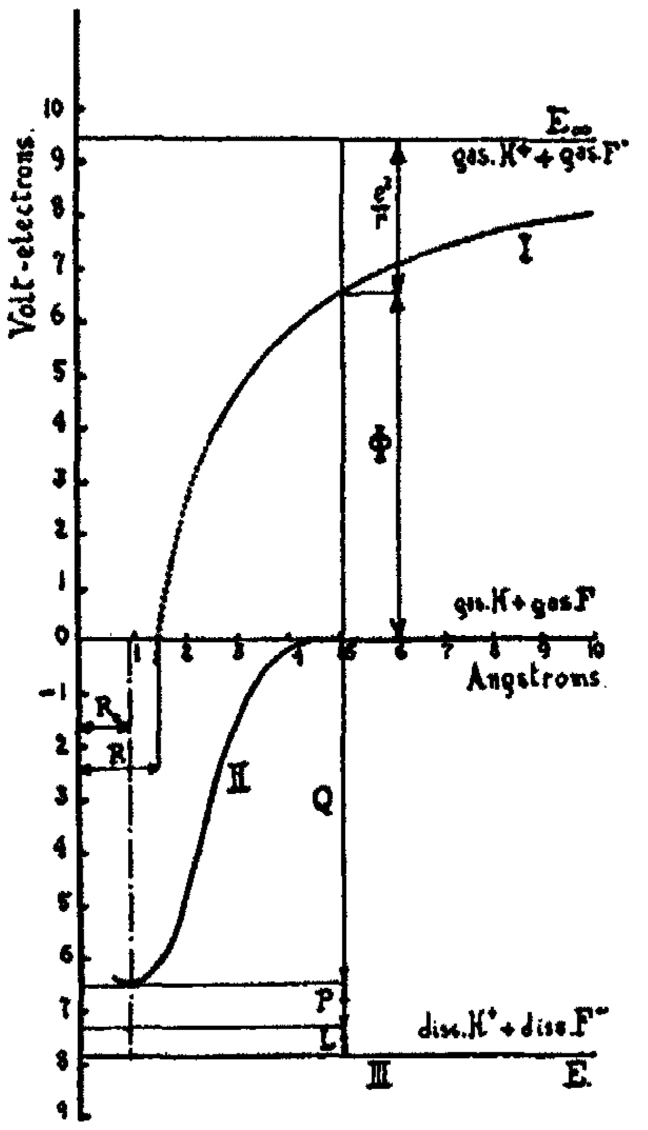

FIG. 1
HF

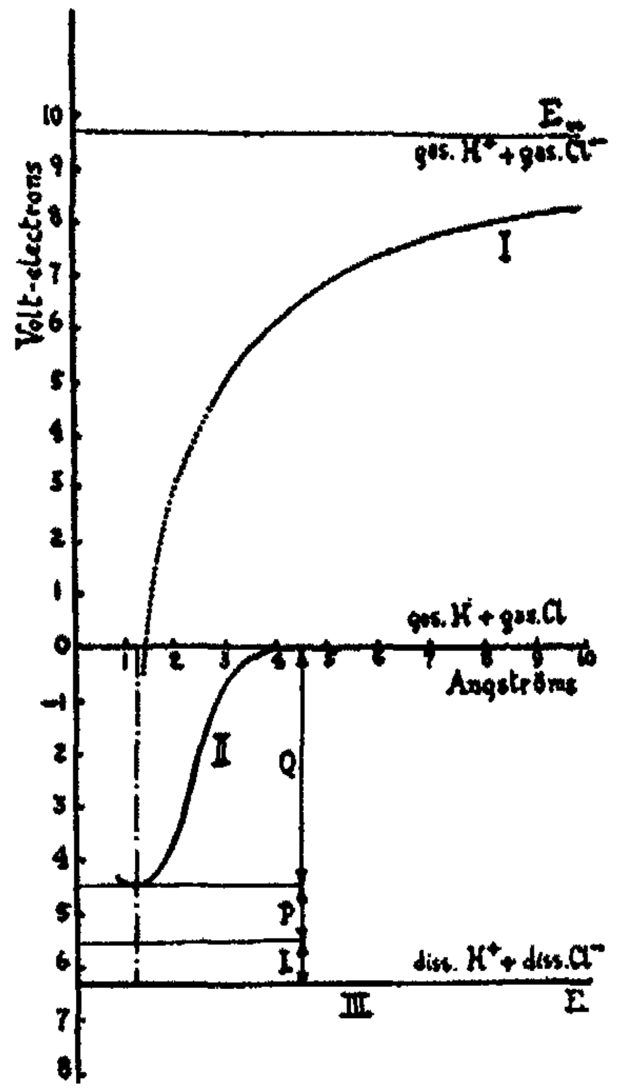

FIG. 2
HCl

TABLE I

	A V.e.	E_∞ V.e.	R Å	R_0 Å
HF	−4.00	9.45	1.51	0.94
HCl	−3.70	9.75	1.47	1.28
HBr	−3.70	9.75	1.47	1.42
HI	−3.40	10.05	1.42	(1.50)

On Figs. 1, 2, 3, 4, curve I represents the interaction potential of the ionic system respectively for HF, HCl, HBr and HI. The curves are not

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[1] K. Fredenhagen: Z. physik. Chem., **128**, 1 (1927); **128**, 239 (1927); **134**, 33 (1928); **140**, 65, 435 (1929); **141**, 195 (1929).

[2] F. London: loc. cit., p. 475.

extended beyond their intersections with the horizontal axis which corresponds to the energy of the atomic system gaseous H + gaseous halogen, taken as a reference energy. The values of R being practically equal to those of R_0, the minima in the ionic interaction curves are on the left of those of the homopolar curves or, more likely, above the horizontal axis and hence do not occur. Therefore the hydrogen halides are homopolar in the gaseous state.

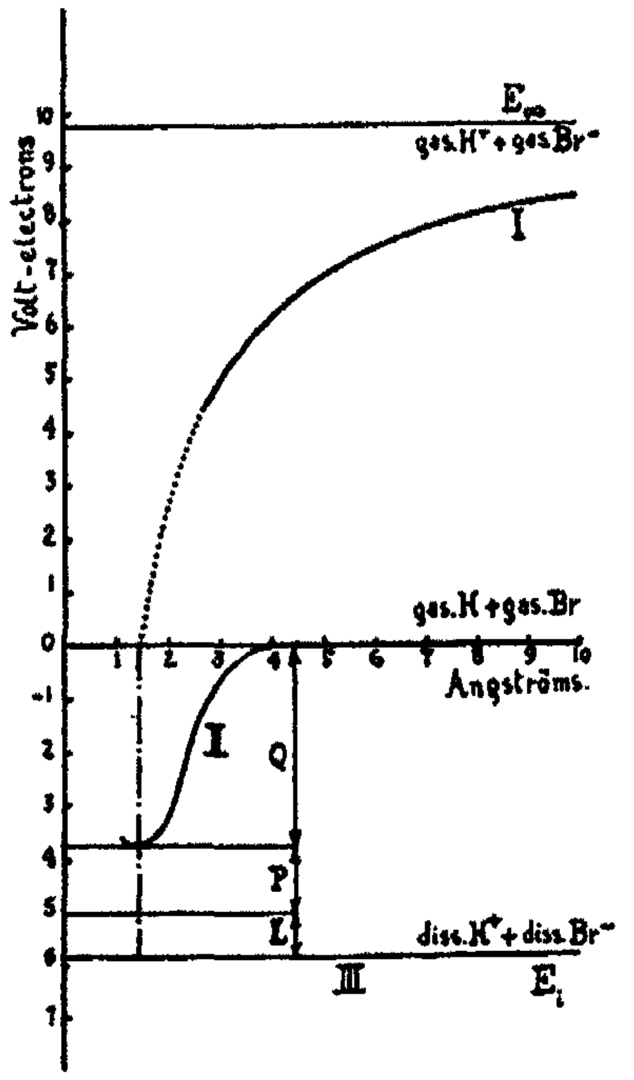

Fig. 3
HBr

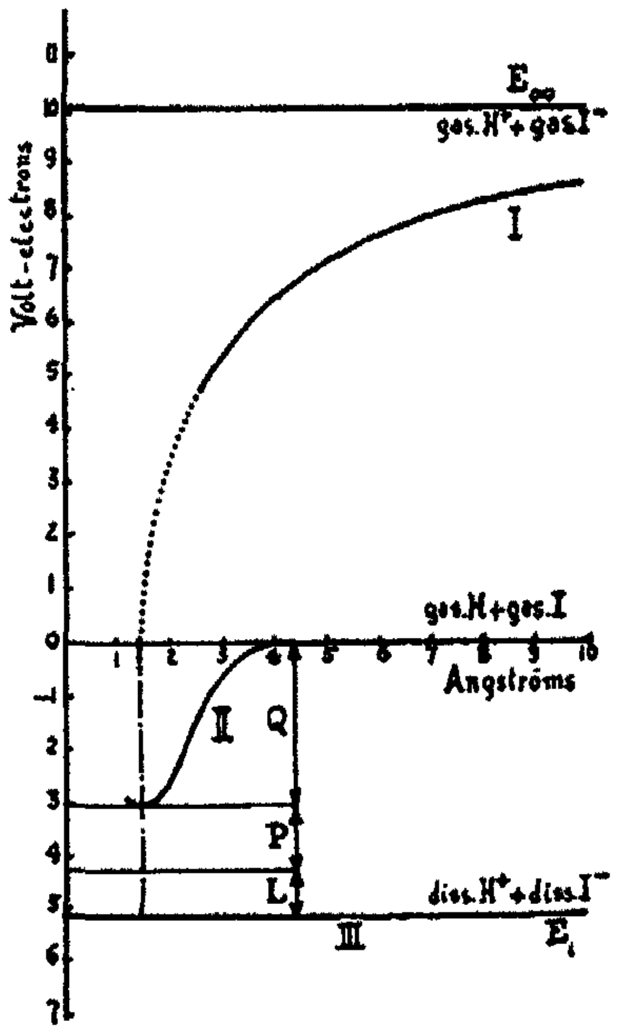

Fig. 4
HI

3. Interaction Curves of the Gaseous Atomic Systems
Hydrogen Atom + Halogen Atom

At all distances down to those of the order of a few angströms the interaction curves coincide with the horizontal axis. Minima appear for the values R_0 given in Table I. These minima are due to the interplay of the electrostatic interaction energy of the charge clouds of the valence electrons and of their exchange energy. Their values cannot be directly computed on account of the mathematical complications of the wave mechanical perturbation problem. The ordinates of those minima correspond to the dissociation energies and could be deduced from thermochemical data. Table II gives the heats of reaction expressed in volt-electrons for the following reactions in which A represents a halogen atom:

$$HA = 1/2\, H_2 + 1/2\, A_2 - Q_1 \text{ V.e.}$$
$$A_2 = 2\, A - Q_2 \text{ V.e.}$$
$$HA = H + A - Q \text{ V.e.}$$

The values of Q_1, Q_2, Q are deduced from the thermochemical data of the Landolt-Börnstein tables. It is recalled that 1 kilogram calorie is equivalent to 4.337×10^{-2} Volt-electron.

TABLE II

	Q_1 V.e.	Q_2 V.e.	Q V.e.
HF	2.78	2.93	6.44
HCl	0.95	2.69	4.49
HBr	0.52	2.00	3.72
HI	0.06	1.50	3.01

The dissociation energy of H_2 is 4.40 V.e. We of course have:[1]

$$Q = Q_1 + 1/2\,(Q_2 + 4.40) \text{ V.e.}$$

The values of Q are then used to determine the minima of the homopolar curves II on Fig. 1, 2, 3 and 4. Those curves can then be drawn in an approximate way.

From the most recent data on band spectra and from computations using the thermochemical values of Q_1 the figures of Table IIa are obtained.[2] The energy of dissociation of H_2 used is 4.46 V.e.

TABLE IIa

	Q_2 V.e.	Q V.e.
HF	—	—
HCl	2.466 ± 0.008	4.417
HBr	1.962	3.73
HI	1.544	3.05

These new values of Q are in good agreement with those of Table II.

4. Interaction Curves for the Ionic Systems Dissolved Hydrogen Ion + Dissolved Halogen Ion

It was shown by Fredenhagen[3] that the following relation holds:

dissolution energy (dissolved ion →gaseous atom)	+	ionization energy (gaseous atom →gaseous ion)	=	solvation energy (dissolved ion →gaseous ion)

This relation was studied in detail for the case of sodium chloride in our previous communication. If we add the dissolution energies of the hydrogen

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[1] For some of these heats of reaction average values were used.

[2] Kindly communicated by Professor R. T. Birge.

[3] K. Fredenhagen: Z. physik. Chem., 140, 69 and seq. (1929).

and halogen ions and draw a horizontal line at a distance below the horizontal axis given by this sum, we obtain the energy level of the dissolved ionic system. At a distance which we suppose equal to the internuclear distance in the molecule (R_o in Table I) an ionic molecule or physical aggregate will be formed. A minimum in the interaction curve appears at this point. Nernst's work[1] showed that the dissociation energies of these ionic molecules is very small. For all practical purposes it is sufficient to assume that the horizontal line III in Figs. 1, 2, 3 and 4 represents the interaction curve of the dissolved ionic system.

The dissolution energy D, the ionization energy I, the solvation energy S of the halogen atoms and the total dissolution energy E_i of the hydrogen halides are given in Table III. The figures are taken from Fredenhagen.[2] The values of D, I and S for hydrogen are, respectively: 3.90, 13.45, 17.35 V.e.

TABLE III

	D V.e.	I V.e.	S V.e.	E_i V.e.
HF	3.92	−4.00	−0.08	7.82
HCl	2.46	−3.70	−1.24	6.36
HBr	1.97	−3.70	−2.03	5.87
HI	1.20	−3.40	−2.20	5.10

The horizontal lines III are at distance E_i below the horizontal axis. We of course have:

$$E_i = D + 3.90 \text{ V.e.}$$

Our energy diagrams are thus completed.

5. Determination of the Heats of Dissociation of the Hydrogen Halides from Data pertaining to the Dissolved Ionic Systems

Representing again a halogen atom by A and calling, respectively L, E_i, Q the energies corresponding to the following processes:

gaseous HA $\longrightarrow$ dissolved H^+ + dissolved A^- + L
gaseous H + gaseous A $\longrightarrow$ dissolved H^+ + dissolved A^- + E_i
gaseous HA $\longrightarrow$ gaseous H + gaseous A − Q

we have the obvious relation:

$$L = E_i - Q \qquad (3)$$

L is the heat of solution of the halide.
$-E_i$ is the total dissolution energy of the ionic system.
Q is the heat of dissociation of the halide in the gaseous state and can then be determined when L and E_i are known.

L can be found, for instance, in the Landolt-Börnstein tables. E_i was determined in the preceding section. The heats of dissociation can then be calculated.

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[1] W. Nernst: loc. cit.

[2] K. Fredenhagen: loc. cit.

On our diagrams, the values of L should give the distances between the horizontal lines III and the minima of the curves II.

The values of L are those corresponding to infinite dilution; no correction for the heat of dilution is then necessary. Table IV gives the values of L, E_i, Q as calculated from $Q = E_i - L$, Q as determined in Table I from thermochemical data, the differences $Q_{calc.} - Q_{th}$.

TABLE IV

	L V.e.	E_i V.e.	$Q_{calc.}$ V.e.	Q_{th} V.e.	$Q_{calc.}$-Q_{th} V.e.
HF	0.50	7.82	7.32	6.44	0.88
HCl	0.76	6.36	5.60	4.49	1.11
HBr	0.86	5.87	5.01	3.72	1.29
HI	0.83	5.10	4.27	3.01	1.26

There is a systematic discrepancy of about 1 V.e. between the two sets of values of the heats of dissociation. No important obvious correction could be introduced in our calculations. All the data correspond to practically the same temperature, namely 18-20°C. The heat of dilution is theoretically 0 at infinite dilution. The heat of solution, as measured, takes automatically into account the work necessary to remove the oppositely charged ions to infinite distance. Moreover this quantity is quite small. There is, of course, some uncertainty in the thermochemical data for the heats of dissociation of molecules into atoms, but the differences $Q_{calc.} - Q_{th}$ are of the same order of magnitude for the four halides. We do not think that they can be accounted for on the basis of a lack of accuracy of thermochemical data, since these agree quite well with spectral data. The average $Q_{calc.} - Q_{th}$ for the four halides is 1.13 V.e. or 26 kilogram calories.

We suggest the following explanation: In relation (3) the quantity E_i corresponds to the process

gaseous H + gaseous A → dissolved H^+ + dissolved Cl^-, in which the atoms are at infinite distance. It means that E_i is larger than Q + L by a term depending on the polarization effect of one atom on the other. When the atoms are close together, as it is the case after the dissociation of a molecule of halide, they exert on each other polarization effects (perturbations of higher order, in wave mechanical language). The energy of the shared electron bond (exchange energy) is of course included in the measured value of Q. Hence, instead of writing:

$$E_i = Q + L,$$

we should write

$$E_i = Q + L + P$$

in which P is the energy corresponding to the mutual polarization of the atoms. The direct calculation of this quantity by wave mechanics is practically impossible. Our computations give for P the average value 1.13 V.e.

Summing up the contents of this paper we may say: the hydrogen halides are, in the gaseous state, homopolar compounds possessing a shared electron bond. In aqueous solution they dissociate into ions like ionic compounds. Combining available energy data and making use of the heats of solution the heats of dissociation of the gaseous halides into atoms can be computed. The heats of dissociation so obtained are equal to those determined by thermochemical data plus the energies corresponding to the mutual polarization of the atoms. The order of magnitude of these energies of polarization is 1 V.e.

6. Summary

1. Previous considerations about homopolar, ionic and polar compounds are reviewed and discussed.

2. Curves representing the interaction energy of hydrogen and halogen ions and atoms in the gaseous state and in aqueous solution in terms of the distance between the nuclei of the two constituents have been drawn.

3. The energy of mutual polarization of hydrogen and halogen atoms is deduced from the combined use of energy data and of heats of solution.

Department of Chemistry,
Stanford University, California,
March, 1931.

THE APPARENT VOLUMES OF SALTS IN SOLUTION
II. THE PROBLEM OF THEIR INTERPRETATION

BY ARTHUR F. SCOTT

The volume of a solute in aqueous solution has been the object of considerable attention because of its theoretical connection with many properties of the solution. Of the numerous attempts to estimate the magnitude of the volume of a solute those based on the volume changes which accompany the formation, mixing, and dilution of solutions have been the most frequent, a consequence, no doubt, of the apparent directness of the method. These studies of volume changes, however, have not led to any clearly defined conclusions regarding the space occupied by the solute. The difficulties encountered in this method of approach can be readily understood from a consideration of the volume change which takes place on dilution of a solution, a subject which will be discussed in this article.

For this case it is customary to make use of the quantity ϕ, termed the apparent molal volume of the solute and defined by the expression:

$$\phi = V - nv_1 \tag{1}$$

where V is the volume of solution containing one gram mol of solute; v_1 is the volume of one gram mol of pure water at the temperature of the solution; and n is the number of mols of water present. The quantity ϕ is a function of concentration and, as a general rule, increases with increasing concentration. The variation in ϕ with concentration, as Tammann[1] pointed out, can be the consequence of changes in the volume of both solute and solvent and includes also any effects arising from an alteration in the degree of dissociation of the solute. The influence of none of these three factors is known independently of the others. Therefore, in attempts to interpret the significance of ϕ it has been found necessary to assume arbitrarily that the volume of either solute or solvent is constant and to ignore completely the effect of dissociation. Conclusions respecting the volume of a solute, which involve the above assumptions, are obviously of limited value.

A somewhat less arbitrary basis for the interpretation of the apparent molal volume of a salt can be proposed. If the concentration of a solution could be increased beyond the actual limits of the solution state, a concentration would be reached at which no water is present, i.e., $n = 0$. This hypothetical state can be regarded as the critical upper limit of the solution state. The limiting value of the apparent molal volume, corresponding to this state, will be designated hereafter as ϕ'. The importance of this concept lies in the fact that ϕ' is by hypothesis the volume of the solute unmodified by any effects arising from the presence of solvent, and that the contribution of the

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[1] Tammann: Z. physik. Chem., 21, 529 (1896).

several factors to the variation in ϕ with concentration need not be known or assumed. Even though the value of ϕ' cannot be accepted as equivalent to the volume of the solute in actual solution, because of the possible dependence of this property on concentration, it should afford a new means of estimating the magnitude of the latter. The possibilities of the above viewpoint will be investigated in the present article. In the first part we shall consider the problem of calculating the quantity ϕ'; in the second part we shall discuss the possible significance of the values which are obtained.

A previous attempt[1] to estimate the magnitude of ϕ' may be mentioned first. For saturated solutions it was shown that the apparent molal volume ϕ_s of the saturating salt is related to the number N of mols of water present in the solution at the same temperature by the empirical expression:

$$\phi_s = -aN^2 + b \qquad (2)$$

where a and b are constants characteristic of each solute. Now, when N equals zero, the condition by which we have defined the critical limiting ϕ' state is explicitly satisfied and accordingly the constant b would appear to be identical to the desired constant ϕ'. However, since the decrease in N is attended by an increase in temperature, the foregoing method of extrapolation introduces a complex temperature factor, the effect of which on the volume of the solute is unknown. Consequently, although the difference in magnitude between b and ϕ' may be small, the two quantities cannot be accepted as equivalent. To indicate the basic similarity between the two hypothetical quantities and at the same time to distinguish between them we shall subsequently refer to b as ϕ_s'.

In order to avoid the uncertainty of the temperature factor we shall, in the present attempt to estimate the magnitude of ϕ', make use of the variation of ϕ in solutions at constant temperature. For the purpose of extrapolation beyond the actual limit of the solution state we shall employ Masson's[2] empirical equation:

$$\phi = km^{1/2} + \phi_0 \qquad (3)$$

where k and ϕ_0 are constants characteristic of each salt at a given temperature; and m is the molal concentration. This equation was critically tested in a previous paper[3] and was found to represent quite satisfactorily the experimental variation of ϕ with concentration. In the same paper there were given values of the constants k and ϕ_0 for solutions of the alkali halide salts by means of which equation 3 best represents the actual data. It should perhaps be emphasized at this point that the results to be set forth in this paper rest ultimately on the validity of Masson's equation and also are subject to errors involved in the values of the above constants.

Since in equation 3 ϕ is expressed as a function of concentration and not as a function of the amount of water present, as in the case of ϕ_s (equation

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[1] Scott and Durham: J. Phys. Chem., 34, 2035 (1930).

[2] Masson: Phil. Mag., (7) 7, 218 (1929).

[3] Scott: J. Phys. Chem., 35, 2315 (1931); Geffcken: Z. physik. Chem., 155, 1 (1931) in an independent test of the same relationship arrived at a similar conclusion.

2), the limiting value ϕ' cannot be calculated directly by imposing the condition $n = 0$. At first glance, however, it would seem that ϕ' is identical to the concept ϕ_m which Masson accepted as the upper limit of his equation. For the quantity ϕ_m is defined by the condition $\phi_m = V_m$, which is equivalent to setting $n = 0$ in equation 1, and therefore formally satisfies the definitive condition of the ϕ' concept.

The matter, however, is by no means so simple as the above discussion would imply. The objection to the above conclusion, which is not obvious, is perhaps best brought out by questioning the applicability of equation 1. This equation merely defines as solute *all* space which is not occupied by solvent and in no way takes into account the mechanism of the solution state. For instance, in solutions which approximate the hypothetical ϕ' state in concentration it is conceivable that there is some space from which water is not excluded but in which no water is present because of the limited amount available. In such a case equation 1 could not be used to determine the domain of the solute, the object of our inquiry. In order to be able to designate ϕ' as the domain of the solute a "free space" term would have to be introduced into the equation and this would mean that the condition $\phi_m = V_m$ is not identical to the condition $n = 0$ and therefore does not define the desired ϕ' state. Although the above objection is purely hypothetical, it nevertheless constitutes a rather serious objection. For the acceptance of ϕ_m as equivalent to ϕ' would commit us to a specific view of the mechanism of the solution state and would thereby preclude from consideration equally plausible possibilities.

The foregoing argument has been outlined to make understandable why an attempt to calculate ϕ' by an entirely different method is permissible. However, before investigating this method it is of interest to examine further the ϕ_m values, especially since their properties were not studied by Masson. Values of this constant for the alkali halides at three different temperatures have been calculated, using the equation constants given in the paper already referred to, and are given in Table I.

TABLE I

Values of ϕ_m in cc.

		Li	Na	K	Rb	Cs
Cl	0.00°	27.3	30.8	39.5	43.8	50.0
	25.00	26.5	29.1	38.4	42.6	49.0
	50.04	26.0	28.7	38.4	42.7	49.2
Br	0.00	31.4	34.8	44.6	48.6	55.0
	25.00	30.7	33.1	43.0	48.0	54.3
	50.04	30.8	33.0	43.2	48.2	54.7
I	0.00	39.7	41.7	52.7	58.0	65.6
	25.00	39.6	41.7	52.2	57.4	63.9
	50.04	39.7	41.7	52.7	58.0	65.6

From these data it can be seen that the effect of temperature on the ϕ_m value of any salt is very slight: in general the values at 0° are a little larger than those at 25.00° and 50.04° which are essentially identical. These temperature differences, it could be supposed, reflect the variations in the properties of water which occur with temperature.

A more explicit analysis of these ϕ_m values encounters the difficulty, which has already been pointed out, that we have no satisfactory picture of this limiting state. Nevertheless, we may consider, because of its suggestive outcome, one of the possible hypotheses which was tested as a means of exploration. If it is assumed that the domains of the solute particles do not interpenetrate with increasing concentration, it follows that the ϕ_m state is reached when the solute particles have come as close together as possible. This idea of "nearest approach" immediately suggests a similarity to the solid, crystalline state. In order to show the nature of this relation values of ϕ_m have been plotted (Fig. 1) against the volumes of the crystalline salts V_c. The data used are for 25° and yield results which are typical of the other temperatures.

The outstanding feature of this diagram is the very definite linear relationship existing between ϕ_m and V_c. It may be noted also that the slopes of the drawn lines are 1.00 and 0.86 ($=\sqrt{3}/2$) respectively, and that the ordinate intercepts of the two lines are practically the same. The difference in magnitude between ϕ_m and V_c is apparently not very great. Even though these facts do not furnish any definite information regarding the condition of the solute in the ϕ_m state, they do imply the existence of a rather intimate connection between the factors which determine the domain of a salt as solute and the complex forces which fix the volume of the salt as a crystalline solid. In connection with this general conclusion we may remark the division of the salts into two groups. The divergence of the cesium salts from the others is due conceivably to the difference in the type of packing of the atoms in the crystal lattice. For when the ϕ_m values are plotted against the hypothetical volumes[1] of the cesium salts with a rock-salt type lattice (indicated by triangles in Fig. 1) they fall on the same line as the other salts. In the case of the lithium salts the divergence from the other alkali halides arises most probably from a unique property of the lithium ion in solution. As was shown in the previous article, equation 2 is applicable to solutions of lithium salts only up to a certain concentration and consequently the ϕ_m values of these salts are not directly comparable to those of the other salts. It can be estimated, however, that the ϕ_m values which would be obtained from the data of solutions of high concentration are somewhat less than those used in drawing Fig. 1.

The above properties of the ϕ_m values do not throw very much light on their significance, particularly on the question whether they can be treated as equivalent to the desired ϕ' values. Even the interpretation to be placed on the interesting relationship portrayed in Fig. 1 is obscured by the neces-

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[1] Pauling: Z. Krist., 67, 392 (1928).

sity of special assumptions regarding the domains of the solute particles. On the other hand, in concluding this digession on the ϕ_m values it may be pointed out that their properties are not in conflict with the hypothesis by means of which we shall attempt to calculate values of ϕ'. As a matter of fact, our subsequent argument could be predicated on the close relationship shown to exist between the ϕ_m values and the volumes of the crystalline salts. For, if the ϕ_m state is not the upper limit of the solution state, it can be shown, as a consequence of equation 2, that the desired ϕ' values cannot differ greatly from the ϕ_m values, unless the so-called free space is a very large fraction of the solution volume.

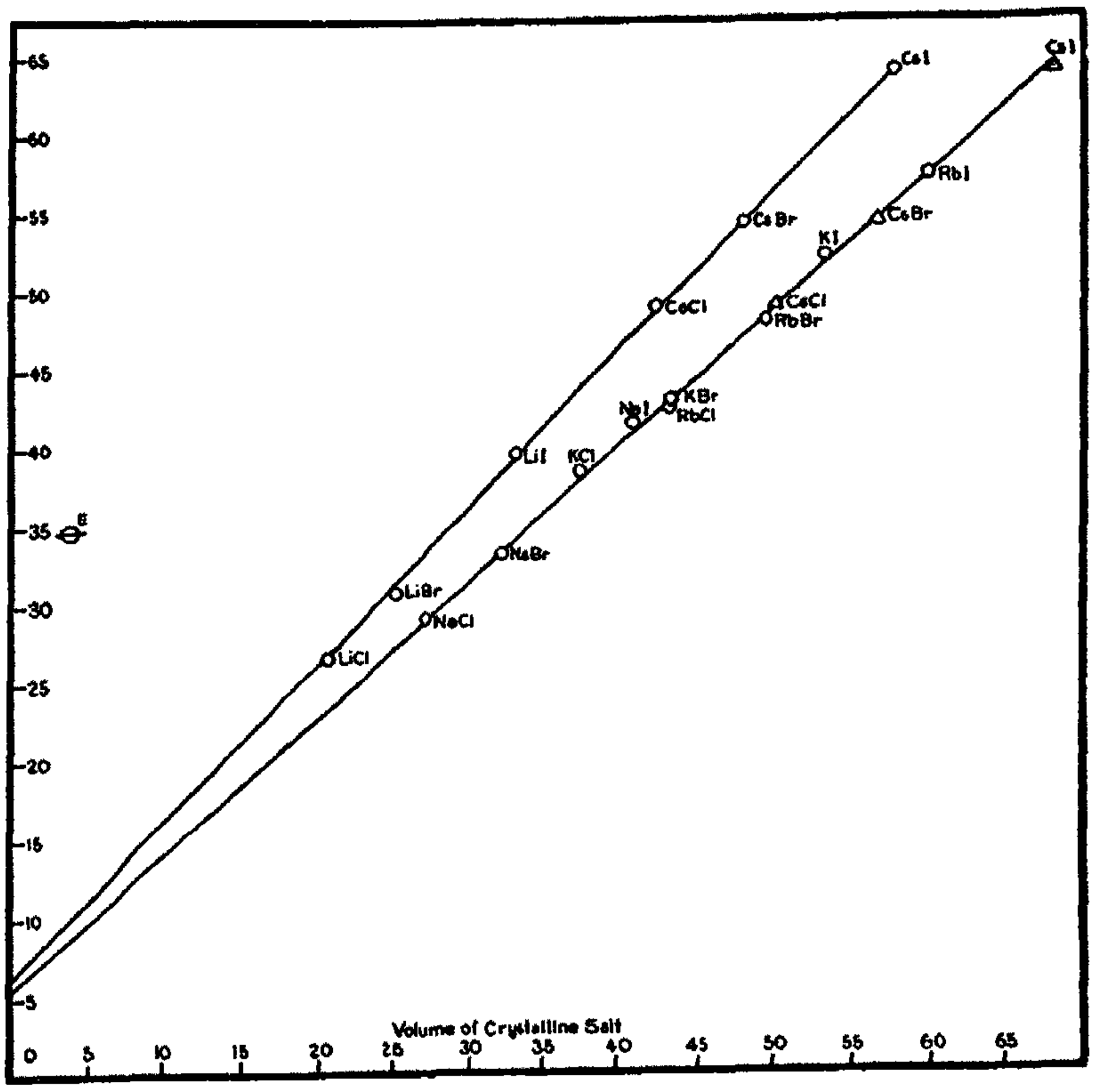

Fig. 1

The Relationship between the ϕ_m and Crystalline Volumes of the Alkali Halides

The condition which we wish to propose for the calculation of ϕ' is most easily formulated in terms of one fundamental assumption. We shall postulate that the transition from the solution state to the crystalline state is not marked by any abrupt change or discontinuity, that with increasing concentration the solute ultimately assumes the properties of a crystalline substance.

Despite the rather broad implications it carries, the assumption is not so novel as it appears at first sight. The implied similarity between the inter-ionic forces in crystalline solids, the inter-molecular forces in water, and ionic-molecular forces in solutions has been suggested by several authors on various grounds. For illustration we may cite the following conclusions of Langmuir[1] which are especially appropriate: "In fact the only essential differences between liquids and solids seem to lie in the mobility of liquids and in those properties which are directly dependent on mobility. As a result of this mobility the definite lattice arrangement of solids gives way to the irregular arrangements characteristic of liquids. . . . . From these considerations it is evident that the forces involved in the structures of liquids are not essentially different from those of solids. . . . . The mobility of a liquids is thus due to a shifting of the relative positions of atoms which are all chemically combined with each other."

The significance of our basic postulate is that it opens the way for a definition of the ϕ' state from the standpoint of the crystalline state instead of from the unknown conditions of the solution state. This reversal of viewpoint may be expressed as follows. In place of attempting to determine the conditions under which a solute ceases to be in a solution state we shall attempt to establish the conditions under which a crystalline substance takes on the properties of a solute in solution. This latter condition, in accordance with our fundamental assumption, would appear to be that at which the regular lattice arrangement of the crystalline substance gives way to a less regular arrangement.

According to the lattice theory[2] of the crystalline state of the heteropolar compounds, such as those we are dealing with, the inter-ionic distance is determined by the cohesive (attractive) forces and the opposing (repulsive) forces of the ions. At the normal, equilibrium distance R the resulting force is zero; on expansion it becomes positive; and on contraction, negative. At some value of the expansion the resulting force reaches a maximum and thereafter decreases in magnitude, approaching zero asymptotically. Since, when this maximum cohesive force is exceeded, the crystal is pulled apart, the volume corresponding to this point of expansion may be designated as the critical disruptive volume V^* of the crystal. Now, for our purpose this critical disruptive volume marks the point of transition from a regular lattice arrangement to some irregular arrangement of the ions. Consequently, we shall attempt to identify the critical volume of the solution state V' (corresponding to ϕ') with the critical disruptive volume of the crystalline substance.

To calculate the critical disruptive volumes of the alkali halides we shall employ the expression derived by Joffe:

$$\frac{R^*}{R} = \left(\frac{n + 3}{m + 3}\right)^{\frac{1}{n-m}} \tag{3}$$

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[1] Langmuir: J. Am. Chem. Soc., 39, 1857 (1917).

[2] A general summary is given by A. F. Joffe in his book "The Physics of Crystals" (1928).

Here R^* and R are the inter-ionic distances in the critical disruptive and normal or equilibrium states, respectively. The attractive exponent m is unity for simple heteropolar lattices such as the alkali halides form. The repulsive exponent n varies with the type of ion involved: with simple ions of the inert gas type its magnitude lies between the limits, 5-12. In our present calculations we shall employ for each substance a value of n which is the mean of the n values of the constituent ions. The latter values are taken from the paper of Pauling to which reference has been made. Values of R^* calculated by means of equation 3 are given below in Table II. Along with them are listed the normal interionic distances R of the crystals.

TABLE II

R^* and R expressed in Angstrom Units.

		Li	Na	K	Rb	Cs	
Cl	R^* =	2.99	3.25	3.60	3.75	4.05	3.93[1]
	R =	2.57	2.81	3.14	3.27	3.56	3.46
	Diff =	0.42	0.44	0.46	0.48	0.49	0.47
Br	R^* =	3.18	3.43	3.77	3.92	4.21	4.09
	R =	2.75	2.98	3.29	3.43	3.72	3.60
	Diff =	0.43	0.45	0.46	0.49	0.49	0.49
I	R^* =	3.48	3.70	4.01	4.15	4.45	4.32
	R =	3.03	3.23	3.53	3.66	3.95	3.83
	Diff =	0.45	0.47	0.48	0.49	0.50	0.49

An inspection of the figures given in Table II shows that the differences between R^* and R are very nearly constant, the mean difference being 0.47Å. In other words the critical disruptive volume of crystalline salts, which marks the transition from a crystalline state to a non-crystalline state, is apparently definable by the condition[2] that the inter-ionic distance is approximately 0.5Å greater than the normal, equilibrium distance in the crystalline state.

Starting with values of R^* it is a simple matter to calculate the critical disruptive volumes V^* of the salts and from these to calculate by means of equation 2 the corresponding values of ϕ^*, employing the constants previously determined. The important qualtities V^* and ϕ^* are presented in Table III. In the same table are also given values of the space-filling quotient $\psi^* = \phi^*/V^*$.

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[1] Hypothetical rock-salt type structure. See discussion of Fig. 1.

[2] In connection with this result the general conclusion arrived at by Langmuir [J. Am. Chem. Soc., 38, 2247 (1916).] from considerations based on the properties of metals is worth noting: "The attractive forces between atoms increase to a maximum when the distance between atoms is about 0.6×10^{-8} cm. greater than the distance at which the attractive force is zero."

Before testing these ϕ^*, V^* values to see whether they can be identified with the ϕ' state a few general comments on them will not be out of place. It appears that the space-filling quotients ψ^*, with the exception of those of the lithium and cesium salts, are sensibly constant. These exceptions, it will be recalled, are the same ones which were found when dealing with the ϕ_m data. As in the latter case the cesium salts seem normal if their calculations are based on the hypothetical salts with a rock-salt structure. Incidentally, since $\psi_m = 1$, the difference between the ϕ_m and ϕ^* states could be expressed as a difference in the condition defined by the space-filling quotients. However, in this connection a significant fact should not be overlooked. While the condition $\psi_m = 1$ is purely arbitrary, the condition $\psi^* = 0.64$ is derived from and therefore represents the salts when they are in a definite, corresponding state. Finally, a comparison of the ϕ^* and ϕ_m values shows the latter to be the larger in every case and consequently to be associated with a more concentrated state of solution than the ϕ^* values. This fact, in terms of our basic postulate, would mean that at the ϕ_m state the solute is already subject to the forces which characterize the crystalline state.

TABLE III

Values of Solution Constants (in cc.)

Salt	V^*	ϕ^*	ψ^*	V'_s	ϕ'_s	ψ'_s
LiCl	32.4	25.3	0.78	—	—	—
LiBr	39.1	30.0	0.77	—	—	—
LiI	51.2	39.2	0.77	—	—	—
NaCl	41.6	26.9	0.65	—	—	—
NaBr	49.0	31.5	0.64	48.0	31.4	0.65
NaI	61.1	40.6	0.66	54.1	42.8	0.79
KCl	56.6	36.3	0.64	69.5	34.3	0.49
KBr	64.7	41.3	0.64	72.0	41.6	0.58
KI	78.0	51.0	0.65	75.7	54.7	0.72
RbCl	63.8	40.7	0.64	63.4	40.4	0.64
RbBr	72.7	46.3	0.64	—	—	—
RbI	86.7	55.9	0.64	—	—	—
CsCl	62.4	48.0	0.77	65.8	48.4	0.74
CsBr	70.4	53.4	0.76	—	—	—
CsI	83.5	63.2	0.76	—	—	—
CsCl[1]	73.4	47.2	0.64	65.8	48.4	0.74
CsBr[1]	82.6	52.8	0.64V	—	—	—
CsI[1]	97.5	62.7	0.64	—	—	—

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[1] Hypothetical rock-salt type lattice structure.

We shall now consider what quasi-direct evidence there is in support of our contention that the ϕ^*, V^* values represent the conditions at the hypothetical upper limit of the solution state. The basis of our test will be the values of ϕ'_s derived from equation 2 and the corresponding values of V'_s derived from the following empirical relationship[1]:

$$V_s^{2/3} = \alpha N + \beta \tag{4}$$

In this expression V_s is the volume of the saturated solution which contains one gram mol of salt; N is the number of mols of water present in the same saturated solution; and α and β are constants characteristic of the salt involved. The volume V_s' of the solution at the critical state where no water is present is equal to $\beta^{3/2}$. Values of both ϕ_s' and V_s' for those salts for which they have been determined are given in Table III.

These ϕ_s', V_s' values satisfy explicitly the condition which we seek to ascribe to the calculated ϕ^*, V^* values, namely, that no water is present in the solution. However, they are not directly comparable to the latter quantities because, as we have already pointed out, they represent the conditions of the limiting solution state at a much higher temperature. The effect of temperature on the critical constants is unknown and is probably not the same for all salts. A possible indication of the effect of temperature is the fact that some of the ϕ_s' values are larger than the corresponding ϕ_m values. Because of this temperature difference the question whether the calculated ϕ^*, V^* values are the desired critical values cannot be answered decisively. It is of considerable significance, however, that with *both* ϕ and V the order of magnitude of the corresponding quantities is approximately the same. That the differences which appear may be caused by the effect of temperature is suggested by the fact that the discrepancies between the V terms is greater than those between the ϕ terms. Finally, it may be pointed out that the ϕ_m quantities which we have already considered as the possible conditions of the limiting state would have to be rejected on the basis of the ϕ_s', V_s' values.

The above discussion renders quite plausible our assumption that the calculated ϕ^*, V^* quantities are, or at least approximate, the critical limiting values of these constants. Of particular interest, therefore, are the ϕ^* values which, according to our hypothesis, represent the volumes or domains of the salts as solutes. Even though these volumes are not necessarily the domains of the solutes in actual solution, it is desirable to determine their possible significance in order to get some insight into the meaning of the latter term.

Attention may be called to two general properties of these ϕ^* values. First, they are additive within the limits of the supposed uncertainty of the basic data; and second, the values of ϕ^* calculated for 0° and 50° are essentially the same as those for 25° which are given in Table III. These two facts may be taken to mean that the domain of each ion is independent of the other ion present in the solute and is also unaffected by small changes in temperature. With this conclusion in mind our problem can be resolved into a simpler one, that of ascertaining the significance of the individual ions in the ϕ^* state.

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[1] Scott: J. Phys. Chem., 35, 1410 (1931).

To introduce this problem the procedure employed in a previous attempt[1] to determine the significance of the analogous ϕ_s' values may be recalled. In that case it was postulated that the ions are spherical in shape and are arranged in a space lattice so that each is in contact with the oppositely charged ion. The results obtained were interpreted to mean that the radii of the cations are the same as in the crystal lattice while the radii of the anions are approximately 0.5Å larger than in the crystalline state. When the above method is applied to the present ϕ^*, V^* data, the calculated radii, although they exhibit roughly the same distinction between cation and anion, are individually very irregular. Since this result signifies that the solute volumes are not additive, it must be supposed that the general method is at fault.

The failure of this method of approach can be understood by a closer examination of the basic premises from the standpoint of the argument which we have developed. Thus the assumption of a lattice orientation of the ions would hardly be consistent with the concept of the solution state. More questionable still is the assumption of a spherical shape for the space occupied by the solute ions. If we consider the origin of these solute volumes (ϕ^* values), we find that they can be defined only in very general terms as, for example, the space within which an ion exerts paramount influence and within which adjacent ions (or water molecules if they are present) never penetrate. In brief, the ϕ^* value is simply the domain of exclusion of a solute. Now, if we grant, as is frequently supposed, that the ions are spherical, the possibility that their domains of exclusion are likewise spherical is practically precluded. This differentiation between the shape of an ion proper and its domain of exclusion compels us to discard the simple picture of the ion with respect to the interpretation of the ϕ^* values.

In order to get some idea of the shapes which these domains of exclusion can assume we shall take recourse to our guiding hypothesis which by implication suggests a similarity between interionic forces and the forces acting between an ion and the surrounding water molecules. One possible conjecture is that the water molecules or ions in the immediate neighborhood of an ion in solution are so disposed about the ion that the arrangement is similar to the arrangement of the oppositely charged ions in the crystal lattice.[2] If we accept this analogy, we have a basis on which to select certain definite shapes which can then be tested. Thus, it can be shown[3] that the domain of exclusion takes the form of a parallelohedron, the particular form depending on the number (coordination number) of adjacent particles and also on the relative dimensions of the two units. For the simplest case where one sphere (ion) is surrounded by spheres (ions or water molecules) of the same diameter we can consider two possibilities: (1) when the coordination number is six, the

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[1] Scott: J. Phys. Chem., **35**, 1410 (1931).

[2] In this connection it is interesting to note that Garrick [Phil. Mag. (7) **9**, 130 (1930); **10**, 76–77 (1930)] has treated the problem of ion hydrates from the standpoint of the electrostatic theory. The values he got for the coordination numbers of the alkali ions are in agreement with Sidgwick's co-valency rule.

[3] A. E. H. Tutton: "Crystallography and Practical Crystal Measurement," 724 (1922).

parallelohedron is a cube; when the coordination number is eight, the parallelohedron is a cubo-octahedron.

Despite the simplifications introduced into the above argument its application to the interpretation of the ϕ^* values is exceedingly suggestive. In Table IV are given the volumes of the two polyhedra circumscribed about the ionic sphere whose radius r is that found in crystals. The calculated volumes are for one *gram-ion* and are expressed in cc.

TABLE IV

Ionic Volumes as Spheres and Circumscribed Polyhedra

	Li^+	Na^+	K^+	Rb^+	Cs^+	Cl^-	Br^-	I^-
r × 10^{-8}cm.	0.60	0.95	1.33	1.48	1.69	1.81	1.95	2.16
Sphere	0.55	2.18	5.97	8.23	12.3	15.1	18.8	25.6
Cube	1.05	4.16	11.4	15.7	23.4	28.7	36.0	48.9
Cubo-octahedron	0.81	3.21	8.78	12.1	18.0	22.1	27.7	37.6

A test of these calculated volumes indicates a rather general rule: the ϕ^* value of a salt appears to be composed of the volume of the cation as a cube and of the volume of the anion as a cubo-octahedron. This conclusion is illustrated rather strikingly in Fig. 2 where the various ϕ^* values are plotted against the sum of the volumes of the constituent ions, calculated according to the above rule. An inspection of this graph shows that the plotted points fall into two groups and that the points of each group lie on a straight line whose slope is unity. Since one of the drawn lines actually passes through the origin while the intercept of the other is only +2 cc., we have in this graph fairly good support of our interpretation of the ϕ^* values as domains of exclusion. The small difference between the two sets of points originates apparently in the properties of the cations.

Before considering further the above results it is of interest to examine from the same standpoint salts which contain more complex ions than those found in the alkali halides. Masson in his article gives values of the constants of equation 3 for a number of uni-univalent salt solutions at various temperatures less than 25°. Since we do not have the necessary data with which to calculate the critical disruptive volumes of these salts, it will be necessary to determine the ϕ^* values indirectly. This can be done supposedly by making use of the condition which has already been shown to characterize this state, namely, $\psi^* = 0.64$. Calculated values of ϕ^* which satisfy this condition are given in column 3 of Table V. A test of these values by plotting them in Fig. 2 would not be very satisfactory because the ionic crystal radii are rather uncertain. It will be more instructive to reverse the process and calculate the radii of the complex, unknown ions. If a ϕ^* value is plotted on the appropriate line (Fig. 2), the corresponding abscissa value is the solute volume in terms of the domains of exclusion of the crystal ions. From the latter by subtracting the volume of the known ion (Table IV) we can get the domain of the unknown ion. It is then an easy matter to compute the radius of the inscribed sphere (ion). The data given below in Table V are self-explanatory. The ionic radii calculated by this method are seen to be in fair agreement with those estimated from crystal data with the exception of the nitrate ion. The discrepancy in this case may arise from the fact that the calculations are based on the assumption of a cubo-octahedral shape for the domain of the nitrate ion. From its structure in crystals it appears that the four atoms of this ion lie in one plane, the oxygen atoms being at the vertices of an equilateral triangle with the nitrogen atom in the center. If this possibility is taken into consideration and the ionic radius is calculated on the assumption that the domain of exclusion of the nitrate ion has the shape of a triangular prism, the value obtained is practically the same as that found in the crystal lattice.

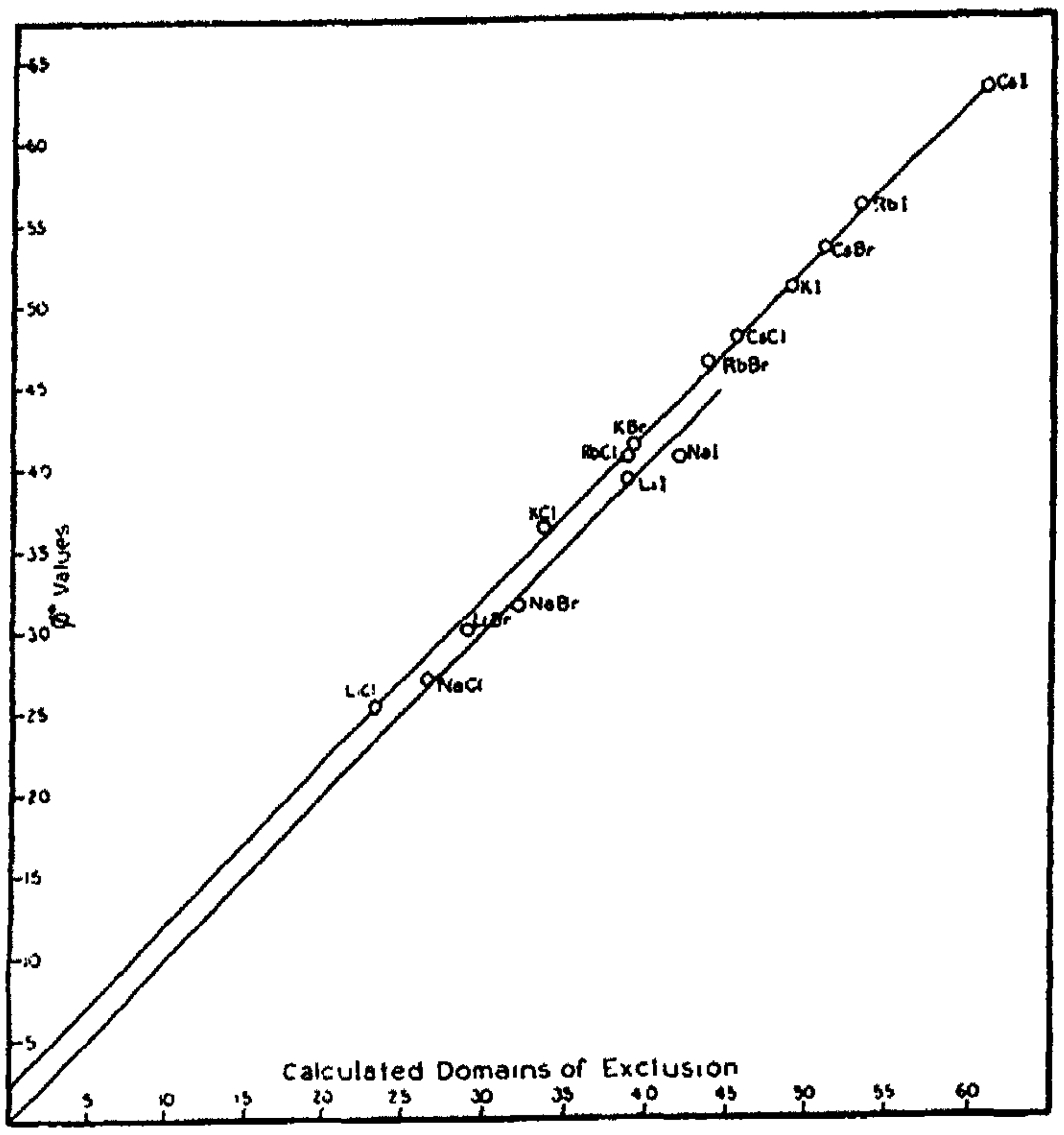

FIG. 2

Graphic Representation of the Conclusion that ϕ^* Volumes equal approximately the Domains of Exclusion of the Crystal Ions.

TABLE V

Data bearing on Salts with Complex Ions

Unknown Ion	Constants given for solutions of		Values of ϕ^*	Radius of unknown ion	Radius estimated from crystal data
NO_3	$NaNO_3$	(20.2°)	37.5	2.08Å	2.60 Å[3]
NO_3	KNO_3	(15.0°)	47.5	2.08	
NO_3	$AgNO_3$	(18°)	39.0	2.08[1]	
NH_4	NH_4Cl	(15°)	41.7	1.52	1.43[4]
NH_4	NH_4NO_3	(17.5°)	51.8	1.49[2]	
OH	NaOH	(15°)	18.9	1.71	1.4-1.5[4]
OH	KOH	(15°)	24.2	1.41	

From the foregoing results it would appear that our description of the ϕ^* values is reasonably confirmed. Unfortunately, however, the usefulness of these results is definitely restricted unless it can be established in what manner the domain of exclusion of an ion, that is, its volume as solute, varies with concentration. As we have already pointed out this prerequisite cannot be met because of the lack of a satisfactory picture of the solution state. Although our interpretation of the ϕ^* values cannot be transferred directly to solutions, it affords at least an advantageous starting point from which to examine further the factors which determine the apparent volumes of salts in solutions.

To avoid the question of ionization we shall consider first the apparent molal volumes ϕ_0 at infinite dilution, for under this condition we can reasonably postulate complete ionization. As a rule the ϕ_0 values are a good deal smaller than the corresponding ϕ^* values. To account for this fact we must imagine that most of this apparent decrease in volume is due to a change in the volume of the solvent when in solution because our interpretation of the domain of exclusion of an ion would not lead us to expect a great change in it. This assumption is essentially the one frequently made, that ions cause a "contraction" in the volume of the water molecules. Despite the uncertainty regarding the nature and the magnitude of the contraction brought about by an individual ion we can safely conclude that in very dilute solutions the amount of contraction is characteristic for each ion.

The general viewpoint which the above discussion leads to is that the apparent molal volume of a salt at infinite dilution is equal to the "volumes" or domains of exclusion of the constituent ions less the contraction in the volume of the solvent which they produce. Since both volume terms are unknown, an unequivocal test of our premise is out of question. However,

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[1] Radius of Ag^+ taken to be 1.26 as given by Pauling. Domains of exclusion found by interpolating on line through the Na points. See Fig. 3.

[2] Radius of NO_3^- taken to be 2.08 A.

[3] Bragg: Phil. Mag., 2, 258 (1926).

[4] Goldschmidt: Trans. Faraday Soc., March 1929, pages 282 and 265.

as a preliminary step we can assume that the domains of exclusion of the ions are the same and equal to their ϕ^* values and then attribute all deviations from these values to alterations in the volume of the water. Such a test was made by plotting the ϕ_0 values of the various salts against the same abscissa values used in the construction of Fig. 2. The interesting and suggestive features of the graph obtained by this method of plotting are brought out more clearly by a slightly different choice of abscissa values.

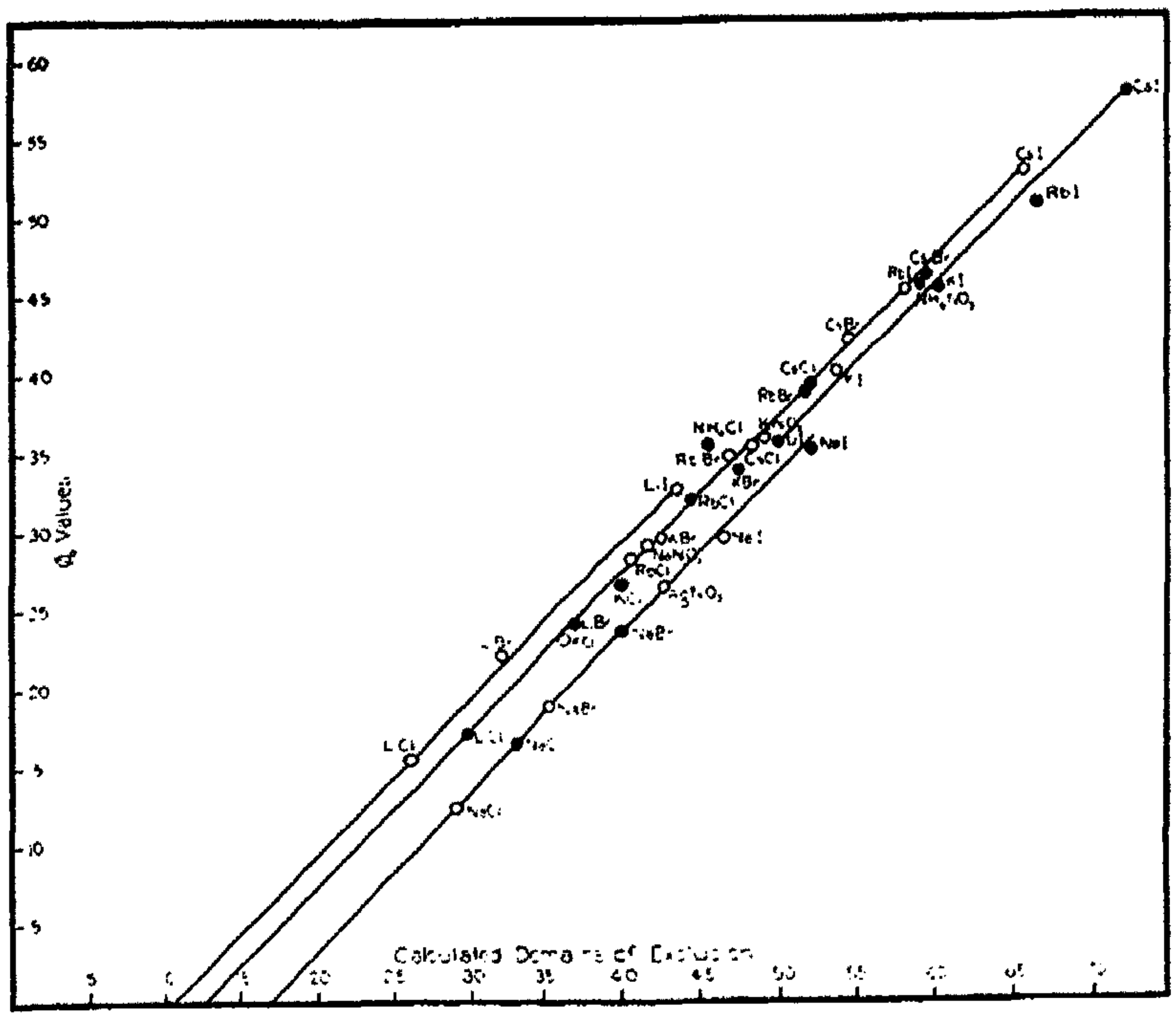

FIG. 3

The Relationship between the Apparent Volumes of Salts at Infinite Dilution and the Assumed Volumes of the Salts as Solutes.

Fig. 3 was constructed by plotting the ϕ_0 values of the salts at 0° (open circles) and 25° (solid dots) against abscissa values determined by the following rules: the cation values at both temperatures are the volumes of cubes circumscribed about the ionic sphere. The anion values employed for the 25° points are also the volumes of cubes; but the anion values employed for the 0° points are the volumes of octahedra and in magnitude lie between the volumes of the corresponding cubes and cubo-octahedra. In general, therefore, the cation volumes are the same as in the ϕ^* state whereas the anion volumes are for both temperatures somewhat larger than in the ϕ^* state.

Considerable caution must be observed in attempting to interpret the rather surprising relationships portrayed in Fig. 3, for it is obvious that the values assigned to the domains of exclusion of the solutes are quite arbitrary. While a test of the reasonableness of these values by means of some theory concerning the nature of water would be desirable, such a test cannot be made because none of the theories so far proposed is free from series criticism.[1] As a matter of fact the only ground we have for attributing any significance to the accepted domains of exclusion is that they are not inconsistent with our general argument according to which the ϕ^* value might undergo a small, but not a large, change with concentration. However, the relationships depicted in Fig. 3 can be interpreted in terms of a simple hypothesis which leads to some interesting conclusions and which consequently will be outlined briefly. The hypothesis can be expressed in terms of two suppositions: First, the contraction in volume of the water is due to the decrease in the domains of exclusion of the water molecules which ensues when, instead of being in contact only with each other, they come into contact, temporarily or permanently, with ions. And second, the amount of this decrease in volume is sensibly the same for each water molecule in contact with an ion and is also practically independent of the ion involved. The bearing of this hypothesis on the interpretation of Fig. 3 is obvious. Since each of the salts yields two ions which together exert an influence on presumably the same number of water molecules, the total contraction should be the same for all the salts. In other words the plotted points for all the salts at a given temperature should fall on the same line whose slope is unity and whose intercept gives the total contraction of the water.

Deviations from what apparently is the normal condition are manifest by the plotted points of the sodium salts at 0° and 25°, and by the iodides at 25°. These points all fall on lines with a slope equal to unity and consequently the deviations indicate either an abnormal contraction of the water molecules or else a uniform alteration in the domain of exclusion of the solute. With respect to the cause of these deviations it can be pointed out that they occur only with salts whose common ion is relatively very large or small. The fact that the differences between the ϕ_0 values at 0° and 25° can be represented as caused only by a change in the domains of exclusion of the anions is indeed curious. Here again the two exceptions to the rule are evidenced only by salts with either a very small ion (Li^+) or a very large one (I^-). For the sake of completeness points have been plotted in Fig. 3 for the salts with complex ions listed in Table V even though their basic data are somewhat less certain.

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[1] For a resumé see Chadwell: Chem. Reviews, 4, 375 (1927). Recently, Stewart [Phys. Rev., 37, 9 (1931)] has indicated numerous objections to the theory of complexes on the basis of x-ray diffraction data. He proposes a new conception of molecular groups (cybotactic condition) and states that it "seems to be in harmony with all the facts." In connection with out viewpoint it is interesting to note a further theoretical conclusion: "The new conception states that the secret of association lies in an understanding of those forces, call them chemical or physical as one will, which binds atoms together in a molecule and which causes stable configurations in crystals and unstable arrangement in liquids."

While the above hypothesis is much simplified it is of interest to indicate briefly its bearing on the general problem of the increase in ϕ with concentration. Because the domain of exclusion of the cation remains constant and that of the anion apparently decreases slightly with concentration, the increase in ϕ would have to be attributed to a diminution in the number of water molecules in contact with the ions. This diminution could come about from the temporary formation of ion pairs or "clusters"[1] which would result in the displacement of the water molecules adjacent to the ions.

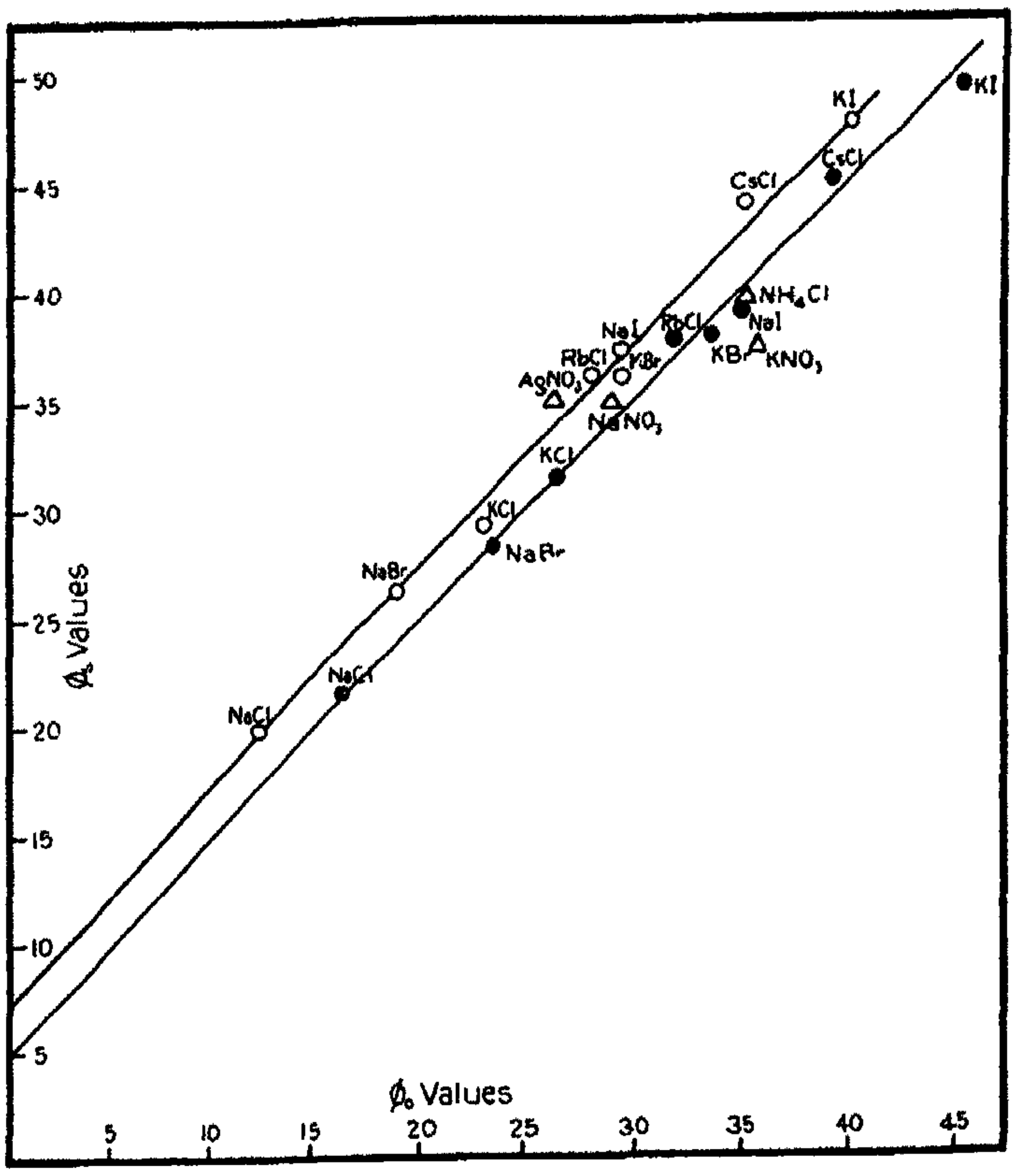

FIG. 4

The Relationship between the Apparent Molal Volumes of Salts in Saturated Solutions and at Infinite Dilution.

In one sense the formation of ion pairs or clusters corresponds to a reduction in the number of free ions in solution and is therefore equivalent to the formation of "unionized" molecules. This viewpoint suggests a connection

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[1] See Bjerrum: Ber., 62B, 1091 (1929).

between ϕ and the degree of ionization of the solute. Thus for ϕ_0 the degree of ionization α would be equal to one and at the other extreme ϕ', would equal zero. At intermediate concentrations ϕ would have to be corrected for the change in domain of exclusion of the anion in order to determine the amount of adjacent water molecules displaced. Without going into the matter further it may be pointed out that Masson, from a distinctly different hypothesis, arrived at a rather similar conclusion and expressed the relationship between ϕ and α by the formula:

$$1 - \alpha = \frac{\phi - \phi_0}{\phi_m - \phi_0} \tag{5}$$

His comparison of the calculated term $1 - \alpha$ with the experimentally determined values at one molar concentration revealed that the former were always too small. The general modifications introduced by our argument, viz., the substitution of ϕ' for the slightly larger ϕ_m value and the use of a corrected value of ϕ slightly greater than the actual value, would be in the right direction.

In conclusion the possible application of the foregoing interpretation of apparent molal volumes to the problem of the saturated state may be touched on. In Fig. 4 values of ϕ_s at both 0° (open circles) and 25° (solid dots) are plotted against the corresponding values of ϕ_0. If the fact that both the ϕ_s and ϕ_0 data are subject to experimental error is taken into account, the drawn lines with slopes equal to unity appear to represent the relationship between the plotted points fairly well. In any case it is obvious that the difference between ϕ_s and ϕ_0 is approximately constant for all the salts at one temperature and is not determined by the total number of water molecules present in the saturated solution, a factor which varies considerably with the different salts. In terms of our hypothesis this would mean that the degree of ionization is roughly the same for all salt solutions when saturated. However, a preliminary examination of some other data of the solutions of sodium and potassium salts suggests that the degree of ionization depends on the cation and is the same for all salts with a common cation. This latter conclusion is apparently confirmed by the evidence to be derived from solutions containing one salt at various concentrations and saturated with a second salt. When both salts have a common cation, the apparent molal volume of each remains constant with varying concentrations in spite of the fact that the number of water molecules present vary over a wide range. In some cases, however, in which the anion instead of the cation is common to both salts, the apparent molal volumes of one or both salts appear to undergo an abrupt change at a specific concentration. This matter, which may throw some light on the mechanism of the saturated state, will be discussed in a subsequent paper.

Summary

The present article gives the results of an attempt to interpret the apparent molal volumes of salts in solution from the viewpoint that at the critical limit of the solution state, defined by the condition that the amount of water present is zero, the apparent molal volume of a salt is an approximate measure

of the volume of the salt as solute. The critical volume of the solution is assumed to coincide with the molal disruptive volume V^* of the crystalline salt. The hypothetical value of the apparent molal volume ϕ^* at this state is calculated by means of Masson's equation.

The properties of these critical constants, as found for the alkali halides, may be summarized briefly. First, the space-filling quotient $\psi^* = \phi^*/V^*$ is sensibly constant and equals 0.64. Second, the ϕ^* value of a salt can be considered equal to the sum of the domains of exclusion of the constituent cation and anion if these quantities are chosen so that the volume of the cation is equal to that of a cube and the volume of the anion is equal to that of a cubo-octahedron. In each case the volume of the parallelohedron is calculated on the condition that it is circumscribed about the ionic sphere whose radius is that of the ion in crystals.

The relationship between the apparent molal volume of a salt at infinite dilution and the above domains of exclusion is also considered. It is found that, if a slightly larger volume is ascribed to the anion, the magnitude of ϕ_0 can be expressed as the sum of the domains of exclusion of the two ions less a constant quality. A tentative hypothesis is developed to account for the above observations and its bearing on the variation in ϕ with concentration is discussed. Finally, a possible deduction from this hypothesis with respect to the saturated state is pointed out.

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6.65 ✓

SOLUTIONS FOR COLORIMETRIC STANDARDS. V

A Study of Certain Systems Proposed for Use in the Determination of pH Values[*]

J. P. MEHLIG WITH M. G. MELLON

Colorimetric methods of analysis in analytical chemistry have long been known, but more recently their development and extension have been so rapid that now such methods are available for many substances. Probably one of the most important fields of colorimetry is that of the determination of the hydrogen ion concentration or pH value of solutions, wherein the color produced by adding a certain indicator to a given solution is matched against the color produced by adding the indicator to standard buffer solutions of known pH value.

Since many indicators are photochemically sensitive and bleach out in time, and are otherwise easily decomposed, various workers have sought to substitute for them permanent standards made by use of solutions of colored, inorganic salts. Kolthoff[1] prepared blends of solutions of ferric chloride and cobaltous nitrate to match the colors produced by neutral red, methyl orange, methyl red, and tropaolin oo. He did not, however, propose a complete set of standards, leaving gaps between pH 4.5 and 5.2 and between pH 5.8 and 7.0. His increments are very uneven, varying from 0.02 to 0.3 pH unit. Taub[2] prepared, by use of the Lovibond tintometer, blends of Arny's[3, 4] "Co-Fe-Cu" solutions to match the colors produced by methyl orange, methyl red, meta-cresol purple (acid and alkaline range), thymol blue (acid and alkaline range), bromcresol green, chlorphenol red, bromthymol blue, phenol red, and cresol red. These standards cover a pH range of 1.2–9.0 at even 0.2 intervals. Taub claimed they have been found to remain unchanged for more than ten years. Bruere[5] prepared blends of solutions of cobaltous nitrate, potassium dichromate, cupric sulfate, and cobaltous chloride to match the colors produced by methyl red, bromthymol blue, and phenol red, covering a pH range of 4.4–8.4 at even 0.2 intervals. Windisch, Dietrich, and Kolbach[6] prepared blends of solutions of potassium chromate and dichromate to match the colors produced by the one-color indicators α-(2:4) and γ-(2:5) dinitrophenol and m- and p-nitrophenol, covering a pH range of 2.8–8.4 at even 0.2 intervals. Kolthoff[7]

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[*] This paper represents a portion of a thesis submitted by J. P. Mehlig to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1931.

[1] Pharm. Weekblad, **59**, 104 (1922).

[2] J. Am. Pharm. Assn., **16**, 116 (1927).

[3] Proc. 8th Int. Cong. Appl. Chem., **26**, 319 (1912).

[4] J. Am. Pharm. Assn., **12**, 839 (1923).

[5] J. pharm. chim., [8] **3**, 377, **4**, 241 (1926); Bull. soc. chim. biol., **10**, 291 (1928).

[6] Wochenschr. Brauerei, **39**, 67 (1922); Chimie et industrie, **8**, 1099 (1922).

[7] Pharm. Weekblad, **60**, 949 (1923).

also used potassium chromate and dichromate as comparison solutions for the mono- and di-nitrophenols and for salicyl yellow, but here again his pH increments are very irregular and so difficult to duplicate that little practical use can be made of the standards.

Careful observation of these matched pairs of inorganic and organic solutions often shows the presence of slight variations in hue, thus raising the question as to whether the two colors, although *seemingly* matched in a colorimeter, really are identical. The present work was undertaken with the object of securing, by means of spectrophotometric analyses, information regarding the colors of the so-called matches. The solutions investigated were the "Co-Fe" blends proposed by Kolthoff,[1] the "Co-Fe-Cu" blends proposed by Taub,[2] and the "Co-Cu-$K_2Cr_2O_7$" blends proposed by Bruere,[5] and the potassium chromate-dichromate blends proposed by Windisch, Dietrich, and Kolbach.[6]

Previous Work

Apparently no previous spectrophotometric study similar to the present one has been reported. Janke and Kropacsy[8] have shown, through a comparative study of the absorption spectra, that solutions of ferric and cobaltous salts, as used by Kolthoff, are not similar in "color tint" and "color depth" to solutions containing methyl orange, methyl red, neutral red, or tropaolin oo. On the contrary the chromates and dichromates, proposed by Windisch and his co-workers, were found to be very applicable for the preparation of inorganic permanent standards to serve for comparison with the mono- and dinitrophenols, since the matches gave closely agreeing absorption spectra.

It should be mentioned that various spectrophotometric studies for individual samples of practically all of the indicators studied in the present work have been made, and the spectral transmission curves have been published;[9] but in these cases the object was not to determine spectrophotometrically differences of color. Recently Mellon and Ferner[10] have published curves showing the effect on certain indicator solutions of the following factors: (1) source (or degree of purity) of the indicator, (2) method of preparation of the stock solution of the indicator, and (3) ageing, particularly the effect of light.

Preparation of Materials

In purifying the materials used in preparing the solutions the usual precautions for careful work were observed, such as using "conductivity water" made by distilling over potassium permanganate and barium hydroxide, calibrating all volumetric apparatus, recrystallizing salts three times and preserving solutions in Pyrex containers that had been cleaned by steaming.[11] Clark's

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[8] Biochem. Z., **174**, 120 (1926).

[9] (a) Baker and Davidson: Phot. J., **62**, 375 (1922); (b) Brode: J. Am. Chem. Soc., **46**, 581 (1924); (c) Gibbs and Shapiro: J. Am. Chem. Soc., **50**, 2798 (1928); (d) Mellon and Martin: J. Phys. Chem., **31**, 161 (1927); (e) Thiel, and Springemann: Z. anorg. allgem. Chem., **176**, 64, 112 (1928); (f) Thiel, Wuelfken, and Dassler: Z. anorg. allgem. Chem., **136**, 406 (1904).

[10] J. Phys. Chem., **35**, 1025 (1931).

[11] Chemist-Analyst, **19**, 23 (1930).

directions[12] were followed in preparing one-fifth normal hydrochloric acid, the buffer solutions, and one-fifth normal solution of sodium hydroxide free from carbon dioxide. The latter solution was kept in a paraffin lined bottle.

Inorganic Stock Solutions for Kolthoff's and for Taub's Matches.—Approximately M/4 solutions of cobaltous chloride hexahydrate, cobaltous nitrate hexahydrate, cupric sulfate pentahydrate, and cupric chloride dihydrate were prepared by dissolving the recrystallized salts in a 1% solution of hydrochloric acid which had been made by proper dilution of constant boiling point acid. The solutions were standardized against a solution of sodium thiosulfate that had been standardized against pure potassium dichromate. In the case of the salts of cobalt the Arny and Taub[4] modification of the Engle and Gustavson iodide method[13] was followed. For the salts of copper the iodide method as given in Mahin's text[14] was used. After the preliminary standardization each solution was diluted to exactly fourth molar and checked by restandardization.

Anhydrous ferric chloride was prepared by passing dry chlorine over clean iron wire (piano-wire grade) according to the directions of H. and W. Biltz.[15] A solution (M/6) was made by dissolving this product in 1% hydrochloric acid and standardizing against a solution of potassium dichromate which had been made by direct weighing of the pure, recrystallized salt.

Bruere's Inorganic Stock Solutions.—Solutions of cobaltous chloride hexahydrate and of cupric sulfate pentahydrate, 10% by weight, and a solution of cobaltous nitrate hexahydrate, 20% by weight, were made by dissolving the recrystallized salts in water, standardizing as in the case of Taub's solutions, and adjusting to the exact strength by the addition of the proper weight of distilled water. A 0.03% solution of potassium dichromate was prepared by direct weighing of the pure salt. Bruere's A, B, C, and D stock solutions[5] were made by proper mixing of the above solutions.

Windisch's Inorganic Stock Solutions.[6]—An approximately M/10 solution of potassium chromate was prepared by dissolving the recrystallized salt and standardizing against a solution of sodium thiosulfate. This solution was then diluted to exactly M/100. A M/60 solution of potassium dichromate was made by direct weighing of the pure salt. From this solution a M/300 solution was made by dilution.

Indicator Stock Solutions.—In an earlier paper[10] of this series attention was directed to the desirability of having a standard method for the preparation of solutions of indicators, and of adopting definite specifications for the purity of the indicators. Since neither of these standards has been established, all that seemed possible in the present work was to follow the methods of preparation used by the individuals whose solutions were to be investigated, and to select those samples of indicators which previous work had indicated to be most dependable.

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[12] "The Determination of Hydrogen Ions," pp. 192-196, 200, 201 (1927).

[13] J. Ind. Eng. Chem., 8, 901 (1916).

[14] "Quantitative Analysis," p. 240 (1924).

[15] "Laboratory Methods of Inorganic Chemistry," p. 68 (1909).

Kolthoff's Indicator Stock Solutions.—Methyl orange was purified by G. W. Ferner of this Laboratory using Hunter's method[16] of recrystallizing three times from hot water and drying in air. A 0.025% aqueous solution of this purified product was used. The other indicator solutions were made as follows: methyl red–0.025% solution in dilute ethanol (3:2); neutral red 0.05% solution in dilute ethanol (1:1); and tropaolin 00–0.1% aqueous solution.

Taub's Indicator Stock Solutions.—A 0.04% solution was used throughout, as directed in the International Critical Tables.[17] One-tenth gram of the indicator, as furnished by the manufacturers, was dissolved in 52 ml. of neutral, 95% ethanol, which had been distilled over barium hydroxide, the amount of N/100 sodium hydroxide designated by Taub[2] was added to neutralize the indicator acid, and the solution was made up to 250 ml. with distilled water.

Bruere's Indicator Stock Solutions.[5]—Two hundredths gram of methyl red, 0.02 gm. of phenol red, and 0.04 gm. of bromthymol blue were each dissolved in 60 ml. of neutral, 95% ethanol and each solution was made up to 100 ml. with distilled water.

Windisch's Indicator Stock Solutions.[6]—Solutions of α-(2:4) and of γ-(2:5) dinitrophenol were made by dissolving 0.1 gm. of the indicator in 21 ml. of neutral, 95% ethanol and diluting to 100 ml. with distilled water. Solutions of m- and p-nitrophenol were made by dissolving 0.3 gm. of the indicator in water and diluting to 100 ml. The sample of γ-dinitrophenol was made by S. B. Lippincott of this Laboratory according to Bantlin's method[18] by nitration of m-nitrophenol.

Spectrophotometric Data

In accordance with the recommendations of various individuals[19,20,21] a spectrophotometer was selected as the proper instrument for determining the colorimetric characteristics of the solutions considered. All spectrophotometric analyses were made with the Keuffel and Esser color analyzer used in the earlier investigations in this series.[9d,10] The procedure followed differed from that reported by Mellon and Martin[9d] only in the use of two 400 watt Mazda lamps for illumination of the samples in 5 cm. and 2 cm. tubes and in less frequent checking of the sector settings and of the wave-length scale. All data were obtained by setting the instrument for a given wave-length at intervals of 10 millimicrons and reading directly the percentage of transmittancy. The reading recorded for each setting represented the average of five readings among which the greatest variation was not more than 0.9%.

A preliminary series of analyses was made of the five standard stock solutions, M/4 cupric chloride, M/4 cupric sulfate, M/4 cobaltous chloride, M/4 cobaltous nitrate, and M/6 ferric chloride, using 2 cm., 5 cm., and 10 cm.

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[16] Biochem. J., **19**, 42 (1925).

[17] "International Critical Tables," **1**, 89, (1926).

[18] Ber., **8**, 21 (1875).

[19] Holmes: Chemicals, **30**, No. 21, 31 (1928); cf. also Am. Dyestuff Reptr., **18**, 2 (1929).

[20] Committee of Revision of U. S. Pharmacopoeia, "Color Names in the U. S. Pharmacopoeia and in the Arts, Sciences and Industries," p. 65 (1930).

[21] Troland et al.: J. Opt. Soc. Am.-Rev. Sci. Instruments, **6**, 527 (1922).

tubes for each. The object was to study the effect on the color of the same solution of using varying lengths of tubes and to study any influence of the anion upon the colors of the cupric and cobaltous cations. Taub[2] states that the color "values" of solutions of cupric chloride and of cupric sulfate are identical when observed with a colorimeter. Arny and Pickhardt[22] had earlier reported that an M/4 solution of cupric sulfate was distinctly darker than an M/4 solution of cupric chloride.

The inorganic matching solutions or blends proposed by Kolthoff,[1] by Taub,[2] by Bruere,[5] and by Windisch[6] and his co-workers were made from the stock solutions by following the respective procedures of these men except as noted for Kolthoff's solutions. The corresponding indicator-buffer solutions were made by adding the specified amount of indicator stock solution to 10 ml. of the recently prepared Clark[12] buffer solutions.

Since Kolthoff's pH increments were very uneven in some cases, and hence very difficult to duplicate, buffer solutions at even 0.2 pH intervals were matched against his inorganic standards as closely as possible by means of a Klett colorimeter, water being added when necessary. As Kolthoff did not specify the amount of water to add in any case, this was found by trial. None of the other matched solutions were compared in a colorimeter, but to the eye the matched colors appeared to be very similar.

Five cm. tubes were used in the analysis of each matched pair of solutions. In certain cases analyses were also made using 2 cm. tubes, since in the usual colorimetric determination of pH value the observer looks through a layer of solution which is more nearly 2 cm. in thickness.

Spectral Transmission Curves

The transmittancy data obtained were plotted on a semi-logarithmic basis, using the percent transmittancy as ordinates and the wave-length in millimicrons as abscissa. Appel and Brode[23] noted that this type of curve gives a good representation of the absorption as it appears to the eye. Representative curves are shown in Figs. 1–15. In Figs. 1–14 all of the curves for a given indicator and its inorganic matches appear on the same graph. Fig. 15 shows an example of the curves obtained for the matched pairs when 2 cm. tubes were used in the analyses. The corresponding curve for the 5 cm. tube is repeated on the same graph for comparison.

Spectrophotometric Calculations

Such curves as the ones shown are often sufficient in themselves for certain purposes as an indication of the properties of the system measured; but when it is desired to know the relative brilliance, colorimetric purity (i.e., saturation), and dominant wave-length of the system (monochromatic analysis), or the percentages of the elementary red, green, and violet excitations constituting the color (trichromatic analysis), further calculation is necessary. After care-

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[22] Drug. Circ., 58, 131 (1914).

[23] Ind. Eng. Chem., 16, 797 (1924).

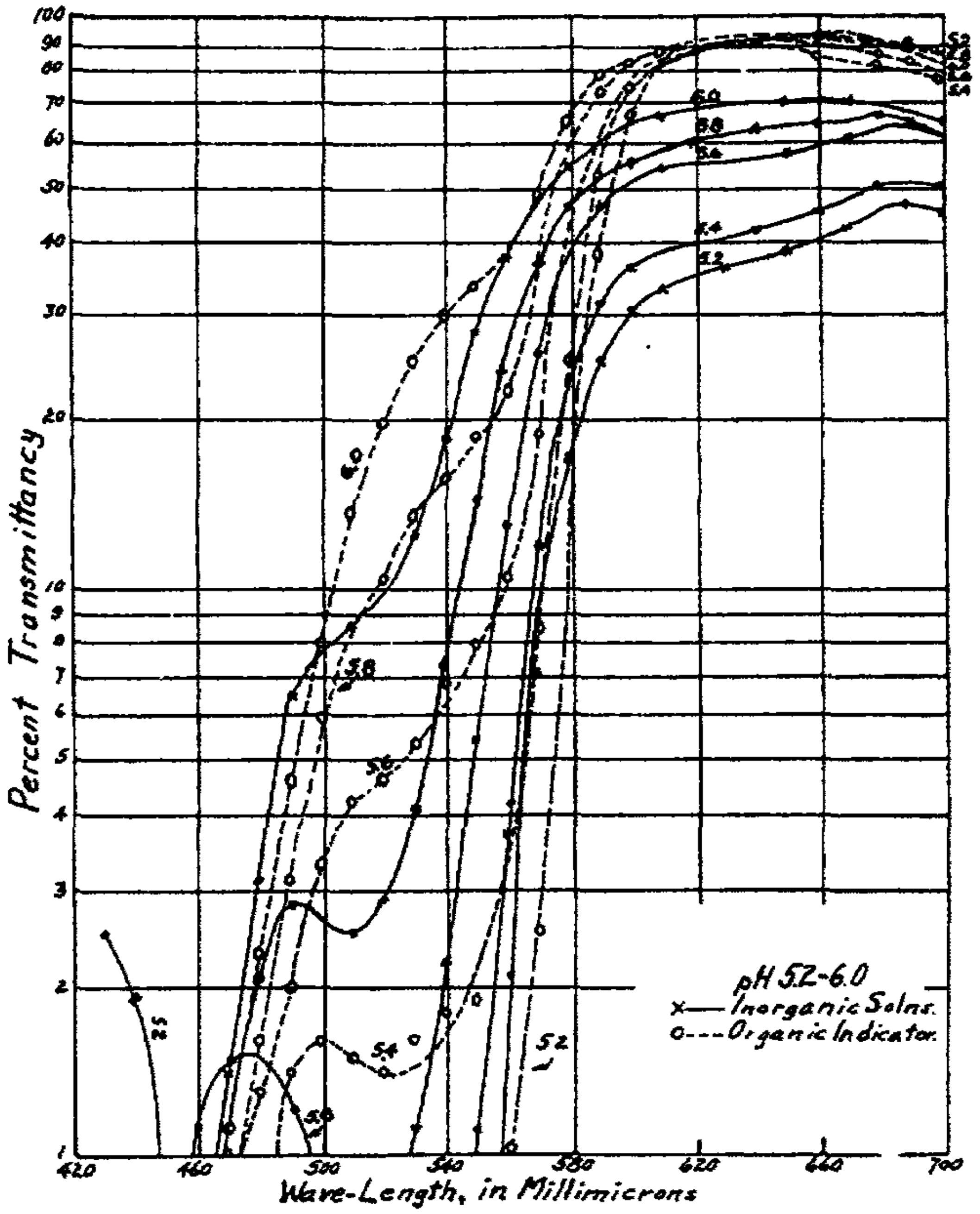

Fig. 1

METHYL RED. Curves showing comparison of spectral transmittancy values for 5 cm. tubes containing (1) a solution made by adding 0.4 ml. of a 0.025% solution of indicator to 10 ml. of buffer solution and (2) Kolthoff's inorganic matching solution.

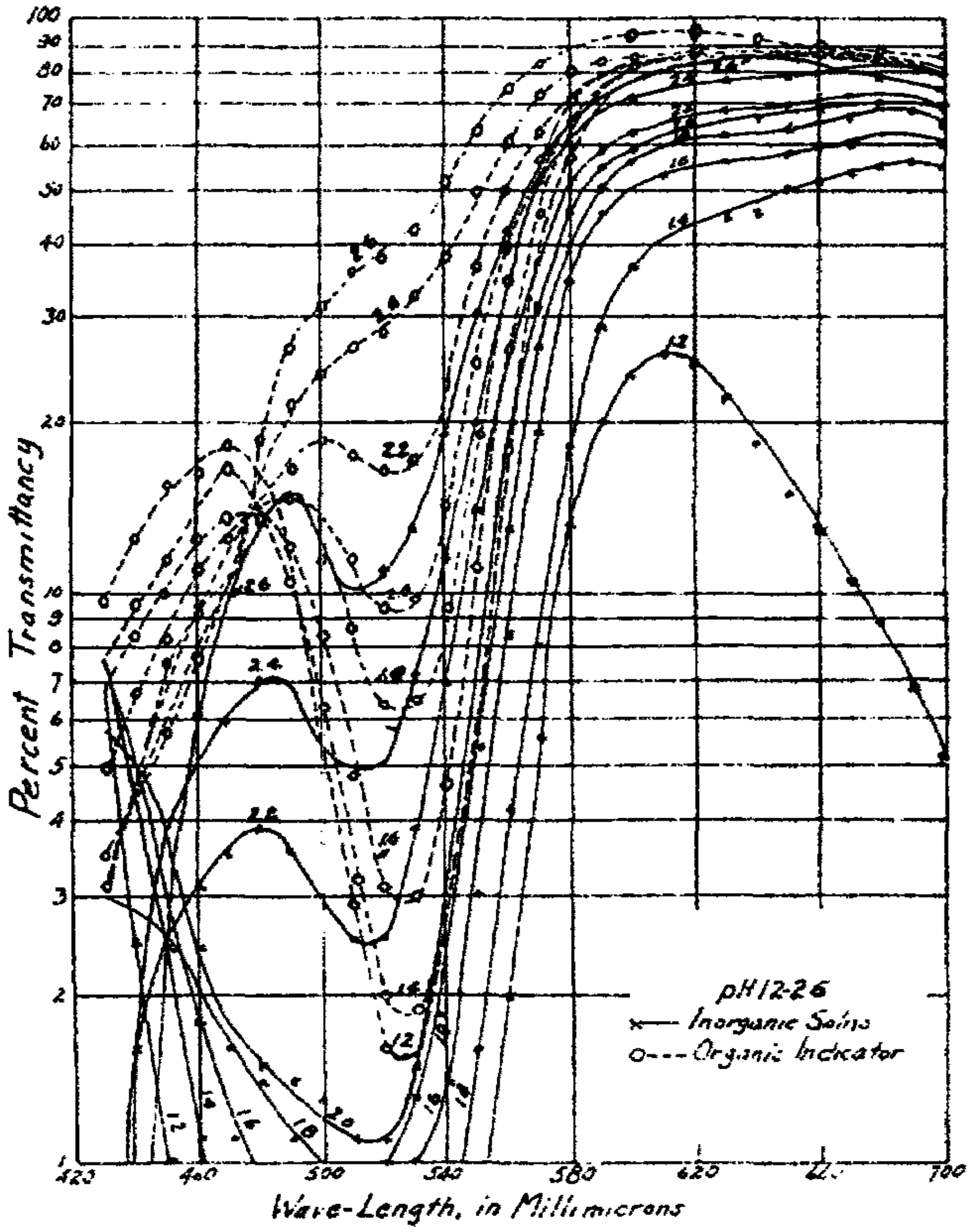

Fig. 2

METACRESOL PURPLE (Acid Range). Curves showing comparison of spectral transmittancy values for 5 cm. tubes containing (1) a solution made by adding 0.3 ml. of a 0.04% solution of indicator to 10 ml. of buffer solution and (2) Taub's inorganic matching solution.

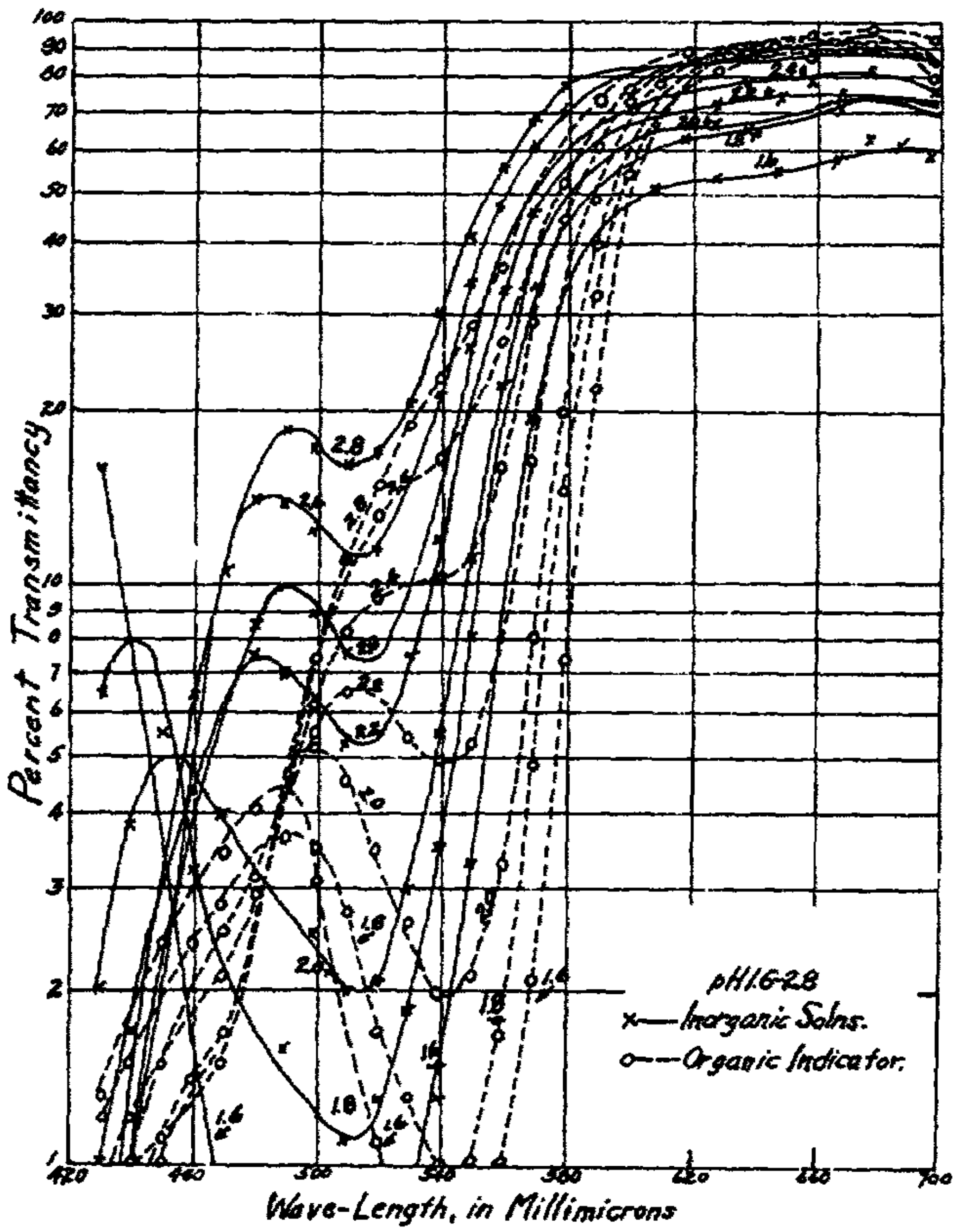

FIG. 3

THYMOL BLUE (Acid Range). Curves showing comparison of spectral transmittancy values for 5 cm. tubes containing (1) a solution made by adding 0.5 ml. of a 0.04% solution of indicator to 10 ml. of buffer solution and (2) Taub's inorganic matching solution.

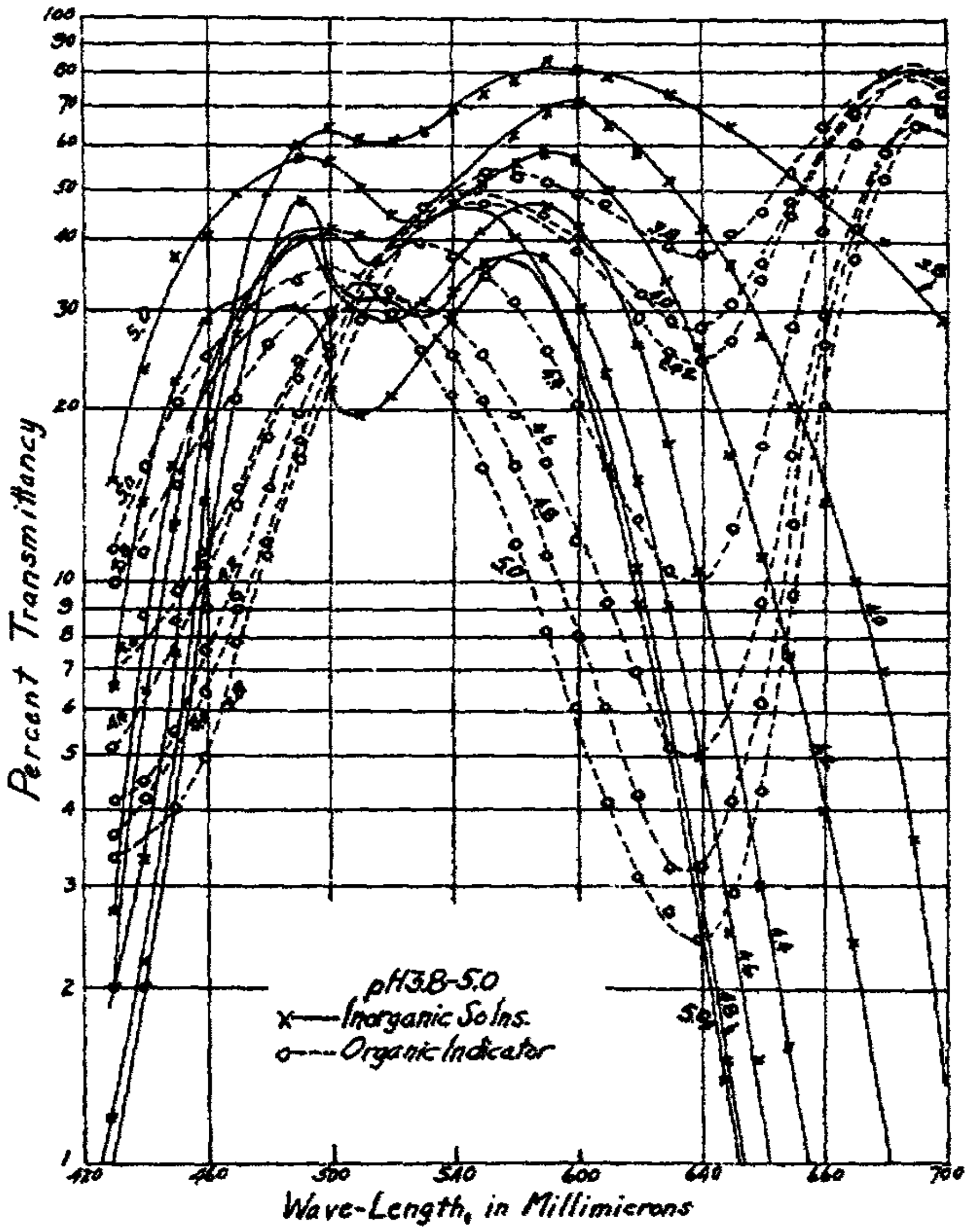

FIG. 4

BROMCRESOL GREEN. Curves showing comparison of spectral transmittancy values for 5 cm. tubes containing (1) a solution made by adding 0.3 ml. of a 0.04% solution of indicator to 10 ml. of buffer solution and (2) Taub's inorganic matching solution.

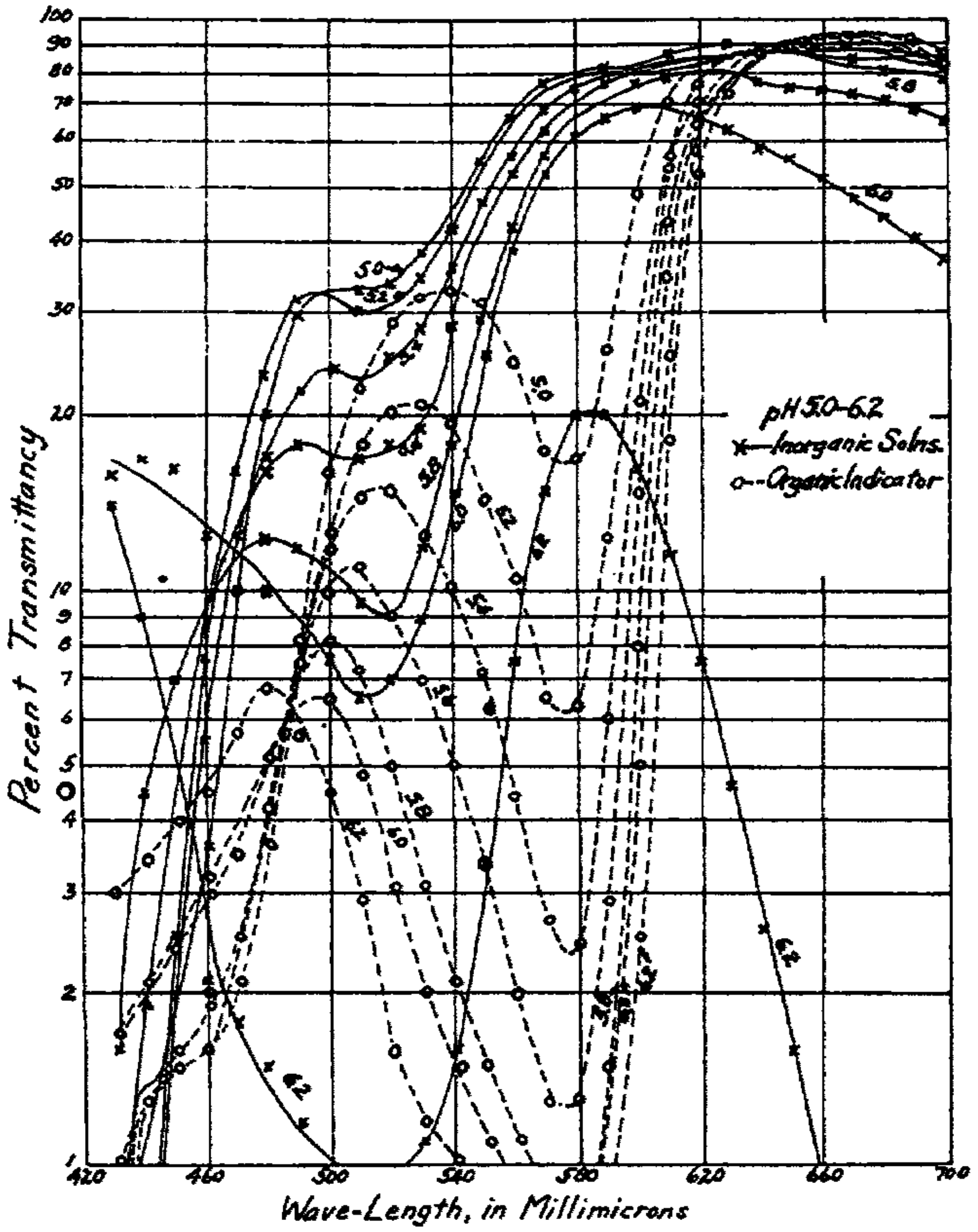

Fig. 5

CHLORPHENOL RED. Curves showing comparison of spectral transmittancy values for 5 cm. tubes containing (1) a solution made by adding 0.5 ml. of a 0.04% solution of indicator to 10 ml. of buffer solution and (2) Taub's inorganic matching solution.

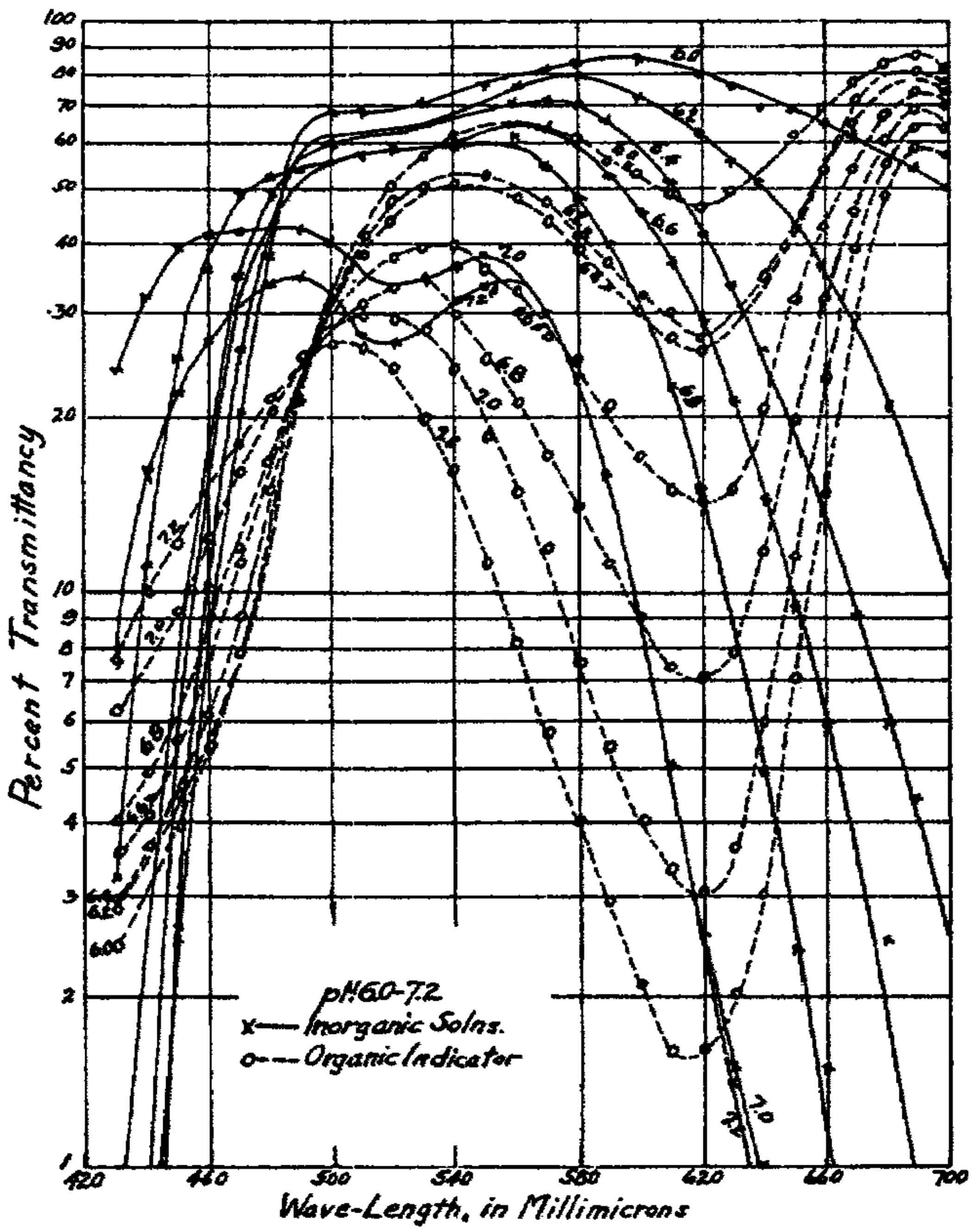

Fig. 6

BROMPHENOL BLUE. Curves showing comparison of spectral transmittancy values for 5 cm. tubes containing (1) a solution made by adding 0.3 ml. of a 0.04% solution of indicator to 10 ml. of buffer solution and (2) Taub's inorganic matching solution.

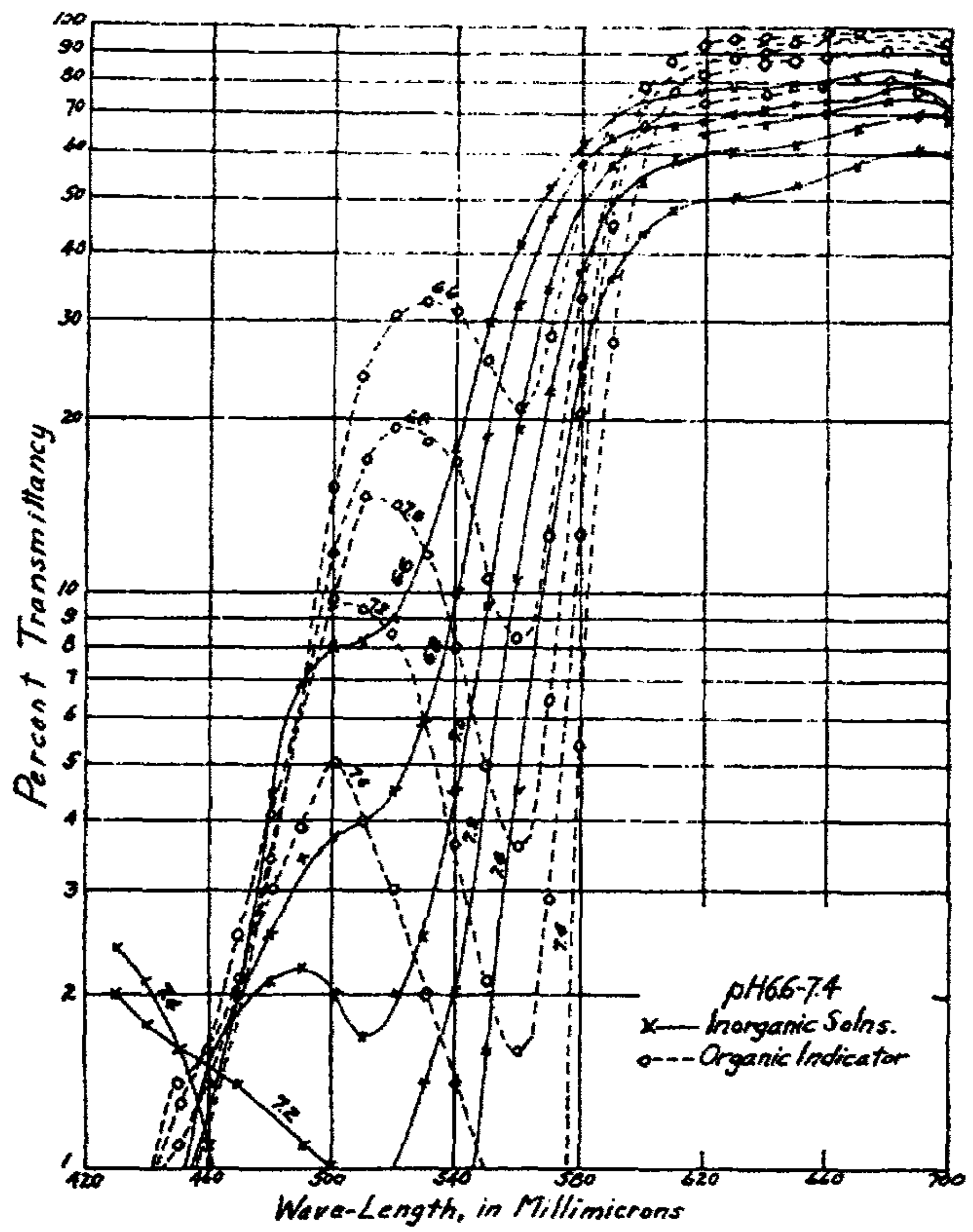

Fig. 7

PHENOL RED. Curves showing comparison of spectral transmittancy values for 5 cm. tubes containing (1) a solution made by adding 0.3 ml. of a 0.04% solution of indicator to 10 ml. of buffer solution and (2) Taub's inorganic matching solution.

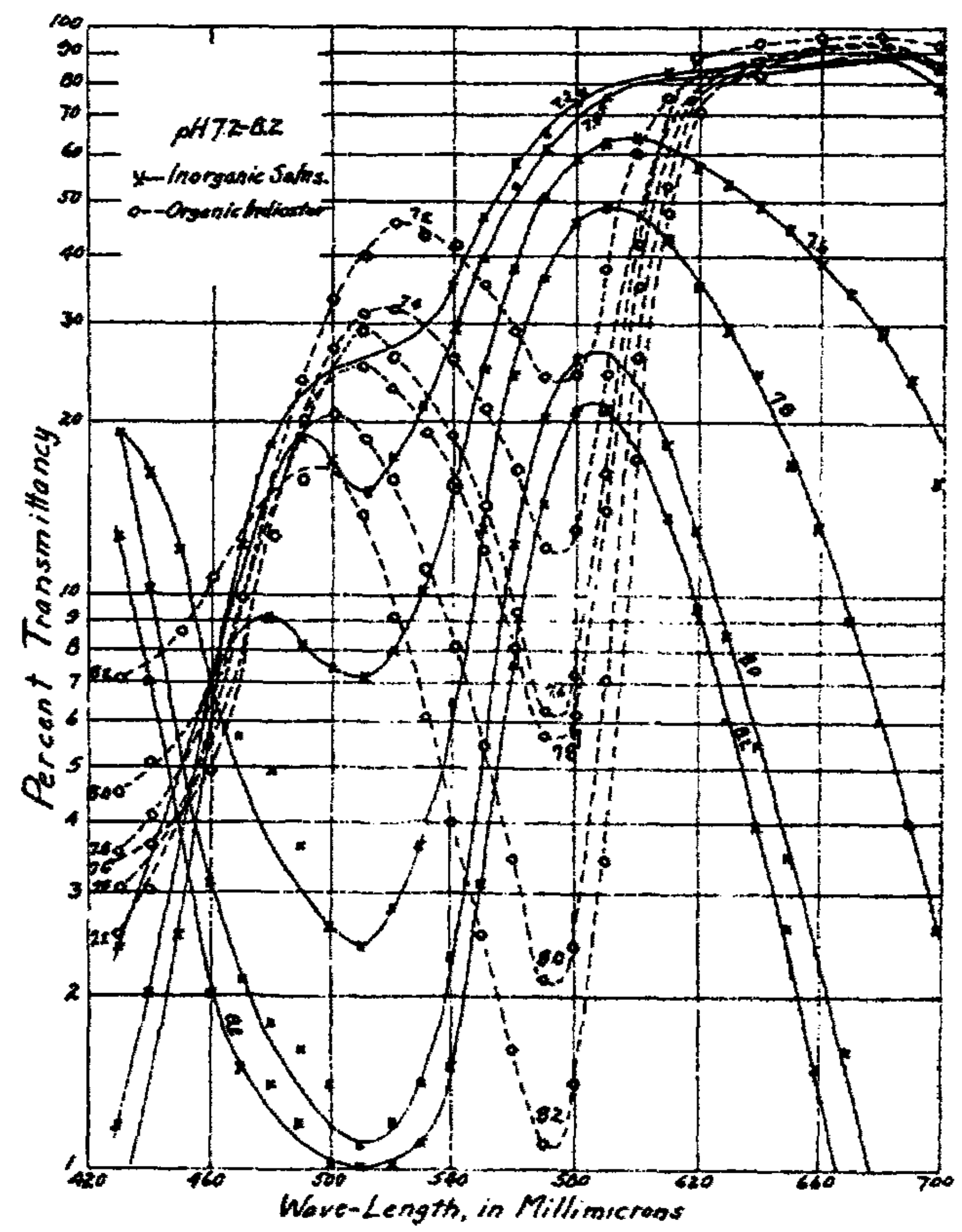

Fig. 8

CRESOL RED. Curves showing comparison of spectral transmittancy values for 5 cm. tubes containing (1) a solution made by adding 0.2 ml. of a 0.04% solution of indicator to 10 ml. of buffer solution and (2) Taub's inorganic matching solution.

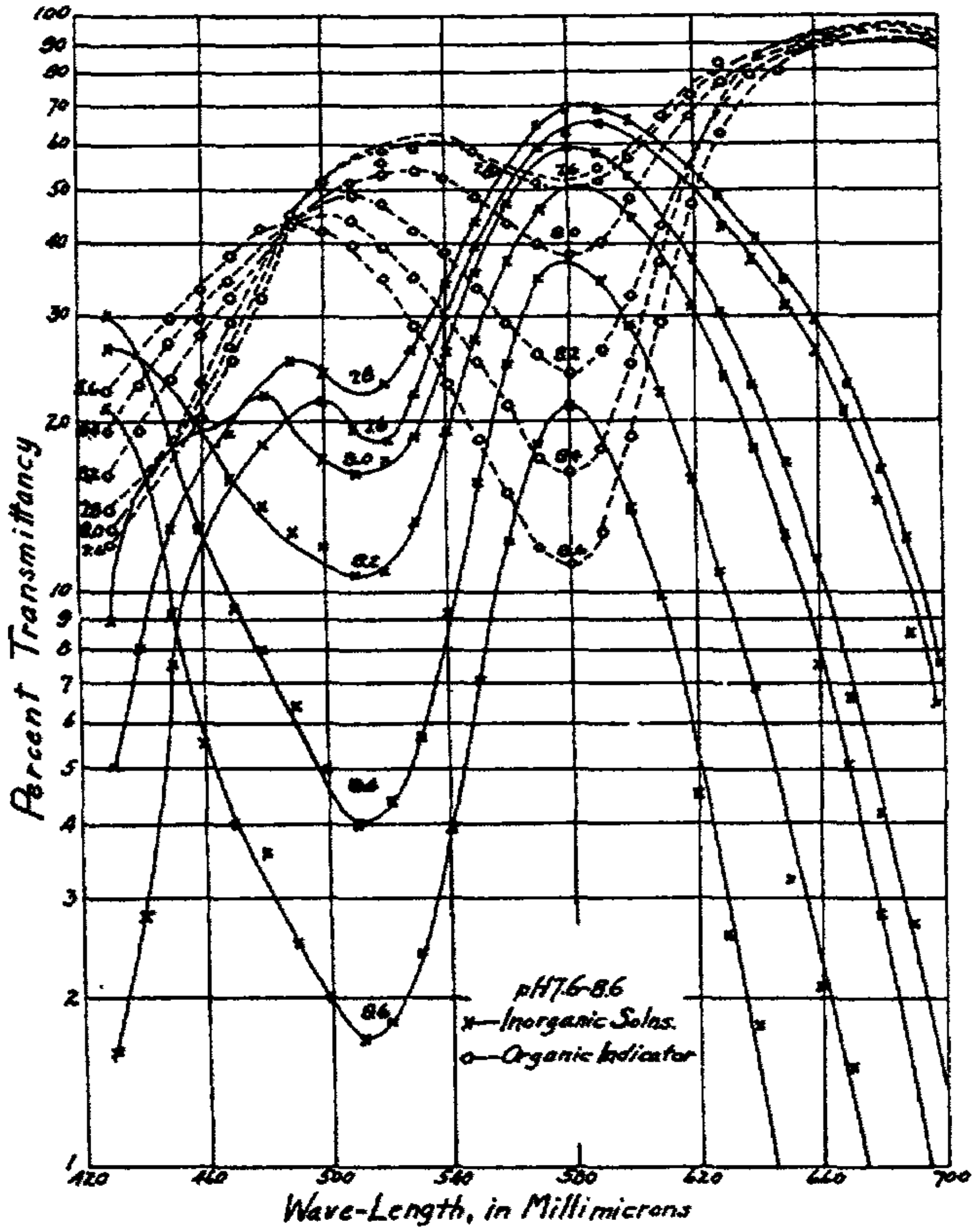

Fig. 9
METACRESOL PURPLE (Alkaline Range). Curves showing comparison of spectral transmittancy values for 5 cm. tubes containing (1) a solution made by adding 0.2 ml. of a 0.04% solution of indicator to 10 ml. of buffer solution and (2) Taub's inorganic matching solution.

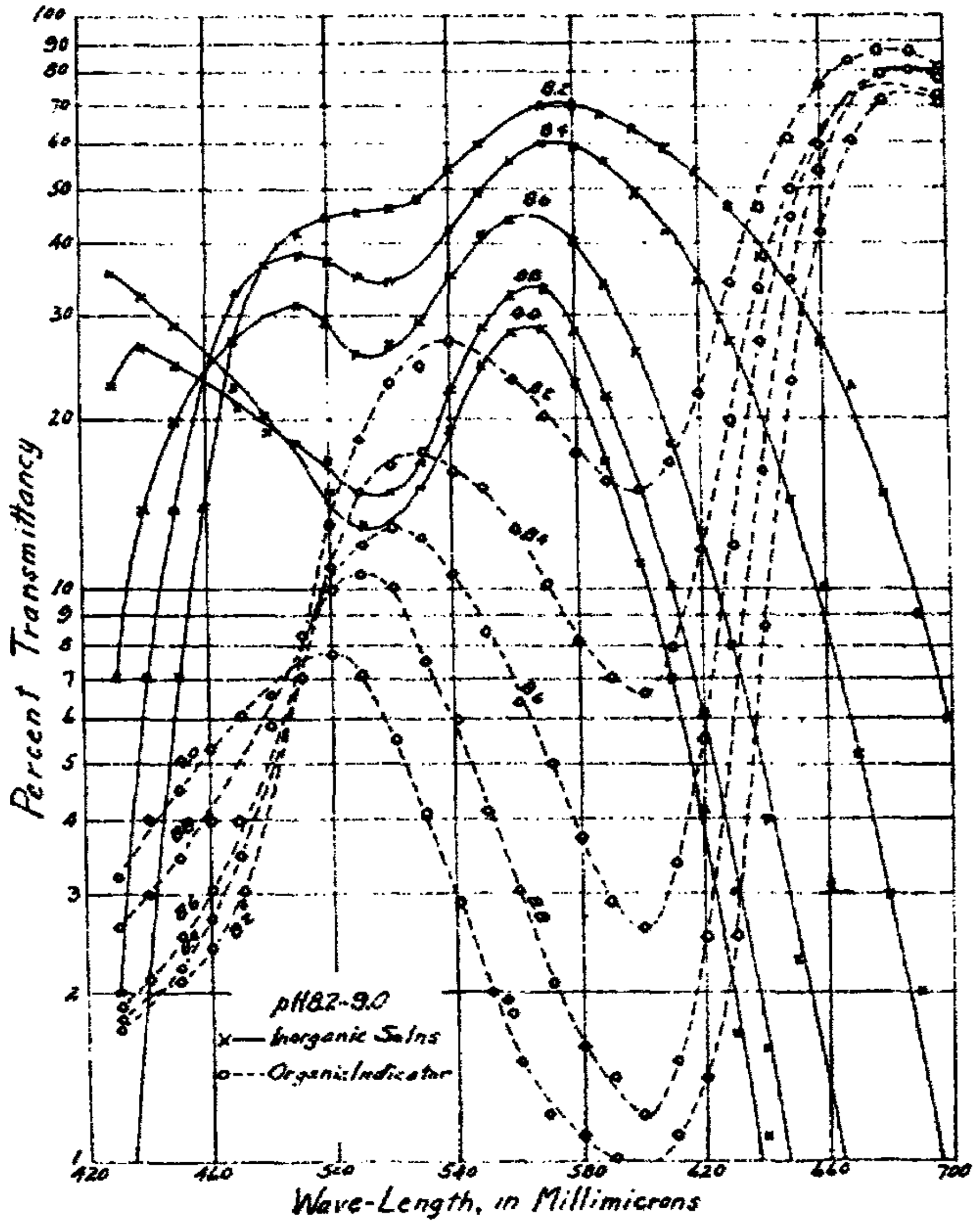

Fig. 10
THYMOL BLUE (Alkaline Range). Curves showing comparison of spectral transmittancy values for 5 cm. tubes containing (1) a solution made by adding 0.4 ml. of a 0.04% solution of indicator to 10 ml. of buffer solution and (2) Taub's inorganic matching solution.

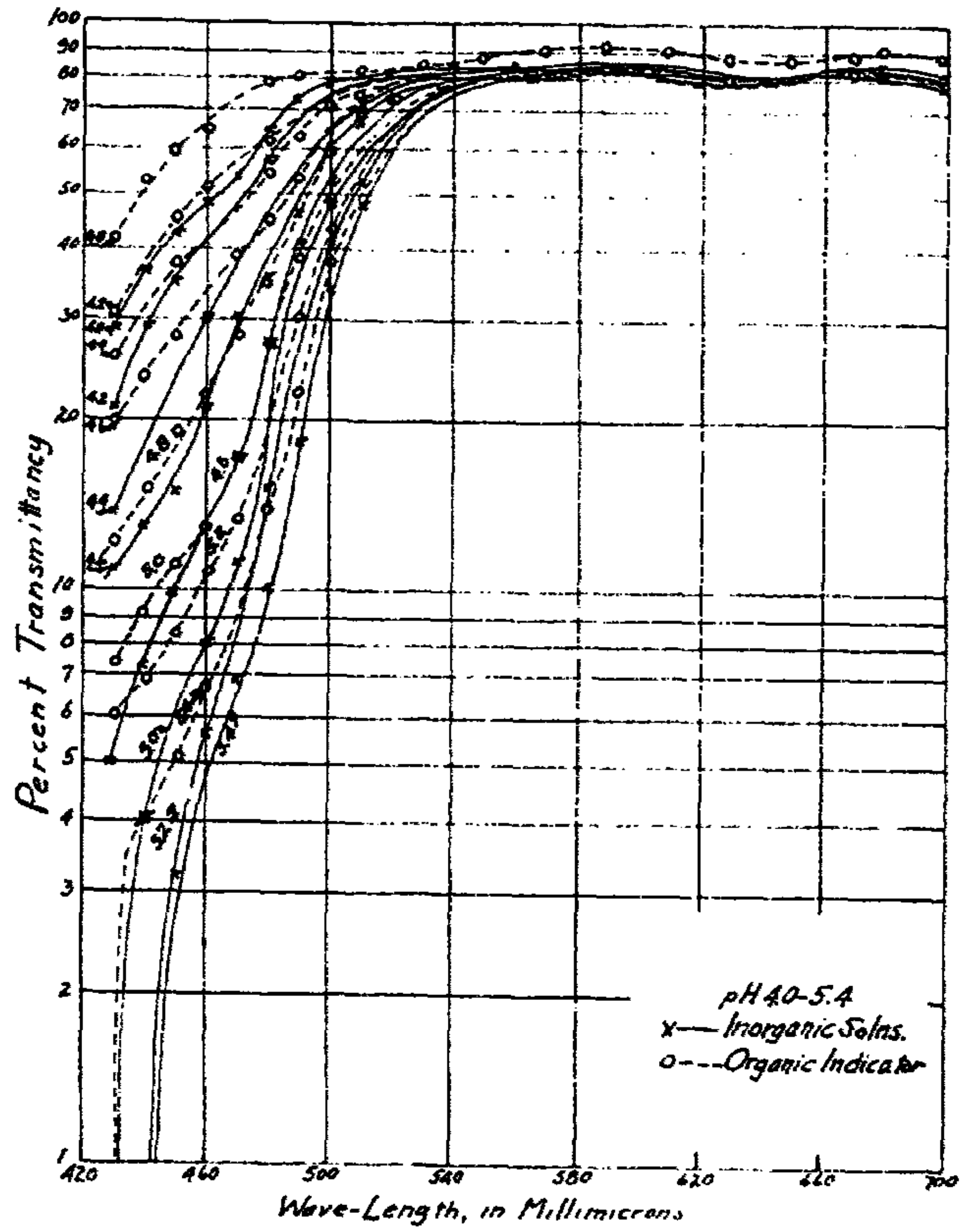

Fig. 11

γ-DINITROPHENOL. Curves showing comparison of spectral transmittancy values for 5 cm. tubes containing (1) a solution made by adding 0.2 ml. of 0.1% solution of indicator to 10 ml. of buffer solution and (2) Windisch's inorganic matching solution.

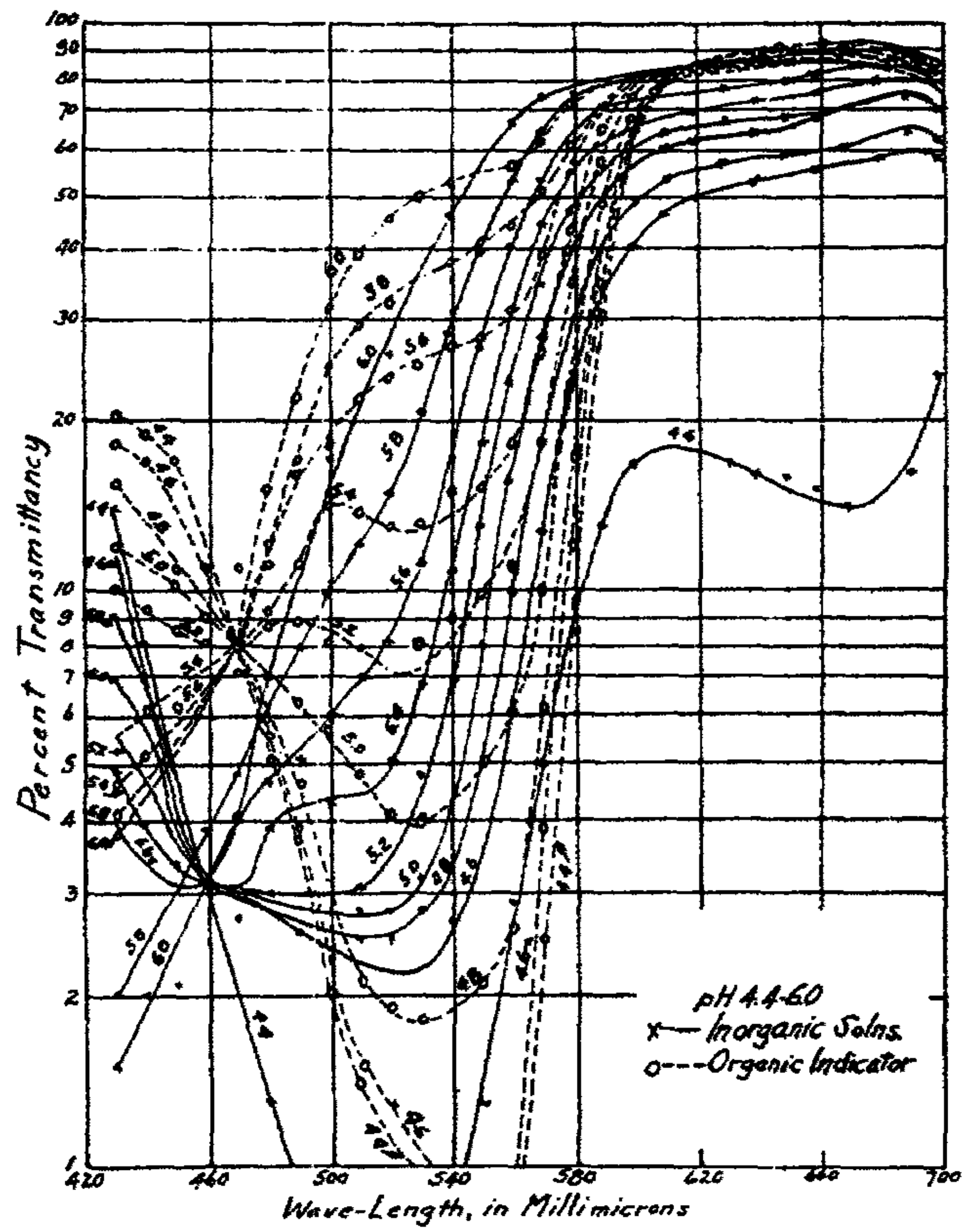

Fig. 12

METHYL RED. Curves showing comparison of spectral transmittancy values for 5 cm. tubes containing (1) a solution made by adding 0.2 ml. of a 0.02% solution of indicator to 10 ml. of buffer solution and (2) Bruere's inorganic matching solution.

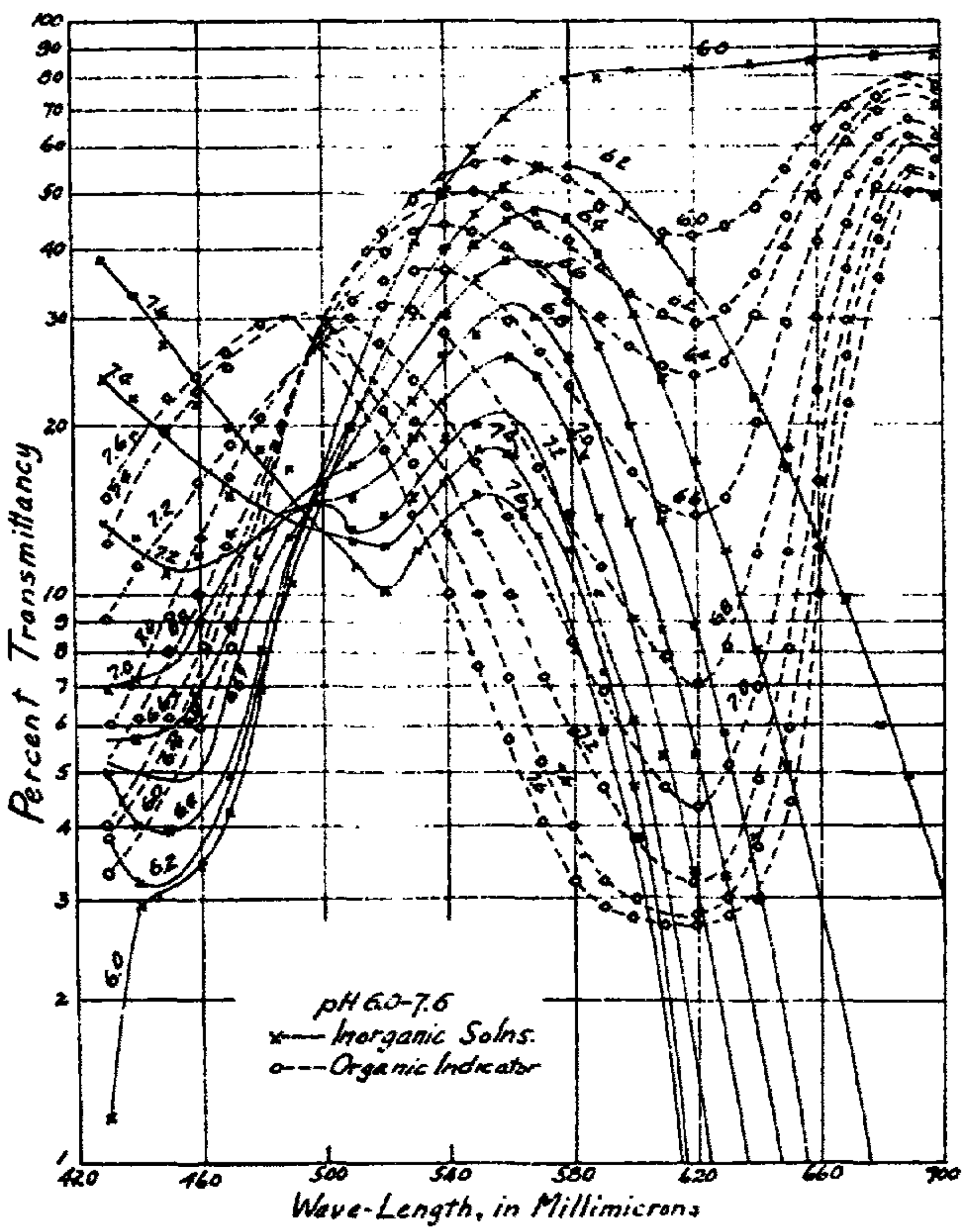

FIG. 13

BROMTHYMOL. Curves showing comparison of spectral transmittancy values for 5 cm. tubes containing (1) a solution made by adding 0.3 ml. of a 0.04% solution of indicator to 10 ml. of buffer solution and (2) Bruere's inorganic matching solution.

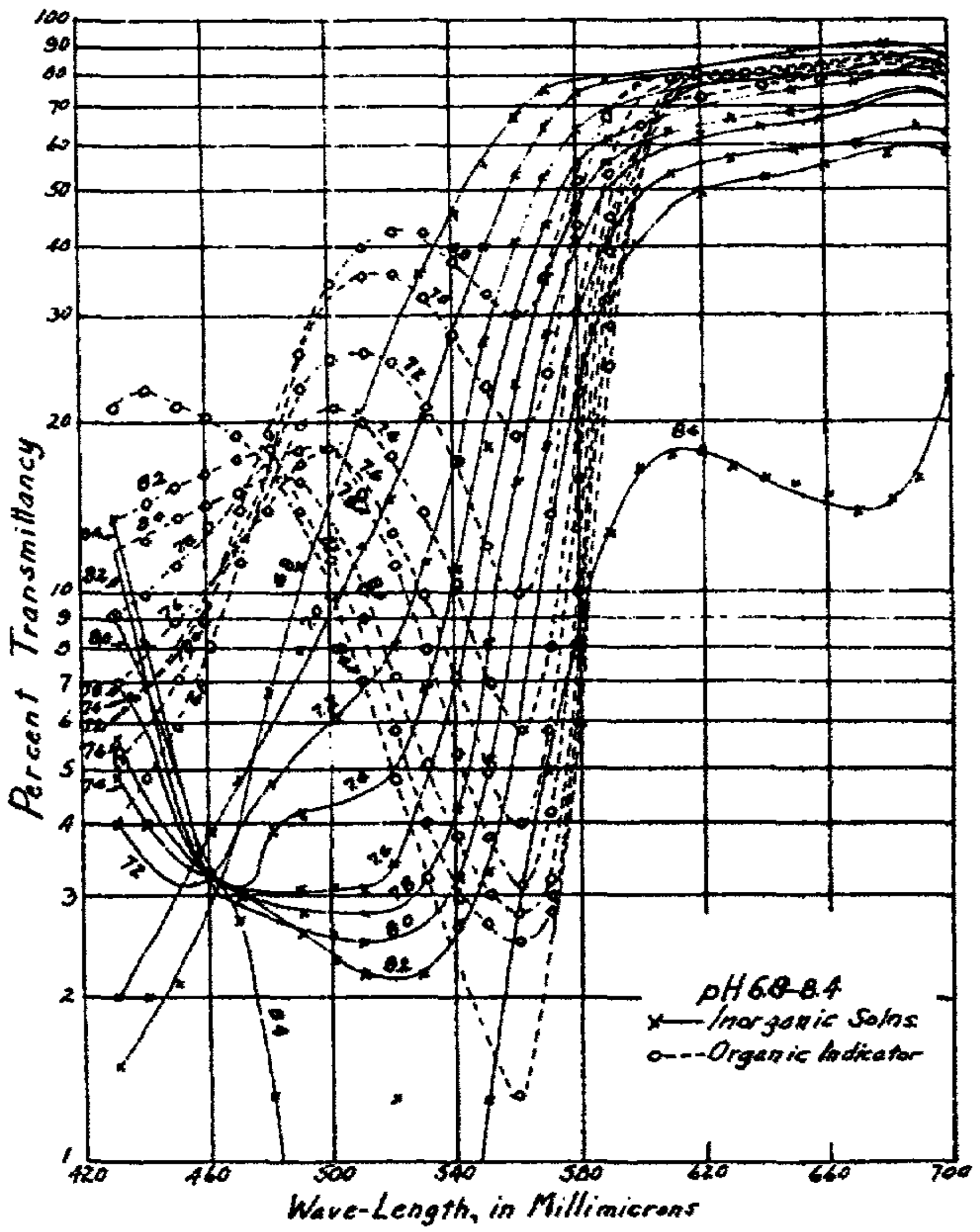

FIG. 14

PHENOL RED. Curves showing comparison of spectral transmittancy values for 5 cm. tubes containing (1) a solution made by adding 0.3 ml. of a 0.02% solution of indicator to 10 ml. of buffer solution and (2) Bruere's inorganic matching solution.

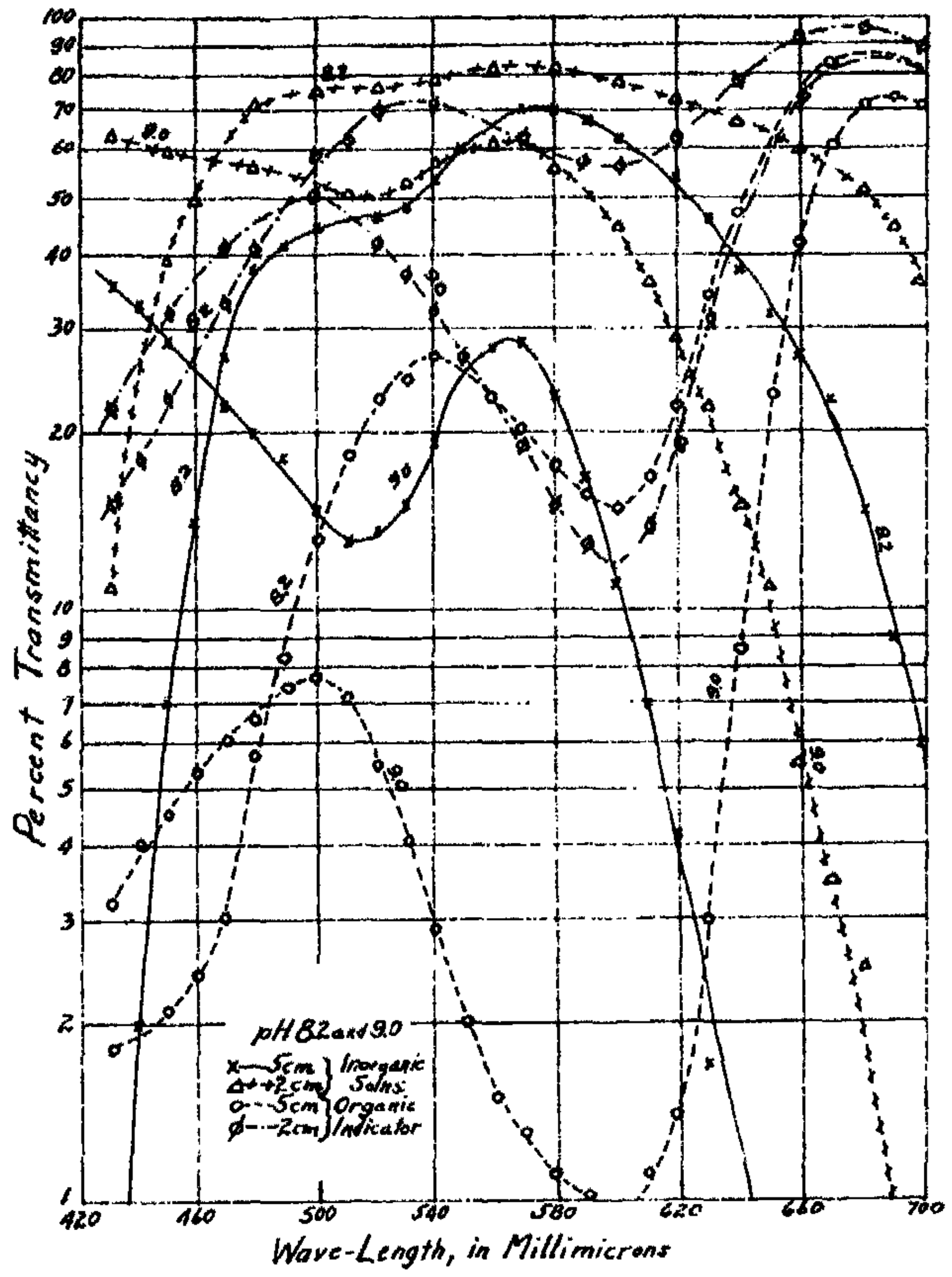

FIG. 15

THYMOL BLUE. (Alkaline Range). Curves showing comparison of spectral transmittancy values for 2 cm. and 5 cm. tubes containing (1) a solution made by adding 0.4 ml. of a 0.04% solution of indicator to 10 ml. of buffer solution and (2) Taub's inorganic matching solution.

ful inspection of the curves, nine pairs of matches were chosen for this calculation with the idea not only of showing any wide variations of colorimetric characteristics, but also of indicating the nature of their agreement in cases where the curves are very similar. The calculations were made according to the method described by Mellon,[24] and similar data were obtained, the summary of which is contained in Table I. It should be pointed out that a purple does not have any real dominant wave-length; that is, no mixture of homogeneous light and "white light" can be found which will match the purple color. In giving the monochromatic specification in such a case, by convention the dominant wave-length of the complementary color, expressed in the table by the use of the letter "C", is indicated. This is defined as that wave-length of

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[24] J. Phys. Chem., 33, 1932, 1934 (1929).

TABLE I

Numerical Specifications of Color for Selected Pairs of Solutions

Indicator	pH	Solution	Trichrom. Analysis. Red	Green	Violet	Monochrom. Analysis Rel. Br.	Dom. λ	Pur.	Spectral Centroid
Bromcresol green	5.0	Indicator	23.4%	37.3%	39.3%	14.8%	491.3mμ	41%	536.0mμ
(Taub)		Inorg. soln.	26.3	41.0	32.7	31.9	497.5	44	540.5
Chlorphenol red	6.2	Indicator	69.8	12.6	17.6	8.2	492.8C	61.5	619.0
(Taub)		Inorg. soln.	38.6	27.2	34.2	7.7	498.0C	27	579.9
Bromthymol blue	7.2	Indicator	24.5	39.2	36.3	11.0	493.8	43	534.8
(Taub)		Inorg. soln.	25.2	37.6	37.2	26.3	492.3	36	542.6
Cresol red	8.2	Indicator	55.7	20.7	23.6	14.2	492.7C	50.5	596.2
(Taub)		Inorg. soln.	40.1	27.1	32.8	7.9	496 C	28	587.3
Thymol blue	9.0	Indicator	33.8	28.0	38.2	3.4	521.2	23	561.6
(Taub)		Inorg. soln.	24.5	30.3	45.2	17.4	482	16	553.0
Thymol blue*	9.0	Indicator	29.9	34.7	35.4	27.1	491.3	14	547.1
(Taub)		Inorg. soln.	29.1	34.0	36.9	50.4	489	13	554.0
Phenol red	8.0	Indicator	55.5	21.4	23.1	20.1	492.5C	49	598.4
(Bruere)		Inorg. soln.	60.3	26.5	13.2	19.6	607.6	66	596.2
p-Nitrophenol	6.6	Indicator	44.9	44.0	11.1	79.7	572.1	75	561.6
(Windisch)		Inorg. soln.	46.8	45.0	8.2	80.4	573	82	562.7
γ-Dinitrophenol	4.2	Indicator	39.9	38.9	21.2	79.1	574	46	561.5
(Windisch)		Inorg. soln.	41.6	40.3	18.1	78.9	574	55	561.9

C Dominant wave-length of complementary.
*All 5 cm. thickness except this one which was 2 cm.

light which is required to be mixed with the sample light in order to match white. Hence, the resulting hue, instead of being like that of the sample, is farthest removed from it.

Discussion of Results

Anomalous Curves.—Inspection of the curves brings to light several anomalies in location that should be pointed out. In Fig. 4 the curve for the indicator-buffer solution for pH 4.0 seems hardly in the right elevation with respect to the curves for pH 3.8 and 4.2. In Fig. 6 the curve for the indicator-buffer solution at pH 6.2 probably should be more nearly midway between the curves for pH 6.0 and 6.4. In Fig. 8 the curve for the inorganic solution corresponding to pH 7.6 seems hardly in the right elevation with respect to the curves corresponding to pH 7.4 and 7.8. None of the curves was actually constructed at the time of making the spectrophotometric readings and when they were constructed later, unfortunately there was not an opportunity of checking any questionable points.

Explanations for peculiarities in other curves follow. In Fig. 2 the location above 600 mμ of the curve for the inorganic solution corresponding to pH 1.2 presumably depends upon the fact that the solution contains cupric chloride and no ferric chloride while all the other inorganic solutions of this set contain ferric chloride and no cupric chloride. In Fig. 9 the curves for the inorganic solutions corresponding to pH 7.6 and pH 7.8 seem to be interchanged in position, but it so happens that the solution for pH 7.8 contains less cobaltous chloride, less cupric chloride, and more water than the solution for pH 7.6. For all the other solutions of the set as the pH increases, the amounts of cobaltous chloride and of cupric chloride increase. Hence the curve for pH 7.8 should lie above that for pH 7.6. In Fig. 12 the odd location above 600 mμ of the curve for the inorganic solution corresponding to pH 4.4 is believed to depend upon the presence of potassium dichromate which none of the other inorganic solutions of this set contains. In Fig. 13 the seemingly inconsistent location above 600 mμ of the curve for the inorganic solution corresponding to pH 6.0 is most likely dependent upon the absence from the solution of cupric sulfate which is present in all the other solutions of the set. In Fig. 14 the questionable location above 600 mμ of the curve for the inorganic solution corresponding to pH 8.4 is ascribed to the absence from the solution of potassium dichromate which is present in all the other solutions of the set.

Since in nearly every case the inorganic solution contains two or more salts possessing different colors, the resulting color is a mixture, and therefore the curve may exhibit irregularities not found in the curves for the indicator-buffer solutions, which do not contain mixtures of colored compounds.

Points of Maximum Absorption and of Intersection.—Brode,[9b] in proposing a spectrophotometric method for the determination of the concentration of hydrogen ions in solutions of dyes, showed that, for azo and phthalein dyes, the absorption band does not shift in wave-length, but simply changes in intensity (height) with a change in the hydrogen ion concentration. Baker and Davidson[9a] confirm this fact for a number of Clark's indicators. Hence, no matter what the concentration or what the pH value of the indicator solution, the spectral transmission curve for such compounds will show a minimum point, that is, a wave-length of maximum absorption, at a definite wave-length. The more dilute the solution, the higher on the graph this point will be, but always at the same wave-length. The present curves bear this out very strikingly. Another interesting fact is that for a number of the indicators there is approximately a point at which all the curves for the various pH values of a given indicator cross.

The curves for the same indicator on the different graphs are, in general, consistent among themselves as to general form(except as affected by concentration), the minimum point, and the point of intersection. This applies to methyl red, Figs. 1 and 12; to phenol red, Figs. 7 and 14; and to bromthymol blue, Figs. 6 and 13. The general form of the indicator curves is very similar to that of the curves of Brode[9b] and of those previously reported from this Laboratory,[9d,10] and the minimum points check very closely. The points of intersection agree with those of Brode.

Principles underlying Comparison of Colors.—Two colors may be compared simply by comparing their spectral transmission curves. If two solutions yield curves practically superimposable upon each other within the limits obtainable with the instrument used, it may be concluded that the samples show the same color; but if there is a marked difference between the curves for the two solutions, it is evident that the two colors may be different. In the use of such curves certain facts should be borne in mind.[25] "Two colors which appear to match under one illumination may not appear to match under another. It is possible for two colors which appear matched in daylight to have the same brightness, dominant wave-length, and purity and yet each yield an entirely different spectral distribution curve when measured on a spectrophotometer. If, however, the two colors yield the same curve, they will not only have the same brightness, dominant wave-length, and purity, but will appear matched under any illumination whatever." Priest[26] has shown that "if any two lights however different in spectral distribution, excite colors of the same quality, the wave-lengths of the centers of gravity of their spectral distributions are coincident," but "two spectral distributions of light may have the same wave-length of center of gravity and not excite colors of the same quality if the lights in the two cases are distributed over different ranges of wave-length."

Curves for Stock Standard Solutions (not shown in this article).—The general form of these curves checked that shown by Mellon and Martin[9d] for one-fourth molar solutions of cupric sulfate, ferric chloride, and cobaltous chloride. The one-fourth molar solutions of cupric sulfate and cupric chloride gave practically identical curves, as did also the one-fourth molar solutions of cobaltous chloride and cobaltous nitrate. Therefore, the colors of the cupric ion and of the cobaltous ion are not differently affected at this concentration by the anions in question, and Taub's statement[2] that the color "values" of the two

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[25] Keuffel and Esser: Technical Bulletin accompanying color analyzer.

[26] J. Opt. Soc. Am.-Rev. Sci. Instruments, 4, 388 (1920).

cupric solutions are the same is borne out by the spectrophotometric analyses. The relative positions, as well as the similar general forms of the curves resulting from the use of 2, 5, and 10 cm. tubes in the analysis of each solution, indicate that these solutions of ferric chloride, cobaltous chloride, cobaltous nitrate, cupric sulfate, and cupric chloride do not exhibit dichromatism. Shortening the tube in a given case is equivalent to diluting the solution.

Curves for Taub's, Kolthoff's, and Bruere's Matches.—The curves shown in Figs. 1–10 and 12–14, together with similar curves not shown, prove conclusively that the solutions containing cobaltous and ferric salts proposed by Kolthoff, the solutions containing cobaltous, ferric, and cupric salts proposed by Taub, and the solutions containing cobaltous and cupric salts and potassium dichromate proposed by Bruere as permanent standards for the colorimetric determination of hydrogen ion concentration, do not possess the same colors as do the indicator-buffer solutions they are said to match. In no case is there even approximate coincidence of the curves for a "matched" pair. The curves obtained for Kolthoff's matches for methyl orange, neutral red, and tropaolin 00 and the curves for Taub's matches for methyl orange and methyl red, which are not shown here, gave similar results. Some of the most striking examples of dissimilarity are bromcresol green, pH 5.0 (Fig. 4); chlorphenol red, pH 6.2 (Fig. 5); bromthymol blue, pH 7.0 (Figs. 6 and 13); cresol red, pH 8.2 (Fig. 8); metacresol purple, pH 8.6 (Fig. 9); thymol blue, pH 9.0 (Fig. 10); methyl red, pH 4.4 (Fig. 12); and phenol red, pH 8.4 (Fig. 14). It should be kept in mind of course, that the data of Mellon and Ferner[10] indicate that some variation in curves may be obtained, due to differences in individual samples of indicators.

Fig. 15 shows that the same general type of curve is obtained for the color of the solutions in question irrespective of whether 5 cm. or 2 cm. tubes are used in the analysis, and that the colors of the "matched" indicator and inorganic solutions are not the same, even when observed through 2 cm. tubes. However, the curves lie closer together when the shorter tubes are used. Curves, not shown here, indicating similar results were obtained for Taub's matches for bromcresol green, bromthymol blue, phenol red, cresol red, and metacresol purple (alkaline range) and for Bruere's matches for methyl red.

Curves for Windisch's Matches.—Inspection of the curves given by the Windisch pairs indicates that the chromate-dichromate matches for the nitrophenols are very satisfactory. Curves are shown for γ-dinitrophenol only (Fig. 11). It is interesting to note that these indicators are one-color indicators whereas those reported above are ones showing two colors.

Numerical Specifications.—The calculated numerical specifications of color for a number of the pairs of indicator and inorganic solutions (Table I) show further the lack of agreement between the colors of the solutions of the indicators and of the matches proposed by Taub and by Bruere, and also show the close agreement of the colors of the nitrophenols and their chromate-dichromate matches. It should be recalled here that mere agreement of numerical specifications does not necessarily mean that the colors are identical, unless the spectral transmission curves are coincident. Two colors which appear matched in daylight may have the same numerical specifications and yet yield entirely different curves. This would mean that the colors would not match under all illuminations. In the light of Priest's conclusions[26] it is evident that if two colors are to match under all illuminations, they cannot have different wavelengths of their centers of gravity. A most pronounced example of this lack of coincidence is shown by chlorphenol red and its inorganic "match."

The results obtained in the present work are in accord with those reported by Janke and Kropacsy[8] in their studies on the absorption spectra of Kolthoff's cobalt-iron matches and of the chromate-dichromate matches of Windisch and his co-workers. While the latter matches are reliable, it is doubtful if the unbuffered aqueous solutions of potassium chromate and dichromate would really prove to be permanent standards. Heintz[27] reported that solutions of a chromate and of a dichromate, used for comparison with indicators in the colorimetric determination of hydrogen ion concentration, changed in color over a period of six months. Jorgensen[28] states that if a definite pH value be given to a solution of a chromate or a dichromate by using a buffer mixture instead of water alone as the solvent, the solution takes on a permanent, definite color tint.

Conclusions and Summary

By this spectrophotometric study it has been shown that,

1. Solutions of cupric chloride and of cupric sulfate have the same color at a concentration of one-fourth molar with 1% hydrochloric acid as the solvent.

2. Solutions of cobaltous chloride and of cobaltous nitrate have the same color at a concentration of one-fourth molar with 1% hydrochloric acid as the solvent.

3. The above mentioned solutions of cupric chloride, cupric sulfate, cobaltous chloride, and cobaltous nitrate, in addition to a similar solution of ferric chloride, do not exhibit dichromatism under the conditions studied.

4. The use, as permanent standards, of a series of solutions of salts of cobalt, iron, and copper for comparison with the color tints produced by two-color indicators in the determination of hydrogen ion concentration is not to be generally recommended. If such standards are used, the comparisons of color should be made preferably through thicknesses of solutions not exceeding 2 cm., and the possible difficulties mentioned in this paper should be kept in mind.

5. The use, as permanent standards, of a series of aqueous solutions of potassium chromate and dichromate for comparison with the color tints produced by the one-color indicators, m- and p-nitrophenol and α- and γ-dinitrophenol, in the determination of hydrogen ion concentration, is recommended, provided precautions are taken to keep the solutions from fading.

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[27] Z. ges. Brauw., **46**, 82 (1923).
[28] Biochem. Z., **186**, 485 (1927).

NEW BOOKS

The Electrochemistry of Solutions. *By S. Glasstone. 23 × 15 cm; pp. viii + 476. London: Methuen and Company, 1930. Price: 21 shillings.* The electrochemistry of solutions is one of the most highly developed branches of physical chemistry. In recent years a particularly intensive study of the subject has been made in relation to modern ideas in physics and chemistry and in connexion with the increasing utilisation of electrochemical methods and processes in chemical and metallurgical industries. In spite of this there has not been hitherto any English text-book which provides a systematic account of the whole subject on modern lines. It is true that the electrochemistry of solutions receives a good deal of attention in text-books of physical chemistry and in the introductory portions of works on applied electrochemistry, and that certain specialised portions of the field are adequately covered by monographs. But a book of the type which Dr. Glasstone has now provided has long been lacking, and the author merits the thanks of all who are concerned with electrochemical matters for filling this notable gap in British scientific literature.

The opening chapter deals with the laws of electrolysis and the concept of electrolytic dissociation, and serves to clear the ground for the subsequent systematic treatment. In the following four chapters which are devoted to ionic migration and electrolytic conduction due reference is made to recent work on the solvation of ions, on the solvent correction in conductance measurements, and on the extrapolation of conductance data. Chapter VI is concerned with the application of the law of mass action and the development of the activity concept, and special reference is made to solubility relations and to equilibria involving complex ions. This is followed by a valuable discussion of the modern theory of electrolytic dissociation. The theory of Debye and Hückel is presented in some detail in relation to the determination of activity coefficients and the variation of ionic mobilities with concentration. In the discussion of evidence supporting the theory it is satisfactory to find reference to recent work on heats of dilution and on conductances with high frequency and high voltage currents. In this connexion, however, a more detailed consideration of the results of measurements of the conductance of non-aqueous solutions would have been welcome, and further attention might have been given to attempts to calculate the true dissociation constants of intermediate and strong electrolytes.

The next five chapters are given over to such matters as the strengths of acids and bases, hydrolysis, pH changes in neutralisation processes, buffer action, indicators, and amphoteric electrolytes. Although most of these subjects are generally discussed fairly fully in text-books of physical chemistry, it is naturally an advantage to have them reconsidered in the light of the modern dissociation theory and set out as part of the general scheme of an electrochemical treatise.

The subject of electrode equilibria and reversible electrode processes commences at about the middle of the book and occupies the next 112 pages. Special mention should be made of sections dealing with the calculation and elimination of liquid junction potentials, the problem of the determination of absolute electrode potentials, and the question of the origin of potential differences in a voltaic cell. On the practical side due consideration is given to the use of quinhydrone, glass, oxide, and controlled oxygen electrodes and to the principles of electrometric titration.

The last 95 pages of the text are devoted to irreversible electrode phenomena. In view of the very inadequate treatment which this branch of the subject generally receives in books on physical chemistry, a larger proportion of the available space could have been allotted to it with advantage. A general introductory chapter is followed by articles on hydrogen overvoltage and the polarisation accompanying metal deposition. The latter contains a discussion of the conditions for the deposition of alloys, an account of work on the mercury dropping cathode, and an examination of the factors which determine throwing power and the physical condition of cathodic metal deposits. The following chapter on anodic polarisation includes sections dealing with the anodic dissolution of alloys, passivity, anodic overvoltages, and valve electrodes, but no reference is made to anodic polymerisation processes such as the formation of persulphate. The book concludes with an account of electrolytic depolarisation, in connexion with which a useful summary of the theory of metallic corrosion is presented, but the depolarisation processes which occur in primary cells receive no attention.

In compiling this volume the author has evidently made a very careful survey of the overwhelmingly extensive literature of the subject and he is to be particularly congratulated on the way in which he has selected and arranged his material. The results and conclusions of the earlier workers have been brought into line with modern views, and those portions of the subject which have tended to develop on independent lines have been kept in proper perspective and brought into relation with the whole. The fundamental principles are clearly brought out and the treatment of controversial matters is critical but unprejudiced. Special attention is given throughout to an examination of the principles underlying practical methods for the determination of electrochemical quantities.

The exposition is admirably clear and is supplemented by tables of reliable modern data and by commendably simple diagrams. Particular mention must be made of the very numerous references to the literature which form a valuable feature of the book. Author and subject indices are appended. In conclusion it should be said that this is a thoroughly good book which can be recommended with confidence to all who are interested in any aspects of the electrochemistry of solutions. *H. J. T. Ellingham*

Katalyse vom Standpunkt der chemischen Kinetik. *By Georg-Maria Schwab. 24 × 16 cm; pp. viii + 249. Berlin: Julius Springer, 1931. Price: 18.60 marks; cloth bound 19.80 marks.* The author of this volume is to be heartily congratulated in having achieved the difficult task of presenting the modern theories of chemical reaction and of the effects of catalysts both homogeneous and heterogeneous in a readable form. The majority of books on this subject are, unfortunately, modelled closely on the lines of "Mrs. Beeton." On the other hand, in the few books purporting to give theoretical treatments, the personal views of the writer are sometimes unduly prominent. The volume is divided into three principal sections: homogeneous catalysis in gases, catalysis in liquids and heterogeneous reactions. Whilst all sections are good, it is only natural since Dr. Schwab is an authority on heterogeneous reactions that the third section is somewhat more complete than the other two.

In the first section, consideration of simple gas reactions leads up to an account of chain reactions; the former would be more complete if the interesting work of Rice and more especially of Kassel had been included. The possibility that many of the pseudo-unimolecular reactions are chain reactions, possibly short ones, is a consideration that should not be overlooked.

In discussing the chain reactions, an account is given of the effect of water in carbon monoxide combustion, of the theories proposed for the hydrogen chlorine reaction and the work of Semenoff on the propagation of chains and the formation of branching chains. The influence of the walls of the vessel in breaking chains and of inert gases in lengthening the chain by retardation of the diffusion process exemplifies well two different types of catalytic action. The specific effects of the walls of the vessel in chain reactions are dealt with in a later section, pp. 213-219, where some attention is given to a frequently neglected aspect of chain reactions, namely the commencement of chains or the formation of a chain link at the walls. Solid surfaces can initiate as well as stop chains and in certain oxidation processes at least specificity of particular solid surfaces for starting or stopping chains is different. In discussing induction periods where intermediate compounds are formed and chains involving oxidation processes, the author cites both the Haber radical theory as well as the "peroxide" theory. Whilst it is possible that the reaction involving peroxide formation may emerge into the radical chain at higher temperatures, the recent work of Bone on the oxidation of methane is not readily intelligible on either of these hypotheses. It is indeed possible that the induction period in this case is due to the removal of a poison from the walls, thus permitting of the starting of the chains. The induction period due to oxygen both in the chemical dissociation of hydrogen at a tungsten surface and in the hydrogenation of ethylene at a nickel surface being well known examples.

In the second section, catalysis in solution is dealt with, pp. 51-132. Attention is first given to the remarkable effect of mixtures of iron and copper salts on the persulphate iodide and the hydrogen peroxide iodide reactions. It would be of interest to examine whether these catalysts started chains in these reactions and whether the catalysts were adsorbed in the walls of the vessel. This section is followed by consideration of ionic catalysis leading up to the work of Lowry, Bjerrum and Brönsted. The work of Orton on the chloramine transformation has shown that the postulates given on pp. 83-84 are invalid. Some ten pages are devoted to consideration of the influence of the solvent on the reaction velocity; the work of Richardson and Soper might well have been included. The section concludes with a discussion on negative catalysis in homogeneous solution, where examples are given of two types of inhibition, removal of a positive catalyst and the breaking of a reaction chain, as shown by Backström in autoxidative processes.

In the section on heterogeneous reaction, attention is first drawn to the current views on the adsorption of gases, and the information which the heats of adsorption can give us on the nature of the adsorption process. From these considerations the formal classification of catalytic reactions as two-dimensional gas reactions is developed and examples of each type are given. This is followed by considerations of selective catalysis, poisons the nature of the catalytic surface and the influence of promoters. There have been at least three different views expressed as to the nature of the active portions of a catalyst. According to Taylor, partly isolated atoms perform the function of an active spot. The reviewer has always held the opinion that the edges and corners were more reactive than the planes and that a group of atoms and not a single atom was necessary for catalytic action. Balandin believes that groups of atoms in certain particular configurations characterise the active patches. These three views have in recent years received their various protagonists. The evidence for the existence of active spots is based primarily on the effect of poisons on reaction velocity; secondly, on the supposed anomalies in the heats of adsorption and thirdly, on calculations on the reaction velocity. Now there is little doubt that in many reactions the whole surface is catalytically active, e.g. in the dissociation of many gases on filaments. These reactions can be divided into two classes; those where adsorption takes place prior to reaction and those in which the ordinary kinetic collision theory accounts satisfactorily for the rate. The heats of adsorption on metals reveal the fact that potential energy stored up in the metal may be released as heat on adsorption of a gas and do not point conclusively to especially catalytically active atoms possessing high heats of adsorption. We are left, therefore, with poisons as the ultimate criterion of the existence of active spots. If the catalyst consists in reality of couples such as are formed in carbon containing traces of iron where for many reactions the catalyst is the carbon-iron system, the influence of small traces of poisons is readily intelligible. It is difficult to avoid the conclusion as to the existence of active spots in a pure catalyst such as copper or nickel unless we assume that the potential field over large areas can be modified by the presence of a poison and that the catalytic activity is dependent on the potential field. The author subscribes to the active patch hypothesis in the form of the edges and corners and believes that two-dimensional gas reactions take place at these places. It is by no means certain that catalysis can only take place, e.g. between hydrogen and ethylene at a nickel surface where both the hydrogen and ethylene are mobile in the adsorbed layer. We know that reaction can take place at very low temperatures and although the evidence from Rupp's work is at present very slender, it is most probable that neither the ethylene nor even the hydrogen is mobile, under these conditions. The volume concludes with a brief discussion on microheterogeneous and biochemical catalysts which scarcely does credit to the rest of the book.

Dr. Schwab's book is really an excellent one and the reviewer can cordially recommend it to anyone who is even but slightly interested in problems of reaction velocity.

Eric Keightley Rideal

Die Katalyse. *Die Rolle der Katalyse in der analytischen Chemie. (Catalysis. The Rôle of Catalysis in Analytical Chemistry). By Gertrud Woker. Special Section II, second division: Biological Catalysts. Second half: Respiratory Ferments. 25 × 16 cm; pp. xix + 592. Stuttgart: Ferdinand Enke, 1931. Price: 76 marks; bound 79 marks.* This is the fourth volume of a series devoted to the rôle of catalysis in analytical chemistry of which the first appeared in 1910 with a series of general catalytic principles, the second in 1915 devoted to inorganic catalysts. The second division of the subject in its special features was to include not only the inorganic catalysts but also the biological catalysts. This latter subject proved to be so comprehensive that it was found necessary to subdivide it still further. Hence in 1924, the first half, devoted to hydrolytic ferments, was published. The second half, which deals with fermentation processes yielding alcohol and with the oxidation reactions in which enzymes intervene, has now become available. A monumental work comprising in all some six hundred pages is devoted to these latter problems.

The book possesses both the advantages and disadvantages of its size and the extended period of time over which it has been produced. In the preface, attention is called to the fact that the approach to the fermentation problem is somewhat different from that which would have been used had it been written after the sections on the oxidation reactions. In the time consumed in the preparation of these latter chapters, the progress in the field of alcoholic fermentation, especially, in the author's opinion, that due to Neuberg, has been so great as to justify other methods of approach than those used. The reviewer sees in such difficulties additional justification for the increasingly popular policy of small monographs, rapidly written, dealing with small islands of knowledge in the whole archipelago. Those however, who prefer to have at hand, in one volume, a detailed and comprehensive treatment of the subject with all the various points-of-view set forth *in extenso*, will welcome this additional volume.

It would require a reviewer of an entirely different orientation in the subject of catalysis to give a critical verdict on the detailed sections of this book. It can, however, be affirmed with how great interest the various achievements in the field of these fermentation processes have been followed and with what respect the record of the penetration into the difficulties of the problem has been received. Here is a comprehensive statement of the chemistry of fermentation, the normal and abnormal reactions that may occur, the fates of the various raw materials, the stimulation of the various processes and the mechanism of such. This is followed by a similar extended treatment of oxidation processes produced by enzymes and by inorganic systems which may serve as ferment models. At all times considerable sections are devoted to the preparative side of the subject and to the analytical technique involved in such work. The book, while doubtless of small expected distribution among individual workers, should be available on all library shelves, technical and educational, where the problems of enzyme action as well as their analytical control are a matter of concern.

Hugh S. Taylor

Gmelins Handbuch der anorganischen Chemie. *Edited by Deutsche chemische Gesellschaft. Eighth edition. 25 × 18 cm; (a) System-number 8. Serial No. 1. Iodine. pp. 244. Price: 37 marks, (b) System-number 45. Germanium. pp. 62. Price: 13 marks, (c) System-number 59. Part B, Serial No. 4. Iron. pp. 657-872. Price: 35 marks. Berlin: Verlag Chemie, 1931.* The three parts of the new edition of Gmelin's comprehensive treatise noticed above carry the publication of this work a further step forward and continue the tradition of its exhaustive character. The text comprises a series of short sentences, followed by the references to the literature, the use of abbreviations contributing to the extreme brevity of style. The work as a whole is not readable in the usual sense, and aims at providing for inorganic chemistry what Beilstein's treatise does for organic chemistry. None of the parts noticed is complete in itself, and the issue of a large number of odd inincomplete parts in this way, unavoidable when many authors are at work on different parts of the whole book, makes it impossible to review the work in the ordinary sense of the word.

The section on iodine (No. 8) deals with the element, its preparation and properties, including solutions and complexes, and analysis. The section on germanium (No. 45) includes germanium and its compounds as far as germanium and aluminium. The section on iron (No. 59, B, 4) deals with iron ferrocyanides and ferricyanides; the nitroprussides; iron thiocyanates, silicates, compounds with oxy-acids of phosphorus, arsenic, and antimony; compounds with chlorides and cyanides of bismuth; general reactions of iron salts, including the interconversion of ferrous and ferric iron and autoxidation, and the beginning of oxidation and reduction cells. This volume, therefore, includes a number of matters of general interest.

It is impossible, in the case of a work of this character, to do more than say that an impression of most detailed and exhaustive treatment was obtained. The great care which is taken by the editors and those responsible for the text to make the work absolutely accurate and exhaustive must be known to those who have used the volumes previously published. The original literature has clearly been consulted, and the great labour necessary in the preparation of such a work should command the gratitude of chemists. When this monumental work is completed (if it is completed before another edition is begun, a failing which sometimes has appeared in the past in the case of large German chemical treatises) it will form an indispensable source of reference which should be available in large libraries. The great expense of the work will be realised when it is stated that the seven parts of the number dealing with iron which have so far been issued are priced at 223.5 Marks and still leave the chemistry of the element in an incomplete state.

J. R. Partington

Strukturbericht 1913-1928. *By P. P. Ewald and C. Hermann. 24 × 16 cm.; pp. iii + 818. Leipzig: Akademische Verlagsgesellschaft, 1931. Price: 45 marks, cloth 47 marks.* This is a critical and ordered survey of all the crystal structures examined by means of X-ray methods and published between the years 1913 and 1928, with many additional abstracts of important papers up to February, 1931. It is typically Teutonic in its comprehensiveness. Only the specialist can fully realise the immense amount of work, much of it routine in character, that has gone to its compilation. The usefulness of the book will, however, be apparent to all who ever need to refer to X-ray work on crystals. It should have a place on the bookshelf of the X-ray worker, crystallographer, metallurgist and chemist; all of whom will find it a most valuable work of reference, even if they have little or no knowledge of German.

All substances about which any structural (X-ray) information is available, are grouped according to their chemical formulae. The system adopted is similar to that found in the Handbuch der Physik (24, Kap. 4, Berlin, 1927) and in the supplementary volume to Landolt-Börnstein, although it is somewhat differently defined. The main divisions are as follows: elements, inorganic compounds of formula AB, AB_2, A_mB_n, etc., alloys (i.e. metallic compounds) and organic compounds. The authors evidently intended originally to have included a section on mixed crystals, but this was not carried out. Each section is introduced by a description of the 'types' of crystal structure found among the substances in that division, following which comes an exhaustive series of abstracts of all the published X-ray work on those substances.

The preliminary descriptions of the various 'types' are likely to be understood only by those readers having some knowledge of mathematical crystallography, but numerous diagrams (276 in all) are included which are largely self-explanatory.

The abstracts which follow are exceptionally good, both in substance and in scope. They include results not only from the rarer periodicals, but also from dissertations which are not easily accessible to the general reader. Each abstract embodies primarily the results as given by the author of the paper referred to; where comments are added by the reviewers (the authors of the book), these comments are in italics. The comments occasionally involve a correction or even contradiction of the publication itself in the light of later research; they correlate the various investigations on each substance and frequently give the results of further calculations based on the experimental observations. In our opinion, these abstracts form the most valuable part of the book. A reader wishing, for instance, to know what X-ray work has been done on the various forms of SiO_2 will find references to, and summaries of, no less than 25 papers, briefly compared and co-ordinated.

The section on alloys occupies some 120 pages, and deals with 83 different metallic compounds, being illustrated by a large number of phase-diagrams and other figures.

The 'Strukturbericht' was originally published in serial parts, as a supplement to the Zeitschr. f. Krist., and this method of publication has enabled a large number of printer's and other errors to be detected. Unfortunately it has not, apparently, been possible to reset the type, the list of corrections (still not quite complete) being given at the end of the text. Excellent indexes make it easy to find any particular reference, whether to author, substance or crystal type.

K. Lonsdale.

Physical Science. *By Herbert Brownell. 23 × 16 cm; pp. xiv + 313. New York and London: McGraw-Hill Book Company, 1931. Price: $2.50.* "This book makes free use of subject matter from all fields of physical science, but no detailed study is made in any single field. Its material and the manner of its use have to do mostly with scientific interpretations of phenomena common in the experiences of life. The theories and the language of science are freely employed, however, for a better comprehension and closer correlation of these phenomena.

"The distinctions commonly observed in college textbooks between the different sciences are here very generally disregarded. The author has considered himself free of the restraints necessarily imposed when teaching a specialized science, particularly with regard to the sequence of topics and the fullness of details. Emphasis is placed upon the importance of acquiring definite meanings for the scientific terms used rather than a mere mastery of words and phrases," p. v.

The chapters are entitled: the nature of heat and of heat transmission; vaporization and condensation, and the heat of vaporization; properties of air, air pressure, and some applications of air pressure; highs and lows in relation to weather, and relation of weather to human welfare; rotation and revolution of the earth; the moon; time and timekeeping; the stars, and other celestial bodies, and studies of constellations; earth structure and geological history—rocks, minerals, and soil materials; metals and ores, coal and petroleum; structure of matter and properties of bodies; matter in motion and the significance of the term energy; energy as the correlating factor in science studies and the relationships of force, energy, and work; the nature of light and of color phenomena, and radiant energy; radiations as electrical phenomena, and radioactivity; changes in matter involving a change in substances; achievements of chemists of great importance to us as contributions to our daily life; achievements of science, and what science cannot do; social aims in science teaching and science in education.

There is a very interesting picture, p. 91, showing the apparent difference in diameter of the sun as viewed at perihelion and at aphelion. "It is estimated that more than 63,000,000 tons of plant food-material are lost annually from the lands of the United States by soil wash in a total soil erosion of 750,000,000 tons. This loss of plant food is twenty-one times the amount removed annually by plant growth," p. 104.

"Rivers, like the Missouri and the Mississippi, have their waters laden with soil washed from land surfaces in their basins, and this earth is almost wholly lost as available productive soil. A similar process, continued through longer periods in some parts of the world, such as northern China, has resulted in large areas of once productive land unfit now for tillage, and for agricultural purposes generally. In the arid and semi-arid regions of the United States large areas of land have been brought into use for crop production as the result of irrigation. But this does not make good the annual losses from erosion of hillsides and the washing away of their most fertile portions—a deplorable waste of the wealth of the nation. Upon the productiveness of the soil the present prosperity of any people, as well as the future greatness of their country is dependent. An impoverishment of soil fertility, on the one hand, and irreparable losses of soils, on the other hand, are national calamities. The rate of soil production may be, possibly, one foot in 10,000 years. Hence the surface wastage ought not to be more than one inch in a thousand years. Wastage of fertile soils is practically irreparable. 'Worn-out soils,' agriculturally speaking, are largely the result of the washing away of the top of the soil, rather than an exhaustion of the plant food from the soil by repeated cropping. Productiveness of soils may be maintained through centuries of farming if serious washing and erosion are prevented. Many of the most fertile soils of the rolling prairie and timbered lands of the state of Missouri have been kept in corn, and subjected to soil washing, until clay spots are in evidence on nearly every hillside," p. 105.

"The vast water tonnage passing through the 'Soo Canal' which connects Lake Superior and Lake Huron far exceeds the amount that passes through the Suez Canal. Much of this traffic is iron ore from the northern Minnesota region en route to the blast furnaces of lake ports such as Milwaukee, South Chicago, Detroit, and Cleveland, which are among the world's great centers of iron and steel manufacture. Return cargoes of coal for the upper lake region swell the volume of an enormous lake traffic. The manufacture of iron and steel is so vitally connected with national life and prosperity, and a general understanding of the operations involved in the production of commercial iron is so readly acquired, that information concerned with the preparation of iron from its ores need not wait until chemistry is studied," p. 129.

"When a horse pulls forward upon a cart to move it, in a very real sense the cart pulls backward with equal force. How, then, can any locomotion be accounted for? Such is an old 'puzzle' propounded by teachers of physics. The fact that at the same time when the pulls are exerted the horse pushes against the ground beneath its feet becomes painfully apparent in cases when by reason of icy pavements this reaction from the pavement is lacking. A corresponding thrust forward upon the horse from the ground occurs.

"The greater the push exerted when jumping, the greater the value of the forward motion of the jumper. To jump from an unmoored boat or from the seat of a swing invites disaster because a forward push is lacking in either case," p. 158.

"Even as late as 1922, automobiles were 'finished' with varnishes and enamels which hardened by oxidation, requiring two or three weeks time to become dry and hard. Now, by use of nitro-cellulose and lacquers, the time required for the same kind of finishing has been cut to a few days only, sometimes two days or less.

"Nitro-cellulose (such as gun-cotton, pyroxylin, and collodion) has long been known. But only in the recent past has nitro-cellulose, fluid enough to be used as a spray, come into use. These solutions dry rapidly by evaporation. Some of the solvents employed are:

"1. Amyl acetate ('banana oil') now made synthetically from a component of natural gas.

"2. Butanol, produced by bacterial fermentation of corn mash under strict bacteriological control.

"3. Cellosolve, made from a gaseous product of the cracking of petroleum. None of these are coal-tar derivatives. But toluene and xylene, used in diluting these solutions, are of coal-tar origin," p. 227.

The author has an unfortunate way of not saying exactly what he means. "A solar eclipse at any one place is a rare event," p. 72. "Marble, as calcium carbonate largely free of impurities, would seem to have been subjected to enough heat *due to pressure* to metamorphose the rock, fusing the particles into a fine-grained mass," p. 124. "Bricks made from clay free of iron compounds are of a light-yellow color," p. 128. "The phenomenon of solution is so commonplace that in a case where sugar disappears in hot water, with an almost complete disappearance of its volume, little or no thought is given to an explanation of the occurrence," p. 148. "The 'sparkle' of diamonds is due not only to reflection of light from their outer surfaces but to light which, having entered the cut surfaces, experiences repeated reflections within the stone before emerging," p. 152. "Providing the force of adhesion remains unchanged, then the less the density of a liquid the higher it will be raised [in a capillary tube]," p. 154. "Some insects and other animals apparently perceive sounds of higher frequency or, it may be, of lower frequency than are audible to man," p. 162. "Calcium cyanamide is made from calcium carbide," p. 177. "In the electrolytic preparation of aluminum, oxygen is liberated at the anode rods which are slowly consumed by the action of the oxygen," p. 215. "Hydrogen is freed at the cathode plate of the storage cell, and oxygen at the anode. . . . The oxygen liberated at the anode converts the PbO into PbO_2 (lead dioxide). The hydrogen at the cathode abstracts oxygen from the PbO there (reduces it), leaving the lead from the former oxide in a spongy condition. . . . When the storage battery is put into circuit as a source of electrical energy, a chemical change occurs in a reversed order," p. 216. "Collodion, forced through capillary glass tubes, becomes at once solidified *into threads of cellulose* when acted upon by water (which dissolves the ether or the alcohol)," p. 226.

The reviewer regrets that the author should have seen fit to adopt the hypothesis of amorphous metals when discussing crystal fracture, p. 33. It is difficult to see the advantage in telling the student something that is not true, merely because it can be made to sound plausible.

It is hard to lay one's finger on what is wrong with this book. To the reviewer it is not interesting. Either the author has not seen his subject as a whole or his command of English is not adequate. The book is really a collection of isolated facts, which is not the impression it should produce.

Wilder D. Bancroft

Constitution et Thermochimie des Molécules. *By A. and M. Gosselin. 25 × 17 cm; pp. vii + 231. Paris: Les Presses Universitaires de France, 1930. Price: 40 francs.* The doctrine of valency and the theory of chemical structure have been the grammar of organic chemistry for decades; the developments that have followed from the work of Werner and which have given us, from the hands of G. N. Lewis, Sidgwick and others the modern electrical theory of valency, have widened and strengthened the original fundamental conceptions of valency theory. Nevertheless, MM. Gosselin ask us to set aside structural chemistry as we know it for a system which they describe as general (p. 25) but which has nothing to say on the subject of benzene theory and which apparently requires us to abandon the whole of stereochemistry. According to MM. Gosselin, molecules are held together by certain central atoms, which attach to themselves other atoms and molecules—particularly molecules—by the operation of two forces, the one electrical and the other "chemical," which is described in a phrase that has an almost mediaeval ring—liaisons où intervient la force chimique, (p. 75). For example, formic acid is represented (p. 101) by $CO.(H_2O)$ and the evidence quoted in support is that the acid is readily dehydrated into water and carbon monoxide. But they omit to mention that, in other circumstances, it is just as readily decomposed into hydrogen and carbon dioxide. Again, the alcohols are written $R.CH_2.(H_2O)$ and are supposed to contain water molecules as such because water is removed by dehydrating agents. But hot copper will liberate hydrogen from ethyl alcohol to give acetaldehyde. These examples are enough to illustrate the most obvious fallacy that underlies the author's system. Except perhaps in the case of ionic reactions, knowledge of the initial step in the reaction of a molecule generally eludes us, owing to the fact that so few reactions are really homogeneous. But MM. Gosselin make no attempt to ascertain the first step, being content to draw their inferences as to molecular compositions from the end products of the most drastic molecular treatment.

The latter half of the book is devoted to an application of thermochemical data to the ideas of molecular structure developed in the first part. Seeing that the heat of formation of an interatomic linkage is a constant and additive quantity, it is not surprising that the heats of formation of the authors' molecules can be calculated from atomic and molecular constants, especially when it is borne in mind that the heat value of the C-C link is not very different from that of the H-H link. A considerable amount of useful thermal data is to be found in this part of the book.

In conclusion one example may be quoted of the way in which the authors use the physical data that are germane to their subject. Their formulae for methane and carbon tetrachloride are $CH_2.(H_2)$ and $CCl_2.(Cl_2)$; on their view methane should be electrically asymmetric and is quoted as being so (p. 114), the recent proof that methane has no dipole moment being ignored. On the other hand, carbon tetrachloride, well known to be nonpolar, should be as electrically asymmetrical as methane; but this fact is not mentioned.

D. Ll. Hammick

Recent Advances in Analytical Chemistry. *By C. A. Mitchell, assisted by nine contributors. Vol. II, Inorganic Chemistry. 20 × 13 cm; pp. xvi + 452. Philadelphia: P. Blakiston's Son and Co., 1931. Price $3.50.* This is the second of two volumes written to present in easily accessible form the latest information concerning analytical chemistry. This volume on inorganic analysis is devoted to the determination of hydrogen ion concentration; the detection and determination of lead, bismuth, mercury, copper, cadmium, arsenic, antimony, tin, selenium, tellurium, platinum and its congeners, iron, chromium, aluminum, beryllium, the constituents of steel, carbon, silicon, cerium and the rare earth metals, titanium, zirconium, thorium, germanium, vanadium, niobium, tantalum, cobalt, nickel, maganese, zinc, molybdenum, tungsten, uranium, magnesium, and the rarer alkali metals; qualitative and quantitative microchemistry and water and sewage analysis. Each chapter has been written by a contributor with special knowledge of the subject.

"The classification of analytical methods under the headings of Organic and Inorganic Chemistry is necessarily somewhat arbitrary, since certain subjects, such as gas analysis, do not strictly speaking come under either heading. Microchemical analysis, which during the period under review has developed into a separate branch of analytical chemistry, also requires a group to itself, for it comprises organic, inorganic and physical methods. Again, the analysis of water and sewage has been included under Inorganic Analysis, although its results have now to be interpreted with reference to biological considerations."

"In the sections dealing with the more common metals, it was not possible to adhere strictly to the plan adopted in Volume I, of giving working details of new methods, for the work of the last ten years has been so voluminous that space would not allow of more than a critical survey of it, with copious references to the original papers."

The information is exceptionally well presented beginning with a general survey of the type of advance which has been made during recent years. This is followed by a detailed account of the specific work done with references to the original literature and in many cases a critical discussion of the work, based on the author's own experience. The authors also point out the determinations which are not satisfactory and where more investigation is necessary.

The book is well written, with very few errors and omissions, and together with Volume I [J. Phys. Chem., **35**, 2464 (1931)] can be very highly recommended as a useful addition to the library of anyone interested in Analytical Chemistry.

M. L. Nichols

Electron Physics. *By J. Barton Hoag. 23 × 15 cm; pp. 212. London: Chapman and Hall, 1930. Price: 15 shillings.* This book is a welcome addition to the very short list of books which can make a real appeal to the experimentalist in either physics or physical chemistry. For it contains not only a brief but clear account of the more common properties of ionising particles and radiations but describes a number of the more important and fundamental experiments which are carried out in the laboratory just before a student embarks upon research. In these descriptions many important practical details are given which usually have to be learnt from experience and bitter experience at that. Included in the volume we find descriptions for the determination of e/m for the electron, experiments on thermionic and vacuum tube electron emission, on the properties of α, β and γ rays and of radioactive substances. What to many may prove the most valuable portion of the book are the appendices on electrometers, electroscopes, vacuum technique and pressure gauges. As is frequently the case in American books, the terminology at times, whilst probably correct English, sounds a little strange on this side of the Atlantic, such as "hook up the apparatus" p. 22. A few corrections, chiefly in the chemistry, might well be made in a future edition in such sentences as "consider now a cubical crystal of rock salt, with alternate sodium and chlorine atoms at the corners" (p. 14), or "the gases found most suitable . . . are methyl iodide, methyl bromide and argon" p. 109. A number of problems as well as tables of fundamental constants are collected at the end of the book, which is well printed and suitably bound.

Eric K. Rideal.

Handbook of Chemical Microscopy. *By E. M. Chamot and C. W. Mason. Vol. I. Principles and Use of Microscopes and Accessories, Physical Methods. 23 × 15 cm; pp. xiii + 474. New York: John Wiley and Sons, 1930. Price: $4.50.* Although based on Chamot's well-known textbook, "Elementary Chemical Microscopy," 1915, "the present work has been entirely rewritten, and expanded in all sections. The optical principles of the microscope have been presented in some detail, as a preliminary to the discussions of the special technique of illumination, photomicrography, and ultramicroscopy. The factors underlying the interpretation of appearances in microscopic objects are formulated in general terms, as is the discussion of the properties of doubly refractive material, in order that they may lend themselves to application in various fields of microscopy. In line with the widening applications of crystallographic principles, their fundamental concepts are exemplified by numerous experiments which have been devised primarily from the point of view of the chemist."

"Much of the material here compiled and discussed for the first time in book form is of paramount importance to all microscopists whether they are workers in the biological or in the physical sciences."

In addition to the wealth of material included, the book is replete with references to the original literature and the appendix contains a two-page biography of textbooks on applied chemical microscopy which are particularly useful for the application of microscopy to special fields. A synopsis of the laboratory experiments in the study of introductory chemical microscopy at Cornell University is also included.

The book is very well written and should be a great help to all those having any occasion to use a microscope.

M. L. Nichols.

Handbook of Chemical Microscopy. *By E. M. Chamot and C. W. Mason. Vol. II. Chemical Methods and Inorganic Qualitative Analysis. 23 × 15 cm; pp. ix + 411. New York: John Wiley and Sons, 1931. Price: $4.50.* "It is the aim of Volume II of this Handbook to describe the essential manipulative methods in detail and to present a compilation of the most dependable tests for the inorganic cations and anions."

In the selection of the tests and methods discussed, the authors have fortunately been guided more by the applicability of the tests to the analysis of complex mixtures, the certainty of the results obtained and the ease of manipulation, than by the sensitivity of the reaction.

"Numerous interesting 'micro' reactions are omitted, either because they are suitable only as identity tests on substantially pure substances and are of little use in mixtures of various unknown materials, or because they require a more precise control of concentrations, acidity, temperature, etc., than is practicable in a single drop of unknown composition on a microscope slide. In other words, with few exceptions reactions have been included only if they will yield results under almost any conditions and in almost any circumstances." Tests requiring special apparatus, color reactions and spot tests have largely been omitted.

"In response to repeated requests, photomicrographs of most of the common and useful tests have been included, not without some misgivings, for the authors believe that the mere examination of pictures will not take the place of the preparation and direct study of actual tests."

The book includes a discussion of manipulative methods of a general character, the handling of small amounts of materials, methods of applying reagents in microscopic qualitative analysis, the detection of the elements arranged according to the grouping of the periodic system, the detection of anions, special reagents yielding reactions with a number of cations, and the qualitative analysis of material of unknown composition.

This book, like Volume I, is very well written and the set comprises an indispensable reference work for the microchemical analyst.

M. L. Nichols.

The Journal
of
Physical Chemistry

Published under the auspices of the American Chemical
Society, the Chemical Society, and the Faraday Society

VOLUME XXXV
JULY-DECEMBER

ITHACA, N. Y.
THE EDITOR

1931

CONTENTS OF VOLUME XXXV

1. JANUARY

2. FEBRUARY

3. MARCH

4. APRIL

5. MAY

6. JUNE

7. JULY

8. AUGUST

9. SEPTEMBER

10. OCTOBER

11. NOVEMBER

12. DECEMBER

FUNCTIONAL PSYCHOSES AND DISPERSION

BY H. BECKETT LANG* AND JOHN A. PATERSON**

The problem of the Dementia Praecox, Manic Depressive and Epileptic psychoses is a very serious one and any explanation tending toward a more accurate diagnostic and therapeutic approach requires earnest consideration. They are the three large groups of functional mental disorders. Many studies have been made as to the etiology, therapy and pathology, with bitterly disappointing results at times, though progress has been made. The present diagnostic classification is based partly on etiology and partly on behavior reaction. The larger groups of mental cases admitted to State Hospitals are of the so-called functional disorders. This study was made to determine whether further clarification as to diagnosis could be achieved.

Bancroft and Richter[1] have made the suggestion that "many of the functional disorders may be nothing more than an abnormal degree of dispersion of the nerve colloids and have been classified erroneously as 'functional' due to the inability of the histological technique to reveal the colloidal abnormalities." This abnormal state may be either over-peptization or agglomeration. They review the work of many authors showing that studies have been made both with agglomerating and peptizing agents, though not systematically or consciously. They draw the conclusion that "disorders of dispersion may be benefited by coagulating agents, and disorders of decreased dispersion would be improved by peptizing agents."

They conclude that catatonia involves over-dispersion while in epilepsy there is a decreased state of dispersion. They discuss sodium amytal as a coagulating agent and sodium rhodanate,[2] (NaCNS) as an example of the peptizing group, which also includes iodides and bromides. In another paper Bancroft and Rutzler[3] have discussed the action of these compounds in more detail.

Our work was begun at the suggestion of Professor Bancroft, who drew our attention to the need for a study of the action of these drugs. His advice and criticism was utilized freely throughout the study. We are indebted to Mr. J. E. Rutzler, Jr. for advice and assistance as to preparation, dosage and administration of sodium rhodanate. Our problem was to determine whether clinical evidence could be found to support the views of Bancroft, Richter and Rutzler. No attempt was made to select cases: a number showed

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[1] Proc. Nat. Acad. Sci., 17, 294; J. Phys. Chem., 35, 1606 (1931).

[2] At the suggestion of Professor Bancroft we are using the term sodium rhodanate instead of sodium thiocyanate to prevent confusion with sodium thiosulphate and sodium cyanide.

[3] Proc. Nat. Acad. Sci., 17, 186 (1931).

marked motor activity with impulsive assaultive tendencies; others were noisy and excited; some were depressed or stuporous. A few showed little abnormal motor behavior. Forty-six cases were studied under both drugs.

Our method was to exhibit sodium amytal orally. The usual dose was 0.4 grams in twenty-four hours; but a few cases were given 0.8 grams and a few others reacted well with 0.2 grams. Cases were tested for five days and a summary made of the behavior. Forty-eight hours were allowed to elapse in order to ensure complete elimination. The sodium rhodanate was started with a dosage of 0.3 grams twice daily by mouth. This was increased at the rate of 0.3 grams per day until the case was receiving 2 grams daily. One case was given as much as 4.6 grams per day for two days with no other result than an increase in stupor. It was found that, so far as diagnostic tests were concerned, a dose of one to two grams per day was quite sufficient and that the majority of cases would show reaction on one gram.

We prefer the terms schizoid and cycloid reactions to dispersed or agglomerated. The blood pressures are given because it has been suggested that the improvement in some cases might be due to the drop in blood pressure and not to the specific action of the sodium rhodanate. Our studies do not confirm this view.

Case 1

J. D. Male, aged twenty-eight, duration five years.
Diagnosis: Dementia Praecox, Catatonic
Behavior:

Before—stupor, seclusive, untidy, refused to care for personal needs. No delusions or hallucinations. Blood pressure, 108/72.

Sodium amytal intravenously, 0.5 grams in 10 cc triple-distilled water. Blood pressure fell to 90/64, but soon recovered. Drowsy, no deep narcosis, awoke feeling refreshed, talked and smiled.

Sodium amytal orally. Slow steady improvement. Asked for work; assisted in cleaning and polishing; fed himself; kept clothes neat, clean; in good contact with surroundings.

Sodium rhodanate. Blood pressure fell to 90/60, confused stupor reaction. Very pale. Head bowed. No response, untidy and dirty.

Sodium rhodanate stopped. Recovered so that he would obey slowly on command.

Comment: This case is one in which the blood pressure fell to the same level with each drug and yet there was marked mental improvement with sodium amytal, while sodium rhodanate made his condition worse.

This case illustrates excellently the arguments of Bancroft, Richter and Rutzler, as it reacted definitely to a coagulating agent and so belongs in the over-peptized or schizoid group. The treatment should be continued, using this type of drug; but must also be accompanied by other therapeutic aids. The mental picture shows predominance of schizoid characteristics with splitting of affect from ideational content (he has put away all feeling).

Case 2

C. S. Male, aged fifty; duration eight months.
Diagnosis: 1. Alcoholic; 2. Apathy and Depression.
Behavior:

Before—shows stupor, depression, is negativistic, generally untidy but not dirty. Has to be coaxed to eat. Was fearful but could not give cause of this fear.

Sodium amytal intravenously. Within three minutes showed slight restless movements; in four minutes he was talking distinctly and responded promptly to commands, was active and alert, later he became drowsy, slept normally and awoke refreshed.

Sodium amytal orally. Became alert and interested, cared for person properly, slept well.

Sodium amytal stopped. Stupor returned promptly but was no worse than before.

Sodium rhodanate. Stupor was increased, was untidy, dirty, did not feed himself properly.

Sodium rhodanate stopped. Returned to original state.

Comment: This case was first diagnosed as alcoholic; but this was changed because of the results reported. When he was in the improved state, he described his depression as due to an unknown fear; he had the delusion that war was to occur all over the world. The schizoid tendencies predominated. There is definite splitting of affect; behavior shows severe regression; therapeutic indications are for exhibition of coagulating agents. The test indicated that a condition of over-peptization existed and that our diagnosis should therefore be schizophrenia.

Case 3

F. P. Male, aged fifty-four, duration four months.
Diagnosis: Manic Depressive, Manic.
Behavior:

Before—excited, confused, assaultive, no delusions or hallucinations.

Sodium amytal, 0.2 grams by mouth. Became very excited, showed a deep narcosis and then excitement.

Sodium rhodanate. Became quiet, showed a slow improvement. Mental condition cleared, normal state recovered. Paroled home.

Comment: We have in this individual one of the benign psychoses. He was extremely excited and his behavior was such that he required restraint. Cycloid tendencies predominated and there was no severe regression; behavior and thought were in contact with reality. From previous experience we believe that this case would no doubt have improved in time, but it is felt that improvement was more rapid under rhodanate. We were therefore dealing with an agglomerated state.

Case 4

W. M. Male, aged twenty-eight, duration one year six months.
Diagnosis: Epilepsy.
Behavior:

Before—repeated convulsions, averaging twelve per month, with two clear periods which were followed by marked confusion, and disturbance of memory. Developed status epilepticus.

Sodium amytal intravenously. Prompt sedation, slept twenty-four hours, mild confusion lasting three days. Disoriented.

Sodium amytal orally. Confused, disoriented.

Sodium rhodanate. Slow steady improvement, confusion cleared, no further convulsions.

Comment: It is too soon to say that convulsive phenomena are controlled. His reaction to the dispersing agent places him in the agglomerated group. Therapeutic indication is for continued exhibition.

Case 5

M. S. Male, aged thirty-four, duration five years.
Diagnosis: Dementia Praecox, Hebephrenic.
Behavior:

Before—excited, restless, untidy, noisy with an occasional clear time when he would speak English. At other times his productions were incoherent and in German, his childhood language. Blood pressure 110/68.

Sodium rhodanate. Slow steady improvement. He requested his own clothes, talked in English coherently and has maintained this improvement for two months. Blood pressure. 102/72.

Sodium amytal. Excited, stimulated, drowsy, short narcosis. Following this he was over-active, destructive. Showed many mannerisms, grimaces and fantastic poses; but, while he was in these bizarre attitudes that appeared catatonic-like, he only adopted them when he knew he was being observed. He enjoyed the effect of this behavior on others. This indicates the presence of a strong affect but mischievous in direction.

Comment: This is an individual whose behavior reaction under amytal would be called Dementia Praecox Catatonia. Actually in his usual state the diagnosis has alternated between Dementia Praecox Hebephrenic and Manic Depressive Mixed according to the observer. This alternation indicates that we have here a case with marked schizoid tendencies; but that affect was not split off, and was still strong, and adapted to the situation at an adult level.

The behavior under sodium rhodanate would, according to our experimental findings, place him in the agglomerated or cycloid group which correlates with the Manic Depressive classification. The prognostic indication should be hopeful. Therapy should consist of exhibition of peptizing agents.

Case 6

C. P. Male, aged thirty-six, duration six years.
Diagnosis: Dementia Praecox, Catatonic.
Behavior:

Before—excited, noisy, restless, resistive, mute for five years; appetite is good but sleep is usually disturbed. This man wrote on the wall that he defied us to make him speak.

Sodium amytal intravenously. Sleepy, nodded in response to questions and spoke once. Narcosis of short duration, following which he was excited and required restraint to prevent injury.

Sodium rhodanate. He was depressed, confused and irritable on large doses. On small repeated doses he began writing numerous letters which were logical to some extent but showed disturbed sentence structure. On the fourth day of administration he began to talk and was over-active and irritable. On the fifth day he was still over-active. He talked steadily. He showed flight of ideas. Conversation was rambling and irrelevant but coherent and correct in choice of words and sentence structure. His ideas were in response to normal stimuli, and if they had not been so rambling and produced so fast (in other words a manic reaction), he would have been normal as to content and production of ideas. He ignored his personal appearance completely but was correct in his habits.

Comment: This is one of the mixed cases, so hard to estimate, diagnose, and treat correctly. He shows many schizoid characteristics and these predominate. The cycloid tendencies are manifested in his irascibility. There are also long mood swings between elation, which leads to excitement, and depression, which produces irritability and negativism.

The interpretation of reaction is difficult in this case. To sodium amytal he reacted with excitement and violence similar to Manic Depressive; to the sodium rhodanate he showed a release of the inhibitory mechanism so that we have uncritical freedom of thought production, undirected and distractible. Our suggestion is that we have here an individual, who responds so readily to these drugs that he is normal only over a slight range. We probably gave him more than enough sodium rhodanate to bring him to the normal state. Considering his five years of mutism, his free production now, at a correct level of adult thought and in response to reality, the reaction would indicate an improved state and therefore Manic Depressive. Therapeutically it remains to find the correct dose level at which he may be maintained.

Case 7

G. B. Male, aged twenty-two, duration two months.
Diagnosis: Dementia Praecox, Catatonic.
Behavior:

Before—stupor, negativistic, incoherent, disoriented, impulsive and assaultive.

Sodium amytal orally. Apparently stimulated. Slowly improved, more neat, tidy, speech clear and distinct. Assists with the ward work.

Sodium amytal stopped. Relapsed into stupor, was not assaultive, nor agitated.

Sodium rhodanate. When this was given, patient became stuporous, untidy and resentful.

Sodium rhodanate stopped. He improved slowly; but did not recover his previous level.

Comment: This case is similar to Case 1.

Case 8

J. L. Male, aged twenty, duration two months.
Diagnosis: Catatonia.
Behavior:

Before—impulsive, assaultive, refused food, went to bed with clothes on, was mute; marked motor activity and confusion.

Sodium amytal orally. Became more disturbed, excited, violent and assaultive, very confused, ataxic gait. Blood pressure 110/80.

Sodium rhodanate. Gradually became quiet, better behaved and clear; would sleep entire night and eat well.

Sodium rhodanate stopped. Resumed restlessness, confusion, soiled bedding and clothing, destructive; but was not assaultive nor agitated.

Comment: This case was found to have a taenia saginata infestation, hgbln 65, RBC 3,510,000. The test would indicate that we are dealing with an agglomerated state and that, upon improvement of physical condition, the mental reaction would show corresponding improvement, in which case a more hopeful prognosis could be made in spite of the patient's retrogression to the vegetative level of behavior.

Comment: This case would substantiate the contention of Bancroft and Richter that there may be two forms of Catatonia, one the peptized and the other the agglomerated. However, we would classify this case more properly as a reactive stupor to a physical state and having a good prognosis although showing infantile behavior.

Case 9

E. B. Male, aged twenty-two, duration four months.
Diagnosis: Mental Deficiency, Excitement.
Behavior:

Before—appeared very fearful, anxious, was noisy, excited, over-active, violent, destructive, untidy, but not dirty in personal habits.

Sodium amytal orally. Excitement, increased restlessness, and over-activity increased. Blood pressure, 110/60.

Sodium rhodanate. Increased periods of quietness, sleeping improved, appeared stupid at times then slow improvement; ate better, was neat and tidy in personal appearance. Is now home on parole.

Comment: In this case not only was the exhibition of sodium rhodanate of diagnostic value indicating a Manic Depressive type but it was also therapeutic in action.

Case 10

F. K. Male, aged forty-two, duration three months.
Diagnosis: Manic Depressive, Manic.
Behavior:

Wildly excited, assaultive, destructive, incoherent and disoriented. Blood pressure 130/60.

Sodium amytal. Showed marked intoxication, over-stimulated, over-active, over-productive and happy, then confused and irritable.

Sodium amytal stopped. Has maintained a clear sensorium, but is irritable and over-active.

Sodium rhodanate. On small dose became quiet, well-behaved, interested and alert. On large doses became confused, depressed, untidy and restless, but sleeps well. Blood pressure 116/68.

Comment: In this patient's history, other members of the family have had manic depressive attacks. He has had several minor episodes, improving quickly from them. This time he was working hard in intense heat and developed heat exhaustion as well as his psychosis. This physical trauma is agglomerating in action. We predicted a beneficial reaction to rhodanate and this did occur. He is now employed on the farm.

Case 11

C. M. Male, aged fifty-six, duration ten years.
Diagnosis: Manic Depressive, Manic.
Behavior:

Before—irritable, uneasy, restless with periods of excitement, over-activity and destructiveness with brief periods of depression and would not sleep well at night. Blood pressure 118/80.

Sodium amytal orally. Patient showed extreme sleepiness; when he aroused from this he was excited, irritable, assaultive and non-co-operative, was tense, did not care for personal needs.

Sodium rhodanate. Became quiet and much more contented with surroundings; slept entire night. Is more co-operative on the ward, eats better and does not become assaultive. Blood pressure 122/82.

Comment: In addition to his cyclic mood changes there is also deterioration present. It is quite possible that, although he may be somewhat improved, the stage of recovery is passed.

Case 12

P. F. Male, aged forty-eight, duration unknown.
Diagnosis: General Paralysis.
Behavior:

Before—assaultive, constant irritability, noisy, restless, agitated and destructive.

Sodium rhodanate. No outburst of violence, will talk, appears less agitated, preserves personal appearance better and sleeps entire night. Blood pressure 120/75.

Sodium amytal. Became uneasy, restless, irritable and assaultive.

Comment: This case had malarial therapy and is also receiving tryparsimide. The findings indicate that his present state is one of agglomeration.

Case 13

W. H. Male, aged sixty-two, duration ten years.
Diagnosis: Manic Depressive, Circular.
Behavior:

Before—shows long periods of excitement, during which he would be noisy, agitated and assaultive following which he would have a brief period of normal state of two or three days, then would go into a depression. At the time of our study he was in an excited condition.

Sodium amytal orally. Narcosis, excitement increased, was more assaultive and irritable.

Sodium rhodanate. Shows a steady improvement, quiet, requested occupation, maintained improvement; is now on convalescent ward.

Comment: From our other cases we should have expected this result; but we must recognize the possibility of a coincidental improvement in the psychosis irrespective of the administration of the sodium rhodanate. Cycloid tendencies predominate.

Case 14

G. Y. Male, aged forty, duration unknown, has been in hospital two months.
Diagnosis: Manic Depressive, Manic.
Behavior:

Before—marked excitement, noisy, restless, agitated, refused food, destructive to clothing, showed impulsiveness and assaultiveness. Mute. Blood pressure 108/66.

Sodium amytal. Showed intoxication, with narcosis following, after which he was more excited and condition was worse.

Sodium rhodanate. Became depressed, brief normal period then stuporous, negativistic, refused food, slept well, would not speak, but would shake hands. Blood pressure 100/62.

Sodium rhodanate stopped. Very slow recovery; is still improving. Will speak at times now.

Comment: In this case sodium rhodanate was given too rapidly; the alteration in dispersion was not of too severe a degree of agglomeration. The dosage carried him through into the opposite state which showed by his stupor and negativism.

Case 15

P. B. Male, aged twenty-nine, duration two months.
Diagnosis: Alcoholic Psychosis, Paranoid.
Behavior:

Before—excellent personal appearance, enjoys banjo music, at night is excited, noisy, restless, agitated, fearful and believes that he is to be attacked.

Sodium amytal. Very deep narcosis with periods of intoxication which were followed by increased fear, anxiety and agitation.

Sodium rhodanate. Slow steady improvement in behavior; would sleep entire night.

Sodium rhodanate stopped. Condition remained as above. Is ready to be paroled home.

Comment: This shows the positive reaction to rhodanate. The case was of short duration prior to hospitalization and no doubt his improvement can be considered due to the fact that agglomeration had not proceeded to a crippling degree. The rhodanate may or may not have had part in the recovery, as alcoholics improve on withdrawal of the alcohol.

Case 16

A. C. Male, aged fifty-one, duration three years.
Diagnosis: Manic Depressive, Manic.
Behavior:

Before—excited, restless, talkative, over-active, untidy, assaultive, irritable, sarcastic, refused to co-operate on the ward. Blood pressure 120/80.

Sodium amytal. Very quick response, very little drowsiness, stimulated, alert, interested, happy, singing on the ward and assisting other patients. Definite improvement.

Sodium rhodanate. Talkative, not restless, works on the ward, sleeps very well at night, appetite is improving; remains irritable and sarcastic. Blood pressure 106/60.

Comment: There is a large schizoid coloring in this case. He has had the disease for three years and is growing a little worse. There is evidently a narrow zone of normal dispersion. Arterio-sclerotic changes are appearing. Blood pressure showed a definite drop.

Case 17

R. M. Male, aged seventy-two, duration twelve years.
Diagnosis: Manic Depressive, Circular.
Behavior:

Before—over-talkative, over-active, restless, agitated, constantly getting into difficulty with others. Blood pressure 220/102.

Sodium amytal. Showed very deep narcosis, restlessness, agitation and excitement.

Sodium rhodanate. Became quiet, was clear mentally, co-operates with care and treatment; sleeps very well. Blood pressure 102/60.

Comment: The behavior picture was one of Manic Depressive, Manic type. He has always been hypomanic. Arterio-sclerosis is marked and there is a severe chronic myocarditis present. The blood pressure was much improved. Because of this and the cardiovascular disease, we cannot place the improvement as due to the action of the rhodanate on the colloidal state.

Case 18

J. K. Male, aged twenty-four, duration three years.
Diagnosis: Epilepsy.
Behavior:

Before—uneasy, talkative, restless, threatening, occasionally terrific excitement when he will require restraint to prevent injury. He would not co-operate with diet. Blood pressure 132/90.

Sodium amytal. Drowsy, deep sleep. On awakening would become irritable, restless, would not work, and refused to co-operate.

Sodium rhodanate. Slow steady improvement, became well-behaved, quiet, worked occasionally on ward which he does very well; sleeps entire night which is in contrast to previous behavior. Blood pressure 128/88.

Comment: This case falls definitely in the agglomerated or cycloid type. His improvement was not accompanied by any change in blood pressure.

Case 19

F. L. Male, aged seventy-two, duration twelve years.
Diagnosis: Manic Depressive, Manic.
Behavior:

Before—irritable, excited, destructive, usually assaultive, did not care for personal appearance. Blood pressure 160/100.

Sodium amytal. No stimulation, deep narcosis following which he became excited, over-active and mischievous.

Sodium rhodanate. Became quiet, well-behaved, worked some on the ward, sleeps well at night, takes care of personal appearance and was not assaultive. Blood pressure 118/74.

Comment: This is subject to the same criticism as Case 17. However, the reaction to each drug was so distinct that he is considered a positive reaction to rhodanate and not alone due to the fall in blood pressure.

Case 20

L. I. Male, aged thirty-nine, duration one month.
Diagnosis: Epilepsy.
Behavior:

Before—restless, over-active, frequent convulsions, marked elation, visual hallucinations present; very difficult to handle because of resistiveness and negativistic attitude.

Sodium amytal. Depressed, hallucinated, active, restless, irritable and disturbed.

Sodium rhodanate. Convulsions controlled, became quiet, worked some on the ward, was clear mentally, hallucinations were not present although he recalled them.

Sodium rhodanate stopped. Irritability returned, became negativistic, hallucinations reappeared. Suddenly developed status epilepticus and a cerebral haemorrhage from which he died.

Comment: The improvement under rhodanate was very positive. Dosage was 0.3 grams three times daily. He would be classified in the agglomerated group.

Case 21

D. D. D. Male, aged twenty-nine, duration twenty-one days.
Diagnosis: Manic Depressive, Depressed.
Behavior:

Before—depressed, worried, fearful, anxious, untidy in personal appearance, confused, constant supervision to prevent him from getting into difficulty; would not eat well. Blood pressure, 118/78.

Sodium amytal. Deep sleep, ataxia, became clear mentally, was happy, alert and able to discuss the situation. While in this state he was able to tell us of his fears, anxieties and delusions of persecution, and ideas of bodily harm.

Sodium rhodanate. Became sulky, sarcastic, noisy, irritable and violent, slept fairly well at night. Blood pressure, 112/70.

Comment: *Again we find our tests indicating that our classification was* wrong, that it was based on the symptoms presented to us by the patient and not on knowledge of his mental state. When contact was made, we then found a delusional state with fears and ideas of persecution, indicating a schizophrenia. He presents an over-peptized state that is improved by agglomeration. Because of our more adequate information we do not now consider that he is a case of Manic Depressive.

Case 22

J. S. Male, aged thirty-nine, duration two years.
Diagnosis: General Paralysis.
Behavior:

Before—quiet, but appeared uneasy, would not talk, had marked delusions of grandeur. Blood pressure 160/90.

Sodium amytal. Deep narcosis, was dizzy, and confused following this.

Sodium rhodanate. Became very quiet, lethargic, slept during day and very deep at night. Blood pressure 128/80.

Comment: This case is also receiving tryparsimide. He shows a severe neurological involvement indicative of wide-spread permanent lesions in the central nervous system. Of the two reactions we considered him improved by sodium rhodanate and therefore of the agglomerated group. In spite of this we classified him as inconclusive. He showed a definite fall in blood pressure.

Case 23

W. C. Male, aged forty-nine, duration six years.
Diagnosis: Manic Depressive, Manic.
Behavior:

Before—restless, uneasy, over-talkative, constantly complaining, assaultive at times, does not care for personal appearance although he had a good education and training. Did not co-operate with care or treatment. Blood pressure 180/90.

Sodium amytal. Drowsy, marked stimulation, intoxication, ataxia, much interested on ward, is over-active and excited. Condition improved.

Sodium rhodanate. Quiet, sleeps well at night, stopped his complaining, co-operates more readily with care and treatment, but does not care for his personal appearance, then became depressed and stuporous on increased dosage. Improvement returned when it was stopped. Blood pressure 142/80.

Comment: This individual has many schizoid characteristics but there are strong cyclic mood swings with affect and ideation still in contact and at an adult level.

Case 24

L. C. Male, aged forty-six, duration two months.

Diagnosis: Involution Melancholia.

Behavior:

Before—depressed, anxious, fearful, worried, constantly complaining of somatic difficulties. Restless at night, could not sleep. Blood pressure, 178/100.

Sodium amytal. More interested, alert, some improvement, deep sleep.

Sodium rhodanate. Appeared uneasy, stuporous, confused, did not talk, but slept well at night. Blood pressure, 146/80.

Comment: We find here that more definite information as to the mental content was obtained when the patient was able to discuss the situation more freely under sodium amytal. The somatic ideas were prominent and delusional in character. Schizoid tendencies predominated; this has been recognized in Involution Melancholia so that in this classification we have two types—one benign or cycloid-predominant which would recover, and the other schizoid-predominant with a poor prognosis.

Case 25

J. M. Male, aged sixteen, duration four years.

Diagnosis: Endocrinopathy.

Behavior:

Before—untidy, periods of explosive irritability alternating with neat, clean and tidy in appearance, co-operative, and well-behaved periods.

Sodium amytal intravenously, 0.5 grams. No narcosis; marked irritability with restlessness and resistiveness following.

Sodium rhodanate. No apparent effect.

Comment: This case is one in which the diagnosis has been deferred until further study on glandular reaction can be made. No conclusive results could be obtained.

Case 26

F. M. Male, aged thirty-one, duration four years.

Diagnosis: Dementia Praecox, Catatonic.

Behavior:

Before—would sit all day in one place, would not eat unless by direct supervision, was surly, irritable and negativistic.

Sodium amytal orally. Became more alert, interested, appetite was better and he assisted with work on the ward.

Sodium rhodanate. Stupor increased, became untidy, disinterested, indifferent and apathetic.

Comment: This also was similar to Case 1. Schizoid predominating. The reaction was very well defined. There had been a question of pulmonary tuberculosis but no positive findings have been obtained in sputum. He has not co-operated on chest examination. No loss of weight, no variation in temperature.

Case 27

P. H. M. Male, aged twenty, duration of psychosis four weeks; duration of diabetes three years.

Diagnosis: Psychosis with Diabetes (Diabetic tabes).

Behavior:

Before—this patient has diabetes. Blood sugar 250 mgms; developed a psychosis characterized by excitement, delusions, anxiety, restlessness, violence and confusion. Neurologically—loss of knee reflexes, changes in sensation (loss) in legs.

Sodium amytal orally. Patient showed brief periods of very deep narcosis, was sleepy, then excited, then normal sleep. On awakening was very irritable and restless, following this he became depressed and cried, then mute and would not co-operate on further examination.

Sodium rhodanate. Became more quiet, talked, gave as explanation of his depression that he is responsible for the death of many people.

Comment: This case is being studied intensively and will be reported by itself when complete data have been obtained. It is placed in the inconclusive group.

Case 28

H. L. Male, aged twenty-one years, duration one year.

Diagnosis: Dementia Praecox, Hebephrenic.

Behavior:

Before—untidy, dirty, slept well at night, usually quiet, many mannerisms.

Sodium amytal. Became drowsy, confused, ataxic, did not grimace, did not show mannerisms.

Sodium rhodanate. Was quiet, mannerisms disappeared. No definite change.

Comment: This case has shown severe deterioration and degeneration. Not much improvement could be expected mentally. Requires further study. This patient is very definitely schizoid.

Case 29

A. M. Male, aged forty-two years, duration six years.

Diagnosis: Dementia Praecox, Catatonic.

Behavior:

Before—quiet, untidy, negativistic, resistive.

Sodium amytal. Quite drowsy, confused, sleep periods increased, slightly more alert, no marked improvement.

Sodium rhodanate. Increased untidiness, more negativistic and more resistive.

Comment: A severely deteriorated case. A longer exhibition of sodium amytal would be indicated from test results.

Case 30

G. S. Male, aged thirty, duration unknown.
Diagnosis: Dementia Praecox, Hebephrenic.
Behavior:

Before—disturbed, noisy, slept poorly, untidy and destructive.

Sodium amytal. Sleeps well, is quiet, appears slightly drowsy, is not so noisy, but agitated.

Sodium rhodanate. Gradually became quiet, stuporous.

Comment: A deteriorated case also. Results inconclusive.

Case 31

A. A. Male, age fifty-five years, duration ten years.
Diagnosis: Dementia Praecox, Paranoid.
Behavior:

Before—always quiet, seclusive, untidy.

Sodium amytal. Drowsy, confused, no material change.

Sodium rhodanate. Became agitated, noisy, restless, did not sleep, became quite excited.

Comment: Although no improvement was obtained with the amytal, the reaction to rhodanate was so marked that this is considered to be an overpeptized state but with deterioration at such level as to make therapy a difficult problem.

Case 32

D. P. Male, aged twenty-nine, duration unknown.
Diagnosis: Dementia Praecox, Hebephrenic.
Behavior:

Before—uneasy, noisy, restless, agitated.

Sodium amytal. Drowsy, confused, short periods of excitement, improved; sleep periods increased; more quiet in behavior, more co-operative and more alert.

Sodium rhodanate. Did not sleep, became restless, uneasy, agitated, noisy and violent.

Comment: Similar to Case 31.

Case 33

H. C. Male, aged thirty-one, duration one month.
Diagnosis: Dementia Praecox, Hebephrenic.
Behavior:

Before—uneasy, restless, noisy, excited, assaultive and untidy.

Sodium amytal. Drowsy, confused, ataxia, then became quiet, slept well, well-behaved.

Sodium rhodanate. Became excited, disturbed, violent, did not sleep.

Comment: Cases 31, 32, 33 all showed the same severe reaction to rhodanate. Dementia Praecox cases, typed as Hebephrenic, Paranoid and Simple may present particulars of each so that typing may be very loose and is often interchanged. The paranoid does not exhibit usually as rapid a deterioration as either the Simple or Hebephrenic types. The test indicates the over-peptized state.

Case 34

E. D. Female, aged forty-five, duration three months.
Diagnosis: Manic Depressive, Depressed.
Behavior:

Before—restless, agitated, anxious, whining, sleeps very poorly.

Sodium amytal. Deep narcosis, followed by agitation, excitement and worry.

Sodium rhodanate. At first agitated, disturbed, became quiet, is clear mentally, is not so noisy, no longer untidy. Condition improved.

Comment: Cycloid predominating; positive response to sodium rhodanate.

Case 35

R. C. Female, aged thirty-nine, duration one year.
Diagnosis: Dementia Praecox, Catatonic.
Behavior:

Before—uneasy, quiet, restless, wanders about disturbed.

Sodium amytal. Deep narcosis, short periods of stimulation, became more alert, was co-operative; increased dosage resulted in excitement.

Sodium rhodanate. Became very noisy, depressed, stupid, unable to help herself, very untidy.

Comment: This case showed a very narrow zone for the improved reaction under amytal.

Case 36

A. G. Female, aged forty-eight, duration two months.
Diagnosis: Manic Depressive, Manic.
Behavior:

Before—over-talkative, excited, restless, untidy.

Sodium amytal. Became drowsy, stimulated, uneasy, alert, very free affect, was interested, co-operative and improved.

Sodium rhodanate. Became very noisy, restless, disturbed, assaultive and obscene.

Comment: This is a third attack. She is of a very unstable personality. Each attack shows a deeper level of regression. Schizoid characteristics predominate. The case is further complicated by the occurrence of the climacterium and resulting glandular imbalance.

Case 37

W. R. Female, aged twenty-two, duration six months.
Diagnosis: Dementia Praecox?
Manic Depressive, Manic?
Behavior:

Before—disturbed, restless, uneasy, violent at times, will stare continuously at ceiling.

Sodium amytal. Deep sleep, no intoxication, has shown steady improvement, is clearing very quickly.

Sodium rhodanate. Became stuporous, untidy, destructive and definitely worse.

Comment: This case was at first diagnosed Manic Depressive, then was changed to Dementia Praecox. From the test she would be considered as of the over-dispersed group. The diagnosis might very properly be catatonic schizophrenia. She would not co-operate in examination and further could scarcely speak English.

Case 38

E. T. Female, aged forty-seven, duration one year.
Diagnosis: Manic Depressive, Manic.
Physical condition—diabetes.
Behavior:

Before—disturbed, singing, restless, uneasy, would not keep clothes on, attacked other patients.

Sodium amytal. Deep narcosis, was more quiet, then became over-active and irritable.

Sodium rhodanate. Became less agitated, but remained quarrelsome, sleep periods increased.

Comment: Because of the presence of diabetes, this case was listed as inconclusive. She showed some improvement under the amytal, then was made worse. She was also improved by the rhodanate. As in the other diabetic, separate study is being done to determine if the variations in reaction have any relation to variations in her physical disease.

Case 39

L. P. Female, aged thirty-eight, duration six months.
Diagnosis: Dementia Praecox, Paranoid?
Behavior:

Before—restless, uneasy, crying, noisy.

Sodium amytal. Showed deep narcosis, marked intoxication, severe dizziness and excitement.

Sodium rhodanate. Became quiet, assisted with work, periods of excitement, short periods of restlessness. Has shown a steady improvement.

Comment: Positive reaction to sodium rhodanate. Therefore of the agglomerated group. No information as to mental content was obtained as she could not speak English and would not talk to the interpreter. She appeared under much fear which is not unusual with these cases.

Case 40

R. N. Female, aged twenty-eight, duration two months.
Diagnosis: Manic Depressive, Manic?
Behavior:

Before—noisy, destructive, disturbed, agitated.

Sodium amytal. Became very nauseated, showed much improvement.

Sodium rhodanate. Became quiet, would cry, was noisy and excited at times, then restless and destructive.

Comment: In this case diagnosis was based solely on observed behavior. No contact with patient could be obtained as she did not speak English. Severe regression in behavior was present. She would masturbate before other patients. The test indicated a state of dispersion.

Case 41

B. B. Female, aged thirty-two, duration two months.
Diagnosis: Dementia Praecox, Paranoid?
Behavior:

Before—disturbed, noisy, over-talkative, agitated, removed clothing.

Sodium amytal. Sleep periods increased, restless when awake, very ataxic, noisy, confused and unsteady, some excitement.

Sodium rhodanate. Gradually quiet, sleeps better at night, remains quiet, has not been noisy, has taken clothes off once.

Comment: Again we have a case in which the classification was based on presented behavior which was a mixture of both schizoid and cycloid tendencies. The test indicates an agglomerated state.

Case 42

E. B. Female, aged thirty-seven, duration two years.
Diagnosis: Dementia Praecox, Paranoid.
Behavior:

Before—agitated, suspicious, delusional, fearful, anxious and restless.

Sodium amytal. Drowsy, appeared slightly depressed, no change in delusions, agitation and restlessness disappeared.

Sodium rhodanate. Became disturbed, restless, crying, delusions increased; she made attempts to grab medicine and throw it out of the window and became excited when the nurses gave the medicine to other patients.

Comment: Although unimproved by sodium amytal she was made much worse by sodium rhodanate. She was considered as of the over-dispersed type; but was classed as inconclusive because of the indefinite result with sodium amytal.

Case 43

A. A. Female, aged fifty-eight, duration one month.
Diagnosis: Manic Depressive, Manic.
Behavior:

Before—disturbed, over-active, uneasy, agitated.

Sodium amytal. Showed marked intoxication, then alert, interested, more rational. After-effect showed increased irritability, was noisy and disturbed.

Sodium rhodanate. Became quiet, rested better at night, slightly irritable, uneasy, but did work on ward, sewing and playing cards.

Comment: This case shows manifestation of both Schizophrenic and Manic Depressive. She showed positive improvement under rhodanate and was considered of the agglomerated group.

Case 44

S. S. Female, aged fifty-one, duration five months.
Diagnosis: Involution Melancholia.
Behavior:

Before—yelling, noisy, restless, agitated and confused.

Sodium amytal. Deep narcosis followed by increased excitement.

Sodium rhodanate. Very disturbed, noisy, increased excitement, gradually became violent.

Comment: Improvement under amytal was not very much; under other barbiturates there was much better response.* The reaction to rhodanate indicates that we have a state of over-dispersion. The psychosis occurred at the climacterium which obscured the response.

Case 45

W. K. Female, aged fifteen, duration two years.
Diagnosis: Epilepsy.
Behavior:

Before—abusive, talkative, disturbed, restless, sulky and excited. No grand mal seizures.

Sodium amytal. Very deep narcosis, severe intoxication followed by excitement.

Sodium rhodanate. Motor activity decreased, became more quiet, slight improvement.

Sodium rhodanate stopped. Irritability and excitement returned.

Comment: This girl shows no grand mal seizures but instead petit mal and the psychogenic equivalents. Following these, acute excitement and assaults will occur. The test was positive indicating a decreased dispersed state.

Case 46

S. M. Female, aged thirty-five, duration two months.
Readmission—Manic Depressive, Depressed.
Diagnosis: Manic Depressive, Manic.
Behavior:

Before—very disturbed, abusive, noisy, screaming, tearing of clothing, crying, unclean.

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*From a study now in process by Dr. Benj. Pollack, Willard State Hospital.

Sodium amytal. Showed deep narcosis with severe intoxication following. Was noisy and disturbed, then drowsy and ataxic, followed by excitement and violence.

Sodium rhodanate. Became very disturbed, abusive, crying, whining, then confused. No definite improvement in the mental condition but improved behavior.

Comment: This is the second admission, the first one being twelve years previous. She shows more disturbed behavior. In the first admission she was depressed.

The forty-six cases are summarized in Tables I and II.

The Schizophrenic group is improved by sodium amytal. The two Paranoid cases with negative reaction to sodium amytal are really Manic Depressive, Mixed. The two inconclusive cases were made worse by sodium rhodanate; they are partial positive and correlate with the over-dispersed type. The Dementia Praecox, Catatonic improved by sodium rhodanate is really Manic Depressive, Mixed; and so is the Hebephrenic case made worse by sodium amytal. The Hebephrenic inconclusive was severely deteriorated. Our Involution cases were improved by sodium amytal, indicating a large schizoid factor. The Manic Depressive group, including the Manic Circular and Depressed states, are of the agglomerated type. Two of the Manic cases with negative reaction to sodium rhodanate are Schizophrenics and the depressed case improved by sodium amytal is really Dementia Praecox, Catatonia. The inconclusive case is so listed because of the presence of arteriosclerosis and chronic myocarditis. The case of Catatonia is really a benign stupor reaction and therefore considered of the agglomerated type.

The epileptics are made worse by sodium amytal and show improvement to sodium rhodanate. In the excited case of Mental Deficiency, the behavior reaction would classify it under the Manic Depressive group. Improvement with sodium rhodanate would be expected and did occur.

In the two alcoholics, one reacted with improvement to sodium rhodanate as might be expected. The other was improved by sodium amytal; but it was found that he had a delusional trend with splitting of emotional field, so that it should more properly be diagnosed as Schizophrenia. Only two cases of General Paresis were dealt with. Both have received large amounts of tryparsimide. One, the inconclusive case, was under treatment at the time, so that the sodium rhodanate had to be discontinued. He furthermore shows very severe neurological involvement.

The two diabetics fall in the inconclusive group. One showed a mixture of schizoid and cycloid characteristics with predominance of cycloid, and is receiving forty units of insulin per day. Much further study on this case is required before positive statements can be made. He, however, was excited under sodium amytal. The other one showed predominance of cycloid characteristics and gave a narcotic reaction to sodium amytal but showed improvement under sodium rhodanate. The case of Endocrinopathy was a mixture of schizoid and cycloid tendencies with mood fluctuation and regres-

TABLE I

Case No.	Initial	Sex	Age	Diagnosis	Duration of Psychosis	Behavior	Sodium Amytal	Sodium Rhodanate	Schizoid	Cycloid
1	J. D.	M	28	D. P. C.	5 yrs.	Stupor	Sedation Stimulation Improved	Depressed Stupor worse	+ + +	
2	C. S.	M	50	1. Alcoholic 2. Depressed	8 mos.	Stupor	Stimulated Alert Improved	Depressed Stupor worse	+ +	+
3	F. P.	M	54	Manic Dep. Manic	4 mos.	Elated Excited	Stimulated Extreme excitement	Quiet Improved Paroled		+ + +
4	W. M.	M	28	Epileptic	1½ yrs.	Convulsion Confusion	Narcosis Confused Irritable	Quiet Improved Cleared	+	+ +
5	M. S.	M	34	D. P. H.	5 yrs.	Agitated Excited	Stimulated Intoxicated Excited	Quiet Improved	+	+ +
6	C. P.	M	36	D. P. C.	6 yrs.	Excited Mute	Sedation Excitement	Stimulated Over-active Talkative	+	+ +
7	G. B.	M	22	D. P. C.	2 mos.	Stupor	Stimulation Improved	Stimulation increased Worse	+ + +	
8	J. L.	M	20	Catatonia	2 mos.	Negativistic Mute	Stimulation Intoxicated Excited	Quiet Improved	+	+ +

TABLE I (Continued)

No.	Initial	Sex	Age	Diagnosis	Duration	Behavior	S. A.	S. R.	Schizoid	Cycloid
9	E. B.	M	22	M. Deficiency	4 mos.	Excited	Stimulated Excitement increased	Quiet Improved Paroled		+ + +
10	F. K.	M	42	M. D. M.	3 mos.	Extreme Excitement	Stimulation Excitement Irritable	Quiet Improved		+ + +
11	C. M.	M	56	M. D. M.	10 yrs.	Irritable Excited	Narcosis Intoxication Irritable	Quiet Improved		+ + +
12	P. F.	M	48	G. P. I.	?	Excited	Narcosis increased Irritability	Quiet Less Agitated	+	+ +
13	W. H.	M	62	M. D. C.	10 yrs.	Alternating Depression Excitement	Narcosis Excited Assaultive	Quiet Improved		+ + +
14	G. Y.	M	40	M. D. M.	2 mos.	Excitement Depression	Narcosis Excited Assaultive	Depressed Negativistic Improved	+	+ +
15	P. B.	M	29	Alcohol	2 mos.	Agitated Fearful	Narcosis Intoxicated Agitated	Quiet Improved	+	+ +
16	A. C.	M	51	M. D. M.	2 yrs.	Excitement Assaultive	Stimulated Intoxicated Irritable Improved	Quiet Still irritable	+ +	+

TABLE I (Continued)

No.	Initial	Sex	Age	Diagnosis	Duration	Behavior	S.A.	S. R.	Schizoid	Cycloid
17	R. M.	M	72	M. D. C.	12 yrs.	Agitated Irritable	Narcosis Excitement	Quiet Clear Improved		+ + +
18	J. K.	M	24	Epileptic	3 yrs.	Convulsions Excitement Agitated	Narcosis Intoxicated Irritable	Quiet Improved		+ + +
19	F. L.	M	72	M. D. M.	12 yrs.	Excited Destructive	Narcosis Excited	Quiet Improved		+ + +
20	L. I.	M	39	Epilepsy	1 mo.	Elation Hallucinated	No change	Improved No convulsion	+	+ +
21	D. D. D.	M	29	M. D. D.	21 days	Depression Fearful	Narcosis Intoxicated Improved	Excited Irritable Worse	+ + +	
22	J. S.	M	39	G. P. I.	2 yrs.	Uneasy Delusional	Narcosis Unimproved	Depressed Lethargic No improvement	+	+ +
23	W. C.	M	49	M. D. M.	6 yrs.	Irascible Disturbed	Narcosis Intoxicated Excitement Improved	Depressed Stuporous	+ +	+
24	L. C.	M	46	Inv. Mel.	2 mos.	Depression	Stimulated Alert Improved	Uneasy Stimulated Confusion	+ +	+
25	J. M.	M	16	Endocrinopathy	4 mos.	Irritable	Stimulated More irritable	No effect	+ +	+

TABLE I (Continued)

No.	Initial	Sex	Age	Diagnosis	Duration	Behavior	S. A.	S. R.	Schizoid	Cycloid
26	F. M.	M	31	D. P. C.	4 yrs.	Negativistic Mute	Alert Stimulated Co-operative	Stupor Increased Worse	+ + +	
27	P. H. M.	M	20	Diabetes	3 mos.	Excitement Negativistic	Narcosis Excitement	Quiet	+	+ +
28	H. L.	M	21	D. P. H.	1 yr.	Untidy Mannerisms	Sedation Intoxication Depressed	Quiet	+ + +	
29	A. M.	M	42	D. P. C.	6 yrs.	Negativistic	Sedation Confusion Slight imp.	Increased Untidiness Negativistic Resistive	+ + +	
30	G. S.	M	30	D. P. H.	?	Noisy Destructive	Sedation Quiet Agitated	Depressed Stuporous	+ + +	
31	A. A.	M	55	D. P. H.	10 yrs.	Untidy Seclusive	Sedation Confusion No change	Agitated Excitement Stuporous	+ + +	
32	D. P.	M	29	D. P. H.	?	Restless Agitated Noisy	Sedation Quiet More alert	Excited Noisy Violent	+ + +	
33	H. C.	M	31	D. P. H.	1 mo.	Resistive Restless Assaultive	Sedation Intoxicated Improved	Excited Violent	+ + +	

TABLE I (Continued)

No.	Initial	Sex	Age	Diagnosis	Duration	Behavior	S. A.	S. R.	Schizoid	Cycloid
34	E. D.	F	45	M. D. D.	3 mo.	Agitated Fearful	Narcosis Agitated Excitement	Quiet Improved	+	+ +
35	R. C.	F	39	D. P. C.	1 yr.	Agitated Depressed	Narcosis Stimulated Alert	Noisy Depressed Stupid	+ + +	
36	A. G.	F	48	M. D. M.	2 mos.	Excited Untidy	Sedation Intoxication Improved	Noisy Excited Assaultive	+ +	+
37	W. T.	F	22	D. P. P.? M. D. M.?	6 mos.	Agitated Confused Mannerisms	Sedation Steady Improvement	Stuporous Destructive	+ +	+
38	E. T.	F	47	M. D. M. Diabetes	1 yr.	Agitated Assaultive Elated	Narcosis Overactive Irritable	Agitated Irritable Normal sleep	+	+ +
39	L. P.	F	38	D. P. P. ?	6 mos.	Agitated	Narcosis Intoxication Excitement	Quiet Improved	+	+ +
40	R. N.	F	28	M. D. M. ?	2 mos.	Agitated Destructive	Severe intoxication Improvement	Noisy Quiet at times Restless Destructive	+ +	+

TABLE I (Continued)

No.	Initial	Sex	Age	Diagnosis	Duration	Behavior	S. A.	S. R.	Schizoid	Cycloid
41	B. B.	F	32	D. P. P.	2 mos.	Agitated Excited	Stimulated Intoxicated Excited	Quiet Improved	+	+ +
42	E. B.	F	37	D. P. P.	2 yrs.	Agitated Suspicious Delusion	Stimulation Intoxication	Excited Delusions increased	+ + +	
43	A. A.	F	58	M. D. M.	1 mo.	Agitated Over-active Excited	Stimulated Intoxicated Alert	Excitement Became quiet Sleep periods increased	+	+ +
44	S. S.	F	51	Inv. Mel.	5 mos.	Agitated Excited Noisy	Narcosis Excitement Some imp.	Excitement increased Violent	+ +	+
45	W. K.	F	15	Epilepsy	2 yrs.	Agitated Excited Assaultive	Narcosis Excitement	Motor- Activity decreased Improved		+ + +
46	S. M.	F	35	M. D. D. (1st Admission) M. D. M. (2nd Admission)	2 mos.	Agitated Assaultive Abusive Excitement	Narcosis Intoxicated Excited	Quiet Confused Stuporous Improved behavior		+ + +

sion in behavior. Because of the alternation between excitement and quiescence, we could not avoid the consideration of a coincidental factor in the exhibition of our drug.

TABLE II

	Sodium Amytal		Sodium Rhodanate			
Diagnosis	Improved	Worse	Improved	Worse	Inconclusive	Total
D. P. Paranoid		2	2		1	3
D. P. Catatonic	6			6	1	7
D. P. Hebephrenic	2	3	3	2	1	6
Alcoholic	1	1	1	1		2
Manic Depressive	3	11	11	3	1	15
Catatonia		1	1			1
Excitement (Mental Deficiency)		1	1			1
Epileptic		4	4			4
Involution Melancholia	2			2		2
General Paralysis		1	1		1	2
Endocrinopathy					1	1
Diabetes					2	2
	14	24	24	14	8	46

The data in regard to blood pressures are tabulated in Table III.

TABLE III

Blood Pressures*

	Case	Before	After	S. A.	S. R.
5	D. P. H.	110/68	102/72[1]	−	+
10	Manic	130/60	116/68[1]	−	+
11	Manic	118/80	122/82[1]	−	+
14	M. D. M.	108/66	100/62[1]	−	+
16	M. D. M.	120/80	106/60[2]	−	+
17	M. D. C.	220/102	102/60[2]	−	+
18	Epilepsy	132/90	128/88[1]	−	+
19	M. D. M.	160/100	118/74[2]	−	+
21	M. D. D.	118/78	112/70[1]	+	−
22	G. P. I.	160/90	128/80[2]		Inconclusive
23	M. D. M.	180/90	142/80[2]	−	+
24	Involution	178/100	146/80[2]	+	−

* From a study, in preparation by Dr. Robt. Wise, Willard State Hospital.

[1] Slight changes that are easily within normal variation.

[2] Very definite changes in blood pressure. Only four show changes in the systolic pressure of over ten points (Hg).

Of the twelve cases observed, six showed slight changes of blood pressure that were easily within normal variation and six showed very definite changes. These are summarized as follows:

Cases showing slight or no change:		
D. P. H.	1	Improved by rhodanate
Manics	4	3 Improved by rhodanate 1 Improved by amytal
Epileptic	1	Improved by rhodanate
Cases showing marked fluctuation:		
Manic	4	4 Improved by rhodanate
G. P. I.	1	No reaction
Involution	1	Improved by amytal

There is no evidence from these observations that a fall in blood pressure is necessarily connected with improvement of the mental state. They indicate, however, two types of cases, in one of which the blood pressure falls appreciably and in the other no definite change occurs.

Conclusions

It is considered:

(1) That this study has demonstrated definitely that the functional psychoses show a correlation between the syndromes presented and the state of dispersion of the cell colloids.

(2) That in schizophrenia (Dementia Praecox) the colloidal system is in a state of over-dispersion.

(3) That in the manic depressive psychoses the colloidal system is in a state of agglomeration or decreased dispersion.

(4) That, although only four epileptics were observed, the reaction was so definite as to indicate an agglomerated state of the colloidal system.

(5) That catatonia is correlated with a state of over-dispersion.

(6) That benign stupor reactions, although appearing very like catatonia, react to tests as though they are of the agglomerated state.

(7) That, based upon the correct appreciation of the colloidal states in these syndromes, a more rational therapeutic approach may be made in the treatment of such cases.

It is not suggested that, in psychoses of either organic or functional origin, these drugs are the sole method of treatment, but only that they may be used as an aid in determining the effect of such mental states on the brain colloids. Known and applicable methods of treatment should and must be used; but a greater appreciation of the effects of such therapy can now be made.

Willard State Hospital,
August 31, 1931.

THE COLLOID CHEMISTRY OF INSANITY. II*

BY WILDER D. BANCROFT AND J. E. RUTZLER, JR.**

So far as we can learn, the theories of insanity vary all the way from the purely pathological to the purely psychological. C. Stanford Read[1] says in regard to insanity. "This term ordinarily connotes more or less severe unsoundness of mind. Though its loose usage is almost synonymous with mental disease, scientifically the term should only be applied to the mental condition of an individual who, through socially inefficient conduct, has to be placed under supervision and control. The mind is the mechanism by means of which we adapt adequately to our environment and when, through its derangement, conduct is exhibited which the community looks upon as evidence of disease and as implying irresponsibility, the individual concerned is said to be insane and the law steps in to certify him as such. Strictly speaking, then, insanity is really a social and legal term and not medical. Mental illness is a broad concept which may include very efficient members of society. No satisfactory definition can therefore be arrived at, since it would be necessary to define what we mean by sanity, which would involve us in equal difficulties.

"It is unnecessary to dwell upon the mystical conceptions of insanity which were held in the middle ages, and it will be sufficient to note that it was only towards the close of the eighteenth century that this sphere of mental disorder was scientifically studied. This was a period in which materialism flourished and research devoted to the anatomy and physiology of the brain gave the workers reason to believe that the nature and cause of insanity would before long be discovered, since the advance of knowledge in the structure and functioning of the central nervous system was progressing at a rapid rate. A school of thought therefore held sway which founded insanity on a physiological basis and endeavoured to base all pathology in terms of organic change in the brain. Although the great value of this method cannot be gainsaid, there is ample evidence that other aspects of approaching the problem of insanity are essentially necessary. Of late years another school has advanced the belief that the majority of cases of insanity are psychogenic in origin and that, even where gross physical disease has been the exciting factor, the symptoms can only be adequately understood at the psychological level. Others, again, prefer to take a wider view-point still and regard insanity in the light of biological or psycho-biological reactions.

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*This work is done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

**Eli Lilly Fellow.

[1] Encyclopaedia Britannica, 12, 383 (1929).

Modern psychological knowledge would lead us to believe that the understanding of much of the subject is made clearer when we regard it in the light of instinctive forces conflicting with environment and resulting in a failure of adjustment. The mental symptoms cannot be rightly spoken of as a disease but as types of reaction through the effort on the part of the individual to meet conditions. . . . The materialistic school would hold that, though in many states of insanity no observable structural changes are found, they exist all the same, only they are such that our imperfect methods cannot detect them, and in time they will be discovered. At present we have insane conditions divided into those that are regarded as functional and those that are organic. In the former we have mania, melancholia and paranoia, and some would include dementia praecox. The psychogenic school would argue that, though mental disease may arise secondarily to physical disorder, the symptoms are psychological reverberations of that disorder and the body of an individual must be regarded as environmental to the ego. In an integrated organism, though the basis of the wrong functioning lies in the physical sphere, some of the effects are manifested at the psychological level. The symptoms, then, are expressions of the personality, and however much we may stress the bodily aspect, that can in no way explain the content of a delusion or a hallucination. The fact that some individuals may take alcohol to the extent of producing severe physical disease without affecting the mind, and others will fall victims to insanity through its use, proves that psychic factors cannot be left out of the calculation. The many structural changes which are found in certain forms of insanity should be reviewed as probably secondary to a perverted mentality. The bodily effects of emotion are well known and it can easily be surmised that long-continued emotional stress should in time be followed by organic change. During the World War we had ample evidence of this. As McDougall says, 'mind has a nature and a structure and functions of its own which cannot be fully and adequately described in terms of structure of the brain and its processes.' If this be true, as he thinks, it does not seem logically impossible that the nature of the mind itself may be disordered or impaired or defective. It seems, then, that we must steer clear of belonging to one or other of the extreme camps when we view the nature of insanity, but take a very wide vista which will embrace the study of the individual, his personal and racial history, his environment, and his physical and mental structure."

In a presidential address before the American Psychiatric Association, Dr. W. A. White[1] of Saint Elizabeth's Hospital in Washington has presented the case for the psychiatrist in an admirably clear manner.

"Since the advent of psychoanalysis we for the first time have our vision directed to where the real trouble has taken place, and our interests centered upon the actual mechanisms that are producing the symptoms. We understand that the deflection of our vision to the body or to the infectious organism are but examples of that mechanism of projection with which we have

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[1] Am. J. Psychiatry, 5, 1 (1925).

become so familiar, and that it was because of the emotional necessity for seeing causes otherwise than in ourselves that we for so many centuries have been unable to face the facts of our own mental life. The tendency to refer all mental diseases to either an exclusively somatic or infectious etiology is, I believe, a regressive tendency in psychiatry. Of course I do not want to be understood as saying that physical disease or infection plays no part in the etiology of the psychoses, although I am not at all sure that such a thesis might not be entertained. Still we are hardly ready for such an extreme position as yet. But the very fact that there are organs that should be removed in whole or in part makes it all the more difficult to discover and to overcome the compromises with tradition and superstition which are hidden behind the concepts of infection or the enucleating operations of surgery. The emphasis is undoubtedly for the first time where it belongs, and when I said that perhaps a thesis could be maintained that would eliminate the consideration of the soma or the pathogenic organism as etiological factors in mental disease I had in mind that one of the results of this new point of view has been, I will not say the development, because matters have not gone far enough perhaps to warrant such a phrase, but the beginning of the development, at least, of a theory of disease, speaking in the large, which for the first time looks as if we might be able to compass the understanding of what we have heretofore spoken of as pathological and abnormal, two terms which have always carried an implication that the things to which they refer were in some way outside of the natural order of things."

At the other extreme from Dr. White is Dr. Henry A. Cotton[1] of the New Jersey State Hospital at Trenton. His book was written before Dr. White's presidential address.

"For years we have been content to consider mental disorders in two large groups, designated as 'organic' and 'functional.' This division was based on the fact that in the first group pathological changes in the brain tissue, which would account for the 'mental disease' were demonstrable, while in the so-called functional group, for a long time, investigations, owing to inadequate methods, failed to reveal changes in the brain which could account for the mental symptoms.

"This led to the erroneous viewpoint that certain mental disorders could occur independently of any changes in the brain. From this view we unhesitatingly dissent. A too literal interpretation of Virchow's cellular hypothesis had led to the hasty and erroneous conclusion that because the cell looked normal in arrangement and outline it was necessarily normal in function. Among others, the English physiologist, Haldane, has recently called attention to the gross error of this view. This erroneous hypothesis that the mind is independent of the brain, was further supported by the fact that no recognizable physical disease was formerly known to exist in these patients. By exclusion, therefore, mental factors came to be accepted

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[1] "The Defective, Delinquent and Insane," 11-15, 16-18, 22-27, 120-122 (1921).

as the sole cause operating in this group. It followed that if mental factors caused 'mental diseases' necessarily mental treatment was the only method which could promise a cure.

"That such a conception is erroneous can be demonstrated by the entire lack of success in such treatment of this type of disease in the last fifty years, during which time the mental picture has been subjected to the closest analysis, and every possible form of psychic treatment has been tried and proved useless. This is evident also from the fact that the percentages of recoveries of this class of patients have decreased rather than increased in the last few years and that at present we have an ever-growing net annual increase in our insane population. In Massachusetts, for instance, the proportion of recoveries to admissions is only 6.9 percent and if improved cases are included the ratio is only 24 percent. It is conservative to state that not over 25 percent of the patients admitted to state hospitals throughout the country are sufficiently improved to leave the institutions permanently. This rate is due entirely to spontaneous recovery, not to any definite therapy, either psychoanalytical or otherwise."

"One has only to turn to works on modern medicine for condemnation of this misinterpretation of the relation of function to structure. Hewlett has recently stated: 'It is true that in the last analysis all disturbances of function must be capable of explanation in terms of physical or chemical changes in the body, cells and fluids.' Anatomical investigations have repeatedly shown that conditions which have been classed among the functional diseases possess, in reality, an anatomical basis."

"Conklin states: 'The mind is related to the body as function is to structure.' Also, 'Any cell may be functionally modified in a thousand different ways without any change being evident to the human eye.' This is entirely in accord with the view of many surgeons who have found that the functional disorders of the stomach and other organs reflexly caused by the appendix have been relieved by the removal of appendices which showed neither gross nor microscopic lesions. The explanation of this relief is that the epithelial cells of the appendix have undergone invisible but extensive biochemical alterations, permitting the passages into the lymphatics of bacteria and toxins which it was their function to prevent but which alterations, either for lack of time or for other reasons, failed to cause distinctly visible changes.

"While psychiatrists, in the past, have held the non-biological view of the nature of the so-called mental disturbances, the biologists have produced evidence regarding function and structure which when applied to mental disorders will, undoubtedly, modify these traditional ideas. The biologists are definite in the assertion that there can be no function without structure. This being true it would also be true that there can be no abnormal function without a correspondingly abnormal structure. Medical men have been willing to admit this fundamental law so far as it related to other organs in the body but there has been some hesitancy in accepting this truth when applied to the brain and the mind. If we could conceive of a mental state independent of the brain, and all known facts refute such a belief, then we could believe that certain forms of insanity were diseases of the mind and not diseases of the brain.

"Conklin is emphatic in his opinion that the mind as well as the body develops out of the germ. It cannot be considered apart from the body. *Every known scientific fact substantiates this viewpoint.* When the brain tissue is affected or destroyed the patient becomes deteriorated or demented and finally there is no evidence of functioning of the mind. When the brain is congenitally abnormal and does not develop properly, as in idiocy and imbecility, the mind is either retarded in development or entirely absent.

"Investigations, in certain types of insanity, as our technique for conducting them has developed, have shown conclusively that a disturbance in the anatomical structure of the brain accompanies the mental symptoms. Thus, in paresis, there are now always demonstrable distinct changes in the brain as a result of the invasion of the brain tissue by the organism of syphilis and finally in such cases the mind ceases to function. In senile dementia, the insanity of old age, it has been found that the disease is a result of definite destructive changes in the brain tissue. In arterio-sclerotic brain disease a similar condition is found, due to the diseases of the arteries and disturbances of the brain tissue. The deterioration in dementia praecox can also be cited as a similar example. In alcoholic mental disorders, on the other hand, while the effect of the poisoning by alcohol is clinically evident, and while the withdrawal of the alcohol and the elimination of the poison from the system causes the mental symptoms to disappear, the transient changes in the brain cells may or may not cause visible lesions.

"With these known facts as a basis one might well inquire why the other types which formerly have been designated as functional and of unknown origin should be considered so entirely different from the types which investigation has shown to bear out the law that function is dependent upon structure. Success in the treatment and prevention of this large group of mental disorders depends upon the establishment of a definite relation between the mental symptoms and pathological conditions in the brain tissue; and while this may be difficult to demonstrate conclusively, sufficient data are at hand to prove that such a relation does exist and that the abnormal mental symptoms disappear when the abnormal brain conditions are corrected."

"It should be said that the primary lesion which determines the abnormal mental state is most frequently not to be found in the brain itself. The brain cells are constantly influenced by abnormal conditions in other parts of the body through the circulation. Anatomical lesions of other organs of the body are known to change the metabolism, contaminating the blood with abnormal products, which in turn disturb the chemical exchange and nutrition of the cells of the brain. Thus, frequently, there is a direct action on the cerebral elements by the morbid agents carried directly through the circulation. The result may be coarse and extensive lesions, such as result from a large hemorrhage, or fine, diffuse, and frequently invisible lesions; either one of these may be the result of the action of various toxins. Or, the brain tissue itself, by the invasion of micro-organisms, such as those responsible for syphilis, may be in part destroyed, leaving instead of the normal nerve cells non-nervous replacements, a condition which actually occurs in paresis. The effect of toxins of any origin, whether produced by alcohol or by bacterial infection, may be temporary or permanent. Thus, in delirium tremens, the result of alcohol poisoning, we have a profound mental disturbance. This, however, may disappear within twenty-four hours after the alcohol is withdrawn and the patient has had a good night's sleep. No lesion may be found in the brain. In other forms of alcoholic mental disturbance the symptoms may not be so profound, in fact they may be mild when compared to delirium tremens, still the degree of poisoning may be so severe and of such long duration that a withdrawal of the alcohol will not alleviate mental symptoms and in such cases brain cell changes may be found.

"In other words, the changes in the brain, the result of poisoning, may have reached such a stage that repair is no longer possible, even after the toxin is eliminated. They are permanent and often visible. It is logical to assume that these conditions hold good in other types of mental disorders, the result of bacterial toxemias. This explains why a certain percentage of patients among the manias and melancholias recover spontaneously, even when the symptoms exhibited are very profound and severe, while in other types, such as dementia praecox, in which the toxemia is chronic, continuous, and of long duration, the patients will go on to rapid deterioration, in many cases showing no tendency towards a spontaneous recovery.

"From the fact that certain serious mental disturbances do permit of spontaneous recovery it has been argued that the brain itself could not have been affected, but this is not necessarily true as we have already seen, on bio-chemical evidence, as well as clinically in delirium tremens. In this condition we know that the brain has been seriously affected but with the removal of the alcohol it becomes perfectly normal again. Therefore, it cannot be argued that because of recoveries in the acute psychoses the brain has not been affected. Moreover we have seen many recoveries among the acute psychoses occur in a day or two after the removal of the chronic foci of infection.

"It is evident from these considerations that the interpretation of the so-called functional mental disorders is following the course already taken in functional diseases of other organs, i.e., *that we have to recognize the physical nature of the disturbance.*"

"The traditional attitude of psychiatrists that mental disorders were in fact diseases of the mind and not, as we are forced to believe today, disorders of the brain, has led students of the subject to concentrate their attention exclusively upon the psychogenic or mental factors, ascribing to them and to heredity the most important role in the causation of these diseases. No attempt is made to eliminate entirely the importance of the mental factors in producing a psychosis for they have their proper place. They are, however, of secondary importance to the toxic factors about to be described.

"It is idle to deny that worry, grief, shock, mental overwork and other factors have a distinct role in this mechanism. They undoubtedly occur in a large number of patients, but, on the other hand, in a number of cases they are absent. Is it not fatuous to suppose that because present in some cases they must be present in all, even when a thorough investigation fails to disclose them? The relative importance of the psychogenic factors diminishes in proportion as they are found to be absent.

"Of what practical value is it to strive to see things that cannot be demonstrated? We are not in accord with the extreme Freudian who wants to account for all psychoses on a sexual basis. Such dogmatic reasoning has led to the conclusion that mental disorders could be cured only by mental therapy and we know that such treatment has been in general very disappointing.

"Mental factors are contributory in the mechanism of the psychoses. Such factors undoubtedly lower the patient's vitality—lower the immunity to infection and produce profound physical disturbances. The loss of appetite, disturbance of nutrition, loss of sleep,—the result of these psychogenic factors—will cause latent infections, which may have existed for years, to become active and virulent.

"It is probable that the emotional reactions, having a profound effect upon the ductless glands, lower the resistance sufficiently to allow the latent infection to become active. It must be admitted that the exact mechanism is not known. Further investigations will help to decide the relation of emotional disturbances to the pathology of the ductless glands and infection.

"No matter what the outcome of such investigations may be, we do know that the infections should be considered far more important in the production of mental disease than heredity, mental factors, environmental defects, personality, and improper training, because they can be directly controlled.

"Many cases occur in which such causes as love affairs, disappointment in love, domestic difficulties, conjugal disharmony, financial reverses,—to mention only a very few,—are considered to be the only cause of the psychosis. In these cases we have never failed to find serious and often extensive local foci of infection. Following the removal of this infection, if the disease has not been of too long duration, the mental disturbance is very apt to adjust itself. Often these patients have to return to the same environment and their domestic difficulties cannot be disposed of as they should be for the comfort of the patient.

"But, in spite of these unfortunate situations, many of our detoxicated and recovered patients have been able to weather the storms and to go through difficulties which would have sent them back to the hospital in former days. One history should be cited to show the effect of detoxication by the removal of focal infection, not only in restoring the patient to a normal mental state, after a period of ten years of almost constant hospital residence, without normal intervals, but also to show how she met and conquered real domestic difficulties after her return to her home.

"This patient had suffered from depression with intervals of slight improvement, during which efforts had been made to keep her at home, but having on two occasions made attempts at suicide she had to be returned to a private hospital. During this time she had no thought for her husband as she was too self-centered and took no interest in his affairs. As a result the husband became interested in other women. Three months after admission to the State Hospital, she recovered, following the removal of her infected tonsils, her infected teeth having been extracted on admission. The change was most pronounced. When admitted, she was thin, emaciated, and spent her time standing in the corner of her room taking no interest in her surroundings, whining and crying. She gained rapidly in weight and her appearance changed from a very pitiful sight to one of great attractiveness.

"When she recovered the husband was reluctant to take her home. She found a very unpleasant condition of affairs. Her husband was infatuated with another woman of ill-repute, and did everything he could to get her back to the hospital, even threatening her with divorce and bringing this woman to live with the patient's children. Our sympathy was aroused and on investigating the circumstances we found her statement correct and not delusional, as her husband would have had us believe. She accepted a position in the hospital for the time being, hoping that matters would improve. Finally, she returned home and after a year or more of extremely bitter experience, the situation adjusted itself and there is no further trouble. She recovered in the fall of 1918 and in spite of this harrowing experience she never had any return of her former depression, although, according to those who place so much stress upon the psychogenic factors, there was ample cause. It is significant to note that at the time of the onset of her trouble no psychogenic factors were present, at least not to the extent following her recovery and return home. It is also important to note that the psychosis was of ten years' duration and recovery followed removal of the tonsils.

"There can be no doubt that the endocrin system plays an important role in the mechanism of mental disorders. The ductless glands, notably the thyroid, thymus, pituitary, adrenals, and sex glands, when they are functioning normally, furnish very definite and specific secretions, which are necessary to the proper development and functioning of the various activities of the entire organism. The activities of these glands are very closely related; disturbance of one undoubtedly causes disturbances in the others. Their function may be inhibitory or stimulating, thus maintaining a proper equilibrium in the body.

"The nervous system is very sensitive to disturbances of the ductless glands and we know definitely that the thyroid exerts a specific influence on it as well as on the sex glands. Cannon and other physiologists have shown that an infinitesimal portion of a grain of the internal secretion of the adrenal gland will cause an amazing reaction in the bodily metabolism.

"Likewise, the absence of thyroid secretion causes a mental condition known as cretinism, in which the patient has all the appearance of an imbecile. If extract of the thyroid gland is fed to these patients, early enough, the mental disease may be arrested. There are also other conditions in the adult, known as myxoedema, and caused by lack of thyroid secretion, which can also be relieved by feeding thyroid extract. An excess of secretion by these glands, or an abnormal secretion, may also exert a toxic influence on the whole body, especially on the nervous system.

"The treatment of conditions due to hyperactivity of the glands is much easier than treatment directed to supplying a deficient secretion. In the former case very often the glands can be partially removed by surgical means and thus rid the system of the excess secretion. This is especially true of the thyroid, a large proportion of which can be removed without danger to the patient. The other glands are not so easily removed.

"It is not altogether clear what factors are concerned in producing these disturbances of the ductless glands. It has been demonstrated that anger, fear, and other emotional disturbances, acting through the sympathetic system, will materially, but transiently, affect the secretions of these glands. Psychogenic factors, then, existing over prolonged periods, may well cause extensive disturbance in the ductless glands, producing at first an abnormal hypersecretion, often followed by a distinct, permanent, structural change. It is possible that such disturbances occur independent of chronic infection, but we have found that these disturbances of the ductless glands are closely related to infection.

"Our experience is entirely in accord with that of Billings, Barker and others, namely that the chronic infections have a direct secondary influence upon the ductless glands. These observers are of the opinion that it is possible to restore the function of the ductless glands by removing chronic foci of infection. For instance, an enlarged thyroid will frequently return to normal, following the removal of infected teeth and tonsils. This restoration, however, is proportionate to the amount of damage caused in the thyroid gland by the circulating toxin. If this damage has gone beyond the point of repair, as is frequently the case, then the abnormal condition can be remedied only by excision of the gland. Very few of our patients were benefitted by efforts to correct conditions in the ductless glands, without first eliminating the infection and toxemia. Consequently, we are inclined to believe that infection and toxemia are the primary factors in the majority of cases, and that the disturbance of the ductless glands is secondary.

"Further investigation in this field is necessary before final and definite conclusion regarding the role of the ductless glands in the mechanism of mental disorders can be reached. Enough is known, however, to make certain that the first step in the treatment is to remove the chronic foci of infection, then, if disturbances of the ductless glands persist, and it can be determined that the failure of the patient to recover is due to such disturbances, measures directed toward this secondary condition should be instituted. It is highly probable that in a small number of our unsuccessful cases the failure is due to the persistance of these disturbances. Much work yet remains to be done in this most important field.

"From the discussion of the factors involved in the production of a psychosis it can be seen that the causes vary in different individuals. In some cases hereditary influences may produce a distinct susceptibility and create a more fertile soil for the development of a psychosis. Emphasis, however, must be laid on the fact that while this influence may favor such a development it is not essential to its production. Furthermore, while psychogenic factors, when present, also exert an important influence, these may be absent and yet a psychosis may develop. The most important and constant factor is the toxemia resulting from chronic infections.

"In the majority of mental cases there is undoubtedly a combination of the factors already discussed and all should be taken into careful consideration in the effort to restore the patient to a normal mental condition. In some instances the hereditary and psychogenic factors may appear to be most prominent and in others the infections and disturbances of the ductless glands. In the treatment of mental disorder it must be realized that hereditary influences cannot be changed. The attack then should be directed upon the factors which can be eliminated from the patient's system, which, in the present state of our knowledge, is limited to the chronic infection referred to above."

"Unfortunately for the many chronic patients confined in hospitals for the insane today, their disease has progressed to the stage where remedial therapy is entirely unsuccessful. There are at the State Hospital at Trenton 900 cases of dementia praecox, none of whom will ever recover. It has been difficult to impress this fact upon the friends and relatives of the chronic patients who apply for admission to the State Hospital. To this class of patients, and especially their friends, undoubtedly the publicity given to this work has been most unfortunate. It has aroused hope for treatment in these cases when as we have explained none can be expected.

"We have stated repeatedly that nothing can be done for the chronic patients, especially dementia praecox in the terminal stage. But, in spite of all this, the idea persists that these methods are applicable to all stages of the disease. Elimination of infection to be effective in arresting the mental symptoms must be instituted *early*, otherwise no favorable outcome can be expected. The reason for this is that the brain tissue has probably become permanently affected as a result of the long-standing toxemia and no repair is possible, even with the elimination of the original infection. But, the situation, in the early stages of the chronic mental disorders, is quite different. When treatment is instituted early it has proven successful in arresting the mental symptoms whether diagnosed as dementia praecox—the deteriorating type of psychosis,—or manic depressive insanity which tends toward spontaneous recovery. This statement is supported by the fact that the chronic cases in the State Hospital have not increased in the last three years, in fact there has been actually a decrease and not an accumulation of those patients as was formerly the invariable rule. Over 50 percent of the permanent residents belong to the dementia praecox group. Practically all of these cases could not only have been prevented but their symptoms arrested after the onset, if the methods of eliminating chronic infection had been applied. There can be no excuse for failure to treat such cases in early stages now that the cause is known. No stronger plea could be offered for the prosecution of the work outlined in these pages than the effect it has had in arresting the ever-increasing number of human derelicts, now consigned, for the rest of their years, to mental obscurity and darkness.

"The 'do-nothing' policy of those who continue to oppose any form of treatment, because they are convinced that insanity is the result of hereditary causes and constitutional defects and, therefore, inevitable and incurable, is beyond comprehension. However, for these afflicted individuals there is the prospect of the dawning of a better day. These relics of medical superstition and barbarism will be supplanted by modern biological conceptions based upon the proper recognition of the true relation of structure to function."

Bolton[1] is on the side of the biologists; but he does not like toxaemia which is the whole thing to Cotton, and it is not absolutely clear to the layman what happens to the cortical neurones and why. At the time this book was published (1914), its author was apparently Professor of Mental Diseases at the University of Leeds and Medical Director of the West Riding Asylum. The preface was written at the West Riding Asylum in Wakefield.

"For reasons which will appear in subsequent chapters, I subdivide all cases of mental disease into two categories, namely: (1) cases which, from the macroscopic post-mortem aspect, exhibit abnormal, no abnormal, no morbid, or slight morbid appearances; and (2) cases which exhibit morbid signs of any higher grade of intensity, and, in some instances, abnormal appearances also.

"The former group, from the clinical aspect, I class under the term Amentia, which I employ to connote *the mental condition of patients suffering from deficient neuronic development;* and the latter under the term Dementia, *which I employ to signify the mental condition of patients who suffer from a permanent psychic disability due to neuronic degeneration following insufficient durability.*

"The subjects of amentia, therefore, as I shall suggest from the macroscopic and prove from the microscopic aspect, *suffer from a more or less marked grade of sub-evolution of the cerebrum.* The chief clinical varieties of amentia are low-grade amentia, or idiocy and imbecility of all grades with or without epilepsy, and high-grade amentia, which includes moral, unstable and excited cases, together with cranks and asylum curiosities, recurrent cases of all types, hysteria, epileptic insanity, and true paranoia and allied cases."

"The subjects of dementia, as I shall indicate both macroscopically and microscopically, *suffer from a more or less marked grade of involution* or dissolution of the cerebrum. I group all such cases into a primarily neuronic class composed of senile, presenile, mature and premature types; into a progressive and secondary class which includes senile and presenile dementia associated

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[1] "The Brain in Health and Disease," 5, 6, 162 (1914).

with gross degeneration of the cerebral vessels, and general paralysis and kindred pathological conditions; and into a class of special varieties following sense deprivation, epilepsy and cerebral lesions.

"This generalisation of amentia and dementia is a gross one, and, as I shall indicate, is based on the fact that cases of mental disease exhibit a lesion of the cortex of the prefrontal region of the cerebrum, which lesion, in the case of amentia, is of the nature of a true sub-evolution, and, in the case of dementia, is of the nature of a true involution or dissolution.

"The existence of amentia does not preclude the onset of dementia, the milder grades of which may in fact be regarded as the normal result of cerebral senility in all persons, sane or insane, who survive to the necessary age-period, which, however, varies greatly in accordance with their individual personal cerebral durability. In many idiots, for example, cerebral senility occurs before the age of forty years, and in some normal persons indications of its onset are absent at the age of eighty.

"The necessity precursor of dementia, whether this be severe or mild, of a rapid or of slow development, is a more or less severe grade of Mental Confusion, which term I employ to connote, in the broadest sense, *the mental symptoms occurring in association with certain pathological states of the cortical neurones, which may be followed by the recovery, or by a more or less extensive dissolution of these elements.* In the former case, in which the symptomatology is incited by temporary or removable causes—e.g. alcoholic excess—complete recovery often occurs. In the latter, a more or less severe grade of dementia ensues. Further, certain clinical indications are frequently, though not constantly present which enable a prognosis to be made as to whether a given case which exhibits mental confusion is recoverable or will develop dementia. Again, it is certain that recoverable mental confusion may occur in persons possessing normal cerebra. Lastly, mental confusion followed by dementia more commonly occurs in cases with cerebra of normal or relatively normal development, though probably of deficient neuronic durability, than in cases with cerebra which exhibit some grade of sub-evolution. The generalisation may in fact be made that the greater the grade of amentia the less is the tendency to dementia, not through a more normal durability of the cortical neurones of the former, but owing to the fact that cases of amentia so readily suffer from symptoms of mental alienation under any form of stress that as a rule little or no irreparable damage to the cortical neurones results from its influence."

"I hope that recognition of the fact that mental disease consists in essence of a large group of cases with varying degrees and types of cerebral degeneracy and of another larger group with varying degrees and types of cerebral dissolution will be of value at a time when, with the object of elucidating the aetiology of insanity with a view to its prevention, even a bacterial origin of mental alienation has been seriously discussed. If the views expressed in the present volume receive credence, I trust that future attempts to deal seriously with the incidence of mental disease will treat the subject, not as a branch of infectious disease or at any rate a toxaemia, but as the greatest of the degeneracies; and that an endeavour will be made on the one hand to discover and to minimise the causes which lead to cerebral degeneracy and on the other to diminish the 'stress' (in the widest sense) to which actual degenerates are subjected, with the object of decreasing the degree and the frequency of cerebral dissolution."

Bolton's views are not necessarily inconsistent with those of Cotton though Bolton thinks they are. Bolton is interested primarily in the anatomical structure and not in the causes that produce it. Cotton is interested primarily in the toxic effects which produce anatomical changes in the brain. Bolton would undoubtedly accept Cotton's dictum that there can be no abnormal function without a corresponding abnormal structure. As chemists it is our duty to hold fast to this dictum until it is definitely proved wrong in some cases. While it is conceivable that there may be conditions under which one may have insanity with a normal brain, it is hopelessly unprofitable to make such an assumption unnecessarily.

Paton[1] takes a sane, intermediate view. "There is no department of medicine in which the investigator needs to be in more intimate touch with the advances of modern science than in psychiatry. The problems to be solved by it are mainly of general, not special, interest. It not only forms a branch of general medicine, but should be classed with other biological studies. Science has demonstrated that the anomalies in thought, action, volition, and emotion, popularly referred to as forms of insanity, are the expression of a disordered functioning of the central nervous system. Gradually we are awakening to an appreciation of the fact that the same general methods of investigation that are applicable in the study of all biological sciences may be successfully adopted in attacking the problems connected with mental diseases.

"Let us consider very briefly the methods which the alienist may employ in dealing with psychic phenomena. The problems to be solved can be approached from several stand-points which for the sake of convenience can be described as psychological, clinical, chemico-physical, and anatomico-pathological. A word may here be said regarding the attitude of the alienist towards the study of mental phenomena or the functions of the cerebral cortex. Instead of contenting himself with a naïve psychology founded upon theory and speculation, he has been taught to rely upon the basis of steady, painstaking observation, substantiating his results whenever possible by experiment. And by these methods alone will it become possible to attain a comprehensive rational understanding of the nature of insanity. The point of view of the modern physiologist, that organic processes are referable to physico-chemical changes, offers another vantage ground, since physiology also teaches that material changes in any organ give rise to disorders of function. The brain is no exception to this rule. Changes in consciousness, anomalies in the emotional life, impairment of volition, are merely expressions of a disturbance in equilibrium of the functions of the brain. In this country,

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[1] "Psychiatry," 2 (1905).

particularly, the alienist is singularly indebted to the physiologist and to the psychologist, not only for keeping alive and stimulating interest in the study of mental phenomena, but also for valuable contributions that have been made by both to our knowledge of the functions of the central nervous system. So little is known, so much still remains to be found out, and the speculative tendency in certain quarters is so strong, that the temptation to substitute theory for observation and experiment has to be met and resisted at every turn. The relation of body and mind is still an enticing theme for the philosopher, but to spend valuable time in theorizing as to the manner in which the ultimate solution of this problem will be effected belongs only to those who live in a realm that is far afield from the path of the clinician. New points of view are always desirable, if they ultimately lead to the discovery of additional facts; but psychiatry cannot afford to build upon shifting sands. The theories of psycho-physic parallelism and of neo-vitalism may afford useful working hypotheses to many investigators, but their adoption as philosophical creeds should be a matter of no concern to the alienist. The attempt to establish a 'psychological basis' for the study of mental disease is quite as undesirable as would be the attempt to limit clinical medicine to the mere study of symptoms. The psychological method is a useful aid to investigation, but to consider its scope and methods as the end-all of modern psychiatry shows no appreciation of the advances that have already been made. Great as has been the stimulus derived from psychological studies, the alienist fully appreciates that his line of investigation differs essentially from that of the psychologist.

"But before pointing out more in detail the positive advantages derived from the new psychology a word of caution is necessary. The facts derived from observation and experiment have thwarted the attempts of those who have tried to transform the useful working hypotheses expressed in the theory of psycho-physic parallelism into dogmas. Even those who were formerly the most ardent supporters of this doctrine are now willing to admit that, while the parallelism may hold in the case of the simpler sensations, it cannot be applied to the more complicated psychic phenomena. Even in the analysis of the simpler mental phenomena it is impossible to correlate the so-called mental and physical events. In all the cerebral processes, from the simplest sensations to the most complex psychic phenomena, there is a series of physico-chemical changes that take place, and these, so far as is known, have no immediate correlates in the mental sphere. A series of ether vibrations strikes the ear and the individual may become conscious of a musical note. How is each event in this physical chain to be correlated with those comprising the psychic phenomenon? And, in fact, do not the teachings of modern science demonstrate the futility of such an attempt? According to the psycho-physical theory the individual events in one place are not contrasted with those in the other, but what is actually attempted is the establishment of a parallelism between a whole series of events on the physical side with those in the mental sphere.

"But it may be asked, Who shall determine exactly the two series of events that are to be contrasted? What is to be called physical and what mental; and what censor shall decide the question for us? The careful analysis of the cerebral functions has resulted in the destruction of the artificial barriers that were supposed to separate them from each other. The differences of gradation but not of quality are recognized. The power of discrimination between violet and yellow, heat and cold, pleasure and pain, represents to each sentient individual important distinctions, but by what right do we assume that in the final analysis these differences are not referable to physical processes that vary only in degree and intensity? For all that we know to the contrary there are no abrupt divisions or chasms to be crossed. The cerebral processes vary, but they do so by degrees, by shading off into each other without gap and without break in continuity.

"It would be superfluous to emphasize the necessity of far more active coöperation in America between psychologist and psychiatrist were there not abundant evidence of the lack of communism of interests. Two facts have contributed to this unfortunate condition. In the first place, too many students of normal mental phenomena start with philosophical speculation and make exact observation and the recording of facts of merely secondary importance. This attitude in a measure accounts for the widespread and not unjustifiable scepticism abroad as to the true merit of many of the so-called psychological investigations. And again, when a recognized leader in the modern school of psychology has actually admitted defeat and declared that his specialty never can become a science, is it to be expected that the wares he offers for sale are to be taken at more than their appraised value? But, happily, although he may have succeeded in demonstrating the inefficiency of his own methods, he has failed signally in the attempt to prove that all others are equally untrustworthy. More hopeful investigators—and, fortunately, they represent the large majority of psychologists—still have faith in the efficacy of patient and well-directed observation. The end is not yet in view, but a bright and brilliant page is being written, and even in the face of what seem to be insuperable difficulties the investigator, in the light of the advances that have been made since Herbart's day, finds reason to take courage and begin the attack anew. Observation, whether it be introspective in character or be applied to the study of mental phenomena noted in others, is being carried on with more rigorous exactitude than ever before. This is still the period of critical analysis. The period of synthesis will come as soon as the methods of introspection, of observation of the normal and abnormal mental processes, and of experiment stand the crucial tests applied to them."

At Cornell the general theory of Claude Bernard in regard to anesthesia has been developed to the point that the next step beyond the position of Cotton has been taken,[1] in that we are able to specify what the abnormal changes in the brain are in incipient insanity, at any rate in the simple cases. From the literature it is evident that there are two general types of insanity,

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[1] Bancroft and Richter: Proc. Nat. Acad. Sci., 17, 294; J. Phys. Chem., 35, 1606 (1931).

one in which the brain colloids are slightly over-coagulated or puckered, and the other in which the brain colloids are slightly over-peptized or mushy. These changes may be so slight that there would be no possibility of detecting them microscopically. Consequently, we must resort to indirect methods if we are going to prove our point. It was shown in the first paper that the abnormal symptoms of the coagulated type should be alleviated by treatment with suitable peptizing agents, while the abnormal symptoms of the peptized type should be alleviated by treatment with suitable coagulating agents. While there is evidence to that effect in the literature, it is purely haphazard evidence. The investigators did not know that there were two types of insanity, and they used specific drugs without knowing that these belonged either to the class of peptizing or coagulating agents. Since nobody tried both peptizing and coagulating agents even accidentally, nobody knew what the failures were due to, and there were failures.

It seemed desirable, therefore, to have tests made on a considerable number of insane patients, starting with the simplest cases and testing them both with coagulating agents and with peptizing agents. In this way it would be possible to tell to what extent it is possible to divide insane patients sharply into two classes, one of which is helped by peptizing agents and is made worse by coagulating agents, while the other class is helped by coagulating agents and made worse by peptizing agents. As coagulating agent sodium amytal was obviously one to try because good results had previously been obtained[1] with it. Previous investigators had used sodium bromide[2] without knowing that it was a peptizing agent; but we are in a position to predict that sodium rhodanate, NaSCN, will be much better. We[3] are using the German term, rhodanate, in the future, because we find that biologists, medical men and newspaper men confuse the terms sodium thiocyanate or sodium sulphocyanide with sodium thiosulphate or sodium cyanide. Since this compound is likely to be used more frequently by medical men in the future than in the past, it seems wiser to adopt an arbitrary but less misleading name for it. By feeding sodium and potassium rhodanate for several weeks Borg[4] has developed insanity in certain patients who were supposed to be suffering only from high blood pressure; but this was only a disturbing incident to him and he failed to see the real significance of his experiments. As was pointed out in a previous paper, sodium iodide, though a good peptizing agent for proteins, cannot be used because of the specific action of the iodide ion.

Dr. Lang[5] of the Willard State Hospital has run tests with sodium rhodanate and sodium amytal on forty-six patients suffering from functional psychoses. These tests were continued for a week or until it was fairly certain whether the patient was or was not made better or worse. In some cases the results were very clear-cut. Case 1 had suffered from dementia praecox cata-

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[1] Lorenz: Psychiatric Quarterly, 4, 95 (1930).

[2] Wright: Am. J. Psychiatry, 5, 365 (1926).

[3] Bancroft and Rutzler: J. Phys. Chem., 35, 3036, (1931).

[4] Minnesota Medicine, 13, 281 (1930).

[5] Lang and Paterson: J. Phys. Chem., 35, 3425 (1931).

tonia for five years. His ordinary characteristics were: stupor, seclusive, untidy, refused to care for personal needs. After oral administration of sodium amytal, there was a slow and steady improvement. He asked for work; assisted in cleaning and polishing; kept his clothes neat and himself clean; was in good contact with surroundings. After oral administration of sodium rhodanate, there was a confused stupor reaction. He was very pale, sat with his head bowed and made no response; was untidy and dirty. After stopping the sodium rhodanate, he went back to the state before the experiment began. There is a marked improvement with sodium amytal and a marked deterioration with sodium rhodanate. The man is obviously of the dispersion type. Dr. Lang uses the term schizoid instead of dispersion and cycloid instead of agglomerated or coagulated. If these words are more satisfactory to the medical profession, they should be adopted. In this phraseology, this case of dementia praecox catatonia is of the schizoid type of insanity.

Case 18 was diagnosed as epilepsy. Before treatment he was uneasy, talkative, restless, threatening, subject occasionally to terrific excitement when he requires restraint to prevent injury. After oral administration of sodium amytal, he fell into a deep sleep. On awakening he was irritable, restless, would not work, and refused to co-operate. After administration of sodium rhodanate, there was slow but steady improvement. He became well-behaved and quiet, worked occasionally on ward which he does very well; sleeps the entire night which is in contrast with previous behavior.

This man is definitely of the agglomerated or cycloid type. His improvement was not accompanied by any change in blood pressure.

Case 34 was diagnosed as manic depressive, depressed. Before treatment she was restless, agitated, anxious, whining, and slept very poorly. Sodium amytal produced deep narcosis, followed by agitation, excitement and worry. After administration of sodium rhodanate, she was at first agitated and disturbed, but became quiet. She is clear mentally, not so noisy and no longer untidy. Her condition is improved and she was definitely the agglomerated or cycloid type.

Case 14 is interesting and shows one of the complications that may occur in short tests. He was diagnosed as manic depressive, manic. Before treatment he showed marked excitement; was noisy, restless and agitated; refused food, was destructive to clothing; showed impulsiveness and assaultiveness. Was mute. On administration of sodium amytal he showed intoxication, followed by narcosis. After that he was more excited and his condition was worse. It is quite clear that sodium amytal made him worse. Consequently sodium rhodanate should make him better. The actual results were not quite what was expected. With sodium rhodanate he became depressed. There was a brief normal period and then he became stuporous and negativistic, refusing food. He slept well; he would not speak but would shake hands. When the sodium rhodanate was stopped, there was a slow recovery and he is still improving. He will speak at times now.

The explanation of this seems to be that the patient responds quickly to sodium rhodanate, that he was given too much, and that he was carried clean over from the cycloid insanity to the schizoid insanity. After stopping the sodium rhodanate he came back to a much more normal period than he was in before treatment. It is probable that small enough doses of sodium rhodanate will improve his condition distinctly.

Case 35 is similar in principle but with the drugs reversed. The diagnosis was dementia praecox catatonic and the behavior before treatment was uneasy, quiet, restless, and wanders about disturbed. When sodium rhodanate was given she became very noisy, depressed, and stupid; was unable to help herself and very untidy. There is no doubt but that she became worse under sodium rhodanate. Sodium amytal produced deep narcosis and then short periods of stimulation. She became more alert and was co-operative, which was all as it should be. Continued dosage with sodium amytal resulted in excitement and she was apparently carried over from schizoid insanity to a mild form of cycloid insanity.

In a number of cases the tests with sodium amytal and sodium rhodanate have led to a change in the diagnosis. Case 2 was diagnosed once as alcoholic and once as apathy and depression. Before treatment the patient showed stupor and depression, was negativistic and generally untidy but not dirty. He had to be coaxed to eat. He was fearful but could not give the cause of his fear. After oral administration of sodium amytal, he became alert and interested, cared for his person properly and slept well. When the sodium amytal was stopped, the stupor returned promptly but was no worse than before. With sodium rhodanate the stupor was increased. The patient was untidy, and dirty, and did not feed himself properly. When the sodium rhodanate was stopped, the patient returned to the original state.

The case could not possibly be an alcoholic one because sodium rhodanate should have helped it and could not have made it worse. The diagnosis was changed because of these tests. When the patient was in the improved state due to sodium amytal, he described his depression as due to an unknown fear. He had the delusion war was to occur all over the world. The test indicated that a state of over-peptization existed and that the diagnosis should have been schizophrenia.

Case 5 was diagnosed as dementia praecox, hebephrenic. Before treatment the behavior was excited, restless, untidy, noisy, with an occasional clear time when he would speak English. At other times his productions were incoherent and in German, his childhood language. With sodium amytal he became excited, stimulated, and drowsy, after which there was a short narcosis. Following this he was over-active and destructive. He showed many mannerisms, grimaces, and fantastic poses; but while he was in these bizarre attitudes that appeared catatonic-like, he only adopted them when he knew that he was being observed. He enjoyed the effect of this behavior on others. This indicates the presence of a strong affect but mischievous in direction.

With sodium rhodanate there was slow and steady improvement. He requested his own clothes, talked in English coherently, and has maintained this improvement for two months.

Drs. Lang and Paterson say that "this is an individual whose behavior reaction under amytal would be called dementia praecox catatonia. Actually in his usual state the diagnosis has alternated between dementia praecox hebephrenic and manic depressive mixed, according to the observer. This alternation indicates that we have here a case with marked schizoid tendencies; but that affect was not split off, was still strong, and was adapted to the situation at an adult level. The behavior under sodium rhodanate would, according to our experimental findings, place him in the agglomerated or cycloid group, which correlates with the manic depressive classification."

Case 9 was diagnosed as mental deficiency, excitement. Before treatment he appeared very fearful and anxious; was noisy, excited, over-active, violent, destructive, and untidy; but not dirty in personal habits. Oral administration of sodium amytal caused excitement with increased restlessness and over-activity. With sodium rhodanate there were increased periods of quietness and he slept well. He appeared stupid at times; but there was slow improvement. He ate better and was neat and tidy in appearance. He is now at home on parole. Drs. Lang and Paterson say that in this case not only was the exhibition of sodium rhodanate of diagnostic value, indicating a manic depressive type; but it was also therapeutic in action.

Case 21 was diagnosed as manic depressive, depressed. Before treatment he was depressed, worried, fearful, anxious, untidy in personal appearance, confused, and required constant supervision to keep him from getting into difficulty. He would not eat well. With sodium amytal there was deep sleep and ataxia. He became clear mentally, was happy, alert and able to discuss the situation. While in this state he was able to tell of his fears, anxieties and delusions of persecution, and ideas of bodily harm. With sodium rhodanate he became sulky, sarcastic, noisy, irritable, and violent. He slept fairly well at night.

Drs. Lang and Paterson say: "Again we find our tests indicating that our classification was wrong, that it was based on the symptoms presented to us by the patient and not on knowledge of his mental state. When contact was made, we then found a delusional state with fears and ideas of persecution, indicating a schizophrenia. He presents an over-peptized state that is improved by agglomeration. Because of our more adequate information we do not now consider that he is a case of manic depressive."

Case 24 was diagnosed as involution melancholia. Before treatment he was depressed, anxious, fearful, worried, and constantly complaining of somatic difficulties. He was restless at night and could not sleep. With sodium amytal he became more interested and alert; showed improvement and enjoyed deep sleep. With sodium rhodanate he appeared uneasy, stuporous and confused. He did not talk but slept well at night.

The comment on this case is that we find here that more definite information was obtained when the patient was able to discuss the situation more freely under sodium amytal. The somatic ideas were predominant and delusional in character. Schizoid tendencies predominated; this has been recognized in involution melancholia so that in this classification we have two types—one benign or cycloid-predominant which would recover and the other schizoid-predominating with a poor prognosis.

Case 37 was diagnosed as dementia praecox (?) or manic depressive, manic (?). Before treatment she was disturbed, restless, uneasy, and violent at times. She would stare continuously at the ceiling. With sodium amytal there was deep sleep and no intoxication. She has shown steady improvement and is clearing very quickly. With sodium rhodanate she became stuporous, untidy, destructive, and definitely worse.

The physicians say: "This case was at first diagnosed manic depressive and was then changed to dementia praecox. From the test she would be considered as of the over-dispersed group. The diagnosis might very properly be catatonic schizophrenia. The patient would not co-operate in examination and further could scarcely speak English."

Case 39 is just the reverse. She was diagnosed as dementia praecox, paranoid (?). Before treatment she was restless, uneasy, crying, and noisy. With sodium amytal there was deep narcosis, marked intoxication, severe dizziness, and excitement. With sodium rhodanate she became quiet and assisted with work. She had periods of excitement and short periods of restlessness; but has shown a steady improvement. Because of the positive reaction to sodium rhodanate, she belongs to the agglomerated group. No information as to mental content was obtained as she could not speak English and would not talk to the interpreter. She appeared under much fear, which is not unusual in these cases.

Case 40 was diagnosed as manic depressive, manic (?). Before treatment she was noisy, destructive, disturbed, and agitated. With sodium amytal she became very nauseated but showed much improvement. With sodium rhodanate she became quiet, would cry, was noisy and excited at times, then restless and destructive. In this case diagnosis was based solely on observed behavior. No contact with patient could be obtained as she did not speak English. Severe regression in behavior was present. The test indicated a state of dispersion, while manic depressive, manic belongs under cycloid insanity.

Case 41 was diagnosed as dementia praecox, paranoid. Before treatment she was disturbed, noisy, over-talkative, and agitated. She removed clothing. With sodium amytal the sleep periods increased. She was restless when awake, very ataxic, noisy, confused and unsteady, with some excitement. With sodium rhodanate, she became gradually quiet, slept better at night, remained quiet, has not been noisy, and has taken clothes off only once. The comment on this is that "again we have a case in which the classification was based on presented behavior which was a mixture of both schizoid and cycloid tendencies. The test indicates an agglomerated state."

The whole forty-six cases are summarized in Table I. Eight out of the forty-six are classed temporarily as inconclusive. Thirty-eight of the forty-

TABLE I

Diagnosis	Sodium Improved	Amytal Worse	Sodium Improved	Rhodanate Worse	Inconclusive	Total
D. P. Paranoid		2	2		1	3
D. P. Catatonic	6			6	1	7
D. P. Hebephrenic	2	3	3	2	1	6
Alcoholic	1	1	1	1		2
Manic Depressive	3	11	11	3	1	15
Catatonia		1	1			1
Excitement (Mental Deficiency)		1	1			1
Epileptic		4	4			4
Involutional Melancholia	2			2		2
General Paralysis		1	1		1	2
Endocrinopathy					1	1
Diabetes					2	2
	14	24	24	14	8	46

six cases are made better by sodium rhodanate and worse by sodium amytal or vice-versa. The remaining eight are classed as inconclusive either because they do not meet this criterion or for some other reason. These eight are Cases 6, 22, 25, 27, 30, 36, 38, and 42, as given by Lang and Paterson.[1]

Case 6 probably should not be included in this list; but rather as one of those in which the original diagnosis was at fault. He was classified as dementia praecox, catatonic. Before treatment he was excited, noisy, restless, resistive, and mute for five years. His appetite was good but his sleep was usually disturbed. He did not want to be helped and wrote on the wall that he dared Dr. Lang to make him speak. He meant "defied;" but he may not have known that word.

When sodium amytal was given intravenously, he became sleepy, nodded in response to questions, and spoke once. There was a narcosis of short duration, following which he was excited and required restraint to prevent injury. With large doses of sodium rhodanate he was depressed and irritable. On small and repeated doses he began writing numerous letters which were logical to some extent, but showed disturbed sentence structure. On the fourth day of administration he began to talk and was over-active and irritable. On the fifth day he was still over-active. He talked steadily in spite of his previously-declared intention not to. His ideas were flighty and his conversation rambling and irrelevant; but coherent in choice of words and sentence structure. His ideas were in response to normal stimuli, and if they had not been so rambling and produced so fast (in other words a manic reaction), he would have been normal as to content and production. He ignored his personal appearance completely but was perfectly correct in his habits.

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[1] J. Phys. Chem., 35, 3425 (1931).

Drs. Lang and Paterson say that "this is one of the mixed cases so hard to estimate, diagnose, and treat correctly. He shows many schizoid characteristics and these predominate. The cycloid tendencies are manifested in his irascibility. There are also long mood-swings between the elation which leads to excitement and the depression which produces irritability and negativism.

"The interpretation of reaction is difficult in this case. To sodium amytal he reacted with excitement and violence similar to manic depressive; to the sodium rhodanate he showed a release of the inhibitory mechanism so that we have uncritical freedom of thought production, undirected and distractible. Our suggestion is that we have here an individual who responds so readily to these drugs that he is normal only over a slight range. We probably gave him more than enough sodium rhodanate to bring him to the normal state. Considering his five years of mutism, his free production now, at a correct level of adult thought and in response to reality, would indicate an improved state and therefore manic depressive. Therapeutically it remains to find the correct dose level at which he may be maintained."

In principle Case 6 seems to us the same as Case 14, previously discussed. The only difference is that that patient was diagnosed originally as manic depressive and this one should have been.

Case 22 was diagnosed as general paralysis. Before treatment he was quiet but appeared uneasy, would not talk, and had marked delusions of grandeur. With sodium amytal there was deep narcosis. Following this he was dizzy and confused. With sodium rhodanate he became very quiet and lethargic, slept during the day, and very deeply at night. The comment on this is: "This case is also receiving tryparsimide. He shows a severe neurological involvement indicative of wide-spread permanent lesions in the central nervous system. Of the two reactions we considered him improved by sodium rhodanate and therefore of the agglomerated group. In spite of this we classified him as inconclusive." Paton[1] gives a reproduction of a drawing of giant cells showing marked agglomeration with a patient having general paralysis.

Case 30 was diagnosed as dementia praecox, hebephrenic. Before treatment he was disturbed, noisy, untidy, and destructive. He slept poorly. With sodium amytal he slept well, was quiet and appeared slightly drowsy. He was not so noisy but was agitated. With sodium rhodanate he gradually became quiet and stuporous. The results were called inconclusive because this was a deteriorated case. To the layman it seems as though this patient was made somewhat better by sodium amytal and somewhat worse with sodium rhodanate, though not very much either way.

Case 36 seems to us a faulty diagnosis. She was classed as manic depressive, manic. Before treatment she was over-talkative, excited, restless, and untidy. With sodium amytal she became drowsy, stimulating, uneasy, and alert, with very free affect. She was interested, co-operative, and improved.

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[1] "Psychiatry," Plate XIV (1905).

With sodium rhodanate, she became very noisy, restless, disturbed, assaultive, and obscene. To the layman this patient was apparently made much worse by sodium rhodanate and somewhat better by sodium amytal, which is quite impossible for manic depressive, manic. The medical comment was: "This is a third attack. She is of a very unstable personality. Each attack shows a lower level of regression. Schizoid characteristics predominate. The case is further complicated by the occurrence of the climacterium and resulting glandular imbalance."

Case 42 was diagnosed as dementia praecox, paranoid. Before treatment she was agitated, suspicious, delusional, fearful, anxious, and restless. With sodium amytal, she was drowsy and appeared slightly depressed, with no change in delusions. The agitation and restlessness disappeared. With sodium rhodanate she became disturbed and restless; cried; delusions increased. She made attempts to grab the medicine and throw it out of the window. She became excited when the nurses gave the medicine to other patients.

The medical comment is: "Although not improved by sodium amytal, she was made worse by sodium rhodanate. She was considered as of the over-dispersed type; but was classed as inconclusive because of the indefinite result with sodium amytal." It seems to us that the disappearance of agitation and restlessness indicates a slight improvement by sodium amytal. It is not known whether a more prolonged treatment with sodium amytal would have helped the delusions. The important thing from our point of view for the moment is that the test did establish the type of insanity.

Case 27 was classed as psychosis with diabetes (diabetic tabes). The comment before treatment was: "This patient has diabetes. Blood sugar 250 mgms; developed a psychosis characterized by excitement, delusions, anxiety, restlessness, violence and confusion. Neurologically—loss of knee reflexes, changes in sensation (loss) in legs."

With oral administration of sodium amytal, the patient showed brief periods of very deep narcosis, was sleepy, then excited, then normal sleep. On awakening was very irritable and restless; following this he became depressed and cried, then mute and would not co-operate on further examination. With sodium rhodanate he became more quiet, talked, and gave as explanation of his feeling, that he is responsible for the death of many.

The medical comment is: "This case is being studied intensively and will be reported by itself when complete data have been obtained. It is placed in the inconclusive group." Superficially considered, there would appear to be improvement with sodium rhodanate and deterioration with sodium amytal, although one must remember that Dr. Lang is probably basing his judgment in part on things which are not set down in the report.

Case 38 was diabetic and was diagnosed as manic depressive, manic. Before treatment she was disturbed, singing, restless, and uneasy; would not keep clothes on, and attacked other patients. Sodium amytal brought on deep narcosis, after which she was more quiet, but then became over-active and irritable. With sodium rhodanate she became less agitated but remained quarrelsome; the sleep periods increased. The medical comment is: "Because of the presence of diabetes, this case was listed as inconclusive. She showed some improvement under sodium amytal but was then made worse. She was also improved by sodium rhodanate [which is what ought to happen under the diagnosis]. As with the other diabetic (Case 27) separate study is being made to determine whether the variations in reaction have any relation to variations in her physical disease." This case is not satisfactory as it stands. Some disturbing factor has not been recognized as yet.

Case 25 is diagnosed as endocrinopathy. Before treatment he was untidy, with periods of explosive irritability alternating with well-behaved periods in which he was co-operative, neat, clean, and tidy in appearance. One-half gram of sodium amytal intravenously produced no narcosis. There was marked irritability with restlessness and resistiveness afterwards. With sodium rhodanate there was no apparent effect. This boy is not put to sleep by an intravenous injection of sodium amytal and is apparently not affected by sodium rhodanate, so he does not fit in to the picture at all for the present. The medical comment is that this case is one on which the diagnosis has been deferred until further study on glandular reaction can be made. No conclusive results could be obtained.

The general summary is that in thirty-eight out of forty-six cases or just under 83 percent, positive results were obtained with both drugs. In five cases, or just under 11 percent, positive results were obtained with at least one of the drugs. With three cases or 6.5 percent, the results were inconclusive. These three cases are the two diabetics and the boy suffering from endocrinopathy. Drs. Lang and Paterson say with reference to these three cases: "The two diabetics fall in the inconclusive groups. One showed a mixture of schizoid and cycloid characteristics with predominance of cycloid, and is receiving forty units of insulin per day. Much further study is required on this case before positive statements can be made. He, however, was excited under sodium amytal. The other one showed predominance of cycloid characteristic and showed a narcotic reaction to sodium amytal, but showed improvement under sodium rhodanate. The case of endocrinopathy again was a mixture of schizoid and cycloid tendencies with mood fluctuation and regression in behavior. Because of the alternation between excitement and quiescence, we could not avoid the consideration of a coincidental factor in the exhibition of the drug."

A positive result in over ninety-three percent of the cases the first time round is entirely satisfactory. The patients did not know which drug they were getting. In fact Drs. Lang and Paterson say that in their opinion "this study has demonstrated definitely that the functional psychoses show a correlation between the syndromes presented and the state of dispersion of the cell colloids." They add that "based upon the correct appreciation of the colloidal states in these syndromes a more rational therapeutic approach may be made in the treatment of such cases.

Dr. Lang has now introduced the tests with sodium amytal and sodium rhodanate as the fundamental diagnostic tests, while the more orthodox methods are now the secondary ones and have to be revised until they agree with the fundamental tests. Dr. Lang has found that, in general, the cycloid cases of insanity require less sodium amytal to cause narcosis than do the cases of schizoid insanity. *These latter are farther from the coagulated state.*

Let us turn back to Table I and consider the conclusive tests. All the dementia praecox, paranoid cases and all the epileptic cases were made worse by sodium amytal and better by sodium rhodanate. All the dementia praecox, catatonic cases and all the involutional melancholia cases were made better by sodium amytal and worse by sodium rhodanate. These classifications are homogeneous so far as the present thirty-eight cases are concerned. Of the dementia praecox, hebephrenic cases two were made better by sodium amytal and three worse. In the alcoholic group one was made better and the other worse by sodium amytal. Of the manic depressive cases, three were made better by sodium amytal and eleven worse. These classifications are therefore not homogeneous. This means that the classification is wrong, that the diagnosis is wrong, or that both are wrong.

In regard to this classification Drs. Lang and Paterson say: "From Table I we find that the dementia praecox groups are improved by administration of sodium amytal. The cases that are apparently made worse and the inconclusive cases are ones that have been in doubt as to exact diagnosis and have alternated between manic depressive and dementia praecox. Our involution cases were improved by sodium amytal. This corroborates very well that in this group there is a large schizoid factor in those cases which do not clear up at all readily. The manic depressive group is definitely improved by sodium rhodanate, while under sodium amytal they are made worse with a tendency to increase of excitement. The discrepant cases are also borderline cases of manic depressive, and show many schizoid factors that have caused the diagnosis to be questioned. They are improved by sodium amytal and so would indicate a more proper diagnosis of schizophrenia. The inconclusive case is so listed because of the presence of arterio-sclerosis and chronic myocarditis.

"The epileptics are made worse by sodium amytal and show improvement to sodium rhodanate. In the excited case of mental deficiency, the behavior reaction would classify it under the manic depressive group and so with sodium rhodanate improvement would be expected and did occur.

"In the two alcoholics, one reacted with improvement to sodium rhodanate, the other was improved under sodium amytal; but it was found that he had a delusional trend with splitting of emotional field so that he should more properly be diagnosed as schizophrenia. Only two cases of general paresis were dealt with. Both have received large amounts of tryparsimide. One, the inconclusive case, was under treatment at the time, so that the sodium rhodanate had to be discontinued. He furthermore shows very severe neurological involvement."

Probably one cannot say more than this until we have more data or until some reckless person breaks a lance in favor of the orthodox methods of classification and diagnosis. Drs. Lang and Paterson decide: that in schizophrenia (dementia praecox) the colloidal system is in a state of over-dispersion; that in the manic depressive psychoses the colloidal system is in a state of agglomeration or decreased dispersion that, although only four epileptics were observed, the reaction was so positive that they would also indicate an agglomerated state; that catatonia is correlated with a state of over-dispersion; and that benign stupor reactions, although appearing very like catatonia, react to tests indicating that they are in the agglomerated state.

One point in regard to sources of infection calls for a few words. Dr. Henry Cotton[1] says that "as early as 1908 Henry S. Upson of Cleveland called attention to the relation of infected teeth to mental disorders. He cites the fact that Savage, the English alienist, in 1876 reported several cases of acute mania recovering suddenly after the extraction of bad teeth. Upson reported his conclusions, based on thorough clinical observations, that many cases of acute psychoses were caused by infected teeth and that after extracting them the patient recovered. He also emphasized the relation of infected teeth and impacted molars to dementia praecox." "A realization of the fact that infected teeth, especially the impacted molars, may occur in very young people and continue throughout the life of the individual, offers a probable explanation for the peculiar personalities and abnormal dispositions noticed in cases of dementia praecox years before the psychosis, as such, develops" (Cotton, p. 47).

On p. 43 Cotton gives photographs of defective teeth from two cases of manic-depressive insanity. On p. 137 Cotton cites a case where the patient exhibited a typical maniacal reaction for a week after admission, but improved rapidly following the removal of her infected tonsils and extraction of infected teeth. She was discharged as recovered six weeks after admission. From these and other passages, we draw the conclusion that infected teeth may cause dementia praecox, catatonic in one patient and manic depressive insanity in another patient. That did not bother Dr. Cotton, who would probably have said that the poison affects the weakest place first and that that might vary from patient to patient. That is perfectly true; but we cannot avail ourselves of it, because we believe in two theoretically opposite types of insanity. We must therefore give some sort of explanation for infected teeth causing agglomeration in one case and dispersion in another. There seem to be only two possibilities. One is that the toxic substance from infected teeth contains a coagulating substance in one individual and a dispersing agent in another individual. That seems so improbable as not to be worth considering further. The other possibility is that the toxic substance from the teeth is not the primary cause of the insanity; but that it stimulates or depresses some gland or glands and that the increase or decrease in the secretion from these glands causes the insanity. We can then have the toxic substance affecting the gland which happens to be most susceptible.

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[1] "The Defective, Delinquent and Insane," 41 (1921).

The difficulty with this is that we are postulating glands with imaginary properties to help us out of the hole. There is, however, some independent evidence that this may be a legitimate explanation. It is generally agreed that if hyperthyroid individuals become insane, they are likely to develop some form of what we are calling coagulation or cycloid insanity. If hypothyroid individuals become insane, they are likely to develop some form of what we are calling dispersion or schizoid insanity. It was reported in the newspaper accounts of the Buffalo meeting of the American Chemical Society that Dr. Hoskins of the Harvard Medical School had extracted a hormone from the thyroid gland which was given to eighteen sufferers from dementia praecox. Five of these became well enough to go home and most of the others showed significant improvement. If this is confirmed, we have an under-active thyroid gland tending to produce schizoid insanity and an over-active thyroid gland tending to produce cycloid insanity. Since there is no reason to suppose that this hypothetical regulatory activity is limited to the thyroid gland, it may appear that over-excited adrenals tend to produce schizoid insanity and under-active adrenals cycloid insanity. Whether this is right or not, it makes a very interesting working hypothesis.

The general conclusions of this paper are:—

1. There are two schools of insanity. One believes that insanity is theoretically a disease of the mind or the psyche and not of the brain, the observable brain lesions and defects being secondary or coincident. This school believes that mental treatment is the rational way of handling a disease of the mind. The other school believes that insanity is theoretically a disease of the brain and that changes in the brain structure are the cause of the insanity.

2. Since there are many cases of functional psychoses in which there is no visible change of brain structure, the Freudian school has claimed that there were actually no changes of the brain structure. This involves the assumption that what one cannot see does not exist.

3. It follows from the theory of Claude Bernard that an abnormal colloidal state of the proper part of the brain will involve abnormal thinking, which is insanity.

4. There can be at least two abnormal conditions of the brain, one when it is over-coagulated and one when it is over-peptized.

5. Two general types of insanity do occur in functional psychoses; dispersion or schizoid insanity; and coagulation or cycloid insanity.

6. Cycloid insanity can be identified by the fact that it is made worse by sodium amytal and better by sodium rhodanate. Schizoid insanity can be identified by the fact that it is made better by sodium amytal and worse by sodium rhodanate.

7. Out of forty-six cases studied by Lang and Paterson, thirty-eight, or about 83 percent gave definite indications with both drugs; forty-three, or about 93 percent gave definite indications with at least one drug, while three, or about 7 percent, are classed temporarily as unsatisfactory.

8. In these forty-three cases there is unquestionably a change of brain structure paralleling the change in insanity, a change which could not be detected by our present methods of microscopy.

9. This means that in about ninety-three percent of the cases studied by Lang and Paterson, the insanity is a disease of the brain. The remaining cases will probably fall in line in time.

10. In a fair number of cases the results by the sodium amytal and sodium rhodanate tests did not agree with the diagnoses previously made along orthodox lines.

11. Dr. Lang has adopted the sodium amytal and sodium rhodanate tests as the fundamental diagnostic tests. When classified in the ordinary way, some of the groups are not homogeneous with regard to the fundamental tests. This means that there are errors in the classification, in the diagnosis, or in both—undoubtedly the last.

12. As might have been predicted, the cases of schizoid insanity require more sodium amytal to produce narcosis than do the cases of cycloid insanity.

13. Epilepsy and manic depressive are clearly coagulation types. The schizophrenia cases (dementia praecox), if properly diagnosed, are all dispersion types.

14. Lang and Paterson consider that catatonia is correlated with a state of over-dispersion and that benign stupor reactions, although appearing very like catatonia, react to tests indicating that they are of the agglomerated type.

15. Since the benign stupor catatonia is an agglomerated state and dementia praecox catatonic is a peptized state, we seem to have been justified in the conclusion drawn in the first paper that there are two kinds of catatonia, which had not hitherto been differentiated properly.

16. The data in Paton's "Psychiatry" are conclusive that general paralysis is of the cycloid type. This is what Lang and Paterson found definitely for their conclusive case and probably for their inconclusive case.

17. We understand that Dr. Henry Cotton and others have found that infected teeth may give rise to either type of insanity depending on the individual.

18. It seems probable that the toxic substances from the teeth do not produce insanity directly; but stimulate or depress some of the glands and thereby cause insanity.

19. When hyper-thyroid people go insane, they usually develop cycloid insanity, while hypo-thyroid people tend to develop schizoid insanity.

20. In view of what has been done at the Harvard Medical School, it is suggested as a working hypothesis that an over-active thyroid gland tends to cause cycloid insanity and that some other over-active gland tends to produce schizoid insanity. This does not necessarily mean that all functional psychoses are due to abnormal glandular activity.

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ABSORPTION SPECTRA OF RARE EARTH GLAZES

BY F. H. NORTON[1] AND D. T. H. SHAW[2]

I. Introduction

The use of mixed rare earths in glasses for special purposes have frequently been met with in the literature,[3,4,5] but the use of rare earths in glazes is seldom mentioned, and no results are available on the separate rare earths in glasses. In connection with color studies of various elements in raw lead glazes,[6] several rare elements were introduced into a lead meta-silicate, $PbO\text{-}SiO_2$, base glaze. Their colors were then recorded and analyzed. It is noteworthy that of all the elements, the rare earths are the only ones that give sharp band spectra in glazes in the visible region, although cobalt, chromium and uranium show broad bands under certain conditions.

II. Experimental Procedure

The preparation and burning of the glazes were described in another article.[6] In short, various amounts of "chemically pure" oxalates of cerium, neodymium, praseodymium, and samarium were weighed out and mixed with the base glaze to which dextrine solution was added to impart adhesion to the body. The glazes were then sprayed on to white biscuit tiles, the weight of application per unit area being kept constant for all samples. These were then burned in an oxidizing atmosphere to 1000°C. and cooled slowly to room temperature. Table I gives the composition, batch weight, and color of the glazes studied.

Spectro-reflecting curves of the glazes were then obtained by means of Professor Hardy's recording photo-electric color analyzer.[7] Figs. 1, 2, 3, 4 and 5 give respectively the family of relative reflecting (standard—$MgCO_3$) curves for Ce, Pr, Nd, Di and Sm, the concentration of the corresponding oxides per unit molecule of $PbO\text{-}SiO_2$ being marked on each curve. The dotted curve is that for the base glaze alone. It will be noted that cerium does not give very distinct bands, as compared with the other rare earths, and these may possibly be due to contamination by some of the other earths.

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[3] F. Weidert: Z. wiss. Phot., 27, 254 (1921), Das Absorptionsspektrum von Didymgläsern bei verschiedenartiger Zusammensetzung des Grundglass.

[4] H. P. Gage: J. Opt. Soc. America, 17, 4, 12 (1928), Glass Color Filters.

[5] K. S. Gibson, et al: Bur. Standards, Tech. Paper, No. 148 (1920). The Ultra Violet and Visible Transmission of Various Colored Glasses.

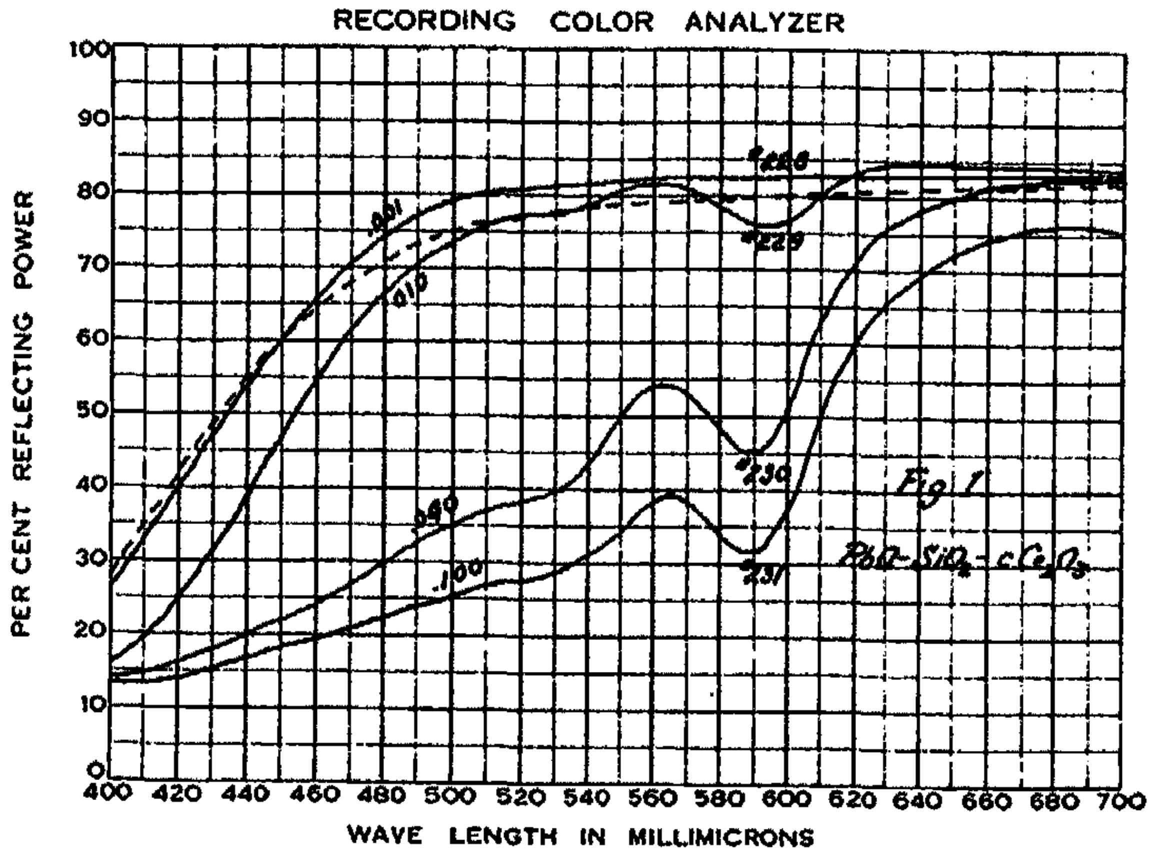
[6] D. T. H. Shaw: J. Am. Ceramic Soc., 14, 11 (1931). Color Formation in Raw Lead Glazes.

[7] A. C. Hardy: J. Opt. Soc. America, 18, 2, 94 (1929). A Recording Photo-electric Color Analyser.

TABLE I

Details of Rare Earth Glazes

No.	Composition	Batch Weight			$C^{1/2}$	Description of color
(A)	Ce_2O_3 Series	Pb_3O_4	SiO_2	$Ce_2(C_2O_4)9H_2O$		
228	PS—.001 Ce_2O_3	9.9	2.6	.0306	.0316	Yellowish ivory, B & S
229	PS—.010 Ce_2O_3	9.9	2.6	.3060	.1000	Light yellow, B & S
230	PS—.040 Ce_2O_3	9.9	2.6	1.2240	.2000	Mottled peach, B & S
231	PS—.100 Ce_2O_3	9.9	2.6	3.0600	.3160	Peach brown, Cryst.
(B)	Pr_2O_3 Series	Pb_3O_4	SiO_2	$Pr_2(SO_4)_3$		
232	PS—.002 Pr_2O_3	9.9	2.6	.0494	.0447	Ivory white, B & S
233	PS—.010 Pr_2O_3	9.9	2.6	.2470	.1000	Ivory white, B & S
234	PS—.100 Pr_2O_3	9.9	2.6	2.4700	.3160	Ivory green, B & S
(C)	Nd_2O_3 Series	Pb_3O_4	SiO_2	$Nd_2(C_2O_4)_3\ 9H_2O$		
235	PS—.001 Nd_2O_3	9.9	2.6	.0309	.0316	White, B & S
236	PS—.010 Nd_2O_3	9.9	2.6	.3090	.1000	White, B & S
237	PS—.040 Nd_2O_3	9.9	2.6	1.2360	.2000	P. Pink, B & S
238	PS—.080 Nd_2O_3	9.9	2.6	2.4720	.2830	Pink separations on white B & S
(D)	Di_2O_3 Series	Pb_3O_4	SiO_2	$Di_2(C_2O_4)_3\ 9H_2O$		
239	PS—.002 Di_2O_3	9.9	2.6	.624	.0447	White, B & S
240	PS—.010 Di_2O_3	9.9	2.6	.3115	.1000	White, B & S
241	PS—.050 Di_2O_3	9.9	2.6	1.557	.2240	White, B & S
242	PS—.100 Di_2O_3	9.9	2.6	3.115	.3160	White, B & S
(E)	Sm_2O_3 Series	Pb_3O_4	SiO_2	$Sm_2(C_2O_4)_3\ 9H_2O$		
254	PS—.001 Sm_2O_3	9.9	2.6	.0314	.0316	White, B & S
244	PS—.010 Sm_2O_3	9.9	2.6	.3140	.1000	White, B & S
245	PS—.080 Sm_2O_3	9.9	2.6	3.1421	.2830	Light yellow, cryst.



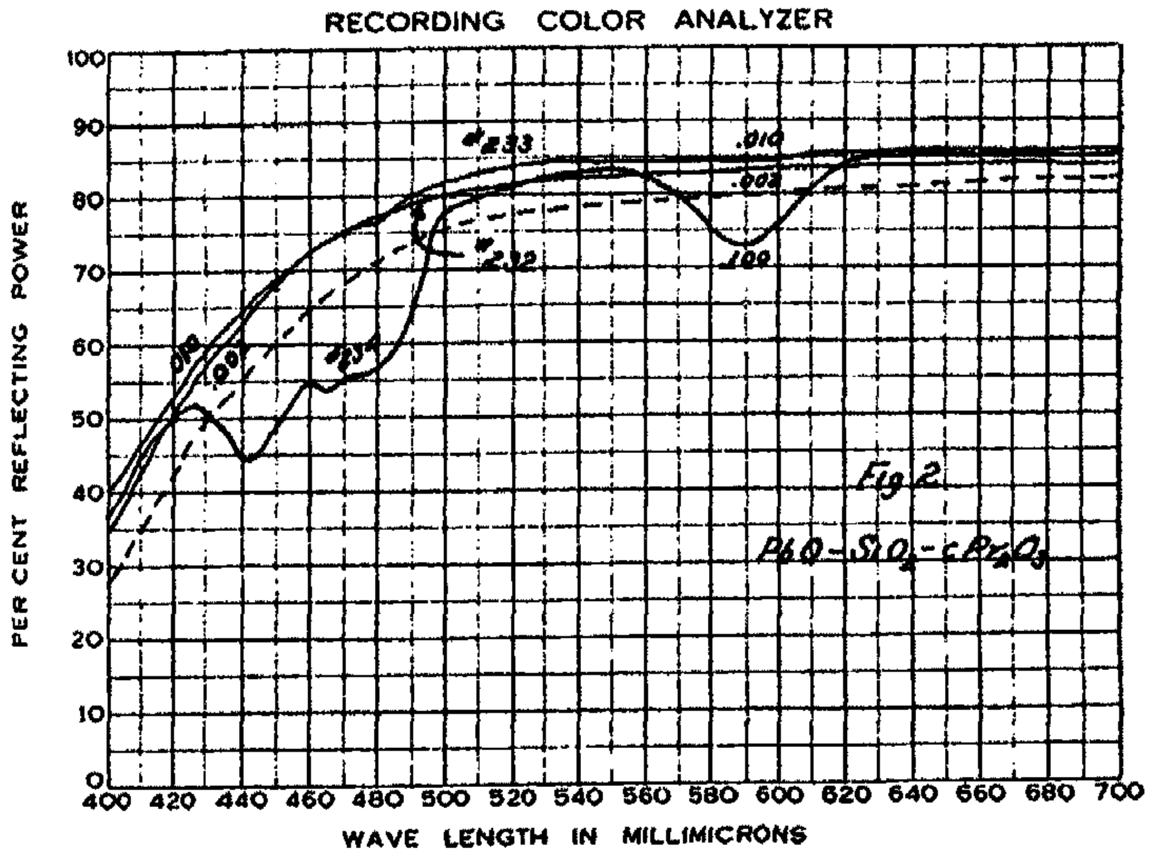


Fig 2

PbO-SiO$_2$-cPr$_2$O$_3$

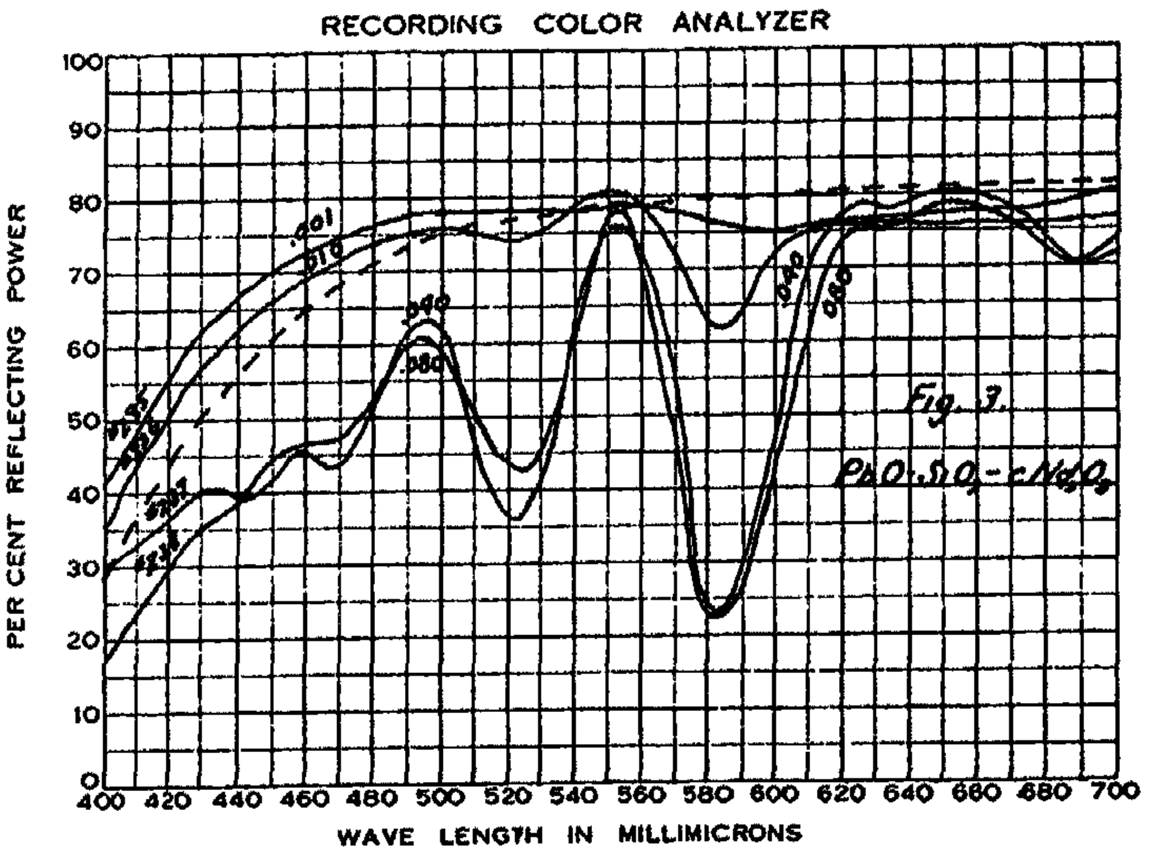
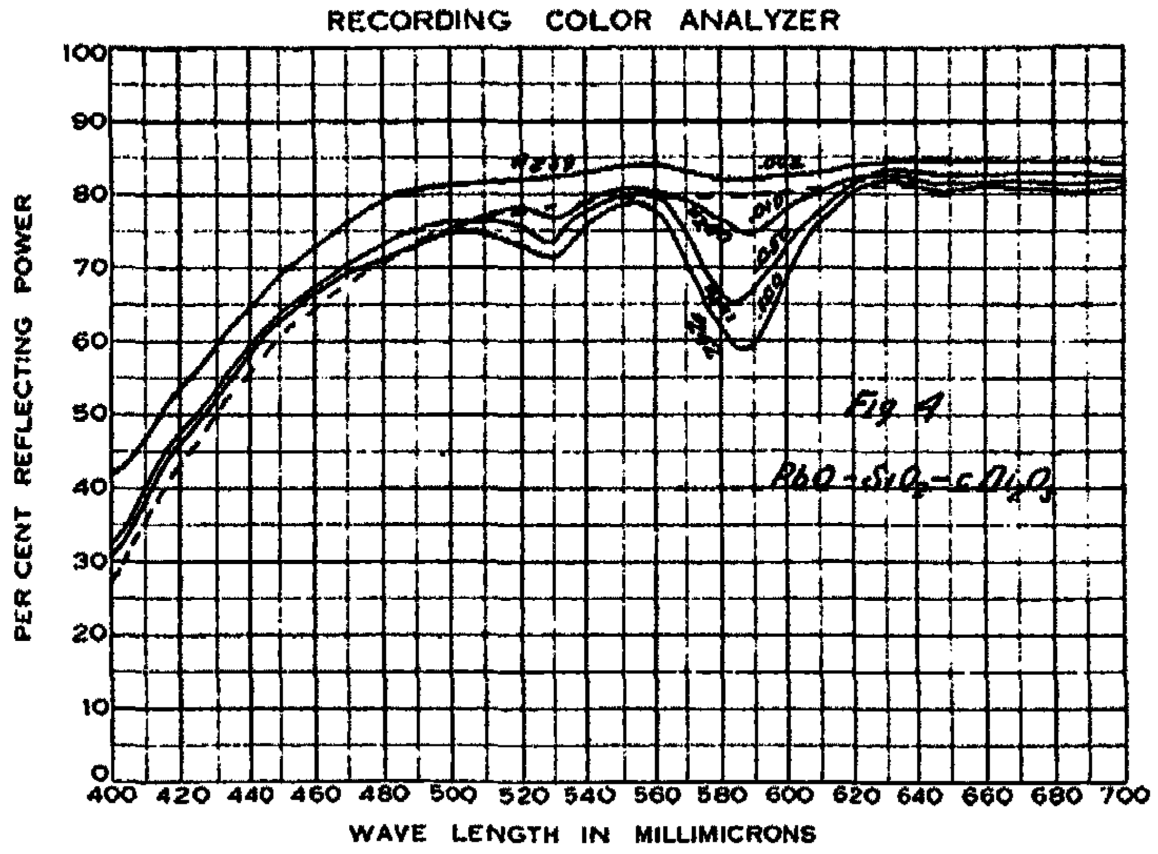
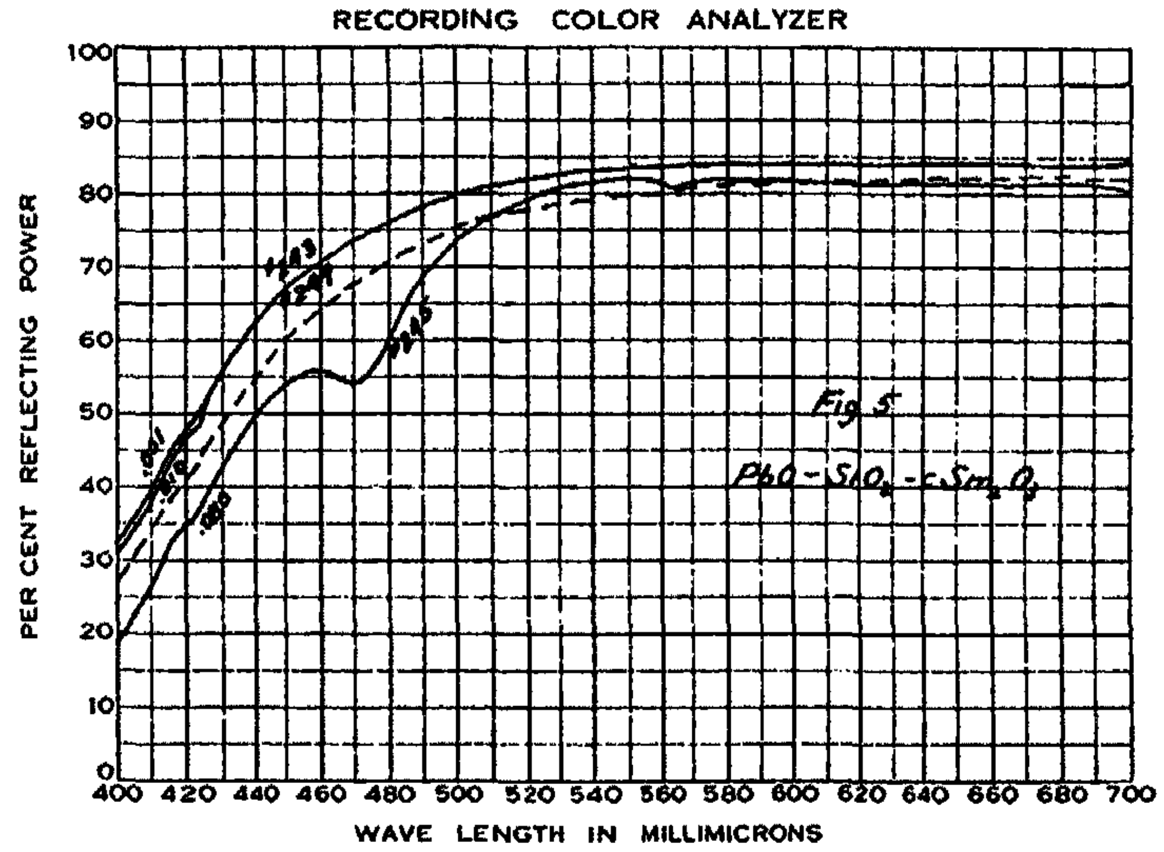


Fig. 3.

PbO.SiO$_2$-cNd$_2$O$_3$


RECORDING COLOR ANALYZER
PER CENT REFLECTING POWER
0
10
20
30
40
50
60
70
80
90
100
400
420
440
460
480
500
520
540
560
580
600
620
640
660
680
700
WAVE LENGTH IN MILLIMICRONS
.002
.010
.050
.100
Fig 4
PbO-SiO2-cDi2O3


RECORDING COLOR ANALYZER
PER CENT REFLECTING POWER
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700
WAVE LENGTH IN MILLIMICRONS
Fig 5
PbO-SiO2-cSm2O3

III. Study of Absorption Spectra

In contrast with the smooth continuous spectro-reflecting curves of most other elements, the rare earth glazes exhibit a number of minima in their reflecting curves. Since rare earths are known for their selective absorbing power of light in the visible spectrum, the minimum points can only be attributed to the presence of the absorption bands at the particular wave length in question. This leads naturally to a comparison of the absorption bands of aqueous solutions with the minima of these spectro-reflecting curves.

In Table II there are shown the principal absorption bands of nitrate solutions of cerium,[8] of praseodymium, as given by Hofmann and Höschele,[9] of neodymium, as given by Hofmann[10] of didymium, as given by Purvis,[11] and of samarium, as given by Prandtl[12] listed side by side with the minima in the reflecting curves of the various glazes at their respective wave lengths in millimicrons.

Table II

Absorption Spectra of Aqueous Solution and Glaze.
Wave Lengths in Millimicrons

Ce		Pr		Nd		Di		Sm	
Aqu. Sol'n	Glaze	Aqu. Sol'n	Glaze	Aqu. Sol'n	Glaze	Aqu. Sol'n	Glaze	Aqu. Sol'n	Glaze
								418	420^{VW}
				427		427			
		442	440^{S}		444^{W}	444^{S}		442^{S}	
		469	465^{W}	469	470^{W}	469			
				475		476^{S}		463^{S}	460
		481^{S}	480^{W}			480^{S}	486^{VW}	480	
								500	
				509		510^{S}			
					525^{S}				
	528^{W}			532^{S}		531^{W}	530	530	
				572		570		560	560^{W}
580	585^{S}	592^{S}	592^{S}	578^{S}	585^{S}	590	587^{S}		
						596^{W}			
		597			635^{W}	623^{W}			
							645^{VW}		
				677					
					690^{W}		690^{VW}		

s = strong w = weak v.w. = very weak

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[8] Determined in the Optical Laboratory of the Massachusetts Institute of Technology with a Zeiss Comparator spectroscope using a saturated solution of cerium nitrate.

[9] Hofman and Höschele: Ber., **47**, 238 (1914). Das Magnesiumchlorid als Mineralisator, mit einem Beitrag zur Spektrochemie der seltenen Erden.

[10] K. A. Hofmann: "Anorganische Chemie," 503-4 (1928).

[11] Purvis: Proc. Cambridge Phil. Soc., **21**, 781 (1923). The Absorption Spectra of Didymium Salts.

[12] Pradtl: Z. anorg. allgem. Chem., **116**, 96 (1921). Über das Absorptionsspektrum des Europiums und des Samariums.

It is to be noted here that didymium is not a single element. It consists of several elements, among which, we can definitely identify two as praseodymium and neodymium. Its absorption bands as shown above, are composed mainly of those of Pr and Nd. It is included in this investigation for the purpose of studying the effect of the mixture of closely related elements on absorption spectra and color formation. In fact, it is probable that none of the rare earths, even though stated to be chemically pure, are free from small amounts of other rare earths. It is possible that the rather indistinct bands shown by cerium are not characteristic of this element, but are due to contamination by neodymium.

IV. Conclusion

An examination of the preceding table will show that on the whole, the positions of the bands in the glaze agree well with those in an aqueous solution. Narrow and faint bands would probably not be recorded by the spectro-photometer as usually set for high speed recording, which accounts for the absence of some of the bands in the reflecting curves. The good agreement suggests a ready way of detecting and identifying the rare earths in a glaze by simply taking its spectro-photometric reflecting curve, and noting if there are minimum points in it. Table III, given below, shows the strong and characteristic absorption bands of the various elements by which they can be easily identified. For glass, the transmission rather than the reflection data would of course be used for this purpose.

TABLE III

Characteristic Bands. Wave Lengths in Millimicrons

Ce	Pr	Nd	Sm
			470
		525	
			560
585		585	
	592		

It is noteworthy that the absorption characteristics of the rare earth atoms are not appreciably altered in the change from an aqueous solution to a silicate glass.

Laboratory of Ceramics
Massachusetts Institute of Technology,
Cambridge, Mass.
September 1931.

ALCOGEL OF SILICIC ACID

BY BASRUR SANJIVA RAO AND K. S. GURURAJA DOSS

Attempts to replace water by alcohol in the hydrogel of silicic acid have given contradictory results. Graham[1] considered the complete replacement of water by alcohol possible, while Neuhausen and Patrick[2] could not secure complete replacement and concluded that the residual small percentage of water in silica gel is held with a force which exceeds that exhibited between atoms of many stable compounds. Firth and Purse[3] found the replacement more complete by a dynamic method than by the static method adopted by Neuhausen and Patrick, the final water content of a sample of gel being 0.57%. They concluded that under the most suitable conditions, ultimate replacement was not impossible.

Results of a comparative study of three methods of replacement of the water in silica by alcohol are described in the present communication.

Experimental

The silica gel employed in the work was prepared by a method which according to Firth and Purse yields a gel showing the best replacement. To a solution of pure sodium silicate, having a density 1.118, was added an equal volume of 3 N hydrochloric acid and the gel allowed to set at the room temperature. The gel was then washed free from sodium chloride and dried at 100°C. The moisture in the gel was 6.8%.

The alcohol used was refluxed with barium oxide, distilled and then treated similarly with metallic calcium till the product was found to be "absolute."

The three methods of replacement employed were:

(a) *The "static" method:* One gram of the gel was immersed in 500 cc. of absolute alcohol. The stoppered "ether" bottle containing the alcohol and gel was placed in a desiccator charged with phosphorus pentoxide. The bottle was occasionally shaken. The alcohol was replaced three times by fresh supplies at intervals of two days.

(b) *The "dynamic" method:* The method described by Firth and Purse was followed.

(c) *The Soxhlet extraction method:* The gel was placed in the alundum thimble of a Soxhlet apparatus and extracted with absolute alcohol. The alcohol was maintained in the anhydrous state by the addition of pure metallic calcium to the flask. A guard tube of barium oxide protected the alcohol from atmospheric moisture.

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[1] J. Chem. Soc., **17**, 318 (1864); Pogg. Ann., **123**, 529 (1864).

[2] J. Am. Chem. Soc., **43**, 1844 (1921).

[3] J. Phys. Chem., **30**, 617 (1926).

For the determination of the water in the alcogel, Firth and Purse used samples having 25 to 30% alcohol. We found that the relative proportions of water and alcohol could be more accurately determined if the alcoholic content of the sample used for analysis, was reduced to about 8% by heating the gel at 180°C. in a current of pure and thoroughly dried nitrogen. The total volatile matter in the gel (alcohol + water) was determined by ignition of the gel to constant weight at blast lamp heat. The alcohol content was estimated by the usual combustion methods of organic chemistry and the percentage of water in the gel got by difference. We thus obviated the difficulty in securing the complete removal of water from the gel in the combustion boat —a process which requires very strong heating.

Results

Method of production of alcogel	wt. of gel combusted	wt. of CO_2	% of EtOH	% loss on ignition	% of water in gel.
"dynamic"	0.5881	0.0988	8.8	9.4	0.65
(76 hours)	0.4279	0.0714	8.7		
			8.75		
"static"	0.3906	0.0944	13.3	13.55	0.30
(8 days)	0.4856	0.1227	13.2		
			13.25		
"Soxhlet" Gel A	0.2128	0.0283	6.95	7.15	0.21
(69 hours)	0.3188	0.0421	6.93		
			6.94		
Gel B	0.3220	0.0419	6.92	7.21	0.39
(53 hours)	0.2330	0.0304	6.82		

Discussion

The gel employed by us appears to have been of the same quality as that used by Firth and Purse since, on replacement of water by the dynamic method, residual water in the gel was 0.65% while in an identical experiment Firth and Purse got a gel with 0.57% water.

Our experiments confirm the view of the authors that the "dynamic" method gives a more rapid elimination of water than the "static" process. The superiority of the dynamic method can be easily accounted for. In this process of replacement of water, the distribution of water between the liquid in the gel and the alcohol-saturated air passed over it, causes an effective loss of water as the volume of air passed is very considerable (450 litres in 3 days—the rate of air flow in our experiments being 100 cc. per minute). In the "static" experiments, however, the water in the gel gets distributed over a comparatively small volume—the volume of alcohol used by Firth and Purse being only 150 cc. per gram of gel, the replacement being repeated three times.

Furthermore, the flow of air over the gel surface would reduce the thickness of the stationary film and thus lead to greater efficiency.

In our experiments we used a much larger volume of alcohol (500 cc. per gram of gel) and we were able to secure a greater replacement—the final product having only 0.3% water.

Of the three methods employed for replacing the water in gel, the extraction method adopted by us seems to be the best in point of efficiency and convenience. In our experiments the Soxhlet used to siphon out once in 20 minutes, thus the quantity of absolute alcohol that came in contact with the gel was about 40 litres. That the water content could not be reduced to below 0.2% in spite of the contact of the gel with 40 litres of absolute alcohol shows how difficult is the ultimate replacement of water.

Summary

(1) Three methods of replacing the water in silica gel by alcohol have been examined.

(2) The most convenient method has been found to be the extraction of the gel with absolute alcohol in a Soxhlet apparatus. This gave a final product having 7% alcohol and 0.21% water.

(3) The ultimate replacement of the water in silica gel by alcohol is extremely difficult.

Central College,
Bangalore, S. India,
August 19, 1931.

THERMAL REACTIONS OF CYCLOPARAFFINS AND CYCLOÖLEFINS*

BY GUSTAV EGLOFF, HARRY T. BOLLMAN, AND BADONA L. LEVINSON

1. Introduction

A field of hydrocarbon chemistry but lightly explored, particularly from the viewpoint of pyrolysis, both catalytic and non-catalytic, is that of the naphthenes or hydrogenated cyclic hydrocarbons. This is true despite the fact that naphthenes are available in enormous quantities from petroleum.

The world's crude oil production for 1930 was 1,418,723,000 barrels. A conservative estimate indicates that one-fourth of this vast volume is made up of naphthenic hydrocarbons.

"Naphthene" was the term applied to certain hydrocarbons obtained from petroleum by Markownikoff and Ogloblin in 1876 (47). The empirical formula C_nH_{2n} classed the simple naphthenes with the olefins, yet the chemical properties of the two groups were quite different. The naphthenes isolated were the five- and six-membered hydrogenated cyclic hydrocarbons which were chemically stable, not reacting readily with concentrated sulfuric acid, nitrating mixture, or halogens.

The widespread occurrence of naphthenes in petroleum has led to their identification in crude oils from many parts of the world. The naphthenes identified in crude oil include cyclobutane, cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, three dimethylcyclohexanes, trimethylcyclohexane, cycloheptane, cycloöctane, decanaphthenes, hendecanaphthenes and naphthenes with 13 to 26 carbon atoms. Some of these naphthenes are monocyclic while others are polycyclic.

Gruse (28) classified crude oils into hydrocarbons of the paraffinic, aromatic, and asphaltic types, the naphthenes being present in varying proportions in all classes of petroleum. Using the triangular diagram, Fig. 1, he illustrated the probable composition of crude oils.

Sachanen and Wirabianz (58) classified the various petroleums according to their hydrocarbon groups. The percentage composition of the 250 to 300° fraction from the distillation of the different classes of petroleum was given as in Table I:

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*Presented before the Organic Division of the American Chemical Society, Buffalo, September, 1931.

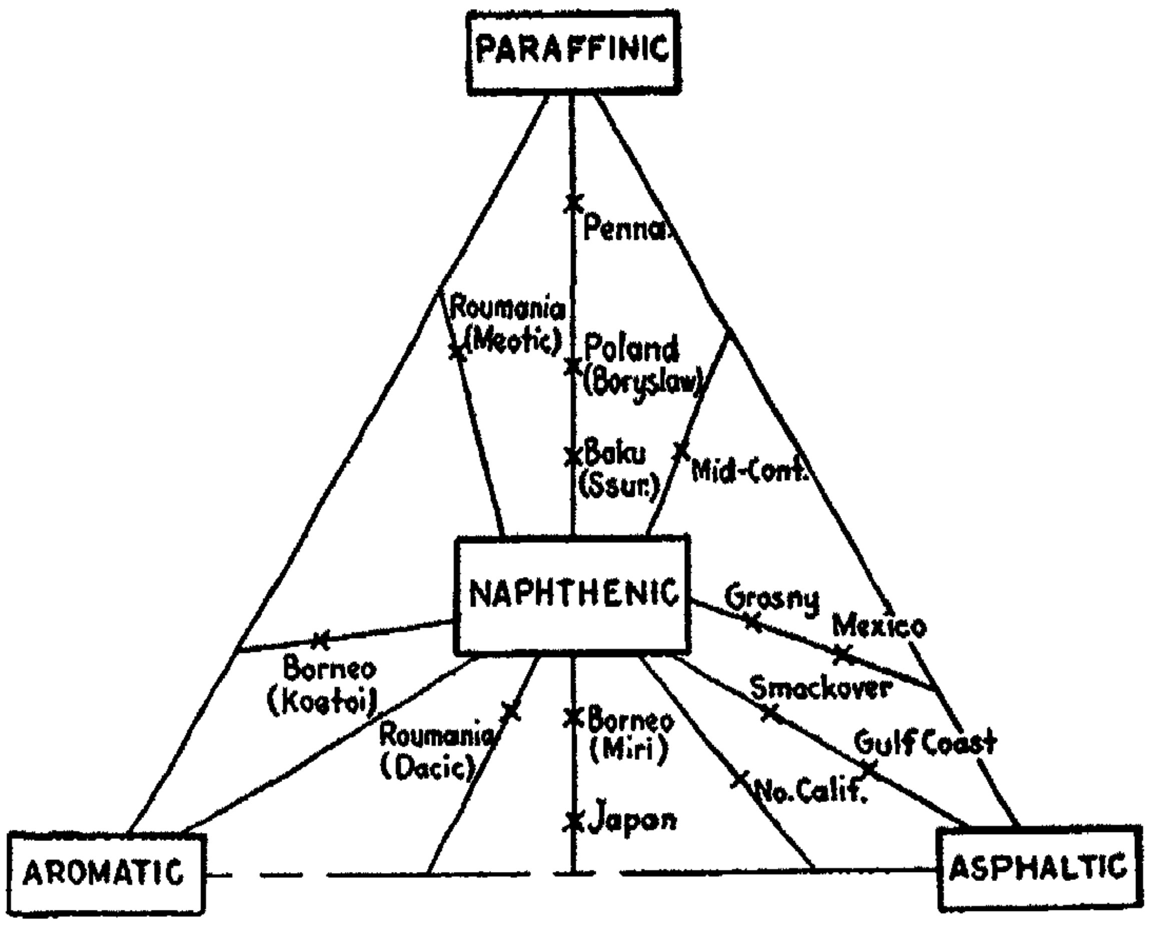

FIG. 1

TABLE I

Crude Oil Classification	Paraffins	Naphthenes (Percents)	Aromatics
Paraffinic	46–61	22–32	12–25
Paraffinic, Naphthenic	42–45	38–39	16–20
Naphthenic	15–26	61–76	8–13
Paraffinic, Naphthenic, Aromatic	25–35	36–47	26–33
Naphthenic, Aromatic	0–8	57–78	20–35

They reported compositions for Russian, Texas, Oklahoma and California petroleums as in Table II. The crude oils were distilled and the different fractions analyzed for hydrocarbon group composition.

TABLE II

RUSSIAN GROZNY CRUDE

"Springeröl"

°C	"High Paraffin" 45.3% over at 300°			"Low Paraffin" 43.9% over at 300°		
	Aromatic	Naphthene Percent	Paraffin	Aromatic	Naphthene Percent	Paraffin
60–95	3	25	72	5	26	69
95–122	5	30	65	8	31	61
122–150	9	35	56	13	36	51
150–200	14	29	57	18	34	48
200–250	18	23	59	18	30	52
250–300	17	22	61	21	28	51

TABLE II (Continued)

"Paraffin Free"

°C	"Lower Level, Light Oil" 45.4% over at 300°			"Upper Level, Heavy Oil" 40.9% over at 300°		
	Aromatic	Naphthene Percent	Paraffin	Aromatic	Naphthene Percent	Paraffin
60–95	5	26	69	4	31	65
95–122	8	33	59	8	40	52
122–150	13	38	49	13	52	35
150–200	18	39	43	21	55	24
200–250	24	40	36	26	63	11
250–300	28	37	35	35	57	8

Texas Crude

Mexia

°C.	47.9% over at 300°		
	Aromatic	Naphthene Percent	Paraffin
60–95	29	17	54
95–122	21	22	57
122–150	19	23	58
150–200	16	21	63
200–250	12	20	68
250–300	12	29	59

°C.	*Oklahoma Crude* Davenport 64% over at 300°			*California Crude* Huntington Beach 34.2% over at 300°		
	Aromatic	Naphthene Percent	Paraffin	Aromatic	Naphthene Percent	Paraffin
60–95	5	21	73	4	31	65
95–122	7	28	65	6	48	46
122–150	12	33	55	11	64	25
150–200	16	29	55	17	61	22
200–250	17	31	52	25	45	30
250–300	17	32	51	29	40	31

The volume of gasoline distilled from crude oil under atmospheric pressure in the United States during 1930 contained approximately 54,000,000 barrels of naphthenic hydrocarbons.

A number of straight-run gasolines derived from different crude oils were analyzed for their hydrocarbon content (Table III). The low-boiling naphthenic members present ranged between one and forty-one percent. The naphthenes in gasoline have special significance because of their high antiknock or low detonating characteristics when burned in automobile engines.

TABLE III

Chemical Analyses of Straight-Run Gasolines

(Percents)

Gasoline source	Naphthenes	Aromatics	Unsaturates	Paraffins
Pennsylvania[1]	13.0	6.9	2.2	77.9
Pennsylvania	1.2	4.2	2.3	92.3
Pennsylvania	23.4	0.0	1.3	75.3
Pennsylvania	23.2	0.0	4.0	73.6
Pennsylvania	11.7	4.9	2.9	80.5
Oklahoma (Cushing)[2]	23.7	4.9	1.6	69.8
Oklahoma (Cushing)	17.9	3.6	3.7	74.8
Oklahoma (Cushing)	26.2	0.0	2.9	70.9
Oklahoma (Seminole)	23.0	4.5	3.4	69.1
Kentucky	23.1	2.8	5.8	68.3
Kentucky (Somerset)[3]	20.6	5.3	3.8	70.3
California	34.9	2.8	5.1	57.2
California	41.2	0.8	2.3	55.7
Kansas	20.3	0.4	2.7	76.6
Arkansas (Smackover)	14.5	11.3	7.9	66.3
Texas (Refugio)	23.1	8.7	2.2	66.0
Texas	27.4	6.0	3.2	69.4
Texas	25.8	2.5	3.2	68.5
Texas	24.7	1.2	3.7	70.4
Texas (Van Zandt)	0.0	2.9	1.7	95.4
Michigan (Mt. Pleasant)	7.4	4.5	2.9	85.2

It will be noted from the above that gasolines derived from the same oil field vary quite widely in hydrocarbon group content.

The cracking process is also producing vast volumes of naphthenic hydrocarbons boiling within the gasoline range. The cracking of petroleum oils produced over 30,000,000 barrels of naphthenes during the year 1930 which were consumed in high anti-knock motor fuel.

Table IV shows the percentage of naphthene, aromatic, unsaturated, and paraffin hydrocarbons present in various gasolines produced from the cracking process.

The discussion of the thermal reactions of the cycloparaffin and cycloölefin hydrocarbons is introduced by the simplest of the cyclic saturated hydrocarbons, cyclopropane. Following this, the hydrocarbons increase in both number of carbon atoms in the ring and in the complexity of the molecule. This complexity of the known hydrocarbons reaches a maximum in the polynuclear compounds and the higher homologs of simple ring compounds, such as cyclohexane.

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[1] Egloff, Nelson, Truesdell: Oil & Gas Journal, 38, (Feb. 12, 1931).

[2] Egloff: World Power Conference, London (1928).

[3] Egloff, Nelson, Truesdell: Oil & Gas Journal, 139, (Feb. 19, 1931).

TABLE IV

Chemical Analyses of Cracked Gasolines

(Percents)

Gasoline source	Naphthenes	Aromatics	Unsaturates	Paraffins
Arkansas (Smackover)	14.3	29.3	13.4	43.0
Arkansas (Smackover)[1]	21.2	27.5	14.7	36.6
California	17.2	20.7	17.2	51.8
California	16.7	22.0	23.0	38.3
Kansas	12.8	17.8	16.1	53.3
Kentucky	18.8	26.0	12.5	42.7
Kentucky	11.1	29.5	9.6	49.8
Kentucky[1]	10.0	22.5	14.4	53.1
Kentucky (Somerset)[1]	11.8	14.9	12.5	60.8
Michigan (Mt. Pleasant)	3.1	33.5	25.9	37.5
Oklahoma	11.6	23.9	6.5	58.0
Oklahoma	14.2	23.0	9.4	53.4
Oklahoma	12.2	28.8	9.3	49.7
Oklahoma	0.0	32.9	32.2	34.9
Oklahoma (Cushing)[1]	18.0	19.8	10.9	51.3
Pennsylvania	13.8	29.0	11.0	46.2
Pennsylvania	13.4	12.0	6.0	68.6
Pennsylvania	10.2	23.5	9.7	56.6
Texas (Cole Bruin)	27.3	26.9	19.9	25.9
Texas (Mirando)	34.0	23.4	17.1	25.5
Texas (North)[1]	11.7	18.6	16.0	53.7
Texas (Refugio)	25.0	32.8	30.0	12.2
Texas (Spindletop)	32.6	17.3	14.7	35.4
Texas (West)	16.8	38.5	27.1	17.6
Texas (West)	38.6	24.7	17.6	19.1
Texas (Van Zandt County)	0.0	35.2	22.2	42.6
Wyoming (Lander)	10.0	20.2	11.6	58.2
Wyoming (Lost Soldier)[1]	14.5	15.9	11.7	57.9
Argentina	9.9	25.0	16.6	48.5
Canada (Wainwright)	13.2	24.7	18.6	43.5
Esthonia Shale Oil	8.6	44.2	30.5	16.7
Germany (Wietzer)	12.5	25.8	10.7	51.0
Mexico (Ebano)	15.9	22.6	13.8	47.7
Roumania	11.6	23.9	13.9	50.6
Venezuela	14.7	25.2	14.7	42.6
Venezuela (Mene Grande)	13.2	24.0	20.3	42.5

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[1] Egloff: World Power Conference, London (1928).

Tabular summaries showing the reactions of the individual hydrocarbons are placed at the end of certain sections. The contact time, an important factor, has been omitted because of uncertainty in almost all of the experiments. Where possible, the contact time has been included in the remarks upon the hydrocarbon.

2. Theory and Mechanisms

One relationship in the stability of the cycloparaffin rings may be obtained if it is assumed that Baeyer's (10) strain theory applies to these hydrocarbons. Although "strainless rings," stable substituted cyclopropanes, and very large monocyclicparaffins have been found, a qualitative comparison of ring stability may be shown by the strain theory. It is claimed by Shemyakin (63A), moreover, that Baeyer's strain theory applies to carbon rings containing less than five members, for it is impossible to arrange the atoms so as to avoid strain. If the carbon atom is considered as a tetrahedron, it is evident that the angles at the four corners are each 109° 28′. The difference between this value and the angle between valence bonds in a ring structure is an index of the stability of the ring. Thus, any ring possessing a large difference in value of the angles between carbon atoms and the theoretical angle, is under a "strain," and hence in an unstable condition. Thus for trimethylene or cyclopropane the difference between angles, or the "strain," is 24° 44′. These values vary with different rings, the five- and six-membered rings showing the least strain. Increasing the number of carbon members in the ring to more than six decreases the stability of the hydrocarbon.

The stability of the rings may be compared by their action over a metal catalyst in the presence of hydrogen. A more direct comparison could be obtained by the non-catalytic pyrogenation of all the ring hydrocarbons under like conditions. Since cyclopropane and cyclohexane, however, are the only hydrogenated cyclic hydrocarbons which have been studied non-catalytically under similar conditions, such a comparison of the complete series of these hydrocarbons is at present impossible. For this reason we must resort to the qualitative relationship shown in the following discussion.

Both cyclopropane and cyclobutane were reduced by Willstätter and Bruce (82) by passing the compounds over nickel together with hydrogen, at 80 to 120° and 180 to 200° respectively, until no further volume reduction was found. Propane and n-butane were produced.

Cyclopentane, passed over platinum black at temperatures up to 300°, was not dehydrogenated according to the work of Zelinsky (85).

Cyclohexane was passed over nickel in the presence of hydrogen at 270 to 280° by Sabatier and Senderens (60), who obtained benzene and methane as products.

Cycloheptane was flowed over nickel with hydrogen at 230° until no further change could be observed. The experimenters, Willstätter and Kametaka (81), found the product of the action to be methylcyclohexane.

Cycloöctane at 205 to 210° over nickel in the presence of hydrogen, gave a mixture of dimethylcyclohexane and perhaps a small amount of alkyl-cyclopentanes. Bicyclooëctane under similar conditions was reduced to a mixture of isomeric monocyclooëctanes. A summary of these comparative data is given in Table V.

TABLE V

Naphthenes with Hydrogen and Nickel Catalyst

Naphthene	Temp.	Time	Substance Obtained	Type of Scission
Cyclopropane	80–120°	Treated	Propane	C-C
Cyclobutane	180–200°	until	n-butane	C-C
Bicyclooëctane	205–210°	no	Mono-cyclooëctanes	C-C
Cyclooëctane	205–210°	further change	(Dimethylcyclohexane Alkyl-cyclopentanes)	C-C
Cycloheptane	235°	took	Methyl-cyclohexane	C-C
Cyclohexane	270–280°	place	Benzene and CH_4	C-C, C-H
Cyclopentane*	300°		Unchanged	None

*Platinum black catalyst.

Although the conditions of the experiments varied with respect to temperature, all the runs were made with excess hydrogen and a sufficient contact time to insure complete reaction. If temperature and decomposition are taken as an index of stability, cyclopropane is apparently the most unstable of these compounds. Cyclobutane, cyclooëctane and cycloheptane are next in order of stability. Cyclohexane follows, exhibiting some carbon-carbon scission judged from methane formation, while cyclopentane is unchanged under the above conditions and is, therefore, the most stable.

Jones (38) obtained from 40 to 80 percent of hydrogen in the gaseous products of decomposition of cyclohexanes and hydronaphthalenes, as shown later. He made the following comparison of these results with those of other investigators on open-chain paraffins, of which n-hexane was representative, and on benzene.

"Haber (30), for instance, has pointed out the difference in behaviour between these two classes of compounds when subjected to thermal decomposition. Whereas with paraffins of more than two carbon atoms, scission takes place between carbon and carbon, with aromatic hydrocarbons it takes place between carbon and hydrogen. Haber quotes as examples benzene and n-hexane. Benzene, when heated, decomposes with some difficulty with loss of hydrogen and formation of diphenyl; hexane decomposes with greater ease, the bond between two end-carbon atoms being ruptured with the resulting formation of amylene and methane.

"The results obtained with cyclohexane, which on decomposition yields gaseous mixtures containing 40 percent of hydrogen, afford a striking contrast to those obtained with hexane and the higher paraffins generally, from which little or no hydrogen is formed."

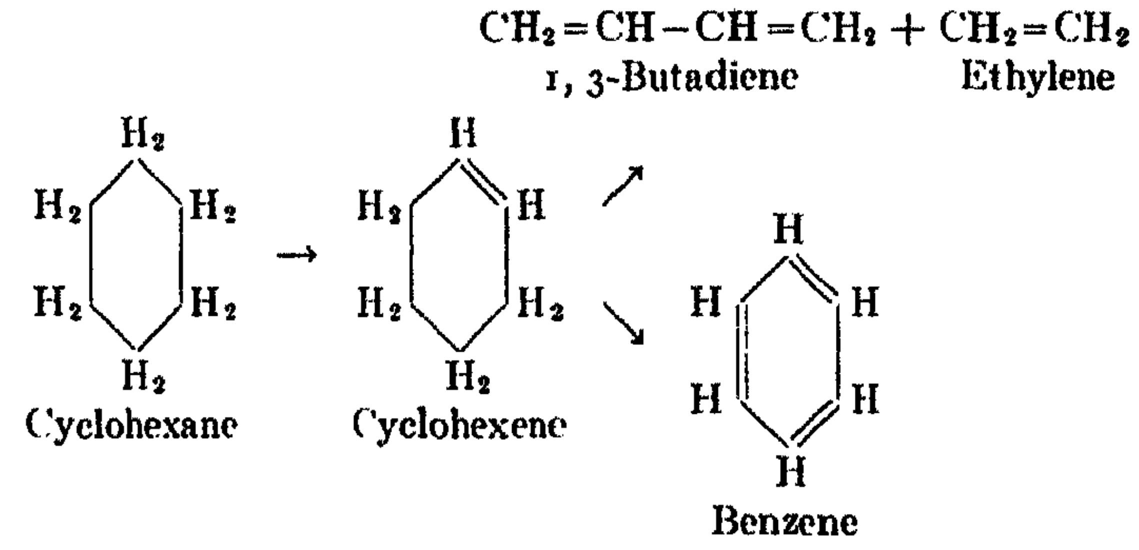
Considering the action that Jones (38) finds for cyclohexane, he says: "Contrary to expectations, it is found that with the cyclohexanes there is a marked tendency to eliminate hydrogen. There must, therefore, be some fundamental difference between these hydrocarbons and the open-chain paraffins insofar as the stability of their carbon-hydrogen linkings are concerned."

Continuing, Jones writes: "The distinction between these two classes of hydrocarbons is made apparent by the results of Zelinsky (85) from which it would also appear that hydrocarbons of five- or seven-carbon ring-systems resemble paraffins rather than cyclohexanes as regards the stability of their carbon-hydrogen linkings. Zelinsky shows that, whereas cyclohexanes readily part with their hydrogen when in contact with palladium at temperatures between 200 and 300°, n-hexane, the cyclopentanes and the cycloheptanes remain unchanged. We are thus driven to infer that the cyclohexanes, hydrogenated naphthalenes, and, we may assume, hydrogenated aromatic compounds generally, retain in some form or other their aromatic structure, or that they possess some form of linking differing fundamentally from that of other carbocyclic and open-chain systems.

"These structural differences cannot be expressed by ordinary graphic formulae, which are based on the assumption that the four carbon valences are permanently equal. If the CH_2-group of an open chain or of a five- or seven-carbon ring be represented by the graphic formula  $-\overset{H\ H}{\overset{\vee}{C}}-$, the CH_2-group of a six-carbon ring must be represented by some other graphic formula in which one or both of the carbon-hydrogen bonds are represented as having some other value than that ordinarily assigned to them. That hydrogenated benzenoid hydrocarbons cannot, however, be regarded as retaining an aromatic structure almost intact, with six extra atoms of hydrogen loosely attached, is demonstrated by the fact that scission of the carbon-carbon bonds takes place apparently with much the same ease as the scission of the carbon-hydrogen bonds, as deduced from the presence of ethylene, methane, etc., in the gaseous products of decomposition."

Jones concludes that "comparison with the results of other investigators (2) suggests that the most probable course of the reaction would be for the cyclohexane first to lose two atoms of hydrogen and form cyclohexene, which then decomposes in two ways, yielding benzene and butadiene."

Mechanism for Cyclohexane Decomposition



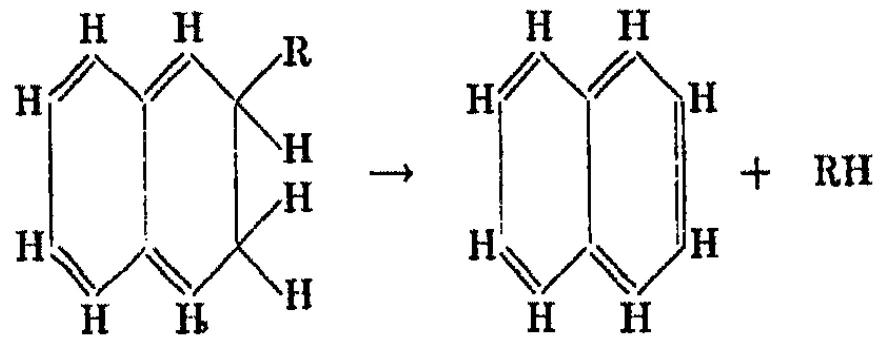
As pointed out by Jones, the decomposition of cyclohexane appears to be intermediate between n-hexane and benzene, if Haber is accepted as correct, while Zelinsky definitely shows that cyclohexane decomposes much more easily than n-hexane in the presence of palladium.

Ipatiev (35) supported the view that n-hexane was less stable than cyclohexane; for, if each of these hydrocarbons was heated in a bomb at 510° in the presence of an alumina catalyst, n-hexane decomposed violently and exploded the bomb, whereas cyclohexane decomposed quite smoothly.

Brooks and Humphrey (11) in studying the cracking of high boiling distillates of petroleum made these statements with regard to the relative stability of paraffins and naphthenes:

"In cracking commercial paraffins, we were surprised to find that this material is more difficult to decompose than light lubricating oil which is composed almost exclusively of naphthenes and polynaphthenes. While the simpler naphthenes whose constitutions are known, such as cyclohexane and methylcyclopentane, are apparently more stable to heat than normal paraffins, and have been found among the products resulting from heating simple paraffin hydrocarbons under pressure, (Engler: Das Erdöl), the instability of the three- and four-membered rings in the terpene series is well established. The properties of cycloheptane, cyclo-octane, cyclononane and their derivatives are not so well known, but their tendency to rearrange to five and six ring systems have been frequently observed. It is probable that the relatively greater ease of cracking petroleum naphthenes such as constitute much the greater part of light lubricating oil, as compared with the cracking of commercial paraffin wax of substantially the same average molecular weight and boiling range, is to be interpreted as indicating that these high boiling naphthenes belong to series other than of five- or six-membered rings. The behavior on heat decomposition of naphthenes of known constitutions such as cyclooöctane, cyclononane, or their derivatives is not known."

Jones and Wheeler (39) obtained aromatic products at 350° by distillation of the following type of compounds in vacuo. They point out that the temperature is less than that necessary to split off hydrogen. They assume this reaction:



Brooks and Humphrey suggest that the action is probably similar to that found for their synthetic "phenyl-paraffin."

$$C_{10}H_7C_nH_{2n+1} \rightarrow C_{10}H_8 + C_nH_{2n} \text{ (Olefin or naphthene)}$$

The conclusions of Brooks and Humphrey as to the identity of the higher naphthenes do not, however, consider the possibility of cyclohexane or cyclopentane rings with aliphatic side chains. The long side chains may account for the relative ease of decomposition of the higher boiling light lubricating-oil stock.

There seems to be evidence that n-hexane and cyclohexane reverse their order of stability under certain conditions. As Jones points out, however, there seems to be a difference between the $-CH_2$-groups in n-hexane and cyclohexane and those in the other polymethylene hydrocarbons, cyclopentane and cycloheptane.

Although the difference in stability of these hydrocarbons under pyrogenic conditions appears to be one of variation depending upon conditions, this difference is not apparent from a study of the structure of the compounds. As shown in a preceding paragraph, the stability of the rings upon a structural basis is such that cycloheptane would be more unstable than cyclohexane, and that cyclohexane and cyclopentane would be comparable in stability. The stability of n-hexane, cyclohexane and benzene may be compared from data reported by Ellis, (22), who finds that the heat of dissociation of the carbon-hydrogen linkage is 94,000 cal. for cyclohexane, 97,000 for n-hexane, and 117,000 for benzene. No data is given for carbon-carbon linkages, however.

Perhaps the question of stability or ease of decomposition may be answered by a study of the stereochemistry of the hydrocarbons in question. n-Hexane, cyclohexane, cyclopentane and cycloheptane are apparently not alike in spatial relations, although the action of cyclopentane and cycloheptane over palladium at the same temperature indicates a possible similarity in structure. The relation of cyclohexane to benzene in the pyrogenic reaction can perhaps be explained by the spatial relations of the atoms or by an assumed stabilizing or unstabilizing effect of hydrogen atoms added to the basic aromatic structure.

Catalysis in the pyrolysis of cyclohexane and closely related compounds has been extensively studied. The metals useful as catalysts are Pd, Pt, Ir, Rh, Cu, Co, Ni, Fe, Zn, Os, and Ru. These metals were found to have structures which make them particularly useful for dehydrogenation. The "multiplet hypothesis" of Balandin (3), however, correlated with results of experiments to be described later, indicated that:

(1) Cyclopentane and cycloheptane, being five- and seven-membered rings, should not be dehydrogenated by metal catalysts.

(2) Cyclohexene and cyclohexadiene should not be obtainable as products of partial catalytic dehydrogenation of cyclohexane.

(3) Di-substituted cyclohexanes should not be dehydrogenated by metal catalysts when the substituted groups are attached to the same carbon atom. This "multiplet theory," which is fundamentally the same as the "spacing theory" of Langmuir, Adkins, and Burk, is based upon the crystal structure of the metal catalysts.

A quantitative study of the dehydrogenation of decalin with catalysts was made by Zelinsky and Balandin (94), with the purpose of developing a new theory of heterogeneous catalysis. This theory, announced later by Balandin, was the "multiplet hypothesis" mentioned above. Platinized activated charcoal was three and one-half times as effective in the catalysis of $C_{10}H_{18}$ to

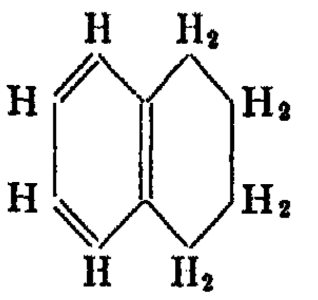
$C_{10}H_8 + 5H_2$ as was platinum when deposited on asbestos. Arrhenius' formula

$$K = K_0 e^{-Q/RT}$$

applied up to 270° where decomposition of the decalin occurred, and the carbon formed covered the catalyst. The decreased catalytic action beyond that point affected only the K_0 and not the activation energy, Q. Comparison of the coefficients K_0 and Q, calculated for the systems cyclohexane-palladium, cyclohexane-platinum and cyclohexane-nickel, showed that the activation energy Q, and the temperature coefficient of the reaction velocity K, depended not on the nature of the substance catalyzed, but only on the nature of the catalyzer used. In general, Q was 18,725 cal. per gram-mol for Pt, 15,780 for Pd, and 9,850 for Ni. With nickel as a catalyzer the reaction also followed Arrhenius' formula up to about 270°, but above this temperature the gas yield increased instead of decreasing as with platinum. The increase was attributed to side reactions, for at 240° the gas was pure hydrogen while at 270° it contained 8.3 per cent of methane. In the presence of platinum the gas was pure hydrogen even at 333°. Dehydrogenation, which in this case transforms a single carbon-carbon bond into a double bond, can be regarded as a process of increasing the distance between carbon atoms by the action of a catalyzer. The influence on dehydrogenation of the time of contact between the hydrocarbon and the catalyzer, and of the addition of one of the reaction products, indicated that adsorption plays an important part in the kinetics of dehydrogenation catalysis.

Balandin (4) studied the kinetics of the action $C_{10}H_{18} = C_{10}H_8 + 5H_2$ at a temperature of 228 to 277° in the presence of osmium. Addition of the reaction products, naphthalene and hydrogen, was found to have little effect upon the speed of the action. At 270° the energy of activation was 10,000 cal. per mol, while the energy of activation increased to 16,500 cal. with the increase of activity noted after prolonged use of the catalyst.

The effect of time and pressure upon catalytic thermal decomposition of tetralin and decalin was emphasized by Hugel (33) in a report of work done in his laboratory. The most interesting points of the discussion were in the assumptions or predictions that were made. A glance at the structure of tetralin,



shows clearly that the hydrogenated ring may disintegrate in several different ways by splitting the carbon-carbon linkages at various points or series of points. The following free radicals may be formed, then, from the splitting of the ring:

$[=CH-CH_2-CH_2-CH=]$, $[=CH-CH_2-CH=]$, $[=CH-CH=]$, and $[=CH_2]$.

These radicals, once formed, may behave so as to:

(1) Dehydrogenate to a more unsaturated radical.

(2) Hydrogenate to a paraffin.

(3) Internally satisfy the bonds, such as the formation of butadiene from $[=CH-CH_2-CH_2-CH=]$.

(4) Further decompose, for example $[=CH-CH_2-CH_2-CH=] \rightarrow CH_2{=}CH_2 + 1.5C + .5\ CH_4$

(5) Disproportionate to form a saturated compound and an unsaturated residue or even carbon as $2[=CH_2] \rightarrow CH_4 + C$.

(6) Polymerize to hydrocarbons such as

$$2[=CH-CH_2-CH=] \rightarrow CH_2{=}CH-CH-CH{=}CH_2$$

Hugel postulated that the cracking reaction proceeded first by loosening the bonds between carbon and hydrogen atoms, or between carbon atoms, by the influence of heat. These loosened bonds could then split into unsaturated radicals, as shown above, which react to form primary products. Further action may take place to form secondary products.

Dojarenko (18) compiled data (see Table VII) showing the action observed when cyclopropane and cyclobutane hydrocarbons were heated. Consideration of these results led to this generalization: "Isomerization takes place in such a way as to form one or more methyl groups, and in the case of three-membered rings this methyl group is formed by the moving of a hydrogen atom from a central atom to an end carbon atom. By use of this rule it would be predicted that diethyltrimethylene would give methyldiethylethylene when passed over heated alumina."

In an earlier paper by Dojarenko (17) a discussion was given leading to these conclusions. "The catalyst causes, by the influx of external energy, the loosening of a C-C linking, with the formation of intermediate labile forms, which give various products depending on the external energy conditions. In all cases the final product has a smaller energy content than the initial compound, as is shown by the values calculated from Fajans' and Hückel's (32) data for C-C and C-H linking in rings and chains."

Much of the work upon unsaturated cyclohexane derivatives is found in Zelinsky's study of the "specific catalyst."

The so-called "simultaneous oxidation-reduction" of unsaturated cyclohexane derivatives by passing them over a palladium catalyst takes place at temperatures lower than those necessary for dehydrogenation of cyclohexane. The action $C_6H_{12} = C_6H_6 + 3H_2$ reaches equilibrium at 200°, and hydrogenation of aromatic compounds take places at lower temperatures. Zelinsky stated that cyclohexene, under the same conditions as cyclohexane, dehydrogenated much more easily and energetically.

From the above, it seems probable that the action consists of dehydrogenating the unstable unsaturated compounds to benzene with the concurrent hydrogenation of the benzene to cyclohexane. Since the temperatures employed are below 200°, it is evident that the equilibrium between benzene and hydrogen and cyclohexane is shifted to the formation of the naphthene. That the equilibrium is shifted above 200° to form benzene and hydrogen was shown by Zelinsky and Pawlow (100) by heating two mols of cyclohexane and one mol of benzene at definite temperatures and comparing the results to the action of cyclohexene over the same catalyst and under like conditions.

The theory and mechanism of the action of cyclopentadiene and cyclohexadiene has been included in the later discussion of these compounds. Similarly, other compounds are discussed in the sections devoted to reactions of the specific type of compound in question, and hence are not included at this point.

3. Cyclopropanes

The simplest ring possible in the hydrocarbon series is made up of three carbon atoms. As previously shown, this ring is the least stable of the cyclic compounds, and hence the non-catalytic pyrolysis might be expected to proceed at low temperatures.

The best temperature for one type of reaction, isomerization, was at 600° with a contact time of 50 minutes. At higher temperatures or with a longer contact time, a second type of reaction began, i.e., the rupture of the hydrocarbon with the formation of carbon, hydrogen, ethylene, and other gaseous products.

A. Non-catalytic

It has long been known that a "dynamic isomerization" existed between cyclopropane and propylene. Tanatar (71) considered that the isomerization was caused by the degradation of the compound with the greater energy to that with a smaller energy content. As was later pointed out by Berthelot (8), the heat of formation of cyclopropane and propylene was 17.1 and 9.4 cal. per mol. respectively. Trautz and Winkler (75) showed this difference to be insufficient to permit the application of Nernst's heat theorem to this isomerization.

Walkoff and Menschutkin (76) attributed the isomerization observed by Tanatar to the presence of propylene as an impurity in the cyclopropane used. They found that a purified cyclopropane did not isomerize at a "red heat" but that an "oxymethylene" and tar were formed. The products observed were undoubtedly formed by the action of air in the pyrolysis tube, hence their criticism has very little weight.

Tanatar (70) replied to Walkoff and Menschutkin in a later paper. He repeated the pyrogenic reaction with cyclopropane purified in the same manner as that used by Walkoff and Menschutkin. Again, the product obtained was propylene. Tanatar concluded that the observed isomerization was the true reaction occurring under his conditions of experimentation. When the gas obtained from the pyrolysis was either treated with sulfuric acid and hydrolyzed, or oxidized, the formation of isopropyl alcohol and of acetone was taken as proof of propylene. It must be remembered, however, that cyclopropane reacts similarly to propylene with the usual reagents, such as bromine, 2 percent permanganate, or sulfuric acid, showing only a slower velocity of reaction.

Berthelot (8) heated cyclopropane in a bulb for 20 minutes at 550°. The gases formed occupied 101 volumes for every 100 volumes of cyclopropane used and were made up of 4 volumes of cyclopropane, 76 volumes of propylene, 7 volumes of ethylene and 14 volumes of saturated hydrocarbons and hydrogen. The products indicated clearly that decomposition as well as isomerization had occurred.

Trautz and Winkler (75) in searching for other examples of gaseous monomolecular reactions, studied the isomerization of cyclopropane to propylene. The curve, Fig. 2, quoted from these authors, illustrates the formation of propylene as a function of time from the treatment of cyclopropane in a porcelain tube at 600°.

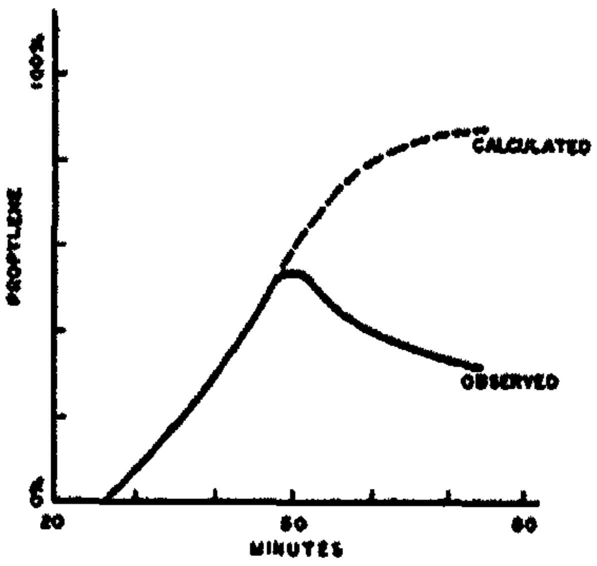


FIG. 2

The isomerization followed the curve calculated from the velocity constant for a monomolecular reaction until a contact time of 50 minutes was reached. At this point the formation of secondary products began, the gas being made up of methane and hydrogen in equal amounts.

Experiments at temperatures of 500 to 700° showed that isomerization was the chief reaction up to temperatures of 600° with contact time of 50 minutes, while temperatures above 600° could be used if the contact time was sufficiently short. Under more vigorous conditions, higher temperature or increased contact time, decomposition occurred to give ethylene, methane, carbon, and hydrogen, together with the propylene formed by isomerization.

The size and shape of the reaction vessel, such as tubing or a bulb, and the material of the vessel—quartz or unglazed porcelain—affected the speed of the reactions. The amount of wall catalysis of the vessel decreased as the temperature increased.

At temperatures of 600 to 700° the isomerization of cyclopropane to propylene was shown to be a monomolecular reaction. The "heat of activation" at temperatures of 550 to 650° was found to have a value of 63,900 cal.

Since the early work upon the pyrolysis of cyclopropane was of doubtful value because of the questionable purity of the hydrocarbon used, the method of preparation of the compounds is included here. The propylene and cyclopropane used by Trautz and Winkler (74) for their experiments were prepared in a pure form by the following reactions:

Trimethylene bromide was treated with zinc dust in a suitable apparatus for generating the gas. A series of tubes was constructed in such a manner that each served as a fractionating column and a condensing bulb. The gas liberated in the action was condensed at −79° and fractionated in the series of tubes. In this manner, pure cyclopropane could be prepared.

Propylene was prepared by catalytic decomposition of isopropyl alcohol at 400°. The alcohol was run through a heated copper tube dehydrating it to form propylene. The propylene and cyclopropane were condensed at −79°, and by a series of fractionations, the pure compounds were found to have boiling points of −47.8° and −34.5° respectively at 750 mm. The specific volumes of the liquids were found to be additive, so that a convenient method of analysis of propylene-cyclopropane mixtures was available.

Ipatiev and Huhn (37) observed that cyclopropane yielded only 1 to 2 per cent of propylene at 360 to 370° when passed through a tube at the rate of 215 cc. per hour. The approximate time of contact was 4.5 minutes.

B. Catalytic

The use of catalysts markedly decreases the temperature necessary to cause isomerization of cyclopropane. No mention of decomposition to other products such as carbon, hydrogen, or methane is made. Tanatar (72) observed that in the presence of platinum black at ordinary temperature cyclopropane isomerized slowly to propylene, while a temperature of 100° slightly increased the rate, as would be expected. At 315°, 2 grams of catalyst in the reaction tube caused a 29 percent yield of propylene when the cyclopropane was passed through the tube at the rate of 285 cc. per hour. With an alumina catalyst Ipatiev and Huhn (37) found that 3 grams of catalyst caused a 20 percent isomerization to occur at 370 to 385°. The gas in this case was passed through the tube at a rate of 343 cc. per hour.

Ipatiev (35) used an iron catalyst at 100° to effect the isomerization of cyclopropane to propylene. The cyclopropane used in this case was purified by shaking with 2 percent permanganate and treating with bromine in the dark. The gaseous product from the pyrolysis was 50 to 70 percent propylene, as proven by oxidation with permanganate and by bromide formation. The other portion of the gas was shown to be cyclopropane.

Dojarenko (18) passed methylcyclopropane at 340-360° through a tube coated with alumina. The gaseous products consisted of 2-butene and isobutylene, while a liquid was found which was a polymer of the butenes, most likely diisobutylene.

Ipatiev and Huhn (37) reported the formation of 7.5 grams of a liquid boiling at 35 to 37° when 8 grams of 1,1-dimethylcyclopropane were passed over alumina at 340 to 345° in one hour and eleven minutes. This liquid was shown to be trimethylethylene, a product of isomerization.

Merejkowsky (49) obtained divinyl or 1,3-butadiene by passing methyleneeyclopropane over alumina at 350°.

Ethylcyclopropane, passed at 300 to 310° through a tube containing asbestos covered with alumina, was isomerized to methylethylethylene as reported by Rozanov (57).

From these results it may be concluded that catalytic action upon cyclopropane compounds consisted of an isomerization of the ring to a straight chain compound. The temperature of the catalytic action was generally between

300 and 350° with platinum black and alumina giving similar results, while iron caused the reaction to proceed at a lower temperature, that is, at 100°. In no case was there any appreciable deposition of carbon noted, nor was mention made of the formation of compounds other than those derived from isomerization.

4. Cyclopropene

Cyclopropene may well be considered as the unsaturated hydrocarbon resulting from the removal of two hydrogen atoms from cyclopropane. It has already been pointed out that cyclopropane has a strong tendency to rearrange to a straight chain hydrocarbon by a scission of the ring when subjected to a temperature of 500 to 700° without a catalyst, or to a temperature of only 300° when a catalyst is used. Since cyclopropene is so closely related to cyclopropane, it follows that isomerization should be expected to occur if the former hydrocarbon is heated with a catalyst.

The ease with which cyclopropene rearranges should be less than with cyclopropane. Hurd and Spence (34) found isobutylene more stable than isobutane when subjected to elevated temperatures, i.e., 600 to 700°. If it may be assumed that a point of unsaturation in a cyclic compound has the same effect as in a straight chain compound, it follows that cyclopropene should rearrange with more difficulty than cyclopropane.

In the preparation of cyclopropene the resulting bromides gave tests for allylene tetrabromide. To prove whether this compound was formed from the cyclopropene or occurred as an impurity, Demjanow and Dojarenko (14) passed cyclopropene through a tube at 270 to 290° over an alumina catalyst. Since the product did not react with ammoniacal cuprous chloride solution, it was concluded that methylacetylene (allylene) was not formed.

In later work Demjanow and Dojarenko (15) again tried this reaction, but at 245 to 255° and at 345 to 350° using unpurified cyclopropene. The product gave a bromide of approximate composition, $C_3H_6Br_2$, but it was concluded that propylene was formed from the methylacetylene present in the original gas. Liquid products consisted of a volatile polymer and a non-volatile, more complex polymer. The conclusion reached was that cyclopropene did not isomerize to allylene.

A theoretical consideration of the pyrolyzed compound would lead to the fact that allene as well as methylacetylene could be formed with equal ease by the breaking of a single bond in the ring. In pyrogenic work a double bond has appeared to be a place of strength in the molecule and any carbon-carbon scission occurs at a single bond in preference to a double linkage. Meinert and Hurd (48) have studied the pyrolysis of allene and methylacetylene and found that methylacetylene gives pyrolytic products identical with those of allene, when similar conditions are employed. This indicates clearly that if the product that Demjanov and Dojarenko expected had actually formed, the product identified would be the isomer, allene. Although the conditions of the two groups of experiments run by the respective authors were not identical, they were comparable, as shown by the decomposition points for cyclopropane; namely, 600 to 700° for the non-catalytic reaction and 300 to 350° when using alumina as catalyst.

The method of analysis for the gases obtained from cyclopropane was the absorption of acetylene or its homologs in ammoniacal cuprous chloride. It is questioned whether this method would show the presence of allene in the gases if it were there.

5. Cyclobutanes

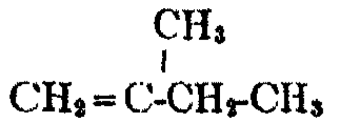
There appears to be no record of any study made upon the pyrolysis of cyclobutane. This hydrocarbon has been catalytically reduced to n-butane, but no reference was found on the heating of cyclobutane without hydrogen.

Methylcyclobutane, however, has been pyrolyzed by Rozanov (56). With an alumina catalyst the pyrolyses were run at 300 to 400°. Heating the methylcyclobutane for three hours at 300° resulted in a small amount of product boiling at 30 to 40°, while methylcyclobutane itself boiled at 39 to 42°. At 350° a product boiling at 25 to 30° was formed by the pyrogenic action. With a decomposition temperature of 400° most of the product boiled at 20 to 22°. Taking some liquid from the 400° run, four portions could be obtained by refractionation, 20 to 22°, 30°, 35 to 37°, and 40 to 200°. The high boiling fraction consisted of polymers, while the other fractions represented isomers of methylcyclobutane, as follows:

$CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CH_3$ b.p. = 36°
2-pentene

$$\overset{\displaystyle CH_3}{\overset{|}{CH_3\text{-}CH}}\text{-}CH{=}CH_2$$

b.p. = 20.2°
3-methyl-1-butene



$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}\text{-}CH_2\text{-}CH_3$$

b.p. = 31-32°
2-methyl-1-butene

Fillipov (25) obtained methylcyclobutene from methylenecyclobutane by passing the vapor of the latter hydrocarbon over alumina at 300°. That this isomerization takes place was known as early as 1901, when Gustavson (29) obtained the reaction by treating methylenecyclobutane with sulfuric acid, alkalis, or small amounts of hydrogen bromide.

The study of the action of methylenecyclobutane above 300° in the presence of an alumina catalyst was made by Dojarenko (18). The experiments were carried out in an apparatus consisting of a tube 1 cm. in diameter and 35 cm. long, coated with 10-12 gm. of alumina and heated in an iron muffle.

Table VI gives the experimental details of the pyrolyses made by Dojarenko.

TABLE VI

Decomposition of Methylenecyclobutane

Temp., °C.	Time Min.	Wt. of Liquid Used Gms.	Liquid Products		Gas cc.
			Low Boiling Hydrocarbons	Polymers	
410–30	30	7.5	4.5 g.	2.1 g.	540
395–405	45	13.5	9.4	2.2	235
400–405	45	7.5	5.2	1.0	160

TABLE VII

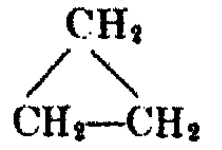
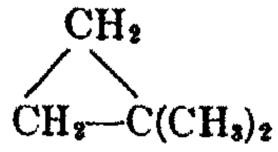
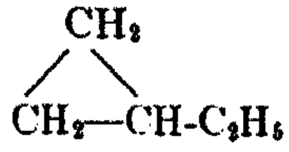
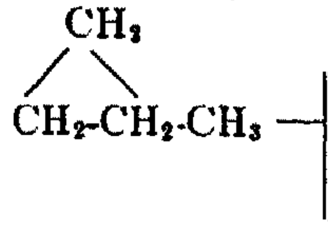
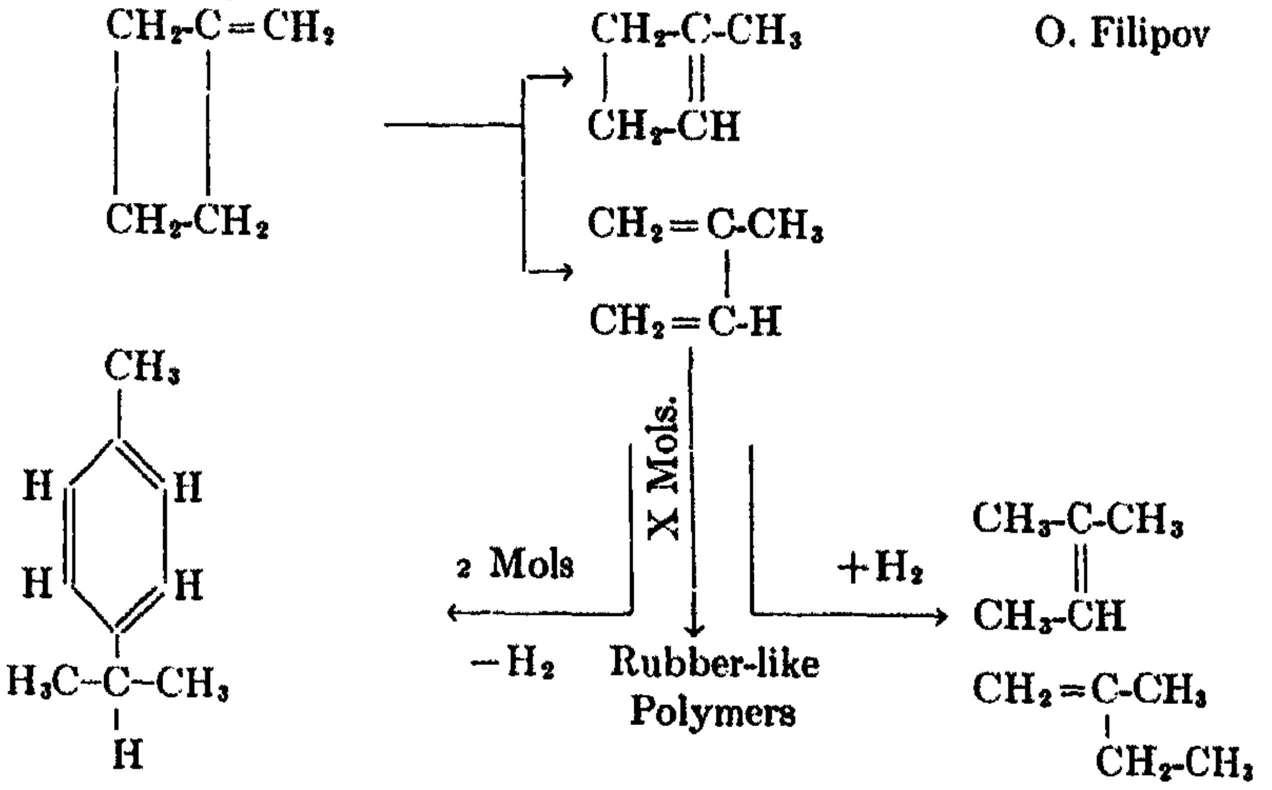
Initial Product	Reaction Product	Observer
I. Trimethylene 	$CH_3\text{-}CH=CH_2$	Ipatiev and Huhn
II. as-Dimethyl-trimethylene 	$CH_3\text{-}CH=C(CH_3)_2$	Ipatiev and Huhn
III. Ethyltrimethylene 	$CH_3\text{-}CH=CH\text{-}CH_2\text{-}CH_3$	Rosanov
IV. Methyltrimethylene 	$CH_3\text{-}CH=CH\text{-}CH_3$ Isomerization $(CH_3)_2CH=CH_2$ $(CH_3)_2CH\text{-}CH_2\text{-}CH=C(CH_3)_2$ Isomerization and Polymerization	Dojarenko
V. Methylenecyclobutane 		O. Filipov

Table VIII shows the conditions of experiment and the products obtained from cyclopropane and cyclobutane hydrocarbons.

TABLE VIII

Cyclopropanes and Cyclobutanes

Reference No.	Hydrocarbon	°C. Temp.	Catalyst	Product
(70)	Cyclopropane	"Red Heat"	None	Propylene
(76)	"	" "	"	Tar Oxymethylene
(8)	"	550	"	Propylene Ethylene Satd. Hydrocarbons Hydrogen
(75)	"	500-700	Quartz Tube or Unglazed Porcelain	Propylene Ethylene Methane Carbon, Hydrogen
(37)	"	360-370	None	Propylene
(72)	"	315	Platinum	Propylene
(37)	"	370-385	Al_2O_3	"
(35)	"	100	Iron	"
(18)	Methylcyclopropane	340-360	Al_2O_3	2-Butene Isobutylene Diisobutylene
(37)	1,1-Dimethylcyclopropane	340-345	Al_2O_3	Trimethylethylene
(49)	Methylenecyclopropane	350	Al_2O_3	1,3-Butadiene
(57)	Ethylcyclopropane	300-310	Al_2O_3	Methylethylethylene
	Cyclobutanes:			
(56)	Methylcyclobutane	300-400	Al_2O_3	2-Pentene 3-Methyl-1-butene 2-Methyl-1-butene Polymers
(25)	Methylenecyclobutane	300	Al_2O_3	Methycyclobutene
(18)	"	395-430	Al_2O_3	Isoprene p-Cymene Trimethylethylene Methylethylethylene Rubbery Mass

Less than one-third of the gases produced dissolved in bromine indicating that the greater portion of the gas was made up of saturated hydrocarbons. The bromide formed from the gases boiled at 141 to 152° at 741 mm. pressure.

The liquid analysis led to the identification of isoprene, trimethylethylene, and unsymmetrical methylethylethylene in the low boiling material, while p-cymene was found in the heavy polymerized product together with a rubber-like mass. The chief liquid product was isoprene.

The decomposition of methylenecyclobutane over alumina at 400 to 430° consisted of isomerization, dehydrogenation, polymerization and hydrogenation. The first reaction, isomerization, resulted in the formation of isoprene. This compound polymerized to a rubber-like mass, hydrogenated and isomerized to the ethylene compounds found, and dehydrogenated and polymerized simultaneously to give p-cymene.

Table VII, compiled by Dojarenko, includes not only the results of work on methylenecyclobutane but also summarizes the actions observed with all the three-and four-membered ring-compounds previously discussed by her.

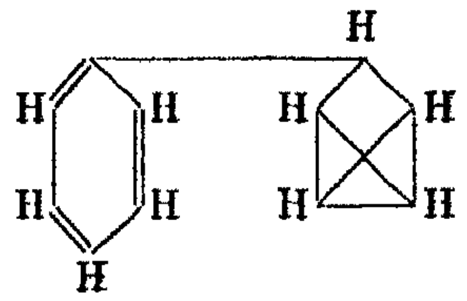
6. Cyclopentane and Homologs

Cyclopentane, the most stable of the saturated cyclic hydrocarbons, as shown in Table V, has not been pyrogenically decomposed. Although the cyclopentane hydrocarbons are obtainable, only one attempt has been made to decompose the simplest member of this series. The more complex members of the series have been subjected to the catalytic action of palladium black which is known as a specific dehydrogenation catalyst. Zelinsky, in his work with palladium or platinum black catalysts, observed that only cyclohexane compounds dehydrogenated, while paraffins or other polymethylene hydrocarbons were unchanged by passage over these catalysts under the same conditions.

Cox (12) refluxed cyclopentane with anhydrous aluminum chloride for a period of eight days, yet no evolution of gas was observed nor was the liquid changed.

Cyclohexylcyclopentane, 1-cyclohexyl-3-methylcyclopentane and phenylcyclopentane have been studied by Zelinsky and Titz (102). These compounds, in the presence of palladium black at 300°, should dehydrogenate in a manner to give phenylcyclopentane, 1-phenyl-3-methylcyclopentane, and unchanged phenylcyclopentane respectively, if the catalyst exercised the selective action claimed by Zelinsky and Balandin.

With cyclohexylcyclopentane, the expected phenylcyclopentane was not obtained. A compound $C_{11}H_{10}$ was produced instead of the anticipated $C_{11}H_{14}$. The compound was not a cyclobutadiene, for it did not react with bromide solution or permanganate. It was concluded that the compound had the following structure in which the excess valences are internally satisfied:



With 1-cyclohexyl-3-methylcyclopentane, under the same conditions, isomerization took place with subsequent dehydrogenation of the isomer. Diphenyl was the final product after the formation and subsequent dehydrogenation of dicyclohexyl.

Zelinsky and Titz (104) later observed that the compound they had analyzed to be $C_{11}H_{10}$ had the properties of diphenyl. The analysis of the compound had given values of 93.25 percent for carbon and 6.81 percent for hydrogen. $C_{11}H_{10}$ gives the calculated values of 92.9 and 7.1 for carbon and hydrogen whereas $C_{12}H_{10}$ is 93.5 and 6.5. Obviously, the values found are between those for $C_{11}H_{10}$ and $C_{12}H_{10}$.

To explain the occurrence of diphenyl in the product, these authors studied their method of preparation for cyclohexylcyclopentane which consisted of reacting cyclohexylmagnesium bromide with cyclopentanone with subsequent reduction of the alcohol. In the preparation of the Grignard reagent, however, the normal course had not been followed, and a Würtz-Fittig type of reaction had occurred, whereby cyclohexyl bromide had been transformed to dicyclohexyl. Thus the product they had studied had been actually a mixture of dicyclohexyl with some cyclohexylcyclopentane.

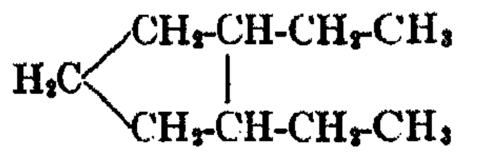
In a like manner cyclohexyl-3-methyl-cyclopentane had supposedly been prepared, so that the reported dehydrogenation and isomerization product, diphenyl, had been really only the simple dehydrogenated dicyclohexyl.

Repeating the work with cyclohexylcyclopentane and cyclohexyl-3-methylcyclopentane, it was found that these compounds gave the expected dehydrogenation products when passed over palladium at 300°.

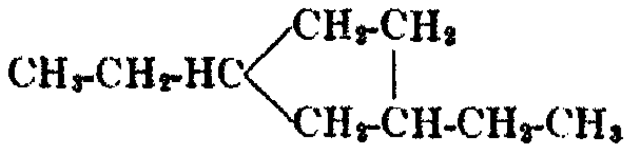
A new hydrocarbon, cyclohexylcyclopentylmethane was prepared and found to dehydrogenate over palladium at 300° in the normal manner, phenylcyclopentylmethane being the product obtained.

Phenylcyclopentane did not change under this treatment as might have been expected from theoretical considerations. Likewise, Zelinsky, Titz, and Fatejew (105) found that dicyclopentane and 3,3-dimethyldicyclopentane were unchanged by similar treatment.

Kizhner (41) reduced 1,2-diethylcyclopentane with concentrated sulfuric acid and with boiling hydriodic acid. In the first case a hydrocarbon C_9H_{18} and a polymer $C_{18}H_{32}$ were obtained, while in the second case a different C_9H_{18} was produced. The first hydrocarbon



did not isomerize to the second hydrocarbon

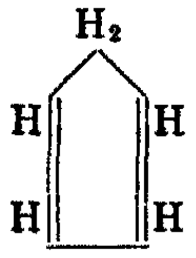


$$\mathrm{CH_3\text{-}CH_2\text{-}HC}\left<\begin{array}{l}\mathrm{CH_2\text{-}CH_2}\\ \qquad\;|\\ \mathrm{CH_2\text{-}CH\text{-}CH_2\text{-}CH_3}\end{array}\right.$$

when it was boiled with hydriodic acid. The ease with which this type of reaction occurs might lead one to expect such isomerization to take place in this case, but knowledge of the compounds was insufficient to predict safely any action or series of actions.

7. Cyclopentadiene

Cyclopentadiene, C_5H_6, may be considered from the viewpoint of structure. The accepted structure



permits us to predict, by analogy, what properties to expect. The cyclic compound may well be considered as a butadiene compound with 1,3-unsaturation. Thus, cyclopentadiene is closely related to isoprene, which is a methyl-1,3-butadiene hydrocarbon. Isoprene is known to give the same type of polymerization as that outlined for cyclopentadiene in the following section. We shall see that conjugated systems of unsaturation in cyclic hydrocarbons exhibit the same characteristic chemical properties as in chain hydrocarbons.

The first observation made upon cyclopentadiene polymerization seems to be limited to the dimeride. Roscoe (55) observed that the low boiling fraction of coal tar, on standing, separated a solid melting at 32.9° and having a formula of $C_{10}H_{12}$. Under a high vacuum the hydrocarbon boiled without decomposing, but distilled under ordinary pressure, it formed a low boiling material. Roscoe concluded that $C_{10}H_{12}$ was a polymer, although the primary substance, C_5H_6, was not isolated. This $C_{10}H_{12}$ hydrocarbon, heated to 180° in an air-free tube, polymerized to an opaque, buttery mass, the solid constituents of which melted at 200 to 220° with decomposition.

Etard and Lambert (23) obtained, from compressed petroleum illuminating gas, a hydrocarbon C_5H_6 which they called "pyropentylene." They found that it polymerized spontaneously to a "dipyropentylene," $C_{10}H_{12}$ (melting point 8°), and that, upon heating, the $C_{10}H_{12}$ depolymerized to C_5H_6. They were the first to observe the equilibrium,

$$2C_5H_6 \rightleftarrows C_{10}H_{12}.$$

They studied the kinetics of the action by plotting the change in density against time. From this they concluded that the process of polymerization was a "regular action."

Kronstein (43) stated that not only $C_{10}H_{12}$, but also the $(C_5H_6)_n$ type of polymers in which n is greater than 2, should be formed. Weger (77) predicted that the products of the reaction would be a great number of polymers with varied properties.

Stobbe and Reuss (68) noted that the use of viscosity measurements was not reliable for this equilibrium study because of the volatility of the cyclopentadiene.

A pure cyclopentadiene was obtained from the dimer by distillation at atmospheric pressure. The values for the refractive index were $n_C^{20} = 1.4413$ and $n_F^{20} = 1.45380$. The dimer gave indices of $n_C^{20} = 1.51047$ and $n_F^{20} = 1.52181$.

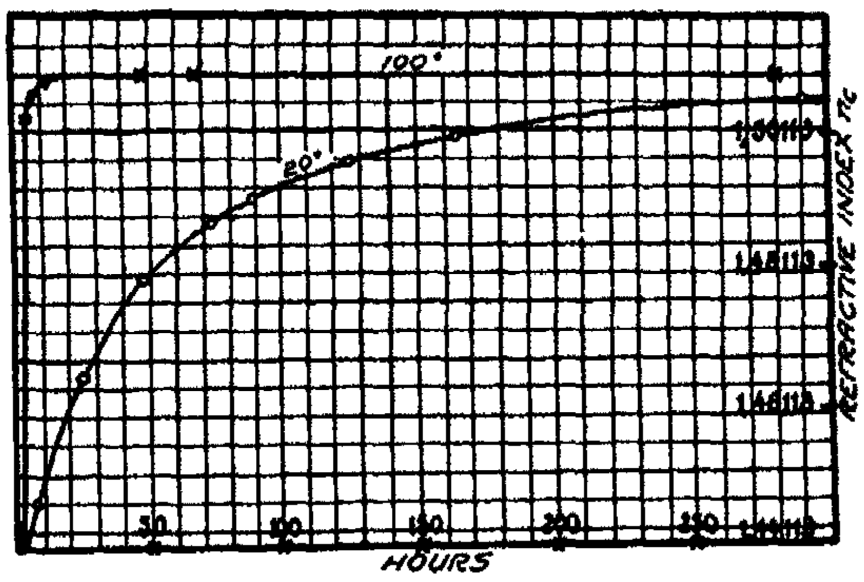


Fig. 3

If the dimer was distilled rapidly, depolymerization did not proceed to completion, and the rising distillation temperature indicated increasing amounts of the dimeride in the product, as shown by refractive index.

The study of temperature influence upon this polymerization showed that at −80° the reaction did not proceed but that at −15° a slow action occurred. At 20° the action was fairly rapid, while 100° fostered a high speed of reaction. By plotting change of refractive index against time, the type of curve, Fig. 3, was obtained:

Light had little influence upon the course of the reaction, but an increase of temperature to 135° caused other polymers to form.

A summary and conclusion of the work of Stobbe and Reuss may be given:

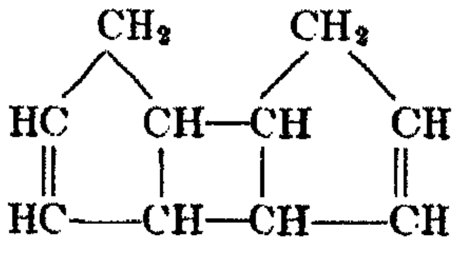
Cyclopentadiene at 100° formed chiefly dicyclopentadiene, while at 135° others polymers were formed:

$$(C_5H_6)_n \text{ where } n > 2.$$

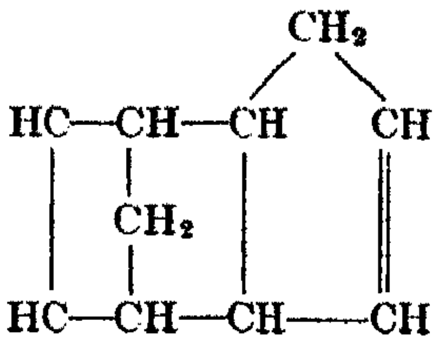
Cyclopentadiene polymerized in the dark quite rapidly at 20°, changing completely in 30 days time. The action was rapid at first, but later stages followed the mass action laws.

Stobbe and Dünnhaupt (67) showed later that this reaction proceeded readily when the materials were shaken at room temperature. They obtained the dimeride and the dimeride oxide, which was formed from the oxygen of the air.

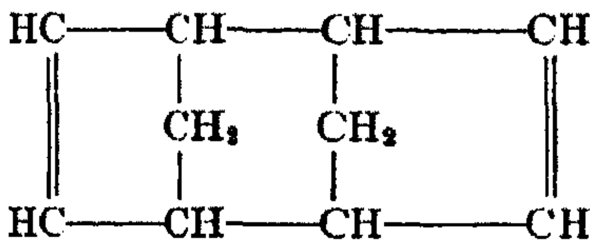
There are several possibilities for the polymerization of cyclopentadiene. The dimer might have one of the following three structures:



(*1*)



(*2*)



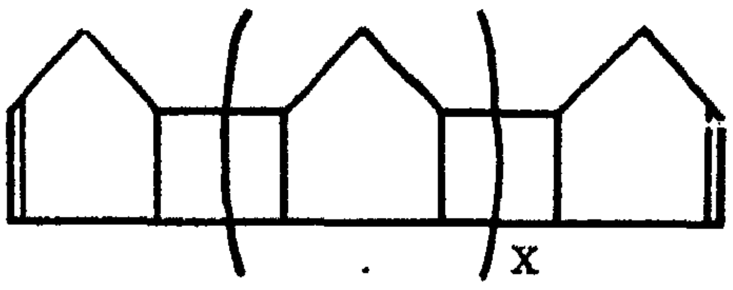
(*3*)

(*1*) Kraemer and Spilker (42).
(*2*) Weiland (78).
(*3*) 1:4 addition. Staudinger and Rheiner (66).

The first formula was assumed to be the correct one, because it allowed the formation of addition compounds. Kronstein (43) formed additional polymers by heating the cyclopentadiene to a higher temperature. Weger (77) also obtained a series of polymers.

Staudinger and Rheiner (66) obtained a tri-, tetra-, penta-, and possibly a hexameride of cyclopentadiene. The polymers were separated by fractional distillation at reduced pressure and by selective solvent action. The various polymers were identified by molecular weight determinations in different media, the compounds being the tri-, tetra-, and penta- polymerides. An insoluble solid was obtained which was probably a hexameride with higher polymers.

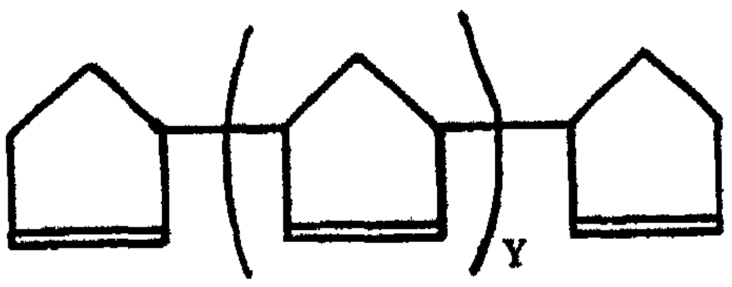
The dimeride heated for 90 hours at 200° also formed higher polymers. These polymers, heated to 500° under low vacuum, yielded cyclopentadiene again. This behavior of the polycyclopentadienes was similar to that of polyoxymethylene compounds. The compounds formed are probably of the type:



where X is relatively small.

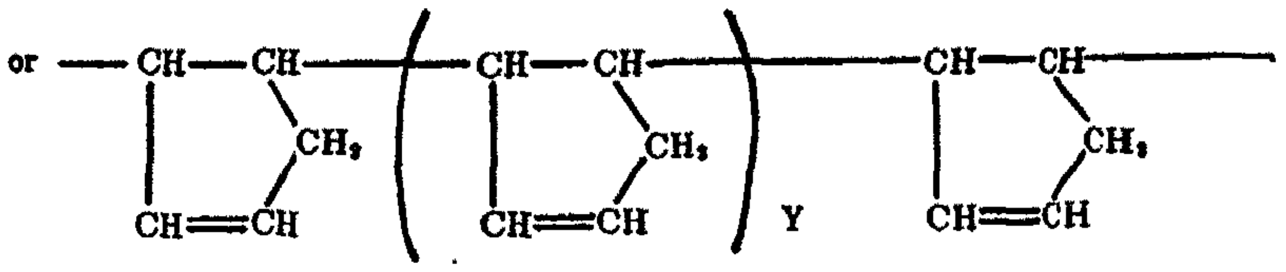
Staudinger and Bruson (65) studied this same polymerization with a catalyst. The halogen salts of all groups in the periodic table were used as catalysts. Those halides having covalences exhibited catalytic power, while halides with ordinary valences were ineffective. The products obtained gave molecular weights varying between 1200 and 6600. The polymers titrated with bromine gave one molecular equivalent for each mol of C_6H_6.

The compounds obtained were formulated as:

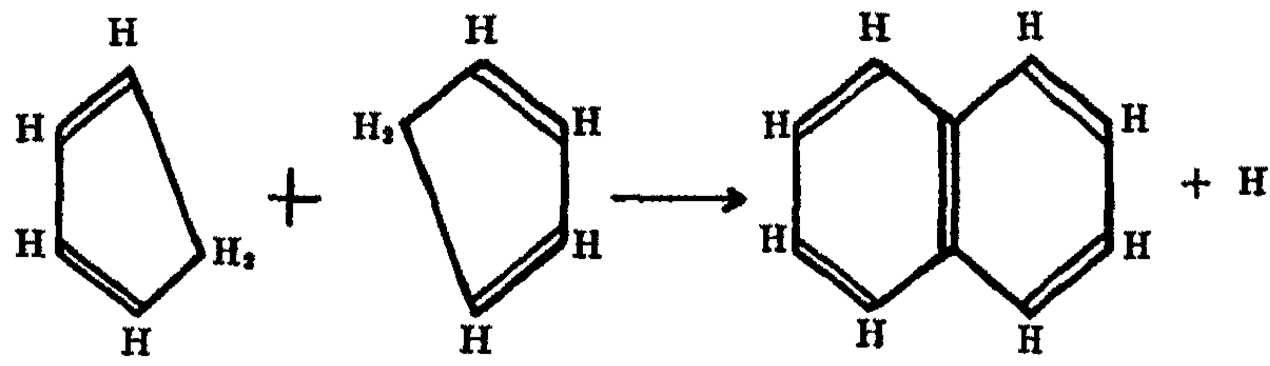


where Y is large, exceeding 20.

or



Weger (77) found that cyclopentadiene or dicyclopentadiene gave a new reaction if passed through a weakly glowing tube. Naphthalene "in good yields," together with some benzene and anthracene, were the products of this pyrolysis.



In this case we find five-membered rings changing to six-membered rings but not by isomerization of a pentamethylene homolog.

Although Weger obtained naphthalene from cyclopentadiene, Meyer and Hofmann (49A) could find none among their amorphous products. Weger had passed vapors through a tube at a dull red heat, whereas Meyer and Hofmann maintained a dull red hot coil of platinum wire in an atmosphere of cyclopentadiene vapors. The explanation offered for naphthalene formation was that Weger's temperature was high enough to form ethylene and acetylene, and that these formed naphthalene, rather than cyclopentadiene joining directly, with the elimination of hydrogen as previously shown.

The reaction products from treating cyclopentanes and cyclopentadiene are shown in Table IX.

TABLE IX

Cyclopentane—Cyclopentadiene

Reference No.	Hydrocarbon	°C. Temp.	Catalyst	Product	Remarks
(12)	Cyclopentane	Reflux	$AlCl_3$	None	No Change 8 Days
(102)	Cyclohexylcyclopentane	300	Palladium	($C_{11}H_{10}$)?	
	1-Cyclohexyl-3-methylcyclopentane	300	"	(Diphenyl) ?	
	Phenylcyclopentane	300	"	No Change	
(105)	Dicyclopentane	300	"	" "	
	3,3-Dimethyldicyclopentane	300	"	" "	
(41)	1,2-Diethylcyclopentane	—	HI	" "	
(67)	Cyclopentadiene	180	None	Dicyclopentadiene	Sealed Tube
	Cyclopentadiene	20	in Dark	"	30 Days
(65)	Cyclopentadiene	—	Halides	Polymers	
(77)	Cyclopentadiene	"Dark Red"	None	Naphthalene Benzene Anthracene	

8. Cyclohexane and Homologs

In the study of cyclohexane there is a strong tendency for most of the workers to include its homologs in a series of experiments. Although the actions of the homologs of cyclohexane are not always strictly comparable to those of the simple hydrocarbon, the difference may be attributed to the action of the side chain and not to the nucleus.

Since the time when Sabatier and Senderens (60) first catalytically reduced benzene to cyclohexane, the interest in the hydrogenated compounds has grown and other homologs and derivatives of benzene have been reduced to the corresponding cyclohexyl compounds.

The non-catalytic decomposition of cyclohexane and methylcyclohexane has been studied in only two cases. Jones (38) was the first to pyrolyze cyclohexane for the purpose of studying the action that takes place. Later, a pyrolysis was made by Frolich, Simard and White (26) using a quartz tube at a temperature higher than that used by Jones.

The catalytic decomposition of cyclohexane and its homologs has been more fully studied, the products of the reaction varying with the catalyst used. At 300° nickel has been found to cause decomposition together with dehydrogenation, while at the same temperature platinum and palladium cause dehydrogenation alone. At a temperature of 550° copper catalyzes both dehydrogenation and decomposition. Several patents have been issued in which the action described is the decomposition of cyclohexane and its homologs, at similar temperatures, to form unsaturated hydrocarbons. Several different types of catalysts such as metals, salts, etc., may be used for this reaction.

With anhydrous aluminum chloride the homologs of cyclohexane which have long side chains behave in a curious manner, the long side chain splitting into a series of short chains which attach themselves to the ring. This action is different from that of the homologs of aromatic hydrocarbons which tend to build one large hydrocarbon molecule at the expense of others. That is, with ethylbenzene and aluminum chloride, the products are di- and triethylbenzene and benzene. Ethylcyclohexane, on the other hand, forms dimethylcyclohexane.

A. Non-Catalytic

The non-catalytic thermal decomposition of cyclohexane and methylcyclohexane was studied by Jones (38). The liquid was heated in a bulb containing porcelain plates, and the gas evolved was collected and analyzed. The analyses were made using concentrated sulfuric acid for benzene and unsaturated hydrocarbons containing more than three carbon atoms; ammoniacal silver chloride for acetylenes; and bromine solution for unsaturated hydrocarbons containing only 2 or 3 carbon atoms. Hydrogen was determined by the action of "oxidized" palladium at 95°. Methane and ethane were measured by oxidation. Table X summarizes the analyses of these gases.

TABLE X

Gas Analysis of Products

Material pyrolysed	Cyclohexane Percent	Methylcyclohexane Percent
Temp. °C.	490 to 510	490 to 510
"Benzene and High Olefins"	26.1	12.8
Acetylene	0.2	Trace
Ethylene	8.5	10.6
Hydrogen	40.3	42.1
Methane	3.0	22.5
Ethane	21.9	12.0

Frolich, Simard and White (26) studied the formation of butadiene from various hydrocarbons, among which was cyclohexane. At a temperature of 654° cyclohexane was passed through a quartz tube, the product of reaction being condensed in two receivers at the temperatures of melting ice and CO_2-acetone mixture respectively. Unsaturated hydrocarbons formed 50.5 percent of the product, 20.6 mols percent consisting of butadiene. These values were based upon the amount of cyclohexane decomposed at the above temperature.

Since the formation of butadiene was of major importance to these investigators, the other products of decomposition were not studied in detail. The analysis of gaseous products was not given, but the liquid consisted of benzene, naphthalene, and tar. No toluene, xylene or other benzene homologs were found.

The results from these sources seem to indicate that besides a large amount of dehydrogenation, a certain amount of carbon-carbon scission takes place. The formation of butadiene, ethylene, and ethane indicates that the mechanism outlined in the patent (2) mentioned previously is correct. (See p. 3496).

B. Catalytic Action

Sabatier and Senderens (60) passed cyclohexane, methylcyclohexane, and ethylcyclohexane over nickel or copper catalysts at a "more or less elevated temperature" with partial dehydrogenation to aromatic hydrocarbons and partial decomposition to other products, such as carbon or methane.

Cyclohexane at 270 to 280° over nickel gave the reaction shown in the equation,

$$3C_6H_{12} = 2C_6H_6 + 6CH_4.$$

Other naphthenes reacted similarly. At about 300° over nickel they were decomposed slowly to aromatic hydrocarbons with the formation of a small amount of carbon, some methane, and hydrogen. Methylcyclohexane decomposed slowly at 240°, but the rate of reaction increased at 275°. The gases formed contained 21.8 percent of hydrogen and 78.2 percent of methane by volume. Ethylcyclohexane decomposed slightly at 220° and slowly at 280 to 300°. The liquids formed were toluene and ethylbenzene, while the gas was made up of 83 percent of methane and 17 percent of hydrogen by volume.

With reduced copper, Sabatier and Senderens found that the action was much more difficult, since a temperature of 300° was required to start the decomposition.

Daramois (13) studied the action of certain metals upon cyclohexane, methylcyclohexane and dimethylcyclohexane, as well as the petroleum oil from which these naphthenes were derived. From 325 grams of cyclohexane, passed over copper at 550°, 130 grams of liquid product were obtained. This was made up of 8 percent olefin hydrocarbons and 5 percent benzene, the remainder being unchanged cyclohexane. The other 195 grams of material was recovered as a gas, made up of 37.8 percent unsaturated hydrocarbons of which 36 percent was ethylene, 30 percent of saturated hydrocarbons with an average composition of C_2H_6 and 32.2 percent of hydrogen.

From 140 grams of methylcyclohexane over copper at 550°, 50 grams of gas were obtained, composed of 35.6 percent hydrogen, 21.1 percent olefins of which 20 percent was ethylene and 43.1 percent of saturated hydrocarbons with the average composition of $C_{1.28}H_{4.52}$. The liquid products consisted of aromatic and unsaturated hydrocarbons as well as unchanged material, the "90° fraction" containing about 30 percent of unsaturated hydrocarbons.

From 200 grams of dimethylcyclohexane, passed over nickel at 550°, the products were composed of 180 grams of liquid and 20 grams of gas. The gas was made up of 50 percent hydrogen, a small percent of higher olefins, 12.5 percent ethylene, and the remainder saturated hydrocarbons similar to those from methylcylcohexane. By fractionation of the 180 grams of the liquid, it was estimated that it contained 3 grams of benzene, 5.5 grams of toluene, and 10 grams of xylene.

The three naphthene hydrocarbons studied by Daramois gave ethylene, but the petroleum containing these naphthenes yielded higher olefins in "important proportions" upon similar treatment.

Using a catalyst of nickel deposited upon aluminum hydrate, Zelinsky and Kommarewsky (98) found that benzene at 180° with hydrogen gave a "good yield" of cyclohexane. At 300 to 310° a mixture of benzene and cyclohexane gave only benzene as a product. Methylcyclohexane at this temperature yielded toluene. Neither benzene run at 300 to 310° with hydrogen, nor cyclohexane under like conditions led to the formation of methane as obtained by Sabatier and Senderens with an ordinary nickel catalyst.

Zelinsky also found that benzene passed over palladium black in the presence of hydrogen at 100 to 110° gave a "good yield" of cyclohexane. Cyclohexane at 300° over palladium black gave almost a quantitative yield of benzene and hydrogen. At 200° the hydrogenation and dehydrogenation was at an equilibrium point. Temperatures above 200° with a palladium catalyst produced dehydrogenation, while below 200° hydrogenation occurred. Zelinsky (85) stated that he believed this dehydrogenation occurred by splitting off 6 hydrogen atoms simultaneously, with no intermediate formation of di- and tetrahydroaromatics.

By a single passage of cyclohexane through a tube at 300°, an 80.5 percent yield of hydrogen was obtained with palladium as the catalyst, and a 62.5 percent yield with platinum. The decomposition of cyclohexane over platinum or palladium black may be concluded, from Zelinsky's work, to be a dehydrogenation reaction and not a ring rupture to form methane such as resulted with a nickel catalyst.

Platinum, palladium or nickel catalysts at temperatures of 150 to 408° had different effects on the dehydrogenation of cyclohexane. Zelinsky and Pawlow (99) showed that nickel was a poor catalyst for dehydrogenation, while platinum and palladium were far superior. The speed of formation of benzene and hydrogen from cyclohexane was increased by a rise in temperature until an almost quantitative yield of hydrogen was obtained at 350°. That platinum or palladium black exhibited "selective dehydrogenation" was shown by Zelinsky (87). A synthetic mixture of cyclohexane and methylcyclopentane passed over the catalyst at 300° gave methylcyclopentane and benzene with the liberation of hydrogen.

The I. G. Farbenindustrie A.-G. (108) obtained a series of patents for the preparation of unsaturated chain hydrocarbons such as ethylene, propylene, butylene, and butadiene, from higher hydrocarbons both cyclic and aliphatic. Natural or artificially prepared hydrocarbons with more than four carbon atoms in the molecule were converted into olefins and diolefins containing a smaller number of carbon atoms. The hydrocarbon vapors were passed through a tube in contact with a catalyst, the temperature being at least 600° and the pressure superatmospheric, normal, or reduced.

The best catalysts were found to be oxides of the metals situated at the maximum of the atomic volume curve. The oxides referred to were:

(1) Alkali and alkaline-earth metals, which included magnesium and beryllium, and their oxygen salts such as aluminates, chromates, tungstates, vanadates, uranates, and phosphates.

(2) Combinations which readily emitted electrons such as strontium and barium oxide in combination, alone, or upon a platinum substratum.

(3) Oxides of scandium, titanium, yttrium, zirconium, lanthanum, tungsten, molybdenum, thorium, and uranium, or mixtures of these. The catalysts were used either in the form of lumps or upon a carrier in the presence of weak dehydrogenators such as copper, molybdenum or tungsten, while iron, a strong dehydrogenator, could only be present in small quantities.

Examples of the reaction were given in the patents as follows: A tube of "V 2 A steel," charged with granular magnesium oxide, was heated to 650° in a stream of nitrogen. The gas was shut off, and cyclohexane passed through the tube. The products consisted of butadiene, butylene, and propylene. No carbon was deposited in the reaction tube.

Tetrahydrobenzene, passed through a tube of porcelain, clay, or noble metal at 625° over lumps of lime, gave products which included ethylene, propylene, butylene, and butadiene.

When cyclohexane was passed through a quartz tube filled with calcium aluminate at 600°, it was decomposed to give a mixture containing 28 parts by weight of ethylene, 14 parts of propylene, 4 parts of butylene, and 40 parts of butadiene.

Zelinsky (88) experimented with the action of cyclohexane homologs in the presence of the dehydrogenation catalyst, platinum black. The hydrocarbon, 1,1-dimethylcyclohexane was tested with the catalyst to see whether the same kind of reaction would occur. This hydrocarbon had been found to react with bromine in the presence of aluminum bromide to form a tetrabromo-p-xylene, and p-xylene might be expected as the product of the reaction if platinum black dehydrogenated and isomerized the 1,1-dimethylcyclohexane. When the compound was passed over the platinum catalyst at 300° no change or isomerization was observed. This non-reactivity of 1,1-dimethylcyclohexane was in agreement with the theory previously expounded by Balandin.

Using the same kind of catalyst, platinum black, at 300 to 310°, Zelinsky (87) found that menthane (hexahydrocymene) or hexahydro-xylenes dehydrogenated to the corresponding aromatic compounds, cymene and xylenes.

Metallic catalysts for the decomposition of cyclohexane and its homologs may be divided into three classes. First, there are the catalysts that form aromatic hydrocarbons by the liberation of hydrogen; second, there are catalysts that foster carbon-carbon scission; and finally, there are catalysts that seem to foster both types of action. It must be remembered, however, that the function of temperature is important. With a catalyst of platinum or palladium, dehydrogenation is completed at temperatures of 300 to 350°, while nickel effects dehydrogenation and carbon-carbon scission at the same temperature. If the nickel is deposited upon a substratum of aluminum hydrate, however, dehydrogenation seems to be fostered.

Copper at 550° gives much the same type of mixed reaction as nickel, resulting in dehydrogenation to produce aromatic hydrocarbons and in carbon-carbon scission to produce propylene, ethylene, butadiene, and similar products.

The quantitative dehydrogenation of cyclohexane hydrocarbons by palladium or platinum catalysts may be emphasized at this point. This so-called "specific catalyst" of Zelinsky has been proven to be inactive or only slightly active when used in conjunction with cyclobutane, cyclopentane, cycloheptane, and cyclooöctane. This fact is mentioned in the sections devoted to these compounds and their homologs.

Various other catalysts have been used to isomerize or decompose the cyclohexanes. Among these may be named aluminum chloride, calcium aluminate, alumina, alcoholic potassium hydroxide and fuming hydriodic acid or its salts.

Ipatiev and Dowgelewitsch (36) found that n-hexane or cyclohexane, run through an iron pipe at 710 and 750° respectively, decomposed to give various products. If alumina was used, the decomposition temperatures were somewhat lower, 660 and 740°. The n-hexane was found to decompose more readily than cyclohexane.

n-Hexane mixed with alumina caused the bomb to explode when heated to 510°. Cyclohexane mixed with alumina under similar conditions developed a pressure of 110 to 120 atmospheres. Heated for four hours and then cooled, the bomb still maintained 15 atmospheres pressure, 3.5 to 4 liters of gas being formed. The gaseous products consisted of 3.8 percent olefins, 22.4 percent hydrogen, and 73.5 percent methane. The liquid product contained olefins, aromatics, naphthenes, and polynuclear aromatics. One of the naphthenes was identified as methylcyclopentane.

When cyclohexane was heated with the same catalyst to 760° at atmospheric pressure, there was no evidence of isomerization. It was concluded, therefore, that pressure as well as temperature was a necessary factor. This same result was obtained when cyclohexane was heated at ordinary pressure, as shown in the preceding part of this section (see p. 3515).

Aluminum chloride catalyst was used in the work of Grignard and Stratford (27). They studied the reactions at temperatures of 120 to 150° with the amount of catalyst varying between 20 and 30 parts per 100 parts of hydrocarbon. The hydrocarbons of the cyclohexane series were identified by catalytic dehydrogenation at 300° over palladium in the manner of Zelinsky (84).

The results obtained from the work of Grignard and Stratford may be summarized as follows:

(1) Cyclohexane and methylcyclohexane were not changed. Ortho- and para-dimethylcyclohexane were isomerized to the meta-compound. Para-dimethylcyclohexane isomerized less easily than the ortho-compound.

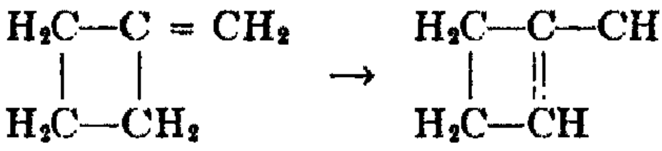
(2) The homologs having side chains of two and three carbon atoms did not crack easily. A portion of the liquid, 1 to 5 parts per 100, was split into saturated aliphatic hydrocarbons corresponding to the chain radical and into cyclohexene which polymerized in the presence of aluminum chloride. The greater portion was isomerized. The side chains gave rise to $(CH_3{-})$ groups which attached themselves to the ring, usually in the meta position.

(3) m-Diethylcyclohexane was changed to tetramethylcyclohexane, while the ethyl groups formed butane if they became detached.

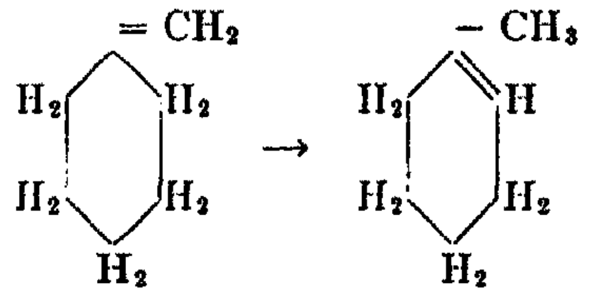
(4) Amyl- and isoamyl-cyclohexane represented a new case. Cracking was more extensive, since 42 to 70 parts per 100 gave butane as a product. The splitting occurred between the first and second carbon atoms to give butane and methylcyclohexane. The other reacting portion of the compound was isomerized to tetra- and penta-methylcyclohexane.

When alkylcyclohexanes were heated with aluminum chloride at 110 to 150°, they isomerized to the corresponding methyl derivatives. Ethyl-, propyl- and butyl-cyclohexanes gave dimethyl-, trimethyl-, and tetramethylcyclohexane respectively (64).

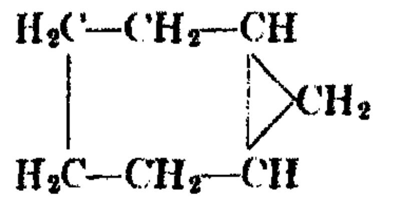
The same type of isomerization was observed with methylenecyclohexane as with methylenecyclobutane. In a former section it was shown that methylenecyclobutane isomerized to methylcyclobutene when subjected to heating over alumina catalysts. Thus



Faworsky and Borgmann (24) found that methylenecyclohexane, heated at 140° with quinoline and quinoline hydriodide, was isomerized to 1-methyl-1-cyclohexene. *Methylenecyclohexane in a sealed tube with benzoic acid at* 150 to 170° showed the same isomerism. This may be written

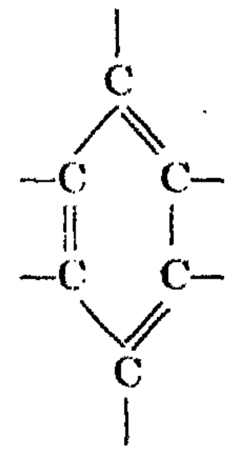
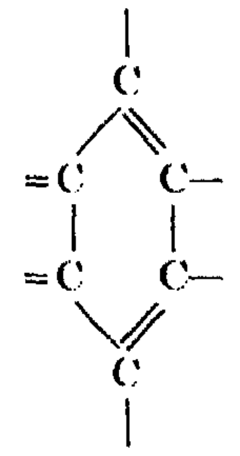
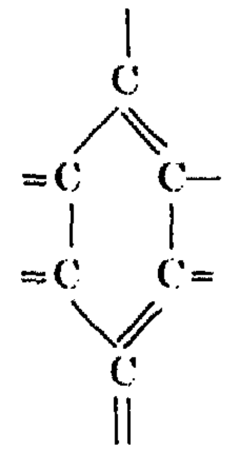


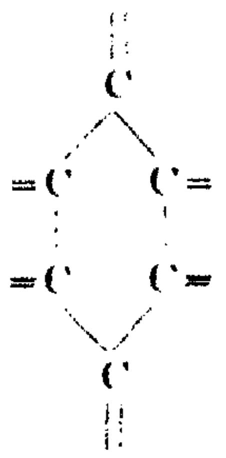
Zelinsky and Gutt (96) obtained a hydrocarbon, C_7H_{12}, boiling at 102.8 to 103°, by removing hydrogen iodide from cyclohexylmethyl iodide. It differed from the methylenecyclohexane, of boiling point 105 to 106.5°, which was obtained from cyclohexenacetic acid. The new hydrocarbon was not isomerized when heated to 300° in a sealed tube, as was the above methylene compound, to give 1-methyl-1-cyclohexene. Heated with quinoline hydriodide, however, it was converted to an isomer of methylcyclohexene. This new hydrocarbon was assumed to have the structure



Hirshfeld, Meyer, and Connell (31A) used cathode rays in the study of hydrocarbon decomposition. Using 10 cc. samples, the hydrocarbons were rayed for half-hour periods. The gases given off during each period were pumped from the reaction vessel and analyzed. The pure hydrocarbons were all run under the same conditions in order to compare the results of the decompositions. In general, this comparison was primarily that of the total gas evolved during the raying period of one-half hour.

The following table quoted from these authors shows the relation of unsaturation in the cyclic C_6 hydrocarbons to the evolution of gas during cathode ray bombardment:

			Total Gas cc. N.T.P.	H_2 % by Vol.	CH_4 % by Vol.	C_nH_{2n+2} % by Vol.
Benzene Boiling Point 79.6°C. Vapor Pressure 81.6 mm. Hg.		C_6H_6	2.2*	—	—	—
Cyclohexadiene Boiling Point 80.5C.		C_6H_8	—	—	—	—
Cyclohexene Boiling Point 83°C. Vapor Pressure 101.2 mm. Hg.		C_6H_{10}	19.4*	39.5	1.2	59.3

Cyclohexane Boiling Point 81°C. Vapor Pressure 104.0 mm. Hg.		C_6H_{12}	41.9*	89.2	2.6	7.2

*Corrected for Vapor Pressure of Compound at Temperature of Test.

The homologs of cyclohexane behave in a manner anticipated by these authors. The results from the hydrocarbons are given as follows:

	Total Gas cc. N.T.P.	H_2 % by Vol.	CH_4 % by Vol.	C_nH_{2n+} · % by Vol.
Cyclohexane	41.9*	89.2	2.6	7.2
Methylcyclohexane	37.7*	78.9	4.0	17.1
Phenylcyclohexane	2.4	66.6	11.1	21.6

*Corrected for Vapor Pressure of Compound at Temperature of Test.

Cyclohexane and methylcyclohexane gave very similar results as would be expected, but phenylcyclohexane, being a partially unsaturated compound, did not evolve as large a volume of gas.

One of the general conclusions drawn by these authors was that: "The cycloparaffins, olefins and cyclo-olefins give off gas in quantities which are generally roughly proportional to the degree of saturation."

Later work by Linder and Davis (45A) indicated a different composition of the gases from cyclohexane and methylcyclohexane. They report:

	H_2	Acetylenes	Ethylenes	Paraffins
Cyclohexane	46.1	13.2	32.2	8.5
Methylcyclohexane	47.0	12.6	16.6	13.8

The effect of temperatures, catalysts, and cathode rays upon cyclohexane and its homologs with the resultant products is summarized in Table XI.

Table XI

Cyclohexane and Homologs

Reference No.	Hydrocarbon	°C. Temp.	Catalyst	Product	Remarks
(38)	Cyclohexane	490–510	Porcelain	Hydrogen Benzene Acetylene Ethylene Methane Ethane	
	Methylcyclohexane	"	"	(Same as above)	

TABLE XI (Continued)

Reference No.	Hydrocarbon	°C. Temp.	Catalyst	Product	Remarks
(26)	Cyclohexane	654	Quartz	"Unsaturated Hydrocarbons" Butadiene Benzene Naphthalene Tar	
(60)	Cyclohexane	270–280	Nickel	Benzene Methane	
	Methylcyclohexane	275	"	Hydrogen Methane Toluene	
	Ethylcyclohexane	280–300	"	Toluene Ethylbenzene Methane Hydrogen	
(13)	Cyclohexane	550	Copper	Liquid olefins Benzene Ethylene Ethane Hydrogen	
	Methylcyclohexane	550	"	Ethylene Hydrogen $C_{1.26}H_{4.62}$ Aromatic and Unsaturated Liquids	
	Dimethylcyclohexane	550	"	Hydrogen Ethylene $C_n H_{2n+2}$ gases Benzene Toluene	
(98)	Cyclohexane	300–310	Ni. on Aluminum hydrate	Benzene Hydrogen	No methane formed
	Methylcyclohexane	"	"	Toluene	
(86)	Cyclohexane	300	Palladium Platinum	Benzene Hydrogen	
(108)	Hydrocarbons of more than 4 C Atoms	Above 600	Oxides of metals	Olefins and diolefins	
(88)	1,1-Dimethylcyclohexane	300	Platinum	No action	
(87)	Menthane	310	"	Cymene	
	Hexahydro-xylenes	310	"	Corresponding xylenes	

TABLE XI (Continued)

Reference No.	Hydrocarbon	°C. Temp.	Catalyst	Product	Remarks
(36)	Cyclohexane	510	Al_2O_3	C_nH_{2n} gas Hydrogen Methane Liquid olefins Aromatics Naphthenes Polynuclear aromatics Methylcyclopentane	Pressure 110–120 atms.
(27)	Cyclohexane	120–150	$AlCl_3$	Unchanged	
	Methylcyclohexane	120–150	"	Unchanged	
	1,2-Dimethylcyclohexane	120–150	"	Meta isomer	
	1,4-Dimethylcyclohexane	120–150	"	Meta isomer	
	1,3-Dimethylcyclohexane	120–150	"	Unchanged	
	1,3-Diethylcyclohexane	120–150	"	Tetramethylcyclohexane Butane	
	Amylcyclohexane	120–150	"	Methylcyclohexane Butane	42-70% cracking
	Isoamylcyclohexane	120–150	"	Butane Tetra- and Pentamethylcyclohexanes	42-70% cracking
(64)	Ethylcyclohexane	110–150	"	Dimethylcyclohexane	
	Propylcyclohexane	110–150	"	Trimethylcyclohexane	
	Butylcyclohexane	110–150	"	Tetramethylcyclohexane	

TABLE XI (Continued)

Reference No.	Hydrocarbon	°C Temp.	Catalyst	Product	Remarks
(24)	Methylenecyclohexane	140	Quinoline HI	1-Methyl-1-cyclohexene	
	Methylenecyclohexane	150–170	Benzoic acid	1-Methyl-1-cyclohexene	Sealed tube
(95)	A C_7H_{12} Hydrocarbon	—	Quinoline HI	Bicyclo (0, 1, 4) heptane	
(31A)	Cyclohexane	—	Cathode ray bombardment	Hydrogen Methane High paraffins	
	Methylcyclohexane	—	Cathode ray bombardment	Hydrogen Methane High paraffins	
	Phenylcyclohexane	—	Cathode ray bombardment	Hydrogen Methane High paraffins	
(45A)	Cyclohexane	—	Cathode ray bombardment	Hydrogen Acetylenes Ethylenes Paraffins	
	Methylcyclohexane	—	Cathode ray bombardment	Hydrogen Acetylenes Ethylenes Paraffins	

9. Cyclohexene and Cyclohexadiene

No case has been found in which cyclohexene or cyclohexadiene have been decomposed at a temperature above approximately 300° without a catalyst. Cyclohexadiene does, however, polymerize slowly at room temperature, as will be shown later.

The "simultaneous oxidation-reduction" action of Zelinsky, previously mentioned, is a description of the phenomenon observed when cyclohexene and cyclohexadiene are heated at 90 to 140° over a palladium catalyst. A review of the results obtained will illustrate the action observed.

Zelinsky (93) catalytically decomposed cyclohexene obtained from various sources. Cyclohexene prepared from cyclohexanol and oxalic acid yielded benzene and hydrogen under the influence of a palladium catalyst much more vigorously than cyclohexane. The cyclohexene prepared from cyclohexyl iodide and quinoline did not react in the same way, for only a small amount of hydrogen and benzene was formed, and a new cyclohexene was found in the reaction. Although no temperature of reaction was mentioned, a temperature above 200° was implied. The new C_6H_{10} formed had a b.p. of 77.5 to 78°, d^{20}_4 of 0.8005, and n^{20}_D of 1.4416. It showed no action with potassium permanganate or bromine. The palladium seemed to exercise selective catalysis in not dehydrogenating the new tetrahydrobenzene. The new compound, therefore, was probably the simplest of the bicyclic hydrocarbons of the $(CH_2)_6$ type.

Cyclohexene or 1,3-cyclohexadiene passed over palladium catalyst at 92° in a carbon dioxide atmosphere were changed to benzene and cyclohexane as represented in the following equations:

$$2\ C_6H_6 \leftarrow 3\ C_6H_8 \rightarrow C_6H_{12}$$

$$C_6H_6 \leftarrow 3\ C_6H_{10} \rightarrow 2\ C_6H_{12}$$

This process of disproportionation could be termed a simultaneous oxidation and reduction reaction. It was an example of non-reversible catalysis, for cyclohexane and benzene could not be made to form either of the partially hydrogenated aromatic compounds in the presence of palladium black.

Zelinsky and Pawlow (100) considered that the catalyst played the part of a ferment, for the labile hydrogen atoms from 3 molecules moved in such a direction as to set up a stable system. It was noted that cyclohexene when passed over the palladium catalyst at temperature of 164.5 and 223° did not give products with the expected refractive indices. The values found at 20° for the above reaction temperatures were 1.4448 and 1.4489 respectively. Pure cyclohexene, however, had a refractive index of 1.4460, and this value should have risen to that for benzene, 1.5010. Instead, the refractive index actually decreased, a fact which led to the investigation of a mixture of cyclohexane and benzene. This mixture, in the proportion of two to one, was found to have an index of 1.4455. Thus the heating of cyclohexene produced first the simultaneous oxidation-reduction action. The subsequent reaction was characteristic of cyclohexane.

If this were true, the action of cyclohexene and of a mixture of two parts of cyclohexane and one part of benzene should give similar results when heated with a palladium catalyst at like temperatures. Table XII substantiates these views:

TABLE XII

Catalyst = Pd. Covered Asbestos

Starting Materials		°C. Temp.	Hydrogen Volumes Obtained	Hydrogen % of Theoretical Yield	N^{20}_{D}
2 Mols Cyclohexane + 1 Mol Benzene	1	225.5	160	6.30	1.4484
	2	240.0	310	12.20	1.4517
	3	262.5	757	29.80	1.4593
	4	281.5	1306	51.42	1.4700
	5	301.5	1838	72.36	1.4827
Cyclohexene	1	222.5	240	9.37	1.4489
	2	243.0	450	17.58	1.4525
	3	262.0	769	30.04	1.4582
	4	281.0	1268	49.53	1.4679
	5	302.0	1896	74.06	1.4817

Although Zelinsky and Pawlow consider the action as simultaneous oxidation and reduction of cyclohexene with the catalyst playing the part of a ferment, the true action is more likely to be the simple dehydrogenation of cyclohexene with the simultaneous hydrogenation of benzene, both of which are known to take place at these temperatures.

Zelinsky (92) found that cyclohexene exhibited the simultaneous "oxidation and reduction" reaction even at room temperature. Cyclohexene, sealed in a tube with palladium black for a period of eighteen days, formed benzene and cyclohexane.

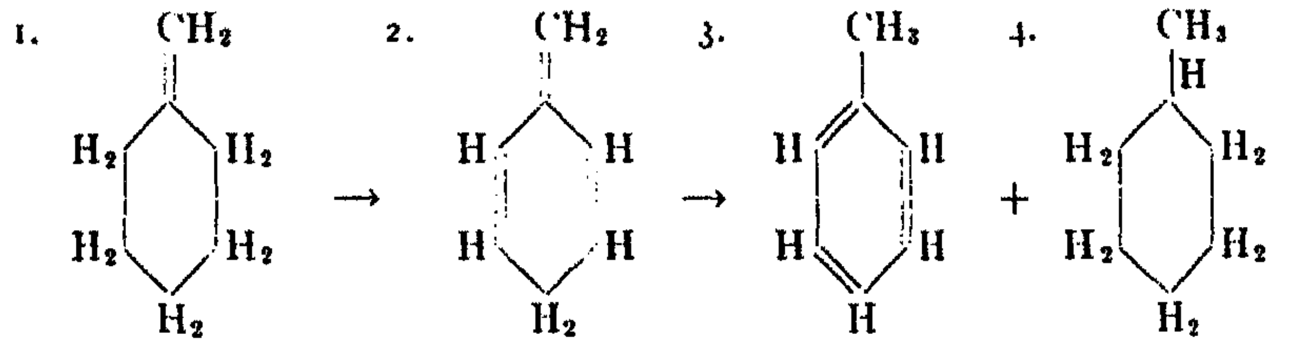
Homologs of cyclohexene gave a similar reaction when treated with a catalyst by Zelinsky and Pawlow (100). The same type of reaction occurred for 1,4-dimethyl-3-cyclohexene. In a stream of carbon dioxide at 140° over palladium, the products obtained were 1,4-dimethylbenzene and 1,4-dimethylcyclohexane.

Similar action carried on at 116 to 118° over the same catalyst yielded toluene and methylcyclohexane from all three of the isomeric methylcyclohexenes.

Radium bromide containing 0.0005 to 0.0006 grams of radium together with 1.5 cc. of cyclohexene was sealed into a tube by Zelinsky (83). Immediately upon introduction, the radium was covered with a black crust of carbon and at the end of a year a "black deposit" could be noted. The cyclohexene, by a series of decompositions, had acquired a dark yellow color. The unidentified products of decomposition were both simpler and more complex than cyclohexene. The complex products were formed under the influence of radiation.

Although methylenecyclohexane was discussed in the section including cycloheyxl compounds, the similarity of the observed action to that of the cyclohexenes seemed to permit the inclusion of the compound in this section.

Zelinsky (91) treated methylenecyclohexane with palladium black at 116 to 118° and obtained toluene and methylcyclohexane. The mechanism was given as follows:



The first step was dehydrogenation. The resulting conjugated system isomerized to toluene, while the hydrogen from the first reaction changed two other methylcyclohexene molecules to hexahydrotoluene.

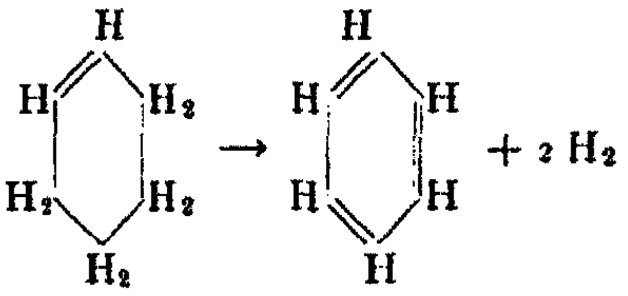
$$3\,C_6H_{10}{=}CH_2 \rightarrow C_6H_5{-}CH_3 + 2C_6H_{11}{-}CH_3$$

Alumina has also been used as a catalyst in the decomposition of cyclohexene, but the bomb method reaction has been employed in place of the flow method used with palladium.

Petrov (53) heated 60 grams of cyclohexene and 6 grams of alumina in a bomb at 400 to 440°. After 24 hours of heating, there was a pressure of 5 atmospheres remaining within the bomb.

The gases contained 31 percent hydrogen and 60 percent C_nH_{2n+2}. The liquid products were fractionated and found to contain a small amount of unsaturated hydrocarbons with a greater portion of aromatic hydrocarbons, especially those of high molecular weight. Benzene was found to the extent of 15 percent in a fraction boiling between 75 and 81°.

If the action was



it must have been accompanied by a secondary hydrogenation to form the stable cyclohexane compounds which were found in the product.

A few cyclohexadiene homologs have been studied but not at high temperatures, since it was found that increased temperature only accelerated the rate of polymerization.

Henderson and Smeaton (31) found that 1-methyl-3-isopropyl-4, 6-cyclohexadiene changed upon standing. The density and refractive index were raised; hence the molecular rotation, which depends on these factors, was decreased. This change was attributed to slow polymerization which occurred upon standing.

The increase in ease of decomposition with increased unsaturation of the cyclic compounds is apparent from the foregoing examples of pyrogenic action. The fairly stable cyclohexane decreases in stability as one, and then two, molecules of hydrogen are removed, the -diene reacting similarly to any 1,3 unsaturated hydrocarbon. Another dehydrogenation, however, forms benzene or aromatic compounds which are more stable than cyclohexane itself.

Working with hydrocarbons of the "semibenzene" type, v Auwers and Ziegler (75A) found two kinds of reaction took place. The "semibenzene" type hydrocarbon was a six-membered ring containing two double bonds, while the third point of unsaturation existed in a side chain, directly bound by the double bond to the ring. If a high temperature was used or the compounds distilled, polymerization was observed to occur, but if a few drops of hydrochloric acid were added to the acetic acid solution of the "semibenzene" hydrocarbon, an isomerization to the benzene compound took place.

1,1-Dimethyl-4-methene-2,5-cyclohexadiene isomerized to pseudocumene.

1,1-Dimethyl-4-propene-2,5-cyclohexadiene yielded asymmetrical propyl o-xylene.

1,1,3-Trimethyl-4-ethene-2,5-cyclohexadiene gave symmetrical ethylpseudocumene.

1,1,2-Trimethyl-4-methene-2,5-cyclohexadiene produced only a small yield of isodurene because of concurrent polymerization.

1,1,3,6- and 1,1,2,6-Tetramethyl-4-methane-2,5-cyclohexadiene yielded pentamethylbenzene.

1,1-Dimethyl-4-ethene-2,5-cyclohexadiene did not polymerize easily as the other compounds did, for it could be distilled at 175 to 178° with little change and even heated for one hour at 150 to 160° without any polymerization. Bromination gave the isomer, for only 1/5 to 1/4 of the theoretical amount of bromine absorbed. Likewise, hydrochloric acid gave the isomer, 1,2,4-dimethyl-ethylbenzene.

Hirshfeld, Meyer, and Connell (31A) found that cyclohexane and 1-methyl-1-cyclohexene when subjected to cathode rays gave these results:

		Total Gas cc. N.T.P.	H_2 % by Vol.	CH_4 % by Vol.	C_nH_{2n+2} % by Vol.
Cyclohexene	C_6H_{10}	19.4*	39.5	1.2	59.3
1-Methyl-1-cyclohexene	C_7H_{12}	14.0*	66.5	6.1	27.3

*Corrected for Vapor Pressure of Compound at Temperature of Test.

Methylcyclohexene did not differ greatly from cyclohexene with respect to the quantity of gas formed, yet the composition of the gas greatly changed. Comparing methylcyclohexene and cyclohexene, it was found that the methyl homolog gave a larger proportion of hydrogen and a smaller percent of paraffins containing more than one carbon atom.

The reaction products resulting from the thermal, catalytic, cathode ray bombardment, and radium treatment of cyclohexene and cyclohexadiene are shown in Table XIII.

TABLE XIII

Cyclohexene—Cyclohexadiene

Reference No.	Hydrocarbon	°C. Temp.	Catalyst	Product	Remarks
(100)	Cyclohexene	92	Palladium	Benzene Cyclohexane	
	1,3-Cyclohexadiene	92	Palladium	Benzene Cyclohexane	
	Cyclohexene	Room	Palladium	Benzene Cyclohexane	18 Days in sealed tube
	1,4-Dimethyl-3-cyclohexene	140	Palladium	Dimethylcyclohexane	
	Methylcyclohexenes 3 Isomers	116–118	Palladium	p-Xylene Toluene Methylcyclohexane	
(91)	Methylenecyclohexane	116–118	Palladium	Toluene Methylcyclohexane	

TABLE XIII (Continued)

Cyclohexene—Cyclohexadiene

Reference No.	Hydrocarbon	C° Temp.	Catalyst	Product	Remarks
(83)	Cyclohexene	Room	Radium Bromide	Oils	Radiation agent
(53)	Cyclohexene	400–440	Al_2O_3	Hydrogen C_nH_{2n+2}Gas Benzene Higher aromatics	Bomb reaction 24 Hrs. heating
(31)	1-Methyl-3-isopropyl-4,6-cyclohexadiene	Room	None	Polymerized	
(31A)	Cyclohexene	—	Cathode ray bombardment	Hydrogen Methane Higher paraffins	
	1-Methyl-1-cyclohexene	—	Cathode ray bombardment	Hydrogen Methane Higher paraffins	

10. Cycloheptane

The results of the hydrogenation and isomerization of cycloheptane to methylcyclohexane, as obtained by Willstätter and Kametaka (81), have been included in Table V. Zelinsky (87) attempted to dehydrogenate cycloheptane by the action of his "specific catalyst," platinum or palladium, but obtained no action. The ineffectuality of these catalysts on the ring structure containing seven carbon atoms is in accord with the multiplet theory of Balandin.

11. Cycloöctane

Cycloöctane has been used as a subject of experimentation in only one instance. Unsaturated eight-membered rings, however, have been of interest because of their relation to benzene as a conjugated, unsaturated system.

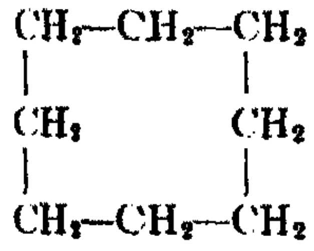
Zelinsky and Freimann (97) further tested the dehydrogenation theory of Balandin by passing cycloöctane over a dehydrogenating catalyst.

If the theory was valid that dehydrogenation occurred only when the space lattice of the catalyst corresponded to the spatial arrangement of the atoms in the molecule, cycloöctane should not dehydrogenate when passed over a platinum catalyst. Zelinsky had shown this to be true for cyclopentane and cycloheptane and also had unpublished results which showed that cyclobutane was passive and did not dehydrogenate.

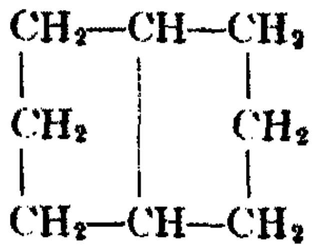
Cycloöctane, passed over a platinum-charcoal catalyst at 300°, did partially dehydrogenate but not in the manner which is characteristic of the catalyst in its action with cyclohexane. The products of the action were hydrogen, bicycloöctane and methylcycloheptane. The bicyclo-(0,3,3)-octane was formed by dehydrogenation, while the methylcycloheptane resulted from isomerization. Further isomerization to dimethylcyclohexane did not occur, although the product was re-run over the catalyst several times. Dehydrogenation to xylene would occur if a cyclohexane homolog had been formed, but no xylene was found.

The reaction was:

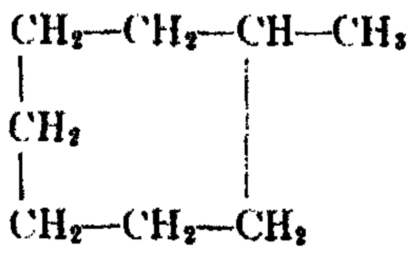
$$2C_8H_{16} \rightarrow C_8H_{14} + H_2 + C_8H_{16}$$



Cycloöctane



Bicyclo-(0,3,3)-octane



Methylcycloheptane

Willstätter and Veraguth (80) in preparing cycloöctadiene from the dibromide observed that the -diene compound formed by use of alkali was unstable while that formed by quinoline was quite stable. The first cycloöctadiene polymerized with almost explosive violence when warmed, while the latter compound was polymerized slowly even on heating, although the addition of hydrogen bromide to either compound gave the same product. The first compound behaved as a conjugated double bond structure, while the latter contained the two double bonds in different positions. Thus the first may be a 1,3-diene, and the second a 1,4- or 1,5 unsaturated compound.

The cycloöctadiene of Willstäter and Veraguth differed from the isomeric tricycloöctane of Döbner (16) which was prepared from vinylacrylic acid by heating with barium hydroxide. The cycloöctadiene polymerized to dicycloöctadiene with almost explosive violence when heated, but the tricycloöctane polymerized only slowly when heated to 250° under pressure.

The reaction products from the treatment of cycloöctane, tricycloöctane, and cycloöctadiene are shown in Table XIV.

TABLE XIV

Cycloöctane—Tricycloöctane—Cycloöctadiene

Reference No.	Hydrocarbon	°C. Temp.	Catalyst	Product	Remarks
(97)	Cycloöctane	300	Platinum	Methylcycloheptane Bicyclo-(0,3,3)-octane Hydrogen	Run until no further change
(16)	Tricycloöctane	250	None	Polymers	Heated under pressure
(80)	1,3-Cycloöctadiene	"Warmed"	None	Polymers	Almost explosive
	1,5-Cycloöctadiene	"Heated"	None	Polymers	Very slow action

12. Polynuclear Compounds

The action predominating in the pyrolysis of hydroaromatic polynuclear compounds is dehydrogenation. All the compounds listed in this section show a tendency to lose hydrogen when heated either alone or with a catalyst, and to return to the corresponding aromatic hydrocarbon.

Dihydronaphthalene, subjected to "red heat" in a sealed tube, was found by Berthelot (7) to regenerate naphthalene and hydrogen.

Bamberger and Lodter (5) also observed that dihydronaphthalene decomposed to naphthalene and hydrogen, when passed through a tube at a "dark red heat."

When Jones (38) heated dihydronaphthalene with porcelain plates, it began to decompose at 390°, and at 420° the decomposition appeared to be complete. The gas formed consisted of 85.4 percent hydrogen and 14.6 percent methane, and the solid obtained was identified as naphthalene.

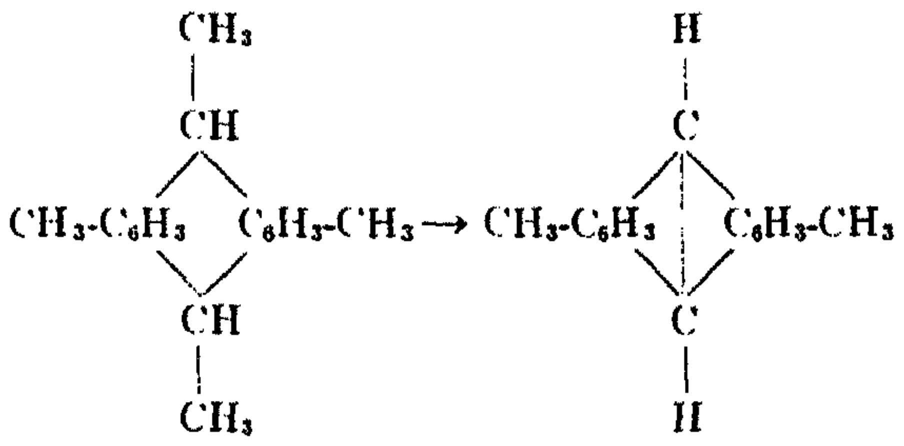
Zelinsky and Pawlow (100) found dihydronaphthalene at 130° over palladium-asbestos catalyst yielded naphthalene and tetralin.

$$C_{10}H_8 \longleftarrow 2C_{10}H_{10} \longrightarrow C_{10}H_{12}$$

This equilibrium reaction was a function of temperature, for Wieland (79) was able to shake dihydronaphthalene with palladium black and obtain naphthalene and tetralin at room temperature.

Alkyldihydroanthracenes passed over pumice at a "low heat," or over zinc dust, yielded anthracene, according to Liebermann (44). Ethyl- or isobutyldihydroanthracene required higher heating, while the isoamyl compound decomposed by refluxing.

Tetramethylanthracene dihydride was studied by Anschütz (1). He heated the compound with zinc dust to a "red heat" and recovered dimethylanthracene. The reaction may be represented as follows:



Tetralin and decalin have been more fully studied than the other polynuclear naphthenes. Both non-catalytic, and catalytic actions have been used for their pyrogenic decomposition.

Jones (38) pyrolyzed 1,2,3,4-tetrahydronaphthalene (tetralin) at 530°, although the action started at 490 to 500°. Naphthalene was the solid product obtained, while the gases were made up of 3.3 percent benzene and higher olefins, 3.5 percent ethylene 80.2 percent hydrogen, 9.0 percent methane and 4.0 percent ethane.

A more complete study of the pyrolysis of tetralin and decalin was made by Sundgren (69). The conclusions reached were that tetralin gave the following reactions at temperatures of 580 to 650°, under atmospheric pressure and under 10, 15, 25, and 30 kg. per sq. cm.:

1. Decomposition to aromatic hydrocarbons with unsaturated side chains.
2. Cracking, characterized by the rupture of the hydrogenated ring to form aromatic hydrocarbons.
3. Dehydrogenation to naphthalene.
4. Decomposition to methane and carbon.
5. Under pressure with hydrogen, decomposition was the same except that methane was the total product from the hydrogenation of the products of complete "dislocation."

Temperature and pressure influences:

1. Increased temperature increased the speed of reaction, but not to the same extent for all of the above actions.
2. Increased temperature decreased the number and length of side chains.
3. Increased temperature changed the manner of rupture of molecules.
4. Increased pressure favored carbon-carbon scission and allowed better heat transfer. More symmetrical rupture of the molecule was also noted.

The use of catalysts slightly increased cracking while decidedly aiding dehydrogenation.

The gases formed showed amounts of methane, ethylene, and hydrogen varying with the different temperatures used. Hydrogen, however, was always the chief constituent of the gases, with methane as the other main portion. Ethylene constituted only a small part of the total. Hydrogen varied from 56 to 85 percent, methane from 13 to 39 percent, and ethylene from 1 to 4 percent.

Analysis of the low boiling liquid products from the pyrolysis of tetralin showed the following compounds resulting from cracking: Benzene, toluene, o-xylene, ethyl-benzene, stryene, allylbenzene, propenylbenzene, methylallylbenzene, propylbenzene and butenylbenzene.

Thermal treatment of decalin resulted in the following reactions:

1. Cracking of the molecule with the rupture of one or both rings.
2. Total or partial dehydrogenation.
3. Condensation or polymerization.
4. Total rupture of the molecule to form carbon, methane, and hydrogen.

The products of cracking are composed almost entirely of aromatic hydrocarbons, the rupture occurring in one ring much more frequently than in both rings.

When decalin was treated under pressure with hydrogen, the products of total rupture, contrary to those obtained from tetralin, were not hydrogenated to methane. The deposit of carbon at 650° became so great as to cause the tube to burst.

The gases obtained contained methane, ethane, propane, butane, ethylene, propylene, butylene, acetylene, and hydrogen.

The liquids were composed, mostly, of aromatic hydrocarbons of from 6 to 20 carbon atoms, while there were small amounts of saturated aliphatic hydrocarbons, and some saturated and unsaturated cyclic hydrocarbons. Among the liquid constituents were: Benzene, toluene, o-xylene, naphthalene, methylnaphthalene, tetralin, cyclohexene, cyclohexadiene, pentane, hexane, and hexene.

Other work has been done on the decomposition of tetralin and decalin using catalysts of various kinds.

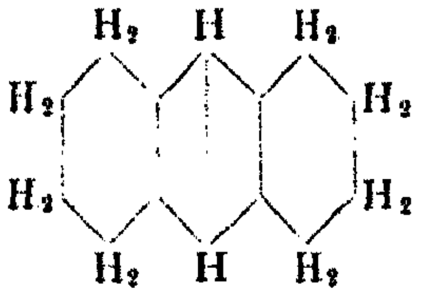
Zelinsky (90) obtained naphthalene and unchanged decalin when he passed the latter compound over palladium black at 300°. Because of the absence of tetralin or other hydrogenated naphthalenes, he concluded that all the hydrogen atoms were lost at once and the action did not proceed in steps with the formation of intermediate hydrogenated compounds of naphthalene.

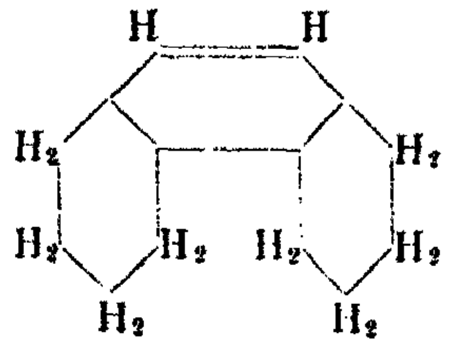
Zelinsky and Turowa-Pollak (107) found that when transdecalol was heated at 290 to 300° with hydriodic acid, the product was isomerized from decalin, for the acid reduced the naphthol to the hydrocarbon. The compound obtained was a hydrocarbon of formula $C_{10}H_{18}$, yet it did not dehydrogenate when passed over platinized active charcoal at 300°. The compound formed, then, could not have been decalin which dehydrogenated under such conditions. The hydrocarbon 2,8-dimethylbicyclo-(0,3,3,)-octane was favored as the most likely form. Ring rupture also occurred, since methyl and 1,2-dimethylcyclohexane were identified in the low boiling products.

Decahydronaphthalene (decalin) at 100° in the presence of aluminum bromide was isomerized from the cis-form to the trans-form. Nuclear isomerization also occurred in this reaction, similar to the transformation described above. At 190° there was less isomerization with a greater tendency toward rupture of the ring and formation of substituted cyclohexanes. The trans-form, obtained by isomerizing the cis-decalin, was quantitatively dehydrogenated to naphthalene by platinized charcoal at 300°.

Schroeter (62) treated tetralin with 1 to 1.5 percent anhydrous aluminum chloride at 30 to 40°. Thirty percent yield of a mixture of hydrocarbons was obtained and then separated into two parts. The higher boiling portion was shown to contain octahydrophenanthrene and octahydroanthracene, while benzene was found in the low boiling portion. The octahydro compounds were identified by dehydrogenation with passage over heated copper. The mechanism of the reaction was postulated as the splitting of the hydrogenated ring to form benzene and a residual radical. This radical combined with a tetralin molecule by hooking to the benzene ring in the ortho position.

By a series of chemical reactions it was proven that the octahydro compounds had the following structures:





Continuing the study of tetralin with aluminum chloride, Schroeter (63) treated 1500 grams of tetralin with 30 grams of anhydrous aluminum chloride. The action was allowed to continue for 6 to 10 hours at a temperature of 50 to 70°. After hydrolysis with dilute acid, the product was distilled.

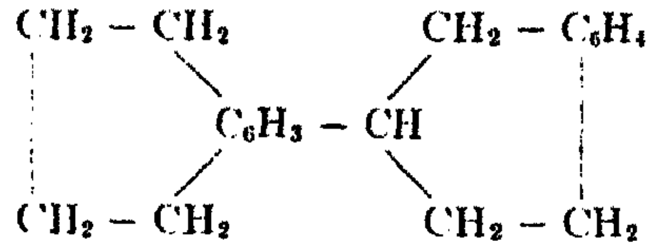
In all, 4.5 kg. of tetralin was used for reaction with aluminum chloride. Distillation of the product gave 3.4 kg. boiling below 120° at 15 mm. pressure. Refractionation of this gave 120 grams of almost pure benzene, while the greater portion was unchanged or was regenerated tetralin. The higher boiling materials will be taken up separately in the following paragraphs.

As shown previously, octahydrophenanthrene, (Octanthrene) and octahydroanthracene, (Octhracene) were identified in the products of reaction, and in this case they occur in the portion distilling at 160 to 190° under 15 mm. pressure. Octhracene, melting at 73 to 74° and boiling at 293-295° under 760 mm. or 167° under 12 mm. pressure, was identified by distilling with sulfur, zinc, or copper at 180 to 220°, and at 550° with copper. The formation of anthracene was the action observed in each case.

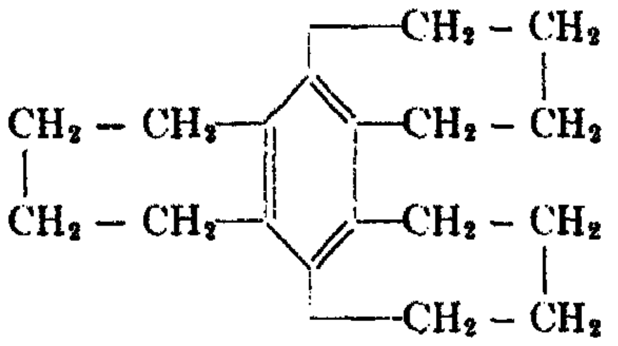
Octanthrene, boiling at 295° under 760 mm. or 167.5° under 13 mm. pressure and melting at 16.7°, was identified by dehydrogenation to phenanthrene.

Another solid was obtained in this same fraction which had an empirical formula of $C_{14}H_{16}$, determined by analysis. This hydrocarbon melted at 54 to 55°.

Another fraction of 450 grams was taken, boiling at 230 to 245° under 15 mm. pressure. The viscous, fluorescent, pale yellow oil was redistilled at 236 to 237° under 13 mm. pressure. This fraction indicates a $C_{20}H_{24}$ hydrocarbon, which by oxidation and dehydrogenation was shown to be α-phenyl-δ-2-tetralylbutane. A second hydrocarbon melting at 53-54° was found in the higher boiling portion of this fraction. By dehydrogenation to 2,2-dinaphthyl and by oxidation to 1,2,4-phthalylacetic acid, this $C_{20}H_{22}$ hydrocarbon was identified as 2, 6′-ditetralyl.



When 250 grams of octhracene were heated with 12.5 grams of aluminum chloride at 70 to 80° for 3 hours, 100 grams of octhracene were recovered from the hydrolyzed product. Octanthrene was obtained in a yield of 100 to 110 grams. After removal of the octahydro compounds, there remained 11-12 grams of an ether-soluble, high boiling material which was divided into two portions, one melting at 233° and the other at 320°. The lower melting substance was identified as dodecahydrotriphenylene:



After ether extraction there remained about 10 grams of high boiling oil which formed tetralin and octahydro compounds when distilled with aluminum chloride.

The author considered this liquid to be a mixture of phenylene-bis-octanthrenylbutane,

$$C_6H_4(CH_2-CH_2-CH_2-CH_2-C_{14}H_{12})_2$$

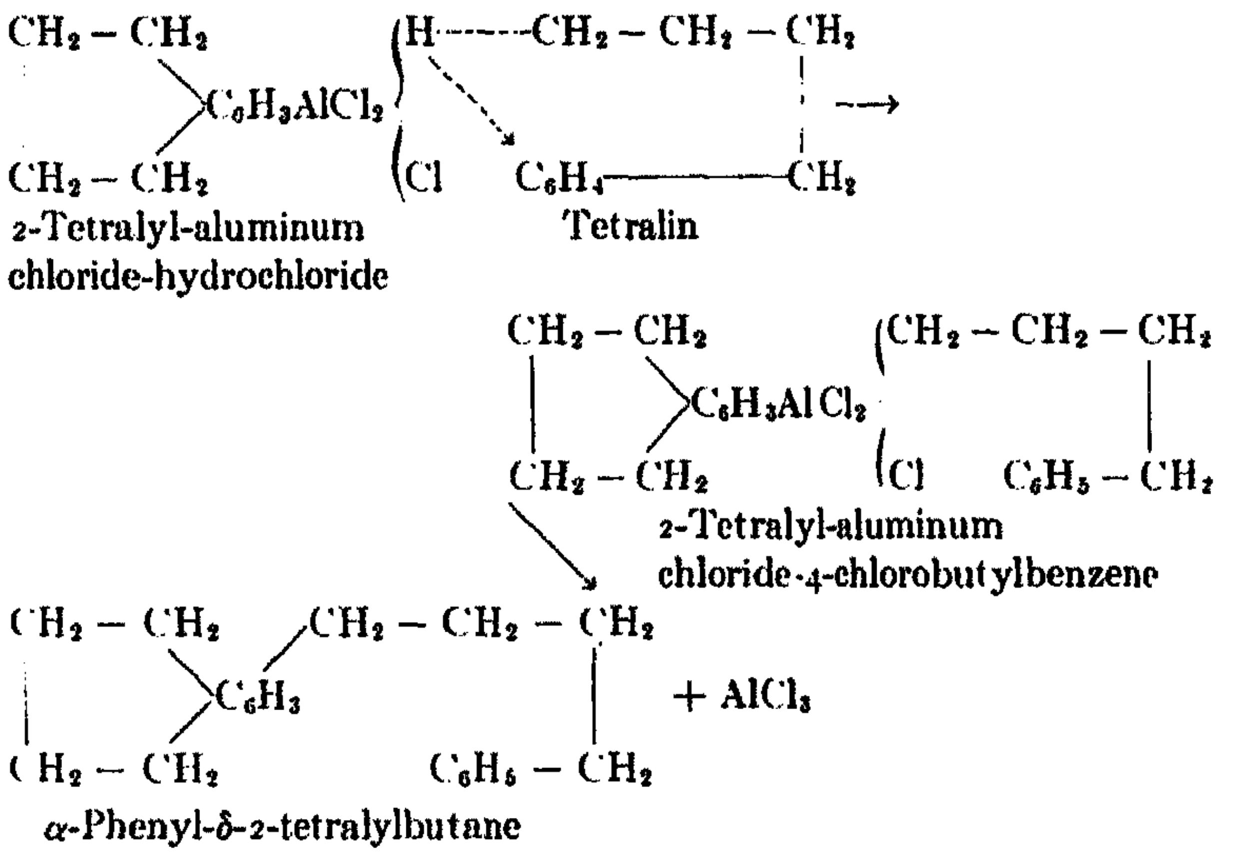
and tetralyl-octanthrenylbutane

$$C_{10}H_{11}-CH_2-CH_2-CH_2-CH_2-C_{14}H_{17},$$

which are intermediate in the formation of triphenylenedodecahydride.

The same results were obtained if octanthrene was used in place of octhracene.

An outline given by Schroeter for the change of tetralin to α-phenyl-δ-2-tetralylbutane may be presented as follows:



2-Tetralyl-aluminum chloride-hydrochloride

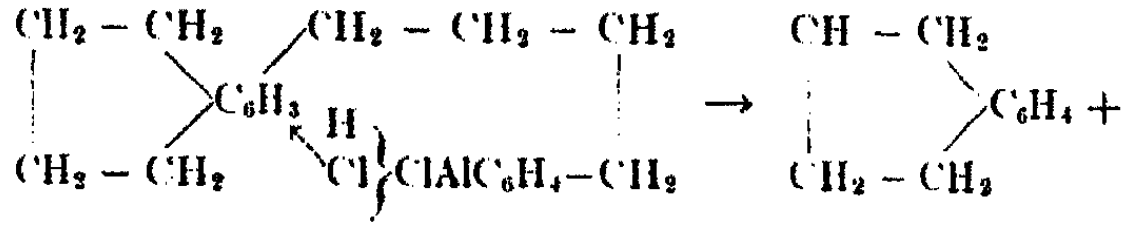
Tetralin

2-Tetralyl-aluminum chloride-4-chlorobutylbenzene

+ $AlCl_3$

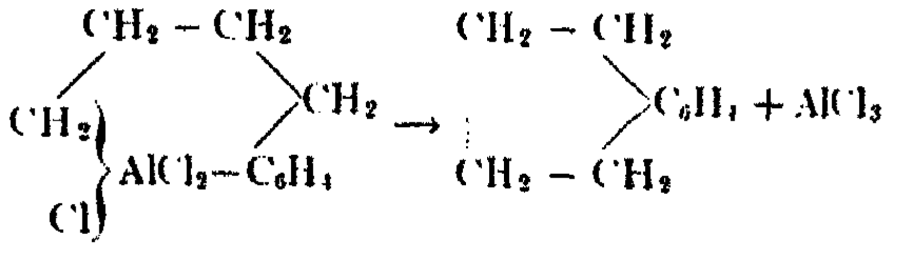
α-Phenyl-δ-2-tetralylbutane

Regeneration of two mols of tetralin from α-phenyl-δ-2-tetralylbutane:



1-δ-Tetrabutyl-4-phenyl aluminum chloride hydrochloride

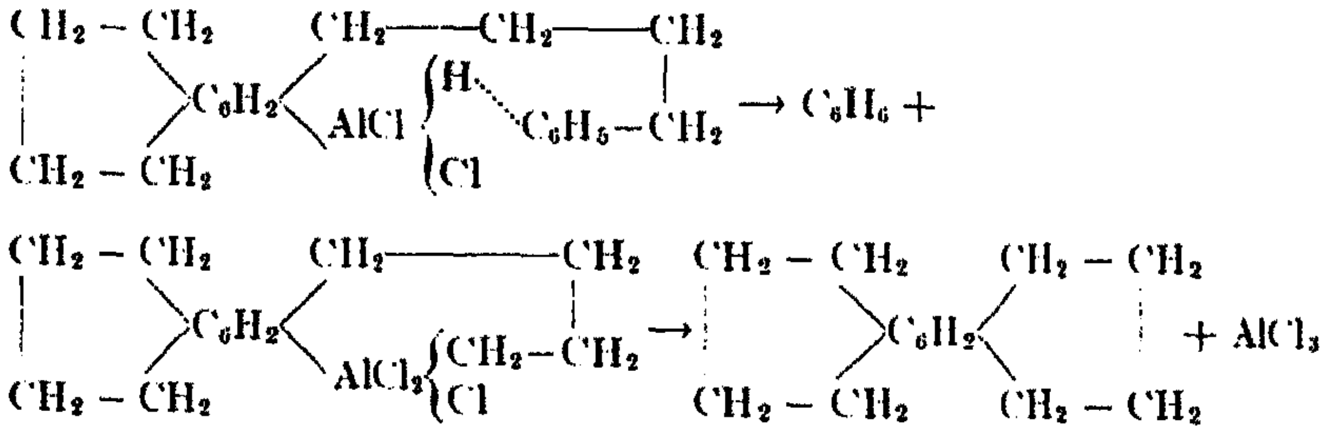
Tetralin



4-δ-Chlorbutylphenyl aluminum chloride

Tetralin

The change of α-phenyl-δ-2-tetralylbutane to octhracene:



A similar graphic presentation could be made for the formation of octanthrene from octhracene.

v. Braun, Hahn, and Seemann (9), interested in a method for the preparation of β-substituted naphthalene compounds, found that a hydrogenated naphthalene such as tetralin, when alkylated, did not give the mixture of α and β compounds in the same proportion as from naphthalene, but gave mostly the β compound. By passage through a "hot" tube, the compound could be dehydrogenated to the corresponding naphthalene. β-Ethyltetralin passed through a tube at 650 to 750° gave a yield of 20 percent β-ethylnaphthalene after purification.

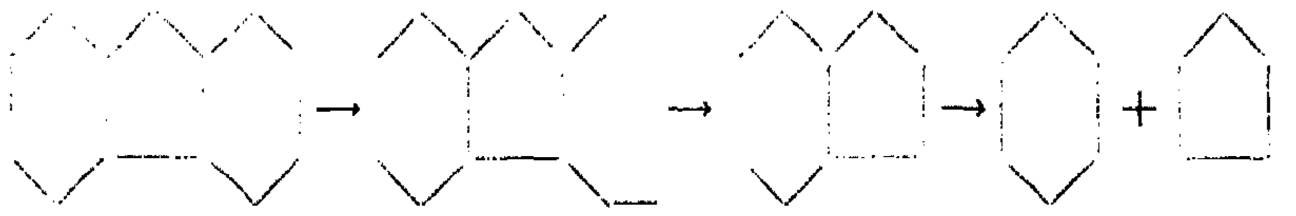
Zelinsky and Borissow (95) heated bicyclo-(0,3,4)-nonane over palladium asbestos catalyst at 300° and obtained bicyclo-(0,3,4)-nonadiene-2, 4. Zelinsky and Kommarewsky (97) used a nickel-aluminum hydrate catalyst with the same hydrocarbon at 300° and obtained similar results. At 320 to 325° the nickel catalyst caused decomposition to products among which benzene and toluene were identified. The same result was obtained with an ordinary nickel catalyst at the same temperature as that used with palladium except that the material was re-run a number of times.

Zelinsky and Titz (103) again tested the action of hydrindane, (bicyclo-(0,3,4)-nonane) over platinized charcoal at 300° to 310°, dehydrogenating it to hydrindene. Zelinsky and Borissow had previously obtained a product, C_9H_{12}, which was now shown actually to be a mixture of two parts of hydrindene and one part of hydrindane. Padoa and Fabris (52) obtained hydrogen and unidentified gaseous hydrocarbons when hydrindene was passed over nickel at 300° in a hydrogen atmosphere.

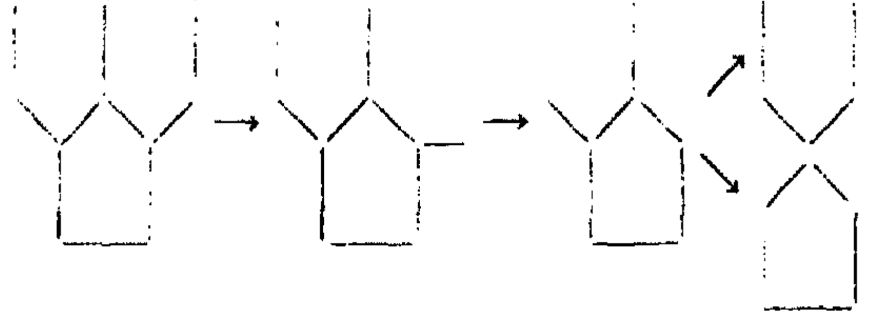
Hexahydrofluorene was obtained by Pictet and Ramseyer (54) from the extraction of a French coal, Montrambert (Loire), with benzene. The hydrocarbon oxidized easily in the air and polymerized upon heating. Subjected to a "red heat" by passage through a combustion tube in a stream of dry hydrogen, it formed fluorene and hydrogen. To show that the fluorene was derived from the hydride, other tests, such as oxidation experiments, were made upon the compound.

Orlov and Belopolski (51) pyrogenically decomposed the perhydrides of fluorene and acenaphthene.

Fluorene perhydride passed through a tinned iron tube at 750° formed cyclopentadiene, indene, and naphthalene. The product boiling at 200 to 235°, which was obtained from Berginization of the fluorene perhydride, was treated in a similar manner. The products identified were cyclopentadiene, benzene hydrocarbons, indene and naphthalene. Thus fluorene perhydride may be postulated as being decomposed according to the scheme:



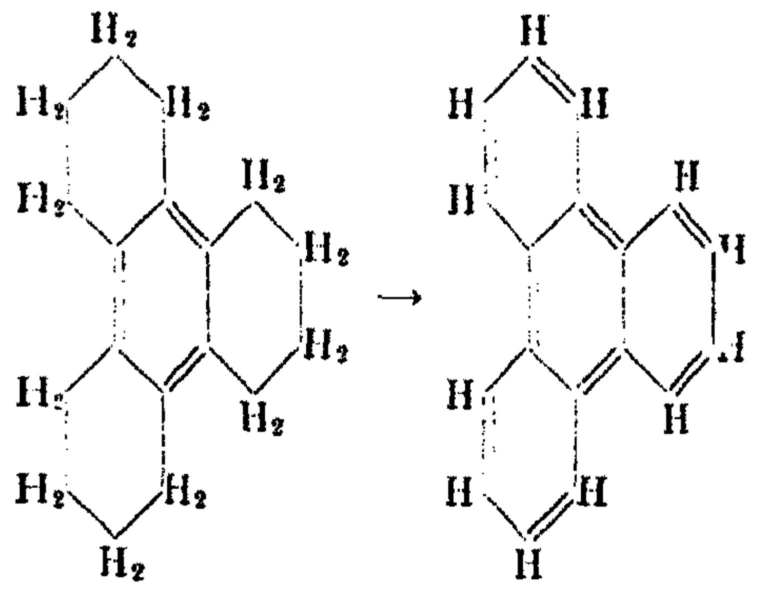
Cracking perhydroacenaphthene at 650° yielded liquid and gaseous products. The gases obtained included 26.8 percent of C_nH_{2n}, 43.9 percent of C_nH_{2n+2}, and 29.4 percent of hydrogen. The unsaturated gases were a mixture of ethylene and propylene. The liquid products consisted of cyclopentadiene, indene and homologs of indene, toluene, and some undetermined unsaturated hydrocarbons. The reaction may be formulated:



Chryseneperhydride, pyrolyzed by Liebermann and Spiegel (45) over pumice at a "low heat," did not yield any chrysene. When zinc dust was used at a "little higher heat," the hydride formed almost all chrysene with little unchanged material. Hexadecahydrochrysene gave similar results when subjected to the same heating conditions.

Mannich (46) passed dodecahydrotriphenylene over copper at 450 to 500° and obtained triphenylene, "the next higher homolog in the series benzene-naphthalene-anthracene." The reaction may be pictured as follows:

$$C_{18}H_{24} \rightarrow C_{18}H_{12} + 6H_2$$



Becker (6) found that passing a high tension discharge through hydrogenated cyclic hydrocarbons in a Siemens ozonizing tube gave a complex mixture of saturated and unsaturated compounds formed from degradation products of the original hydrocarbon.

Decalin yielded butane and various unidentified unsaturated hydrocarbons with as high as 25 percent of resinous condensation products of high molecular weight, having a boiling point above 200° under less than 1 mm. pressure.

Tetralin, when treated in air, yielded hydrogen cyanide and other nitrogen compounds, but if hydrogen was used, and the tetralin was treated in the vapor phase, a yield of 25 percent of a colorless, almost solid resin was obtained.

If the operation was conducted in a Geissler tube, the resin produced yielded, after extraction with acetone, colorless crystals of ditetralyl, $C_{20}H_{22}$, formed by the condensation of two mols of tetralin with the elimination of one mol of hydrogen. From the remaining resin, vacuum distillation gave two fractions, a yellow oil, n_D^{13} 1.5948, and colorless crystals.

The bombardment with cathode rays of decalin, tetralin, and naphthalene by Hirshfeld, Meyer, and Connell (31A) showed very clearly the difference in the behavior of a naphthene, unsaturated naphthene, and aromatic hydrocarbons. The naphthene, decalin, gave off the greatest volume of gas when bombarded by cathode rays, while tetralin, an unsaturated naphthene, gave an intermediate amount, and naphthalene, an aromatic hydrocarbon, the least.

		Total Gas cc. N.T.P.	H_2 % by Vol.	CH_4 % by Vol.	C_nH_{2n+2} % by Vol.
Naphthalene	$C_{10}H_8$	0.6	—	—	—
Tetralin	$C_{10}H_{12}$	2.8	86.2	3.5	8.1
Decalin	$C_{10}H_{18}$	37.2	98.7	0.2	1.3

The effect of temperature with and without catalysts and electric discharge on the polynuclear hydrocarbons is shown in Table XV, along with the products of the reactions.

TABLE XV

Polynuclear Compounds

Reference No.	Hydrocarbon	°C. Temp.	Catalyst	Product	Remarks
(7)	Dihydronaphthalene	"Red Heat"	None	Naphthalene Hydrogen	Sealed tube action
(5)	Dihydronaphthalene	"Dark Red"	None	Naphthalene Hydrogen	Flow method
(38)	Dihydronaphthalene	420	Porcelain	Naphthalene Hydrogen Methane	
(44)	Ethyldihydroanthracene	"Low Heat"	Zinc Dust	Anthracene	No other products given
	Isobutyldihydroanthracene	"Low Heat"	Zinc Dust	Anthracene	No other products given
	Isoamyldihydroanthracene	Refluxed	Zinc Dust	Anthracene	No other products given
(98)	Dihydronaphthalene	130	Palladium	Naphthalene Tetralin	Flow method with indefinite contact time
(79)	Dihydronaphthalene	"Room"	Palladium	Naphthalene Tetralin	Materials shaken together
(1)	Tetramethylanthracene dihydride	"Red Heat"	Zinc Dust	Dimethylanthracene	Hydrogen likely the gaseous product
(38)	Tetralin	530	Porcelain	Naphthalene Benzene Hydrogen Ethylene and "Higher Olefins"	
(69)	Tetralin	580–650	None	Hydrogen Methane Ethylene Benzene Toluene o-Xylene Ethylbenzene Styrene Allylbenzene Propenylbenzene	

TABLE XV (Continued)

Reference No.	Hydrocarbon	°C. Temp.	Catalyst	Product	Remarks
				Methylallylbenzene Propylbenzene Butenylbenzene	
(69)	Decalin	580–650	None	Methane Ethylene Hydrogen Ethane Propane Butane Acetylene Propylene Butylene Benzene Toluene o-Xylene Naphthalene Methylnaphthalene Tetralin Cyclohexene Cyclohexadiene Pentane Hexane Hexene	
(62-63)	Tetralin	30–40	$AlCl_3$	Octahydrophenanthrene Octohydroanthracene Benzene α-Phenyl-δ-2-tetralylbutane Dodecahydrotriphenylene Phenylene bis-octanthrenylbutane Tetralyloctanthranylbutane	
(90)	Decalin	300	Palladium	Naphthalene Hydrogen	
(107)	Decalin (trans.)	300	HI	2,8-Dimethylbicyclo-(0,3,3)-Octane	

TABLE XV (Continued)

Reference No.	Hydrocarbon	°C. Temp.	Catalyst	Product	Remarks
				Methylcyclohexane o-Dimethylcyclohexane	
	Decalin (cis.)	100	$AlBr_3$	Decalin (trans.)	Other isomerization also
	Decalin (cis.)	190	$AlBr_3$	Alkylcyclohexanes	Less isomerization
(6)	Decalin	—	Silent Discharge	Butane	Resin b. p. above 200° Less than 1 mm. pressure
(6)	Tetralin + Air	—	Silent Discharge	HCN Nitrogen compounds	
(6)	Tetralin + H_2	Vapor	Silent Discharge	Resin Ditetralyl A yellow oil Colorless crystals	
(9)	β-Ethyltetralin	650–750	None	β-Ethylnaphthalene	
(95)	Bicyclo-(0,3,4)-nonane	300	Palladium	Bicyclo-(0,3,4)-nonadiene-2,4	
(97)	Bicyclo-(0,3,4)-nonane	300	Ni-aluminum hydrate	Bicyclo-(0,3,4)-nonadiene-2,4	
	Bicyclo-(0,3,4)-nonane	300	Nickel	Bicyclo-(0,3,4)-nonadiene-2,4	Contact time longer
	Bicyclo-(0,3,4)-nonane	325	Nickel	Benzene Toluene	Other products not identified
(103)	Bicyclo-(0,3,4)-nonane	300–310	Platinum	Hydrindene Hydrindane	
(52)	Hydrindene	300	Nickel	Hydrogen Unsaturated hydrocarbon gases	
(54)	Hexahydrofluorene	"Red Heat"	None	Hydrogen Fluorene	Decomposed in stream of dry hydrogen
(51)	Fluoreneperhydride	750	Tinned Iron Tube	Cyclopentadiene Indene Naphthalene	
	"Berginized" Fluorene perhydride	750	Tinned Iron Tube	Cyclopentadiene Benzene homologs Indene	

TABLE XV (Continued)

Reference No.	Hydrocarbon	°C. Temp.	Catalyst	Product	Remarks
(51)	Acenaphthene-perhydride	650	Tinned Iron Tube	Hydrogen Ethylene Propylene C_nH_{2n+2} Gases Cyclopentadiene Indene Indene homologs Toluene Unsaturated liquids undetermined	
(45)	Chryseneperhydride	"Low Heat"	Pumice	——	No products stated
	Chryseneperhydride	"Low Heat"	Zinc Dust	Chrysene Hydrogen	
	Hexahydrochrysene	"Low Heat"	Zinc Dust	Chrysene Hydrogen	
(46)	Dodecahydrotriphenylene	450–500	Copper	Triphenylene Hydrogen	
(31A)	Decalin	—	Cathode rays bombardment	Hydrogen Methane Higher paraffins	
	Tetralin	—	Cathode rays bombardment	Hydrogen Methane Higher paraffins	

13. Unclassified Hydrogenated Cyclic Hydrocarbons

The action of dicyclohexyl hydrocarbons at 300° with platinum black as catalyst would be expected to split off hydrogen from the cyclohexyl group with the formation of aromatic hydrocarbons.

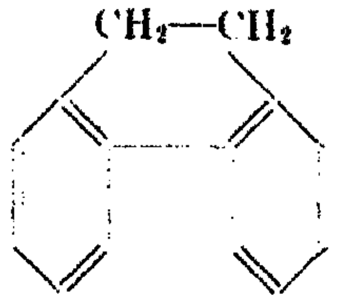
Dicyclohexyl was dehydrogenated to diphenyl in the usual manner over platinum black at 300° by Zelinsky, Titz and Fatejew (105). Dicyclohexylmethane dehydrogenated over the platinum catalyst at 300°, but the expected product, diphenylmethane, was not obtained. Zelinsky, Titz, and Gaverdowskaja (106) identified the product as fluorene.

Zelinsky and Titz (103) also decomposed 1,2-dicyclohexylethane over platinum. The decomposition was shown to occur in steps, for diphenylethane was obtained under certain conditions, but dihydrophenanthrene was not found because of its ease of dehydrogenation.

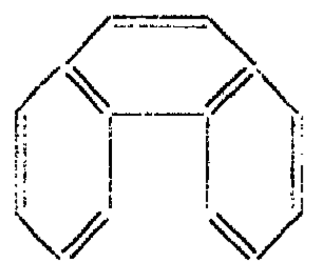
Zelinsky, Titz and Gaverdowskaja found that both diphenylmethane and diphenylethane dehydrogenated at 200° over a platinum catalyst to give fluorene and phenanthrene respectively.

$C_6H_{11}-CH_2-CH_2-C_6H_{11}$
1,2-Dicyclohexylethane

$C_6H_5-CH_2-CH_2-C_6H_5$
1, 2-Diphenylethane



9,10-Dihydrophenanthrene



Phenanthrene

Egorova (21) obtained cyclohexylideneethylene, $C_6H_{10}=C=CH_2$ by heating cyclohexylacetylene at 140° with alcoholic potassium hydroxide. The newly formed allene compound isomerized to 1-vinyl-1-cyclohexene when heated with benzoic acid in a sealed tube at 170°.

These hydrocarbons and their reaction products are shown in Table XVI under the heading of unclassified hydrogenated cyclic hydrocarbons.

TABLE XVI

Unclassified Hydrogenated Cyclic Hydrocarbons

Reference No.	Hydrocarbon	°C. Temp.	Catalyst	Product	Remarks
(105)	Dicyclohexylmethane	300	Platinum	Fluorene	
(103)	Dicyclohexylethane	300	Platinum	Anthracene	
(21)	Cyclohexylacetylene	140	Alc. KOH	Cyclo-hexylidene-ethylene	
	Cyclohexylidene-ethylene	170	Benzoic Acid	1-Vinyl-1-cyclo-hexene	Sealed tube

14. Petroleum Products

The pyrolysis of hydrocarbons obtained from petroleum fractions necessarily includes more than one compound. The hydrocarbons designated as heptanaphthene or octanaphthene imply an analysis of C_7H_{14} and C_8H_{16} respectively, the exact structure of the compounds being unknown or uncertain. Thus, a fraction of unknown chemical constitution may be postulated to be made up of certain compounds because of the appearance of specific decomposition products.

A. Non-Catalytic

Oglobin (50) pyrogenated crude naphtha in order to produce benzene by dehydrogenation and decomposition of the naphthenes in the charging stock. The pyrolysis consisted of passing the naphtha through a tube heated at 525 to 550°, the products being separated into three fractions, (1) that boiling above 200°, (2) that boiling below 200°, (3) and the gas. The second fraction was further subjected to heat by a passage through a tube at 1200°, under a pressure of two atmospheres.

Fractionation of the products gave gas, liquid, and solid substances. One fraction of the liquid contained benzene, toluene and xylene, while the solids were naphthalene and anthracene. This process of dehydrogenation gave a yield of over 6 percent benzene from the crude naphtha used.

From the cracking of machine oil from Baku crude at 463° under 12 atmospheres pressure, Sachanen and Tilitschejew (59) concluded that the cracking of naphthenes consisted of two chief reactions: (a) the splitting of the side chain; and (b) isomerization and dehydrogenation to the corresponding aromatic hydrocarbon. Dehydrogenation without a specific catalyst took place more readily with the higher homologs than with cyclohexane itself.

Egloff, Twomey and Moore (20) subjected two "naphthene base" oils to temperatures of 550, 600, 650, and 700° under pressures of one and eleven atmospheres.

Oil #1 gave 15.8 to 19.3 percent of gasoline at one atmosphere, while at eleven atmospheres pressure the percent of gasoline increased to a maximum of 26.2, based upon the starting material. Oil #2 gave 5.3 to 15 percent gasoline and a maximum of 20.1 percent respectively for the above conditions.

TABLE XVII

Oil No. 1

One Atmosphere Pressure

Temperature, °C.	550	600	650	700
	Percent by Volume			
Benzene	0.2	1.1	2.6	3.9
Toluene	1.8	2.3	4.7	2.5
Xylene	5.7	6.7	6.8	6.5

Eleven Atmospheres Pressure

Benzene	0.9	2.7	4.4	5.0
Toluene	3.8	5.5	6.0	5.2
Xylene	7.4	8.1	5.3	3.6

Oil No. 2

One Atmosphere Pressure

Temperature, °C.	550	600	650	700
	Percent by Volume			
Benzene	0.9	0.9	2.6	4.2
Toluene	2.0	2.2	4.0	4.5
Xylene	2.3	2.7	3.4	2.0

Eleven Atmospheres Pressure

Benzene	0.4	2.0	7.2	6.5
Toluene	2.1	6.1	5.9	3.3
Xylene	3.3	5.9	5.1	2.3

The unsaturated hydrocarbons in the fractions boiling up to 175° varied from 12 to 52 percent and 6 to 48 percent at one and eleven atmospheres pressure respectively for oil #1. In oil #2 the results were 10 to 54 percent and 4.5 to 45 percent respectively.

The formation of benzene, toluene, and xylene, which are constituents of the gasoline mentioned above, is best shown in Table XVII quoted from these authors.

The percentage of starting oil which decomposed to form carbon and gas increased with increase of temperature and pressure. The minimum of 10 percent formed at 550° under one atmosphere pressure, the maximum of 69.3 percent at 700° under 11 atmospheres pressure.

The importance of the composition of oil in the thermal reaction was brought out clearly by these authors. Thus we find:

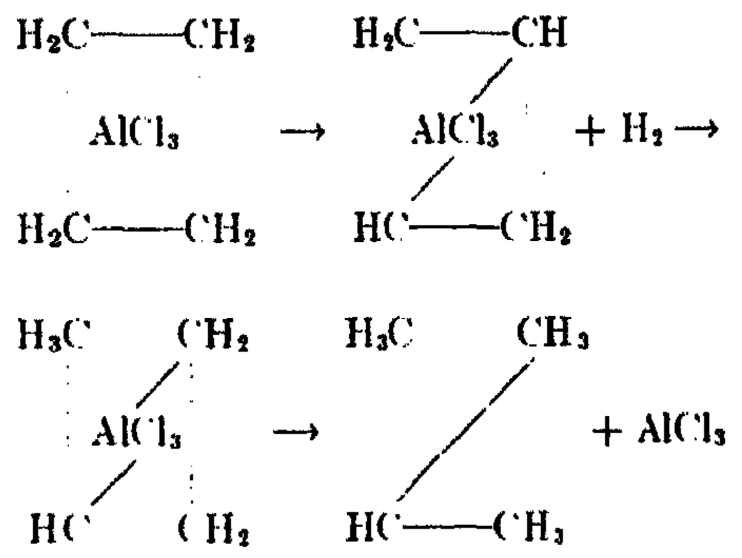
"The two naphthene base oils, although somewhat similar in characteristics as to distillation and specific gravity analysis, gave widely different percentage yields of gasoline, unsaturates, benzene, toluene, and xylene under the same conditions of temperature and pressure. This emphasized the importance of the starting oils in cracking phenomena when yields of certain types of hydrocarbons are desired in maximum quantity."

B. Catalytic

1. *Aluminum Chloride.* Zelinsky and Smirnow (101) decomposed "heptanaphthene" obtained by fractionation of Baku petroleum (b. p. 101 to 102° at 740 mm. $d_{15} = 0.7695$) by heating in sealed tubes at 100 to 300° with varying proportions of aluminum chloride. Fifteen grams of "heptanaphthene" was heated with 18 grams of aluminum chloride at increasing temperatures from 100 to 300°, and the gas was removed after certain periods of heating. The yield of gas corresponding to the empirical equation:

$$3C_7H_{14} = 4C_4H_{10} + (5C + H_2)$$

The isobutane formed may be assumed to come from the cyclobutane-$AlCl_3$ complex formed by the decomposition of the "heptanaphthene." The C_4H_8-$AlCl_3$ complex may hydrogenate and split, thus:



Egloff and Moore (19) treated the six 25° fractions boiling from 150 to 300° from a naphthene base oil with aluminum chloride to about 100° for a period of twelve hours. The material boiling below 100° was removed from the sphere of action as soon as it was formed.

The change in the original oils with respect to gasoline formation—that is, the liquid boiling below 150°—was studied as well as the specific gravity and refractive index. The formation of aromatic hydrocarbons is most important because of the relation of naphthenes to aromatics.

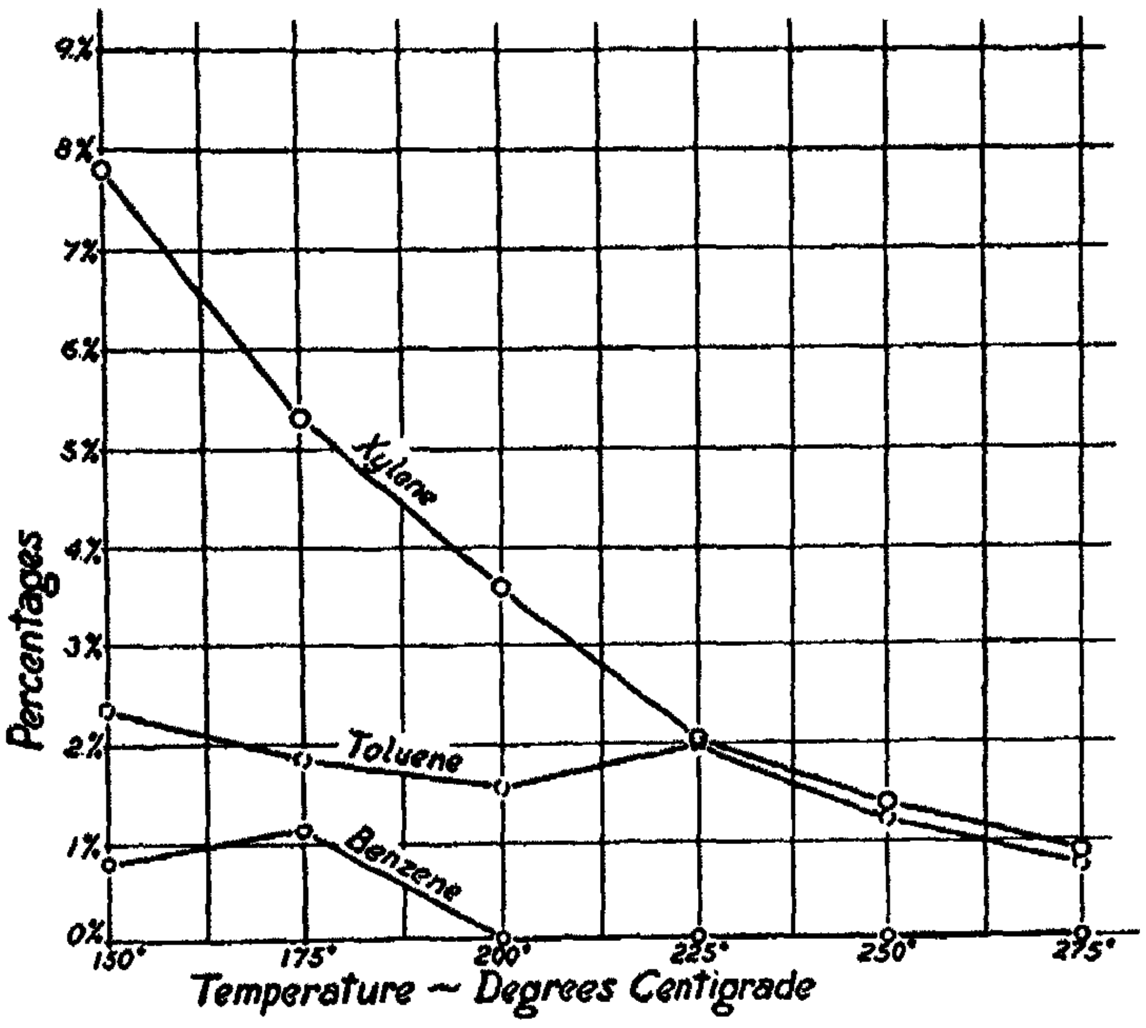


FIG. 4

Gasoline was formed from the oil, using aluminum chloride as catalyst, to the extent of 18.4 to 32.1 percent. The maximum conversion occurred with the oil of higher boiling point.

The graph given by the authors shows the results of the action of aluminum chloride upon the six oil fractions with respect to aromatic hydrocarbon formation.

2. *Metals.* Zelinsky (86) (89) passed various fractions of petroleum distillate from Baku crude over a platinum catalyst at 300°. The fractions 102 to 104° and 100 to 100.5° were similarly treated with the catalyst. The first fraction was untreated before use, but the second portion had been treated with nitric-sulfuric acid mixture. The results of dehydrogenation were similar in both cases, indicating about 50 percent cyclohexane derivatives in each of the original fractions, based upon the hydrogen evolved. The residue was analyzed for naphthenes, and it was concluded that they were

TABLE XVIII

Naphthenic Petroleum Hydrocarbons

Reference No.	Hydrocarbon	°C. Temp.	Catalyst	Product	Remarks
(50)	Naphtha	525–550	None	Gas Liquid boiling above 200° Liquid boiling below 200°	Decomposition of naphtha carried out in two steps
	Liquid boiling below 200°	1200	None	Benzene Toluene Xylene Naphthalene Anthracene	Two atmospheres pressure
(100)	Baku petroleum fraction 101–102°	100–300	$AlCl_3$	Carbon Hydrogen Isobutane	Sealed tube
(86)	Fraction 102–104°	300	Platinum	Hydrogen	The aromatics not determined
(89)	Fraction 100–100.5°	300	Platinum	Unchanged cyclopentanes	
	Fraction octanaphthene 100–100.5°	300	Platinum	No change in liquid Little hydrogen evolved	Naphthenes consist of other than cyclohexanes
(40)	Decalin	320–330	Platinum	Naphthalene	
	Methyldecalin	320–330	Platinum	α-Methylnaphthalene	
	Dimethyldecalin	320–330	Platinum	1,6 and 2,6-Dimethylnaphthalenes	
(61)	Naphthenic oils	—	Cathode Rays	Hydrogen Methane Higher gaseous paraffins	
(19)	Naphthene base oil	100	$AlCl_3$	Gasoline Benzene Toluene Xylene	
(20)	Naphthene base oil	550 600 650 700	None	Gasoline Benzene Toluene Xylene Unsaturated hydrocarbons Carbon Gas	Under pressures of 1–11 atmospheres

cyclopentane derivatives. "Octanaphthene, isoöctanaphthene, and nonanaphthene" fractions were passed over the catalyst under similar conditions, but not much hydrogen was evolved. It was evident, then, that these fractions did not consist of cyclohexane homologs, which produce quantitative amounts of hydrogen, but were made up of other cyclic compounds and of mixtures of cyclic and paraffinic hydrocarbons.

Tausz and Putnoky (73) applied Zelinsky's method to the analysis of mixtures of cyclohexane and aliphatic hydrocarbons and of the lower boiling fractions of petroleum that might contain cyclohexane. Calculation from the amount of hydrogen liberated from any mixture gave a good approximate value for cyclohexane. A synthetic mixture of hexane and cyclohexane, analyzed by this method, gave fair results, usually within one-half of one percent of the true value for cyclohexane.

Kaffer (40) used Zelinsky's dehydrogenation catalyst as a means of identifying decalin in crude oil. The fraction of crude oil which contained the naphthenes, decalin, methyldecalin, and dimethyldecalin, was used as a starting material. This mixture was passed several times over a platinum-charcoal catalyst at 320 to 330°. After each passage, the aromatic compounds formed were removed by concentrated sulfuric acid.

The decalin present formed naphthalene; methyldecalin gave α-methylnaphthalene; and the dimethyldecalin gave a mixture of 1,6 and 2,6-dimethylnaphthalenes. These products were identified by physical constants such as the melting point and the picrate melting point. Mixed melting points were made with each material used.

Schoepfle and Connell (61) studied the action of cathode rays upon hydrocarbon oils. Using a "naphthenic" oil of unknown source, but of "moderate or high refinement," they subjected the oil to cathode rays at 0°.

When "moderately refined" oil was used, one-half hour of bombardment gave 10 cc. of gas while with "highly refined" oil 35 cc. was obtained under the same conditions. This gas was found to be about 90 percent hydrogen, while the remainder was methane and higher saturated hydrocarbons in the proportion of 1 to 2.

Table XVIII records the treatment of naphthene mixtures from petroleum and the reaction products obtained.

15. Summary

The hydrocarbons incorporated here have been limited to hydrogenated cyclic compounds. Although unsaturated compounds of the type which includes tetralin and cyclohexene are not, strictly speaking, naphthenes or polymethylenes, the class has been included because of a similarity in reactions with those of pure naphthenes.

Reactions found to take place under the various stipulated conditions may be divided into the following types: (1) Carbon-carbon scission, (2) hydrogenation or dehydrogenation, (3) polymerization or depolymerization, and (4) isomerization. Any one of these reactions, combinations, or all of them may take place when a hydrocarbon is treated with some activating agency, such as heat or a chemical. The stability of the ring structure, and the relation of this ring to the whole molecule are the criteria by which the hydrocarbon reaction may be postulated.

The decomposition of the various polymethylene rings may be reviewed briefly. Cyclopropane, cyclobutane, cycloöctane, and cycloheptane undergo a breaking of the carbon-carbon bond, the ease of rupture decreasing among the hydrocarbons in the order named. On the other hand, cyclohexane gives a carbon-hydrogen scission more readily than a carbon-carbon break, while cyclopentane is apparently resistant to either type of scission.

These decompositions are evidenced by the fact that in the first four polymethylenes named, ring rupture and isomerization occurs to form more stable compounds. Cyclopropane yields propylene, cycloheptane gives methylcyclohexane, while cycloöctane produces methylcycloheptane, although some dehydrogenation also occurs to form bicycloöctane. Cyclohexane, however, breaks the carbon-hydrogen linkage more readily, although with a nickel catalyst a carbon-carbon break also occurs.

Unsaturated ring compounds, such as cyclopentadiene, exhibiting conjugated double bonds, are analogous with the chain hydrocarbons containing the same type of unsaturation. Polymerization, the characteristic reaction of the diolefins, also takes place with the doubly unsaturated ring compounds.

The so-called "oxidation-reduction" reaction, or simultaneous hydrogenation and dehydrogenation, occurs with the unsaturated six-membered ring hydrocarbons in the presence of palladium or platinum catalysts.

The more complex naphthenes such as the hydrogenated naphthalenes or anthracenes show dehydrogenation as the chief reaction.

With an aluminum chloride catalyst the homologs of cyclohexane are found to give a peculiar reaction. Paraffinic side chains consisting of more than a single carbon atom produce methyl radicals, equal to the number of carbon atoms in the chain, which attach themselves to the nucleus.

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107. Zelinsky and Turowa-Pollak: Ber., **58**, 1292 (1925).
108. I. G. Farbenindustrie A.-G. British 269,593, 272,539, 296,694, 296,752, 297,398, 302,203, 317,303, 317,359.

THE SYSTEM: SODIUM METASILICATE—SODIUM FLUORIDE*

BY HAROLD SIMMONS BOOTH AND BERNARD A. STARRS**

In contrast with ordinary soda-lime glass vitreous enamel frits are made from a relatively large number of raw materials. The reactions which these raw materials undergo in the smelting process are little understood, and it was for the study of these reactions that the late Mr. H. D. Cushman, president of the Ferro Enamel Corporation, founded the Cushman fellowship. The first five years[1] have been devoted to the study of the possible reactions that may take place based on the gases evolved during the given reaction.

Of the various combinations studied in this preliminary work the system, sodium fluoride-sodium oxide-silica, showed the need of further study by the methods of thermal analysis. Little work has been done on this system with the exception of the component binary system, sodium oxide-silica. Data[2] of this system reveals the existence of an orthosilicate, pyrosilicate, metasilicate, and disilicate as compounds with congruent melting points. While the data of the literature is in fair agreement, the interpretations are different. Kracek found the orthosilicate to be unstable at 1118° ± 5° and 40.7% silica, and did not carry his experimental study beyond this point, i.e., into the high Na_2O region.

On the other hand, D'Ans and Löffler found a pyrosilicate to adjoin the metasilicate and then the orthosilicate adjoined the pyrosilicate. The orthosilicate existed in two forms and had a congruent melting point. The pyrosilicate was very similar to the orthosilicate in optical properties which may explain Kracek's probably mistaken identification of the orthosilicate.

Considerable information on the ternary system should be gained by studies of the binary systems composed of one of the sodium silicates and sodium fluoride. It was decided first to make a thermal analysis study of the system sodium metasilicate-sodium fluoride. This is now of added interest because it has recently been suggested[3] to use the metasilicate as a raw material for enamel frits. Also, these studies would definitely establish the nature of the phases in the mixtures at different temperatures and inference could be made as to the phase, or phases, causing opacity.

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* Presented by Bernard A. Starrs in partial fulfillment of the requirements for the degree of Master of Arts at Western Reserve University, 1931.

** Holder of the Cushman Fellowship for fundamental research in vitreous enamels, 1930-1931.

[1] This introductory work has not yet been published. It is on file at Western Reserve University in the form of theses and reports, and will shortly be published.

[2] (a) F. C. Kracek: J. Phys. Chem., **34**, 1583 (1930). (b) J. D'Ans and J. Löffler: Z. anorg. allgem. Chem., **191**, 4 (1930).

[3] M. E. Manson: J. Am. Ceramic Soc., **14**, 490 (1931).

Experimental Procedure

Chemicals: Pure silica was obtained by powdering large quartz crystals. The surfaces of the crystals were first cleaned by scraping off adhering material and then treating them with boiling aqua regia. These covered surfaces were often etched. The powdering was performed by heating the crystals in a platinum dish and then cooling rapidly with a stream of cold distilled water. The shattered pieces were at first large and those with etched surfaces were rejected. This process was repeated several times and the particles became smaller, and they were finally ground to a fine powder in a large agate mortar. 8.5166 grams of this powder gave 0.03% residue on treatment with hydrofluoric acid.

The sodium oxide component was obtained by the use of sodium carbonate monohydrate. The percentage of water in this hydrate was in agreement with its formula percentage, and qualitative testings showed the absence of appreciable quantities of impurities.

Sodium metasilicate and sodium disilicate were made by careful fusion of the correct amounts of silica and sodium carbonate monohydrate in a platinum dish. The disilicate solidified to a glass which was crystallized by heating at a temperature below dull red heat.

Chemically pure sodium fluoride was recrystallized once from water, dried in an air bath, but still retained from 0.6-0.8% water depending upon the time of drying. Careful conversion of this sodium fluoride to sodium sulfate gave 99.07% sodium fluoride, and since this particular sample had 0.81% water, a total of 99.8% was accounted for.

Apparatus: The furnace employed was built by T. C. Morris (previous Cushman Fellow) and was suggested by that of Orton and Krehbiel.[4] It is a vertical cylindrical resistance furnace with two heating coils. The inner coil consists of 41 ft. of No. 24 BS platinum-20% rhodium alloy wire; the outer coil, "the booster coil," is made up of 20 ft. of No. 18 BS Chromel resistance wire. 110 volt AC was used on both coils, the current being controlled by two Cenco water-cooled rheostats.

The potential measuring instruments were the standard set provided by Leeds and Northrup using the student type potentiometer with the wall type galvanometer. The galvanometer had the following characteristics: sensitivity, 97 megs.; period, 8.5 sec.; and resistance, 132 ohms.

The thermocouple was made from standard platinum, and platinum −10% rhodium, wire 0.020 inches in diameter, provision being made for differential temperature measurements. The differential junction was about 2½ inches above the charge junction and was surrounded by a "neutral body" of nickel.

An elevator device was used for raising and lowering the thermocouple in the furnace, and a means provided for hanging the platinum melting point crucible rigidly below the thermocouple junction. The melting point crucible was a cylinder of platinum ⅝" inside diameter and 2" high with heavy walls.

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[4] E. Orton, Jr. and J. F. Krehbiel: J. Am. Ceramic Soc., 10, 373 (1927).

The thermocouple was carefully calibrated using potassium dichromate[5a] 398°, potassium chloride[5a] 770°, sodium chloride[5a] 800°, potassium sulfate[5b] 1076°, and sodium metasilicate[5a] 1089°. The bare thermocouple was immersed in the material in all cases. The rate of heating was usually less than 5° per min. In this connection F. M. Jaeger[6] has found "that the discontinuities in (the temperature-time curve of sodium molybdate) all lie at practically the same temperature although the rates of heating for the three curves are in the ratio 4:2:1. Temperature readings of the charge were taken every minute, the time between readings being one-half a minute whenever the charge was undergoing a phase change. A charge of 10.00 gms. was always used. The components were accurately weighed out, carefully fused in platinum over a blast lamp (slight contamination being incurred), and then ground to a powder in an agate mortar. This powder was placed in the platinum melting point crucible, the thermocouple carefully inserted, and the mixture was then usually fused—the heating curve of a finely ground powder is apt to be somewhat erratic. At least two heating curves and one cooling curve of each charge was made.

TABLE I

The System: Na_2SiO_3 – NaF

			Low Temp. Approach		High Temp. Approach	
Pts.	Wt. % NaF	Molar % NaF	Monovariant Arrest Pt.	Invariant Arrest Pt.	Invariant Arrest Pt.	Duration at Invariant Pt. (min.)
1	0.00	0.00	—	1089°C.	(a) 1015 (b) 1057	
2	4.96	13.16	1074	915	903	<0.2
3	9.94	24.28	1049	913	904	0.8
4	14.90	33.71	1002	915	910	1.0
5	17.89	38.77	985	914	909	2.5
6	19.89	41.91	962	914	905	2.9
7	22.88	46.30	946	913	909	3.5
8	25.66	50.08	935	912	909	4.2
9	26.86	51.63	926	914	909	4.6
10	29.85	55.29	916	911	909	5.8
11	31.86	57.61	926	912	908	4.8
12	34.84	60.86	931	913	907	
13	40.60	66.52	947	913	907	3.5
14	44.82	70.24	950	913	907	3.3
15	49.82	74.26	960	913	907	3.3
16	54.82	77.91	970	914	907	2.5
17	64.84	84.27	979	915	908	2.0
18	79.89	92.03	990	914	896	1.0
19	100.0	100.0	---	995	994	

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[5] (a) I.C.T. Vol. 1, p. 54 (1928). (b) "Chem. Rubber Handbook," p. 257, 14th Ed.; I. C. T. 1, 54, gives 1069°.

[6] F. M. Jaeger: "The George Fisher Baker Non-Resident Lectureship in Chemistry" at Cornell University (1930).

Results

The data obtained for this system are given in Table I and plotted in Fig. 1. This system is a simple V type, the eutectic temperature being at 913° ± 2°, and the eutectic composition is 28.5 ± 1.0 wt. per cent of sodium fluoride in the liquid.

The melting point of sodium metasilicate has been determined by previous workers with sufficient precision for it to be used as a calibration point for a thermocouple. Jaeger[7] gave the m.p. of sodium metasilicate to be 1088°; Morey and Bowen[8] as 1086.5°; Ginsberg and Nikogosian[9] as 1093°; and Kracek[2a] as 1089°. The authors' results were in agreement with the value 1089°.

However, the published melting points of sodium fluoride vary much more widely. Ruff and Plato[10] obtained the value 980°; W. Plato[11] 992.2°; Kurnakow and Zemazuznyz[12] 997°; Puschin and Baskow[13] 1040°; and Grube[14] 992°. The authors obtained the value of 995° ± 1° for sodium fluoride recrystallized twice from water and heated only in an electric furnace. It was found that sodium fluoride heated in a covered platinum crucible over a gas flame gained weight due to carbonate formation. In 18.1 hrs. of heating there was a gain in weight of 1.11 per cent. and on treating the solid with dilute acid gas evolution occurred which proved to be carbon dioxide. Seemingly, the burner gases cause hydrolysis and carbonation.

It may be noted in Fig. 1 that the points of the sodium metasilicate liquidus are only in fair agreement. This is partly due to the arrests not being very well-defined and partly to the large change in the equilibrium temperature for a small change in composition. The composition was obtained from the careful weighing out of the components, and are as given in columns 2 and 3 of Table I.

The arrest points determining the sodium fluoride liquidus were much better defined than those of the sodium metasilicate liquidus.

The arrest points given in columns 3 and 4 of Table I were secured from at least two heating curves. The heating curves (temperature-time) were oblique, but the differential curves usually definitely located the temperature of change. W. P. White[15] has discussed the principal causes of oblique melting curves.

Column 6 of the table gives the eutectic temperature for different mixtures of the components as determined from cooling curves. A slight supercooling is evident. Column 7 of the table gives the time that the charges stayed at the eutectic temperature, and it may be noticed in Fig. 1 that a plot of these points is in agreement with the nature of the system as disclosed by the other results.

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[7] F. M. Jaeger: Z. Kristall., **53**, 632 (1914).

[8] Morey and Bowen: J. Phys. Chem., **28**, 11 (1924).

[9] Ginsberg and Nikogosian: Chem. Zbl. I_2, 3383 (1926).

[10] Ruff and Plato: Ber. **26**, 2363 (1903).

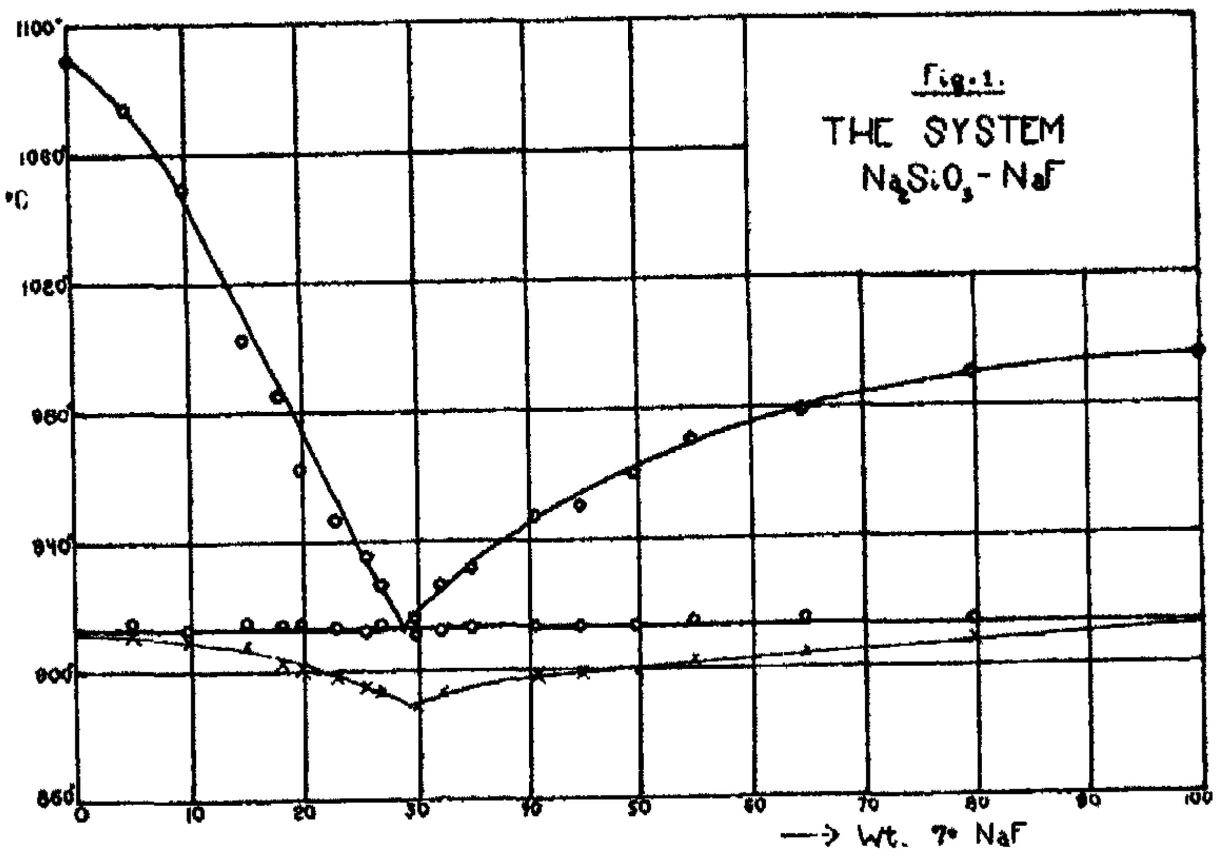
[11] W. Plato: Z. physik. Chem., **58**, 350 (1907).

[12] Kurnakow and Zemazuznyz: Z. anorg. Chem., **52**, 186 (1907).

[13] Puschin and Baskow: Z. anorg. Chem., **81**, 347 (1913).

[14] G. Grube: Z. Elektrochemie **33**, 481 (1927).

[15] W. P. White: Am. J. Sci., (4) **28**, 453 (1909).



An attempt was made to study the system: sodium disilicate-sodium fluoride by means of thermal analysis. However, the fused disilicate-sodium fluoride mixtures easily form glasses, and so, but one heating curve could be obtained without recrystallization.

A melting point of 875° was obtained for the crystalline sodium disilicate and a distinct arrest was also obtained at 837°. The cause for the arrest at 837° is unknown and cannot be interpreted from the nature of this region as given in Kracek's[28] work.

From the heating curves of a number of different compositions, this sodium disilicate-sodium fluoride system also appears to be a V type. The addition of sodium disilicate has slight effect on depressing the melting point of sodium fluoride until about 65% by weight of sodium disilicate has been added. Then the liquidus curve rapidly falls to the eutectic which is at 798° ± 3° and 13.5 ± 5.0% by weight of sodium fluoride.

The nature of this system, sodium disilicate-sodium fluoride cannot be satisfactorily determined by the use of heating curves alone, and resort must be made to other methods, preferably the quenching method. Since the heating curve data was not supplemented by other methods, the information given must be considered as tentative only.

Summary

The system, sodium metasilicate-sodium fluoride, is a one eutectic type, and the eutectic occurs at a composition 28.5 ± 1.0 weight per cent of sodium fluoride in the liquid and at a temperature of 913° ± 2.0°C.

Some tentative data for the system, sodium disilicate-sodium fluoride are also presented.

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PARTIAL PRESSURE ISOTHERMS. II

BY SIANG CHIEH LEE*

It has recently been shown by Professor Bancroft[1] that the disturbing factors which will cause a deviation of partial pressure curves from straight lines as demanded by the laws of ideal solutions, may be polymerization or depolymerization, solvation, heat of dilution, or the tendency to separate into two layers. These factors may be present at the same time and one may dominate the other. It is only when they are entirely absent that we can get the limiting case of ideal solutions.

The tendency to separate into two layers is emphasized because its importance as a disturbing factor has not been realized before. Dolezalek[2] and his followers considered polymerization and solvation as the main causes for the deviation from Raoult's law, while the van der Waals and van Laar school[3] attributed the deviations to the intermolecular forces between the components. Hildebrand,[4] on the other hand, criticized both schools and boiled down the disturbing factors to two, internal pressure and polarity. Recently, Errera[5] discussed the nature of the molecular association from the point of view of Debye's dipole theory and van der Waal's force. He concluded that there are two kinds of associations: one is due to the dipole moments of the component molecules and the other due to the van de Waals force. The polarization measurements measures only the "dipole association," while the vapor pressure experiments give a measure of the total association. For non-polar components, the van der Waals force is the only decisive factor. Tinker[6] said that the deviation of the vapor pressure from the straight line law is determined by the magnitude of the differences between the molecular heats of vaporization of the components in the mixture and the corresponding latent heats for the pure liquids. Butler[7] considered that the partial heat of solution is a better measure of the deviation from the law of Raoult. Washburn[8] thought fit to have a name for the sum total of all disturbing factors in solutions and has invented the phrase "thermodynamic environment" for such purpose.

In spite of much work done on the subject of solutions, an adequate theory of concentrated solutions is still lacking. The knowledge of the

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* Research Fellow of the China Foundation for the Promotion of Education and Culture.

[1] Bancroft: J. Phys. Chem., **35**, 3160 (1931).

[2] Dolezalek: Z. physik. Chem., **64**, 727 (1908).

[3] Van der Waals: Z. physik. Chem., 5, 133 (1890); van Laar: **72**, 723 (1910); Kohnstamm: **36**, 41 (1901).

[4] Hildebrand: J. Am. Chem. Soc., **38**, 1452 (1916); "Solubility" (1924).

[5] Errera: Z. physik. Chem., **138**, 332 (1928); **140**, 273 (1929).

[6] Tinker: Phil. Mag. (6) **32**, 295 (1916).

[7] Butler: J. Am. Chem. Soc., **47**, 117 (1925).

[8] Washburn: "Principles of Physical Chemistry," 165 (1921).

phenomena of vapor pressure lowerings stands almost in the same way as it was first advanced by Raoult and van't Hoff. The only discovery that is worth mentioning is perhaps the fact that the so-called Raoult's Law holds true for certain binary solutions in all concentrations. Dolezalek's[2] assumption that solutions composed of normal substances obey Raoult's formula is not of much use in view of the facts that many normal substances, benzene and hexane, for example, do not obey the law, while methyl alcohol and ethyl alcohol, both associated, do. Evidently, the phenomenon is complex and the disturbing factors involved have to be recognized and analyzed before any general conclusions can be made.

Theoretically, the problem of vapor pressures from solutions has been treated in two ways: the thermodynamic treatments with and without the concept of osmotic pressure, and the thermokinetic treatment of van der Waals. By a cyclic reversible process, van't Hoff obtained his famous osmotic pressure equation, the second form, connecting the osmotic pressure with the vapor pressure, and giving an exact derivation of Raoult's empirical equation. An imperfect understanding of van't Hoff's equation has resulted in much confusion and mis-applications. Fortunately, the cloud has been cleared away by the important work of Bancroft and Davis,[9] and there is no further excuse for not understanding it rightly. However, when applied to the vapor pressure lowering, assumptions have to be made, which are not justified in many cases. A detailed discussion is given in the papers of Bancroft and Davis.[9,10]

By using purely thermodynamic functions, the same problem can be approached in different ways. The studies of Duhem[11] and of Margules[12] led them to the formulation of what now known as the Duhem-Margules' equation. In this equation the partial pressures of the components are related to their respective concentrations in solution. As the equation is in a differential form, it has to be integrated before it can be used directly. If it is to be integrated, some assumptions must be made in regard to the relations between the variables involved in it, namely, p_1, p_2, and x, where p is the partial pressure and x the mol fraction. This is as if we are defeating our own purposes, because what we are searching for is a relation between p and x so that we can calculate the former from the latter, thus, the lowering of the vapor pressure. Margules, from the parabolic nature of the partial pressure isotherms, made the assumption that p could be represented by a power series of x. This is simply a mathematical way of recording the expermental data and nothing else. Porter[13] has recently suggested another method to integrate this equation, based upon the symmetrical form of the differential equation, and claimed that the experimental data could be represented by the following form:

$$e^{\vartheta} = \frac{\alpha}{u}$$

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[9] J. Phys. Chem. 32, 1 (1928).

[10] J. Phys. Chem., 33, 370 (1929).

[11] Am. de l'École normale, sup. (3) 4, 9 (1887); (3) 6, 153 (1889); "Traite élémentaire de Mécanique chimique", Trav. et Mém. des Facultés de Lille, nos. 12 and 13 (1894).

[12] Wien. Ber., 104, 1243 (1895).

[13] Trans. Faraday Soc., 25, 343 (1928).

where α is the ratio of the partial pressure to the pressure of the pure component; u the molfraction of one component and ϑ is a function of u, the terms of which can be chosen from the following, multiplied by the constant coefficients A, B, ... ,

$$\log u,\ (1-u),^2\ (1-u)^3(1+3u),\ (1-u)^4(1+4u+10u^2),$$
$$(1-u)^5(1+5u+15u^2+35u^3),\ \text{etc.}$$

This treatment is essentially the same as that of Margules.

Wagner[14] has more recently published a series of papers on the thermodynamics of mixtures of two or more components, after the trail blasted by Planck. Fisher[15] did his share in another series of publications. This author has given an equation[16] for partial pressure isotherms, but I have not seen it. The former investigator treated the subject rather thoroughly and has studied different special cases. He classified the solutions, or mixtures, into two main types, purely physical and physico-chemical mixtures, each of which is again divided into two, ideal and non-ideal. This classification is based on the heat effects upon mixing; which is said to be the sum of two terms, Q_p, the heat occurred due to the act of mixing, and Q_c, that due to chemical reaction. In purely physical mixtures, Q_c is zero. Different systems were then studied according to whether Q is a lineal function of the concentration (ideal), or not (non-ideal). He gave equations for partial pressure isotherms for different systems, but in general, the following equation may be written, in reminiscence of the so-called Raoult's equation,

$$p = PXe^{\frac{1}{RT}\frac{\partial\sigma}{dx}}$$

$$\text{and } \sigma = -Q_p + T\int_0^{T_1} \frac{\partial Q_p}{T\ \partial T}\,dT$$

where Q_p as defined above, and X is the mol-fraction of one component. Up to here, assumptions were made that need an expert in thermodynamics to approve or to disapprove. He emphasized at the outset, however, that the components should be normal substances in the usual sense.

As the heat effect is written as a function of concentration, and the function is unknown, it is natural to play upon assumptions. Here Wagner did as Margules had done and assumed that the function of concentration could be expanded into Taylor's series. The resulting equation, as expected, is just the same as that given by Margules as a solution to his differential equation.

The treatment of van der Waals[3] is of course based on his kinetic theory. Along this line, the works of Kohnstamn[3] and van Laar[3] may be mentioned.

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[14] Z. physik. Chem., **94**, 592 (1920); **95**, 15, 37 (1920); **96**, 287 (1914); **97**, 229, 330 (1921); **98**, 81, 151 (1921). Reference is especially made to the first paper.

[15] Z. Physik, **43**, 150 (1927); **46**, 427 (1928); **48**, 706 (1928); **50**, 419 (1928); **53**, 138 (1929); **54**, 715 (1929). The last paper is especially referred to.

[16] Z. tech. Physik, **5**, 458 (1924).

Judging from the success of the kinetic study of gaseous mixtures, we do not expect at present any exact solution to the problem of liquid mixtures from this source. Not till a complete, or nearly complete, theory of liquids is developed, can we modestly hope of any success in extending it to mixtures.

Van Laar,[17] employing the concept of thermodynamic potential, has derived repeatedly his equation for partial vapor pressures. In the midst of his derivation, he used the equation of state of van der Waals. His equation, though essentially of the same form as the others mentioned above, differs from them in that the constants in the equation can be calculated from the van der Waals' constants, a and b, of the pure components, while in other equations the constants are arbitrary and must be determined experimentally. It has been complained that this equation is too complex, but this is no objection, for the problem is a complex one, unless there is a simple one just as good. The trouble is in the fact that van der Waals' equation is not exact, not to say that the constants in the equation of most substances are not known. Even these constants are known, there still remains the question how to calculate the constants of the mixture from its components. Weisenberger[18] had attempted to test the equation of van Laar and measured the vapor pressures of solutions with one volatile component so that the pressure of the other one can be neglected. He found that the calculated values did not agree with his experimental values. This made him rather skeptical about van Laar's equation and led him to the conclusion that not only the attractive forces exist between molecules, but also repulsive forces. According to him, when the attractive forces are extremely large chemical combinations will occur, and, on the other extreme, when the repulsive forces highly predominate, the liquids will separate into layers. Between the extremes, the mixtures will behave according to how these two forces balance each other. Van Laar[19] however, came forth and pointed out to Weissenberger that the latter's calculations were all wrong. α, a factor in van Laar's equation, was found a large negative number instead of a small positive one as calculated by Weissenberger. This indicates the difficulties involved in the applications of the equation in question, and also that there is no experimental proof that the intermolecular forces are purely attractive in nature and are the only factors affecting the behaviors of solutions.

With the advance of the x-ray examination of materials, many new ideas have been formed. The investigations of liquids with x-rays, such as the works of G. W. Stewart, the inventor of the term "cybotaxis," seem to indicate that the liquid molecules have a definite though temporary arrangement as if forming a labile lattice form. We, therefore, expect that some forerunners should apply this novel idea to liquid mixtures, and this has been done by Herzfeld and Heitler.[20] These authors assumed the validity of the

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[17] Z. physik. Chem., **72**, 723 (1910); **83**, 599 (1913); **137** 421 (1928); Z. anorg. allgem. Chem., **171**, 42 (1928).

[18] J. prakt. Chem., (2) **115**, 78 (1927); data given in Tables Ann. de Constantes, **7**, p. 247-57 (1930).

[19] Z. anorg. allgem. Chem., **171**, 42 (1928); *Also Tables Ann. de Constantes*, **7**, 247 (1930).

[20] Z. Elektrochemie, **31**, 536 (1925).

idea of liquid crystals and derived an equation for partial vapor pressures of the following form,

$$p = PXe^{\lambda/RT(1-X)^2}$$

where λ is the heat of the mixture. This equation was applied to acetone-carbon disulfide mixtures with fair success. Bredig[21] claimed that it was also applicable to his results on methyl alcohol-water mixtures. Van Laar was alert enough to notice the similarity of this one to his equation and pointed out that it was only a special case of the one suggested by him.

From the study of surface energies Langmuir[22] derived the following equations for partial pressures,

$$p_A = P_A\,X_A\,e\,\frac{S_A\varphi}{RT}\beta^2;\; p_B = P_B\,X_B\,e\,\frac{S_B\,\varphi}{kT\varphi^2}$$

where S_A and S_B are surface areas of components H and B φ is a function of γ, the surface energy, independent of concentrations, A and B are surface fractions, and k is the Boltzman constant. This equation was studied experimentally by Smyth and Engel and was found not applicable to systems containing associated components.

Washburn[23], using his concept of "thermodynamical environment" summarized the existing equations in what he called "the fundamental vapor pressure law"; which was stated mathematically by the equation,

$$dp = + f\,(T.\,E.)\,dx.$$

In words, "when the molecular fraction of any component of a solution is increased by a very small amount dx, the corresponding increase, dp, in its vapor pressure above the solution is equal to dx multiplied by a quantity which is a function of the thermodynamic environment which prevails in the interior of the solution." In infinitely dilute and ideal solutions, this function of thermodynamic environment is supposed to be constant. For other solutions, this function varies with the "number, nature and relative proportions of the different constituents of the solution." In regard to other empirical equations, he said, referring to the power series formulation of this unknown function, "This method of formulation is neither more nor less general than our equation and amounts to nothing more than a mathematical method of saying what has been said above in words."

Any new approach to this problem will be welcome, and we hope for more of them. But from the above brief review of the different treatments from different points of view by different authors, we can not help of concluding that the theoretical deductions must end where the experimental inductions should begin. From the equation of van't Hoff to that of Herzfeld and Heitler, all sorts of assumptions were made either to simplify the equation or to give it a mathematical solution. As soon as a doubtful assumption

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[21] Z. physik. Chem., **130**, 1 (1927).

[22] Langmuir: Colloid Symposium Monograph, **2**, p. 57 (1925).

[23] Washburn: "Principles of Physical Chemistry," 163-4 (1921).

is made to an equation, the general validity of the equation will be inevitably lost. This situation can only be saved by experimental work and by subjecting the equations to test. Van Laar's equation, for example, still remains an equation without any supporting data, not even from its originator. Maybe we should not hope too much from "pure" theorists.

Since the van't Hoff-Raoult's equation is closely connected with the osmotic pressure equation, which has been the foundation of our theory of solutions, and, besides, there has been collected under its head a large amount of facts, it seems to afford a much surer and better ground to start from than any other approaches. Of course, this doesn't mean that the other roads are either forbidden or closed. Let the adventurer go any way he pleases. As whether the osmotic pressure should be the starting point or not, for a general theory of solution, opinions differ, and one is referred to the recent paper by Bancroft and Davis, and the following is quoted from Nernst:[24]

"It is remarkable, and, I may say, inexplicable, how often we find the statement in modern literature that osmotic pressure is only of secondary importance for the theory of solutions.

"It is of course admitted that the laws of lowering vapor pressure, freezing-point, etc., and in fact all questions of physical and chemical *equilibrium*, may be treated thermodynamically without the introduction of osmotic pressure. Whether the thermodynamic method is as clear and convincing as van't Hoff's treatment is another question; in this connection the strength of the generalization of Avogadro's rule by the analogy between gaseous and osmotic pressure may well be pointed out. But when it comes to hydro-diffusion, an essentially dynamic phenomenon, the theory of osmotic pressure is indispensable; and as, when a doubt exists, we should always choose as our theoretical basis that conception which allows the *most complete and extensive treatment*, so every rational *general* theory of dilute solutions should, in my opinion, start from the conception of osmotic pressure."

Though Nernst was referring to dilute solutions only, there is no reason why the same should not be said of concentrated solutions, since it is simply a matter of concentration and a degree of complexity; and, besides, the term "dilute" is used only relatively. In fact, it is necessary to have the same basical conception in order to develop a unified theory of solutions.

As pointed out before, no matter which way we take to approach the problem, experimental measurements are necessary if progress beyond merely assumption is desired. At this junction, it is best, I think, to quote from Professor Bancroft[25] who made the following statement more than a quarter of a century ago:

"Before we can hope to work out a satisfactory theory of concentrated solutions, we must have accurate measurements on concentrated solutions and at present we have practically none. We need experiments at constant temperature on the compositions of co-existent liquid and vapor phases for

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[24] "Theoretical Chemistry," 157 (1916).

[25] J. Phys. Chem., 9, 218 (1905).

binary systems with one volatile component and with two volatile components. These measurements are not easy to make and that is one reason why they have not been made. We have measured boiling points and freezing points, because they are easy to measure, but for a theory of concentrated solutions the value of such measurements is very small. This is because we are measuring the combined effect of the change of the pressure with concentration and with temperature, whereas we ought to study the two separately."

This statement still remains true and our measurements on concentrated solutions are not much more than none. The partial pressure experiments on binary systems are surprisingly few in view that there had been many theoretical discussions and controversies on this subject. The International Critical Tables recorded only a little more than a dozen of cases, most of which were furnished by Zawidski for non-aqueous solutions. It again shows the urgent need of experimental measurements.

Professor Bancroft[1] has shown that the abnormality of the partial pressure isotherms of the lower alcohols in water increases as the increasing of their molecular weights. The fact that butyl alcohol is only partially miscible with water indicates that the higher the alcohol in the series the greater the tendency to separate into two layers with water. As the polymerization and heat of dilution were shown not the main disturbing factors in these cases, the increasing abnormality of the partial pressure isotherms must be due to this increasing tendency to separate into two layers.

On the other hand, the fact is known that water is immiscible with benzene and that methyl alcohol is a water-like substance and its chemical and physical properties lie midway between that of water and that of ethyl alcohol. Therefore it is expected that methyl alcohol will be more miscible with benzene than water, and ethyl alcohol will be much more so. This is very natural because the hydrocarbon character increases as we go up the series. It had not been shown before, however, that methyl alcohol is only weakly miscible with benzene until it was found that the mixture of the two can be easily separated into two layers with sodium iodide. It can also be separated with anhydrous calcium chloride, but in this case the separation is less complete and, besides, much heat is evolved and chemical combination probably takes place. The mixture of benzene and ethyl alcohol was not separated with either of them. This is partly due to the greater miscibility of ethyl alcohol in benzene and partly due to the smaller solubility of the salts in ethyl than in methyl alcohol.* If a substance could be found which is very soluble in ethyl alcohol, or in benzene, it might be possible to effect a separation, too. In fact, water may be used to separate the two. There is no doubt, however, that the higher the alcohol the greater the miscibility with benzene.

It is seen from the above considerations that the behavior of the alcohols in water is just the reverse of that in benzene. It was therefore predicted that the vapor pressure isotherms will vary also in the reverse direction, and that the abnormality from the normal behavior will decrease as we ascend

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* Solubility of sodium iodide at room temperature in methyl alcohol is 77.7% and 43.1% in ethyl alcohol.

the alcohol series. Since only the measurement of the system benzene-ethyl alcohol[26] is available it is proposed to determine the isotherms of both methyl alcohol and propyl alcohol with benzene in order to compare the deviations due to the tendency to separate into two layers, and also to compare with that of ethyl alcohol. The experimental results, as will be seen later, came out as predicted, and the idea that the tendency to separate into two layers is an important disturbing factor in such weakly miscible solutions, is further substantiated by other measurements, which will be also discussed.

I. Experimental

The experimental methods for measuring partial pressures of volatile liquid mixtures have been devised by different investigators. The chief feature of these methods is to determine some physical properties of the liquid and vapor phases so that their compositions may be calculated. A detailed discussion was given by Young[27] on the earlier methods and a critical review of some of the methods was given by Rosanoff.[28] More recently, Dornte[29] gave a brief review including some of the new developments. It is therefore not necessary to give any further discussion here.

The method used in this investigation is the distillation type used by Sameshima.[30] The apparatus and its arrangement, however, is somewhat different from his. Two modifications are distinct and may be mentioned with emphasis. First, the superheating effect, which has been the main objection to this type of dynamic determination of vapor pressures, is completely eliminated by the use of the Davis-Brandt[31] apparatus. This is a modification and improvement[32] of Cottrell's boiling-point apparatus, and the pumping device is very effective in discharging the entrapped bubbles and in relieving the hydrostatic pressure. It is found that when a flame is concentrated at the bottom of the flask and the liquid brought to boiling, the thermometer registers a temperature which will not vary with the size of the flame. The superheating and the bumping is further reduced by the use of rugged glass tubes of about 1½ cm. long, which are very effective in preventing bumping even to rather low pressures. With this kind of boiling flask, the electrical device as used by Sameshima for stirring is unnecessary, and no thermostat is required.

The second modification is the receiving cup for the condensed vapor. In Sameshima's arrangement, the cup was placed midway between the condenser and the boiling flask. The condensed vapor was collected as soon as the liquid boiled even before the establishment of true equilibrium between the liquid and its vapor. The result is that a long time is required to reflux the

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[26] Lehfeldt: Phil. Mag., **46**, 42 (1898).

[27] "Fractional Distillation," 72-88 (1903).

[28] J. Am. Chem. Soc., **31**, 448 (1909).

[29] J. Phys. Chem., **33**, 1309 (1929).

[30] J. Am. Chem. Soc., **40**, 1482 (1918).

[31] A sketch is given in "Laboratory" vol. 3, No. 3, p. 42 (1930).

[32] Bancroft and Davis: J. Phys. Chem., **33**, 591 (1929).

liquids so that the condensed liquid will have a chance to flow back to the main body of the solution several times, and, eventually, an equilibrium may be established between the condensed and the main liquids. This is not only time-consuming, but also has the danger of not reaching a true equilibrium which is the first requirement for success in this kind of experiments. Sameshima was wise in allowing the boiling up to two hours. In the modification, the receiving cup is directly connected to the condenser and a device is made to let the condensed liquid flow into the main solution before the true equilibrium is reached. When the temperature and pressure are well adjusted as wished, and equilibrium is assured by boiling the liquid steadily for a while, a stopcock is so turned that the receiving cup begins to collect the condensed liquid. In this way, there is ample time allowed to adjust the pressure carefully so that the thermometer will register the temperature desired and remains constant, under which conditions the liquid boils and gradually comes into equilibrium with its emitted vapor above it.

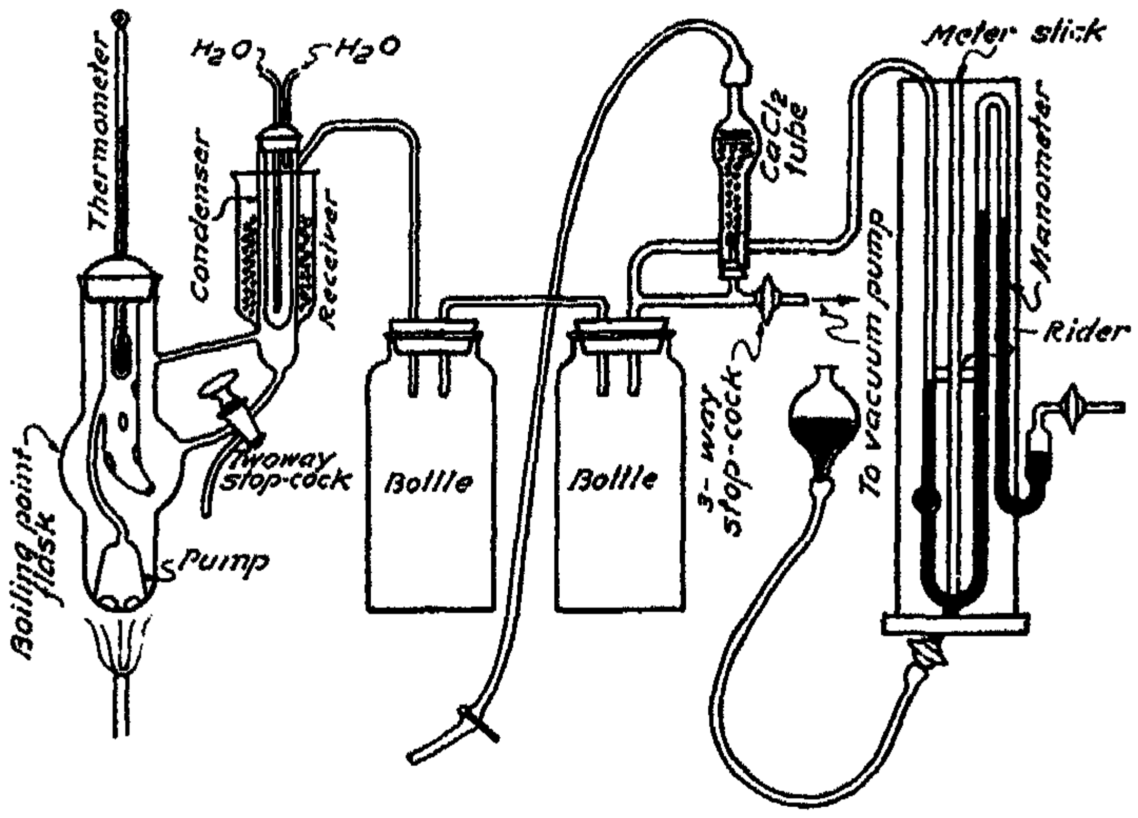

Fig. 1

A diagrammatic sketch of the arrangement of the whole apparatus is shown in Fig. 1. The whole system is air-tight and is connected to a vacuum pump. The pressure is read from a manometer, and two four-liter bottles are used to steady the pressure. The thermometer is graduated in 0.5 of a degree and is calibrated against one standardized by the Bureau of Standard. It is of German make with a ground joint which is sealed into the ground-glass stopper. The latter is in turn sealed on the Davis-Brandt pumping device, so that the whole thing is of one piece and is convenient to handle. The thermometer is of course removable. The condenser is as shown and either water or ice can be used as the cooling material. In the following experiments, cracked ice was used in order to assure a complete condensation of the oncoming vapor. The receiving "cup" is connected to the main flask with a capillary tube provided with a two-way stopcock, which can be open or closed depending whether the collecting of the condensed liquid is in operation or not. On the stopcock an outlet is furnished to draw out the sample for analysis. The whole system communicates with the outside air through a calcium chloride tube which helps to remove any moisture.

To draw a sample from the main solution for analysis, a 10 cc. pipette was used, and a small vessel, about 10 cc. capacity, is found convenient to draw the condensed liquid from the receiving "cup." For the source of heat, a micro Bunsen burner may be used. A liquid bath is not suitable.

Before going to the procedure taken, some sources of error inherent in this method of determining vapor pressures may be mentioned. It has been objected that the rate of distillation affects the vapor composition somewhat. If the objection is real, this source of error seems unavoidable in the distillation method. It might not be a true objection, however. Those who observed the difference in the vapor compositions due to the rate of distilling may have overlooked the superheating effect. As pointed out before in this experiment the size of the flame does not affect the boiling temperature, and it does of course affect the rate of distillation. Thus, if the rate of distillation changes the compositions of the vapor, consequently that of the liquid, the temperature should be changing with the size of the flame. Therefore, we may conclude that if the objection is true, the effect must be very small so that the thermometer is not sensitive enough to tell the change.

Another source of error is from the rather large bulk of vapor above the solution, which is not all condensed and removed from the liquid in equilibrium. The ideal way is of course to cut off the whole bulk of vapor above the liquid and condense it for analysis. In practice, this cannot be done, and a part of the vapor is always condensed back to the main solution as soon as the flame is removed and the pressure increased. The condensation of the vapor in the upper part of the boiling flask before reaching the condenser increases the uncertainty of the equilibrium composition of the liquids. In the following experiments, the upper part of the flask was wrapped with asbestos cords to reduce the radiation and keep the temperature as near to the experimental temperature as possible. It is not known to what extent this source of error may be. Probably it is not large since the volume of the solution studied is comparatively large and a slight change in composition will not be appreciable. This is evidenced by the fact that during the distillation, when about 8 cc. of condensate was collected, the temperature remained practically constant, until the concentrated solutions of the less volatile component where the fractionation was relatively large. The uncondensed vapor above the solution is certainly much smaller in amount and will not be able to change the liquid composition appreciably. There is no doubt, however, that this is an error inherent in this method and cannot be eliminated completely.

A third source of error, and a serious one, is the fractionation upon distilling. The methods employed by Lehfeldt and Zawidski, for example, are especially subjected to this source of error. To obviate this error, either the solution has to be very large, or the condensate reduced to a minimum. To do both is better but not practical. In this respect, Sameshima's method is superior in that the condensed liquid is allowed to flow back to the main solution and an equilibrium is established gradually. Thus the fractionation appears only as troublesome and mischievous, but will not do much harm if conducted carefully. However, large fractionations still constitute a source of error because it will make the adjustment of the temperature and pressure much more difficult and the true equilibrium hard to obtain. In this study, the volatilities of the pairs of liquids are not so far apart as to make the fractionation a serious factor. In the end of the less volatile component, however, fractionation becomes quite appreciable, and manipulations are accordingly more troublesome.

For a complete determination, the following procedure was used: A solution with an approximately known composition of about 200 cc. was put into the boiling flask, and the heat was applied at the bottom. Then the pump was set in operation and began to evacuate the system. The evacuating was done slowly by regulating with the pinch-cock attached to the rubber tube in order to prevent too much evacuating so as to cause a sudden ebullition. As soon as the solution began to boil either above or below the temperature chosen for experiment, the pressure was regulated accordingly by increasing or decreasing the evacuation so as to bring the temperature to the desired point, 40°C. in this study. Usually this was easily done, but sometimes it took patience to get the exact temperature. When the adjustment was successfully made, the solution was allowed to boil for a few minutes to allow it to come into equilibrium with its vapor. Then the stop-cock connecting the receiving cup to the main flask was closed so that the condensed vapor was now collected. During all this time the temperature must be closely watched. If the temperature began to rise due to fractionation, it must be stopped by reducing slightly the pressure. The main thing is to keep the temperature constant by regulating the pressure, even when fractionation takes place. In this way, though the collecting of the condensed vapor was going on all the while, the vapor was kept in equilibrium with the liquid at the constant temperature. It took about five minutes to fill the cup which was about 7-8 cc. in capacity. After the cup was filled, the temperature would not change very appreciably if the pressure was kept constant. Let the solution boil under these conditions for twenty or thirty minutes so as to insure the equilibrium between the two liquids. During that interval the newly condensed vapor was continually intermingling with that already collected in the cup and causing some to overflow into the main solution. At the end, the collected vapor would truly represent the vapor composition under the experimenting conditions. The temperature and pressure were then read and recorded.

If during the above experiment any change of temperature occurred owing to an ill adjustment of pressure, especially when the collecting of the condensed vapor was taking place, the experiment should be stopped and started over again. The maximum variation in temperature in this study was around ±.2 of a degree.

When the collection of the condensed vapor was successfully carried out, the experiment was discontinued and air was drawn in through the calcium chloride tube. Both the main solution and the collected liquid were then ready for analysis. Samples were taken as indicated before, and the analysis was done by specific gravity measurements. For each pair of liquids a density composition curve was prepared beforehand, and when the density was measured, the composition could be read off at once. From the vapor composition thus obtained the partial pressure was calculated.

The first pair of liquids thus studied was benzene and methyl alcohol. Benzene was thiophene-free and redistilled before use, B.P. = 80°C at 754 mm. Hg., d_{24}^{24} = 0.8746, and p = 183.5 mm at 40° C. Methyl alcohol was the best grade from Eastman Kodak Company and acetone free. It was redistilled over lime before use, B. P. = 63.8° C. at 736.2 mm. Hg. d_{4}^{25} = 0.7883, p = 263.5 at 40°C. As the alcohol is highly hygroscopic, it was not absolutely dry when used. Care was taken not to expose it to air any longer than necessary during manipulations. The results are given in Table I, also shown graphically in Figs. 2 and 4.

TABLE I

Benzene and Methyl Alcohol at 40° C.

Composition (mol% alcohol)		Total Pressure (In mm. mercury)	Partial Pressures (mm. mercury)	
Liquid	Vapor		Benzene	Alcohol
14.1	50.7	349.0	172.	176.9
22.7	52.4	356.6	170.5	186.1
30.4	53.1	362.5	170.0	192.5
40.2	54.0	364.2	167.5	196.7
46.8	54.3	365.6	167.1	198.5
55.2	54.8	366.0	165.4	200.6
64.3	56.6	366.2	158.9	207.3
70.2	58.0	362.5	152.2	210.3
75.0	57.8	357.5	150.9	206.6
83.4	64.1	345.2	123.9	221.3
87.8	67.0	334.0	109.6	224.4
89.6	72.3	325.2	90.1	235.1
91.5	75.3	322.5	80.6	241.9
100.0	100.0	263.5	0.0	263.5

Mixtures of benzene and propyl alcohol were then studied. Propyl alcohol was from Kalbaum and was dehydrated over lime. As well known, this alcohol is especially hygroscopic and very hard to get dry. Upon distilling, the walls of the receiving cup became somewhat cloudy. This was certainly due to moisture. A further dehydrating didn't do much good. Its d = 0.8003 at 24° C. and p = 50.2 at 40° C. The results are given in Table II, also graphically shown in Figs. 3 and 4.

TABLE II

Benzene and n-Propyl Alcohol at 40° C.

Composition (mol% alcohol)		Total Pressure (mm. mercury)	Partial Pressures (mm. mercury)	
Liquid	Vapor		Benzene	Alcohol
3.9	8.4	191.7	175.6	16.1
18.0	14.6	196.0	167.4	28.6
30.0	16.3	193.0	161.6	31.4
49.2	18.7	183.5	149.2	34.3
58.4	20.5	175.0	139.1	35.9
64.0	21.5	168.4	132.2	36.2
70.9	24.0	156.0	118.6	37.4
79.1	29.4	134.2	95.0	39.6
87.0	32.3	114.0	77	37
90.1	41.6	102.0	59.6	42.4
100.0	100.0	50.2	0.0	50.2

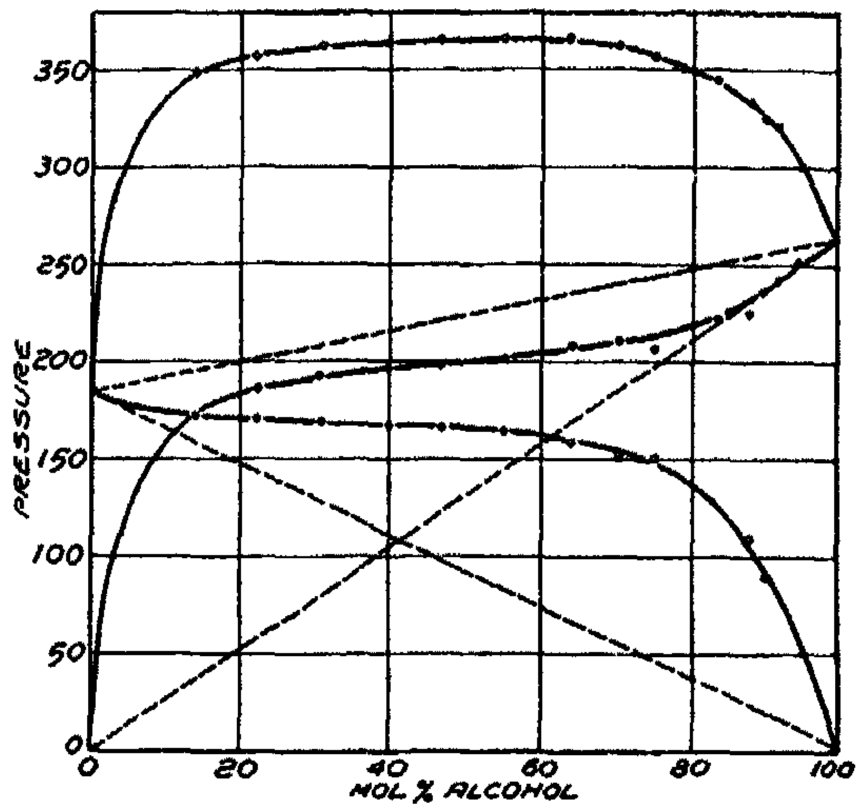

FIG. 2
Benzene-Methyl Alcohol at 40°

II. Discussions

From the Tables I and II, and Figs. 2 and 3, we see that the vapor pressures of these mixtures give strongly positive deviations from normal straight line curves. In Fig. 4, the fractional vapor pressures p/p₀ are plotted against the mol fractions for both pairs. It is clear from these curves that the benzene-propyl alcohol mixtures are more normal than those of benzene and methyl alcohol. The curves of benzene and ethyl alcohol, from the values of Lehfeldt, lie apportionately between the two as expected. In comparison with the curves for water-alcohol solutions as shown in Professor Bancroft's paper, the order of normality is just reversed.

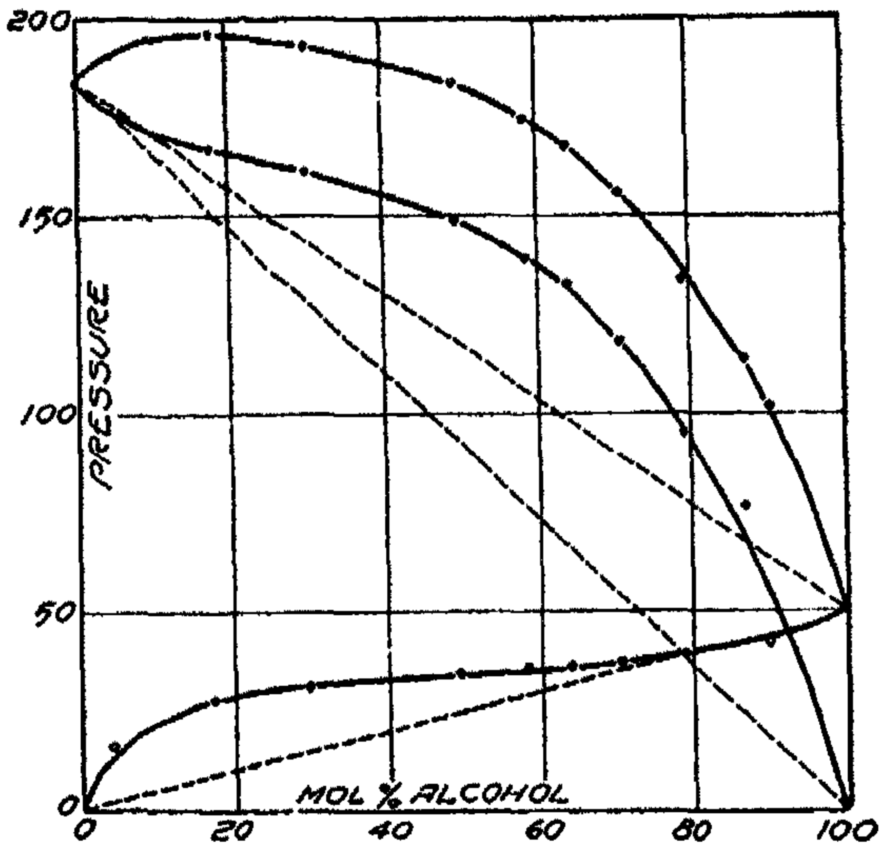

Fig. 3
Benzene-n-Propyl Alcohol at 40°

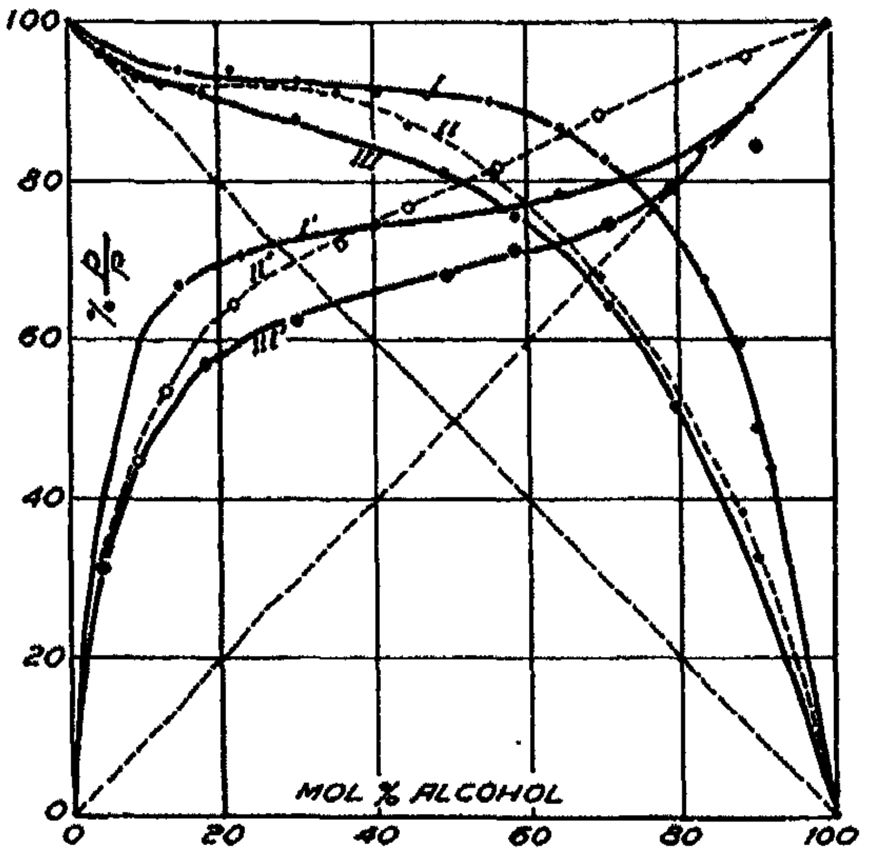

Fig. 4
Benzene (I) —Methyl Alcohol (I')
Benzene (III) —Propyl Alcohol (III')
Benzene (II) —Ethyl Alcohol (II') [Lehfeldt]

The empirical equation for partial pressures found by Bancroft and Davis[10] has been applied to a great number of systems by the authors, Morton,[33] and Dornte.[29] For the systems studied by them, the experimental data could be represented with unexpected accuracy for most cases. Being an empirical equation, the real significance of the two constants involved is yet uncertain, and, besides, it is not known whether all the disturbing factors are included or not. When this equation is applied to the present results, it is found that for the system benzene-propyl alcohol, the data can be fitted to equations of the "exponential" form, very well for propyl alcohol but less so for benzene. The equations and the calculated values of partial pressures are given in Table IV, and the logarithmic graphs are shown in Fig. 7. No adequate equations could be found for the benzene-methyl alcohol system, to represent the whole range of concentrations. A glance at the logarithmic curves, Fig. 5, will show that it is not possible to make a straight line equation for either of them. It is seen, however, that equations could be constructed to represent a certain range of concentrations. This is done and the values are given in Table III. As in the other system the alcohol is better represented than benzene.

TABLE III

Benzene and Methyl Alcohol at 40° C.

x = mol fraction alcohol; p_A = partial pressure alcohol; p_B = partial pressure benzene; P = vapor pressure of the pure components respectively. Partial pressure equation for alcohol:

$$\log (P_A - p_A)/p_A = 0.259 \log (1-x)/x - 0.513$$

Partial pressure equation for benzene:

$$\log (P_B - p_B)/p_B = 1.130 \log x/(1-x) - 1.083^*$$

x × 100	p_A (obs.)	p_A (calc.)	Diff.	p_B (obs.)	p_B (calc.)	Diff.
0.0	0.0				183.5	
14.1	176.9	176.8	−0.1	172.1	172.2	+0.1
22.7	186.1	185.3	−0.8	170.5	171.3	+0.8
30.4	192.5	190.8	−1.7	170.0	170.2	−0.2
40.2	196.7	196.6	−0.1	167.5	169.0	+1.5
46.8	198.5	200.0	+1.5	167.1	168.2	+1.1
55.2	200.6	204.1	+3.5	165.4	166.2	+0.8
64.3	207.3	208.6	+1.3	158.9	158.2	−0.7
70.2	210.3	211.4	+1.1	152.2	151.0	−1.2
83.4	221.3	219.2	−2.1	123.9	121.7	−2.2
87.8	224.4	222.6	−1.8	109.6	104.1	−5.5
89.6	235.1	224.1	−11.0	90.1	94.8	+4.7
91.5	241.9	226.0	−15.9	80.6	83.4	+2.8
100.0	263.5				0.0	

* This equation is only good for the upper part of the curve in Fig. 6. The first five values in column 6 in the above table were calculated from the equation.

$$\log (P_B - p_B)/p_B = 0.221 \log x/(1-x) - 1.029.$$

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[33] J. Phys. Chem., 33, 384 (1929).

Table IV

Benzene and n-Propyl Alcohol at 40°C.

x = Mol fraction of alcohol; p_A = Partial pressure of alcohol; p_B = partial pressure of benzene. P = Pressure of pure components respectively. Isothermal equation of alcohol:

$$\log (P_A - p_A)/p_A = 0.387 \log (1 - x)/x - 0.344$$

Isothermal equation of benzene:

$$\log (P_B - p_B)/p_B = 0.928 \log x/(1 - x) - 0.587$$

x × 100	p_A (obs.)	p_A (calc.)	Diff.	p_B (obs.)	p_B (calc.)	Diff.
3.9	16.1	19.5	+3.4	175.6	181.1	+5.5
18.0	27.7	28.6	−0.9	167.2	172.5	+5.1
30.0	31.4	30.8	−0.6	161.6	164.1	+2.5
49.2	34.3	34.4	+0.1	149.2	146.5	−2.7
58.4	35.9	35.9	0.0	139.1	135.4	−3.7
64.0	36.2	36.8	+0.6	132.2	127.2	−5.0
70.9	37.4	38.0	+0.6	118.6	115.3	+3.3
79.1	39.6	39.5	−0.1	95.0	96.9	+1.9
90.1	42.4	42.1	−0.3	59.6	60.5	+0.9

Table V

Benzene and Ethyl Alcohol at 50°C. (Lehfeldt)

x = Mol fraction alcohol; p_A = Partial pressure alcohol; p_B = Partial pressure benzene; P = Vapor pressure of pure components respectively.

Partial pressure equation for alcohol:

$$\log (P_A - p_A)/p_A = 0.633 \log (1 - x)/x - 0.598.$$

Partial pressure equation for benzene:

$$\log (P_B - p_B)/p_B = 1.066 \log x/(1 - x) - .729.$$

x × 100	p_A (obs.)	p_A (calc.)	Diff.	p_B (obs.)	p_B (calc.)	Diff.
0.0	0.0	--	—	270.9	—	—
8.8	98.5	102.1	+6.6	251.9	268.2	+16.3
12.1	118.8	116.9	−1.9	250.2	264.9	+14.7
21.5	141.6	139.6	−2.0	255.3	258.7	+ 3.5
35.5	158.7	160.4	+1.7	247.2	246.6	− 0.6
44.4	168.6	170.0	+1.4	235.8	236.1	+ 0.3
56.1	179.3	180.5	+1.2	218.3	218.3	0.0
69.7	194.1	191.1	−3.0	184.3	186.3	+ 2.0
88.6	210.4	205.4	−5.0	104.6	101.9	− 2.7
100.0	219.5	—	—	0.0	—	—

Simply for the sake of comparison, the equation is applied to the system ethyl alcohol and benzene. The results are given in Table V and Fig. 6. It again shows that this pair is intermediate between the other two.

This gradually increasing normal behavior of the alcohols may be explained by the assumption that the degree of association decreases with the higher alcohols. It has become almost a habit to the investigators to attribute any deviations from ideal behaviors, not only for the property of vapor pressures, but for many other properties of solutions and others as well, to associations. In the pure state, methyl alcohol is more associated than ethyl alcohol, and ethyl alcohol more than propyl alcohol. But in solutions the phenomena become more complicated, and there are no absolute methods of measuring the extent of association in any case. If no other factors of influence present, the deviations of partial pressures from Raoult's law may serve as a method for calculating the degree of associations in solutions. Professor Bancroft has done this for the system benzene-ethyl alcohol. For the two systems studied here, the results from the calculations are given in Table VI. Professor Bancroft has shown why these values of associations are not absolute but only apparent. When comparison is made between these systems it should be remembered that the system benzene-ethyl alcohol was measured at 50°C.

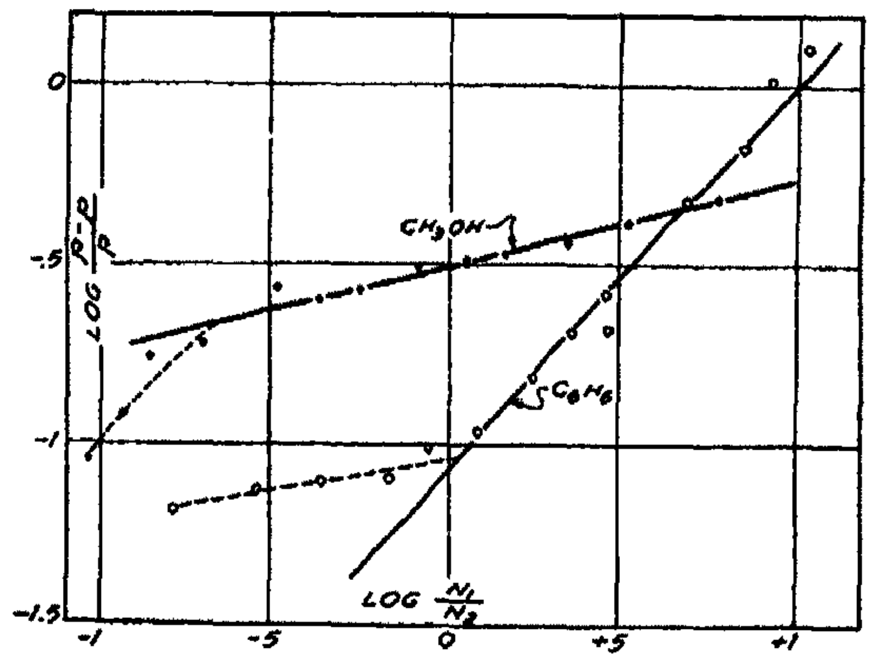

Fig. 5
Methyl Alcohol and Benzene

The apparent degree of associations of the alcohols in benzene can also be calculated from the freezing point depressions, again, of course, neglecting other disturbing factors. The freezing point lowerings of methyl alcohol in benzene had been measured by Auwers[34] up to 15.1 mol%; those of ethyl alcohol by Beckmann[35] to 35.5 mol%; and propyl alcohol by Paterno[36] to 20 mol%. More recently, Perrakis[37] measured the freezing points of the first two

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[34] J. Phys. Chem., 12, 689 (1892).

[35] Z. physik. Chem. 2, 715 (1888).

[36] Gazz., 24 II, 179 (1894).

[37] J. Chim. phys., 22, 290 (1925).

mixtures covering all concentrations. He also measured the system of isopropyl alcohol with benzene. The earlier workers aimed at the determination of the molecular weights, which were therefore given by them. Dividing these apparent molecular weights by the true values respectively, we obtain the apparent degree of association, which are given in Table VII. Comparing with the values calculated from the vapor pressure lowerings for corresponding concentrations, we see that the alcohols are more associated in the freezing point determinations. This is in agreement with the rule that association will increase if the temperature is lowered. If Perrakis' results are used to calculate the apparent degree of association, it will certainly bring out the same fact.

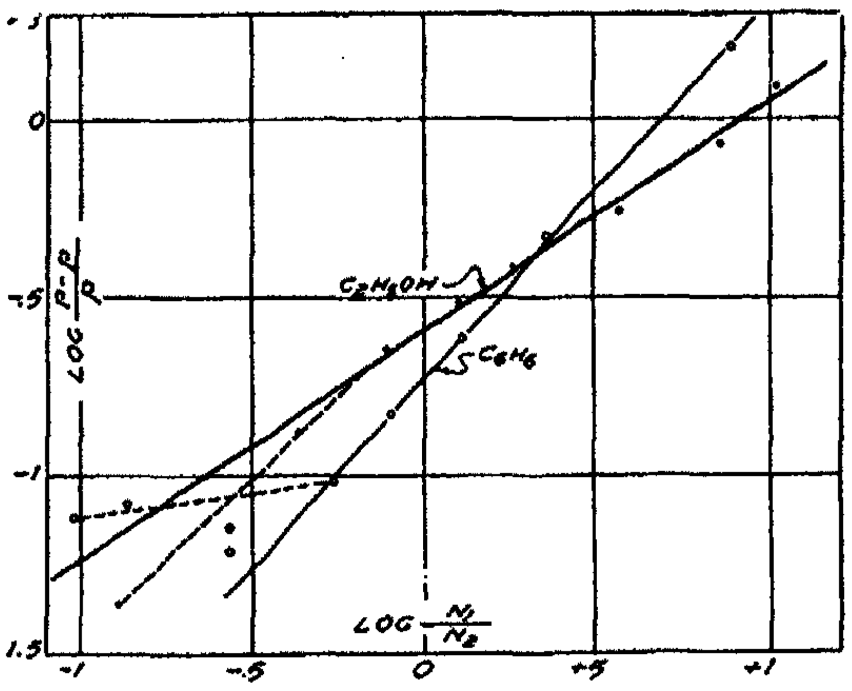

FIG. 6
Ethyl Alcohol and Benzene

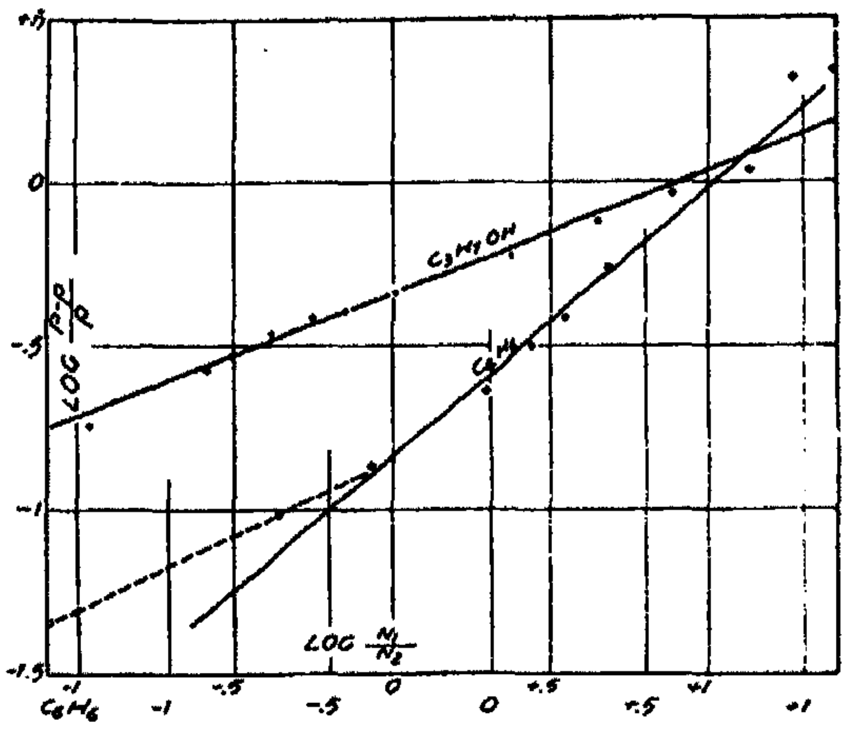

FIG. 7
Propyl Alcohol and Benzene

In Fig. 8 the percent deviations of the apparent molecular weights from true molecular weights are plotted against the concentration. These curves are reproduced from Auwers' paper. It is clearly shown that the lower alcohols are more abnormal in benzene solutions than the higher alcohols, as already shown by their partial pressure isotherms.

TABLE VI

A. Benzene and Methyl Alcohol at 40°C.

x = mol fraction alcohol; 1 − x = mol fraction benzene; p_A = partial pressure alcohol; p_B = partial pressure benzene; A = apparent coefficient of polymerization of alcohol; B = apparent coefficient of polymerization of benzene.

x	p_B	A	1-x	p_A	B
0.0	183.5	—	1.0	0	—
0.141	172.1	2.5	0.859	176.9	12.4
0.227	170.5	3.8	0.773	186.1	8.2
0.304	170.0	5.5	0.676	192.5	6.2
0.402	167.5	7.1	0.598	196.7	4.4
0.468	167.1	8.9	0.532	198.5	3.5
0.552	165.4	11.1	0.448	200.6	2.6
0.643	158.9	11.6	0.357	207.3	2.1
0.702	152.2	13.7	0.298	210.3	1.7
0.834	123.9	10.4	0.188	221.3	1.0
0.878	109.6	10.6	0.122	224.4	0.8
0.898	90.1	8.3	0.104	235.1	1.0
0.915	80.6	8.4	0.085	241.9	1.0
1.0	0	—	0	263.5	—

B. Benzene and n-Propyl Alcohol at 40°C.

x	p_B	A	1-x	p_A	B
0.0	183.5	—	1.0	0	—
0.039	175.6	1.0	0.961	15.7	11.
0.180	167.4	2.2	0.820	28.6	6.0
0.300	161.6	3.1	0.700	31.4	3.9
0.492	149.2	4.1	0.508	34.3	2.2
0.584	139.1	4.4	0.416	35.9	1.9
0.640	132.2	4.5	0.360	36.2	1.5
0.709	118.6	4.4	0.291	37.4	1.2
0.791	95.0	4.1	0.209	39.6	1.0
0.901	59.6	4.4	0.099	42.4	0.6
1.0	0.	—	0	50.2	—

The fact that the apparent degrees of association calculated from the freezing point experiments are higher than that calculated from Raoult's equation, may be explained in another way. It is known that when alcohols are mixed with benzene large amounts of heat are absorbed. For partially miscible liquids, the miscibility of such solutions will increase with rising temperature, as a consequence of the Law of Le Chatelier. On the other hand the tendency to separate into layers will increase if the temperature is lowered. As shown before, methyl alcohol can be separated from benzene by some salts, and other alcohols by water, or possibly by certain salts too. Theoretically, such weakly miscible mixtures may be separated into layers by sufficient cooling, if they remain fluid at very low temperatures, that is, may reach a hypothetical critical solution temperature. At any rate, the tendency to separate into two layers will be increased at low temperatures. As indicated by Professor Bancroft that this tendency tends to increase partial pressures, the presence of this disturbing factor may well be the cause of the apparent associations in the freezing point measurements. Since this tendency is greater at lower temperature, the apparent degree of association should be greater too. In this case the tendency to separate into layers will of course tend to decrease the lowering of the freezing points.

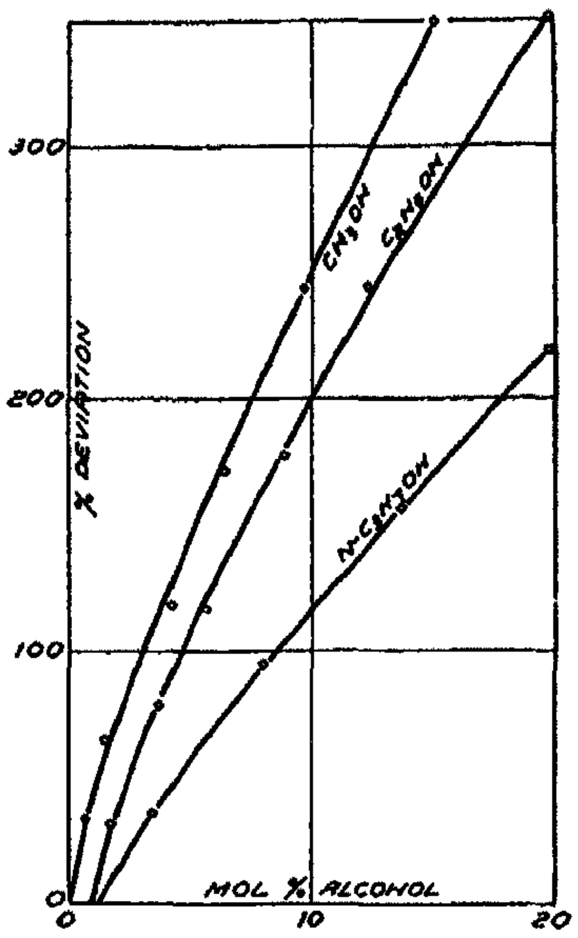

Fig. 8
Deviations

The vapor pressure isotherms of partially miscible mixtures had been studied by several workers, especially Roozeboom. The general course of these isotherms is such that when two layers are present, that part of the isotherm is flat and independent of the concentration. The vapor pressure isotherm of benzene-methyl alcohol, Fig. 2, also shows a flat part, from 30 to 70 mol% of alcohol, and at this interval the concentration effect is very slight. In isotherms of mixtures just above their critical solution temperatures, like methyl alcohol and hexane, the flatness is more pronounced. On the other hand, in the isotherms of ethyl and propyl alcohols with benzene, the flat part becomes less and less. Correlating these facts, one may conclude that in such mixtures, the deciding factor to determine the course of the vapor pressure isotherms is the degree of miscibility between the constituting components.

The flatness of the vapor isotherms due to the tendency to separate into layers is also shown in other property-concentration curves. Perrakis had studied many other physical properties of binary solutions, such as specific heats, heat of mixing, freezing-points, volumetric changes, etc., and came to the conclusion that at the vicinity of the critical state, by which he meant a state at which a slight change of conditions would cause a separation of the mixture, there is always a flat portion in the plotted curves. While the validity of this general statement is still uncertain, it certainly holds true to the vapor pressure isotherms. The volumetric measurements of his for example have been questioned by recent authors.[38] The changes in volume upon mixing for methyl alcohol and benzene, according to Schmidt,[39] are negative, increasing with the concentration of benzene; Perrakis' results give negative

TABLE VII

Freezing-Point Lowerings of Alcohol in Benzene

x = Mol fraction alcohol; d = Depressions; M′ = Apparent molecular weights of alcohol; A = Apparent coefficient of polymerization of alcohol; % = % deviation from true molecular weight.

x	d	M′	A	%
		A. Methyl Alcohol		
0.008	0.360	43	1.3	34.4
0.016	0.612	53	1.65	65.6
0.042	1.265	70	2.2	118.7
0.065	1.610	87	2.7	171.9
0.097	1.978	110	3.5	243.8
0.151	2.475	144	4.5	350.0
0.250	3.000	233	7.3	628.1*
0.369	3.30	371	11.6	1059*
		B. Ethyl Alcohol		
0.003	0.175	45.9	1.0	0
0.013	0.480	50.4	1.1	9.6
0.018	0.875	60.9	1.3	32.4
0.038	1.360	82.5	1.8	79.3
0.057	1.705	100	2.2	117.3
0.089	2.22	128	2.8	178.2
0.123	2.725	159	3.5	245.6
0.199	3.445	208	4.5	352
0.293	4.180	265	5.8	476
0.355	5.000	318	6.9	591
		C. n-Propyl Alcohol		
0.007	0.269	61	1.0	0
0.035	1.007	82	1.4	36.5
0.080	1.711	117	1.9	95.0
0.137	2.376	154	2.6	156.7
0.198	3.029	189	3.2	220.0

* These values were calculated from Perrakis' data.

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[38] Washburn and Lightbody: J. Phys. Chem., **24**, 2701 (1930).

[39] Z. physik. Chem., **121**, 221 (1926).

changes too, but first increase, then decrease to zero, and finally increase again, always negatively. The recent results of Washburn and Lightbody show a positive change at first, but with increasing concentration of the alcohol, the changes become negative. None of these results, when plotted show any distinctly flat portion in the curve. Perrakis' results of the system diphenyl ether-ethyl alcohol, however, do give a flat part in the plotted curve. This may be due to its greater tendency to separate into layers than the system benzene methyl alcohol.

Some attempts had been made to correlate the volume and heat changes with the deviations of vapor pressure isotherms from straight lines. There seems no direct relationships between the volume changes and the deviations. In the system benzene-methyl alcohol, for example, the volume changes, according to Washburn and Lightbody, change signs with the concentration, but the deviations of the isotherm remain positive through out the whole range of concentrations. A positive change, that is, evolution of heat, is found to accompany a negative deviation, while a negative heat change gives a positive deviation. This is true with the benzene-alcohol systems.

The heat changes of methyl alcohol and benzene mixtures had been studied by Schmidt[39] at 15 C., and by Washburn and Lightbody, at 25°C. The values given by them are only approximate because the specific heats of the mixtures were not measured. They were calculated from temperature changes. The mixtures of ethyl alcohol and benzene were measured by Perrakis, also by Washburn and Lightbody. The former measured also the specific heats at the same temperature, 20°C., and his values are therefore more exact. The system benzene-propyl alcohol was studied by Schmidt at 15°C. All these results, though measured at different temperatures, point to the same conclusion that with benzene, propyl alcohol absorbs more heat than ethyl alcohol and the latter more than methyl alcohol. This is surprising if we wish to compare the magnitude of the heat changes with that of the deviations of the vapor pressure isotherms from the normal curve. As one of the requirements for the formation of ideal solutions is that the heat change should be zero, we naturally expect that the larger the heat change, the greater should be the deviation. But as shown in Fig. 4, the deviations become smaller as we pass through benzene-methyl alcohol to benzene-propyl alcohol, though the latter experiences a greater change of heat. This indicates that the heat effect is not the main disturbing factor in these cases.

The idea that the tendency to separate into two layers is an important disturbing factor is further strengthened by another set of experiments reported by Smyth and Engel.[40] These authors measured the partial pressure isotherms of a dozen or so pairs of organic liquids, some of these having an alcohol as a component. In Fig. 9 is the graphical result of the system heptane-ethyl alcohol at 30°C. It is at once seen this pair of liquids gives the same type of vapor pressure isotherm as the system benzene-methyl alcohol. The flat portion of the curve is especially prominent and suggests a great

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[40] J. Am. Chem. Soc., 51, 2646 (1929).

tendency to separate into two layers. From the lesson on the benzene-methyl alcohol system, one may anticipate that ethyl alcohol could be salted out from heptane by some salt. Indeed, the same salt, sodium iodide, that separated methyl alcohol from benzene was capable of separating these two also. This leaves us without doubt that the abnormal behaviors and the flat-

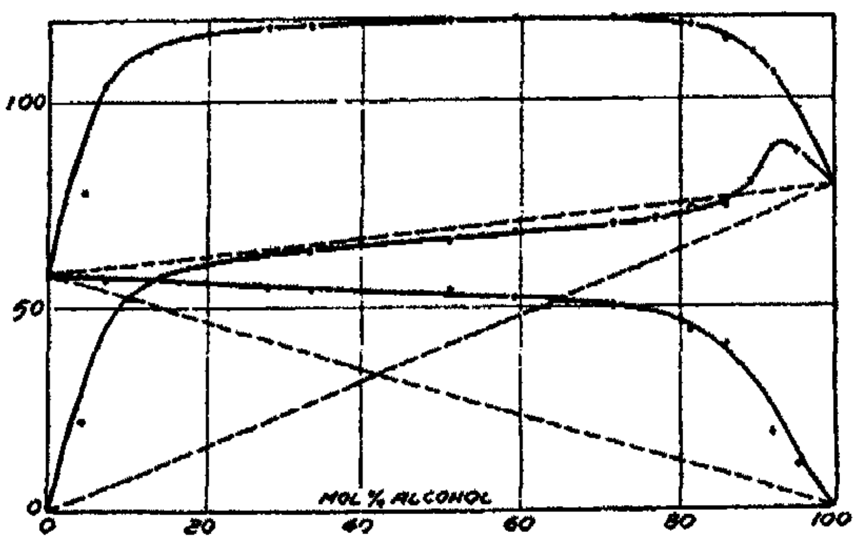

Fig. 9
Ethyl Alcohol and Heptane at 30°

TABLE VIII

Heptane and Ethyl Alcohol at 30°C.

x = Mol fraction alcohol; p and P, Pressures of alcohol in solution and pure state respectively.

Partial pressure equation for alcohol:

$$\log (P - p)/p = 0.388 \log (1 - x)/x - 0.757.$$

x	p (obs.)	p (calc.)	Diff.
0	0	—	
0.0400	22.0	50.6	28.6
0.0684	47.2	54.9	7.7
0.1236	56.1	56.9	0.8
0.2803	62.9	62.5	0.4
0.334[illegible]	63.5	63.6	0.1
0.5151	65.9	66.7	0.8
0.5934	68.1	67.9	0.2
0.7174	69.7	69.7	0.0
0.7687	71.0	70.5	0.5
0.8154	73.5	71.2	2.3
0.8550	73.9	71.9	2.0
0.8902	79.2*	72.6	6.6*
0.9173	87.9*	73.4	14.5
0.9545	87.0*	74.2	12.8
0.9913	77.8	76.1	1.7
1.0000	78.2	—	

* These values are doubtful as they are higher than that of the pure state.

ness of the vapor pressure isotherms of these two systems are due to the same cause, namely, the tendency to separate into two layers.

On the other hand, the vapor pressure isotherms of mixtures of n-butyl alcohol and heptane, as measured by the same authors, appear to be analogous to that of the system benzene-propyl alcohol. They could not be separated into two layers by sodium iodide, and their isotherms do not have portions distinctly flat. This is due to the greater miscibility of butyl alcohol with heptane. It is thus expected that methyl alcohol should be less miscible than ethyl alcohol, and, in fact, it is only partially miscible, with heptane. Thus, the alcohols form a series, according to their miscibility, with heptane just as they do with benzene with the exception that it is methyl alcohol, instead of water, being the partially miscible component. Incidentally, it brings out the interesting fact that methyl alcohol is in some ways more similar to benzene than to heptane, in spite of the fact that they are both straight chain compounds. It is also to be remembered that ethyl alco[illegible] can be separated from heptane but not from benzene by adding sodium iodide.

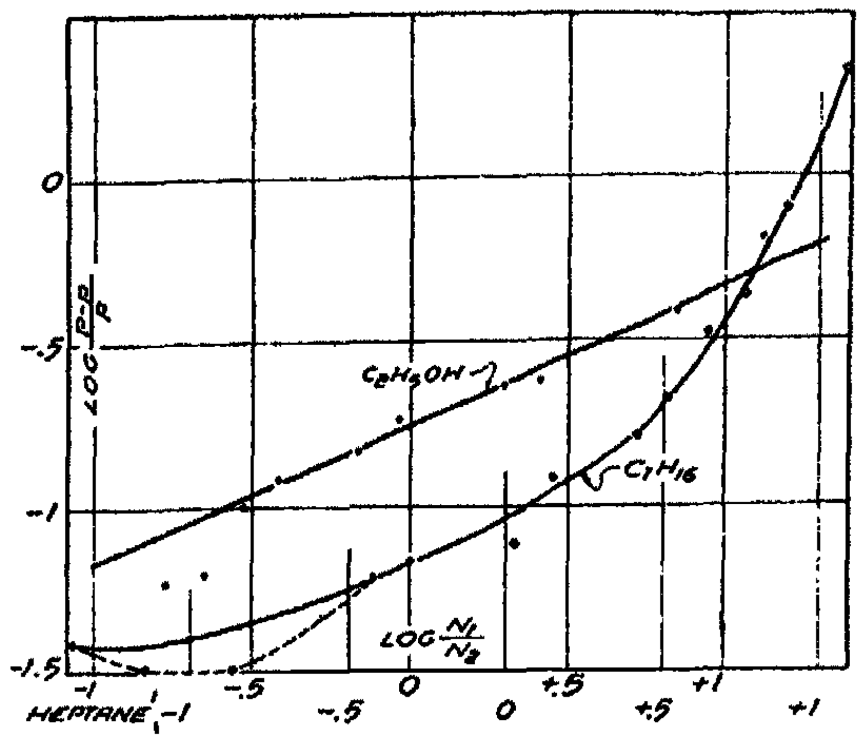

Fig. 10
Ethyl Alcohol and Heptane

For the sake of comparison the equation of Bancroft and Davis is applied to the system heptane-ethyl alcohol. As shown in Fig. 10 and Table VIII, the agreement is fairly satisfactory for the alcohol, but it is not possible to find an equation for heptane. As in the benzene-alcohol systems the more associated component alcohol is better represented by the experimental equation.

Summary

1. A review of the theories and mathematical equations proposed and derived by different authors from different points of views indicates that most of them are based on assumptions that have no sufficient experimental support.

2. Experimental studies on the compositions of co-existent liquid and vapor phases for binary systems with one volatile component and with two volatile components are needed if a complete and satisfactory theory of concentrated solutions is desired. This was pointed out by Professor Bancroft more than twenty-five years ago.

3. The binary systems benzene-methyl alcohol and benzene-propyl alcohol are studied. Their partial pressures at 40°C. were determined by a modified form of the apparatus used by Sameshema.

4. The data thus obtained, and in conjunction with that of benzene-ethyl alcohol, proved successfully the idea that the tendency to separate into two layers is one of the disturbing factors in such cases.

5. The freezing-point data point to the same conclusion. Also the heat of mixing.

6. The flat portions on the vapor pressure-concentration curves are due to the weak miscibility between the components. The greater the tendency to separate into layers, the more prominent will be the flatness in such curves.

7. The vapor pressure-concentration curves of the system heptane-butyl alcohol have flat portions just like that of benzene-methyl alcohol systems, and like the latter the separation into two layers can be easily effected by sodium iodide.

8. The Bancroft-Davis equation was applied to the obtained data with only a partial success. This is probably due to the serious disturbances of the tendency to separate into two layers.

This work was done under the direction of Professor Bancroft, and the writer wishes to take this opportunity to express his hearty appreciations and sincere gratitude. It is a great pleasure to work with him and to attend his lectures. The writer is also indebted to Dr. Davis for his suggestions and interests in this problem.

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THE ADHESION OF GLUE

BY MAYNARD F. WITHERELL

The object of this work was to determine the factors influencing the adhesion between glue and a high-grade alundum, and to bring about the best possible adhesion between the two. The alundum used was a product of the Norton Company, Worcester, Mass., and is an electrically fused grain, white or nearly so in color, and designated as "99" white alundum, for polishing. The size of the grit is 36-mesh. The glue was a 145 millipoise hide glue, "400 A," with a moisture content of 14.23%, after 24 hours drying at 105°C.

The method of measuring the adhesion between the glue and grit is that given by C. E. Lanyon[1] who was determining the adhesive strength of glue, using a standard grit. In this case a single glue is used throughout and the grit is varied. The details of the method are as follows:

23.55 gr. of the glue are placed in a 150 cc. beaker and 76.5 cc. of distilled water are added. This is allowed to soak for 30 minutes, then it is placed in boiling water and warmed for 10 minutes. About three minutes before the glue is ready to remove from the hot water, 400 grs. of the grit is weighed into a small pan. Then 85 grs. of the 20% glue solution are poured onto the grit and rapidly and thoroughly mixed in with an 8 inch porcelain spatula. This glue and grit is then packed into the standard cement briquet moulds which have been slightly altered for this use. (The ordinary mould has a cross-section of one square inch and it was found that six or eight weeks drying was necessary to bring the briquet to equilibrium with the atmosphere. To shorten this time, a section 1/4 in. × 1 in. × 1 in. is affixed to the mould so as to put a hole of the given dimensions in the middle of the briquet. Thus the thickness at the breaking point of the briquet is 3/8 of an inch. The total area there is 3/4 sq. inch). These briquets are found to have reached a maximum strength after 11 or 12 days, or slightly longer depending on the weather. Unless otherwise stated, the briquets have dried 14 days, a period which insures their maximum strength having been attained. The dried briquets are then broken in a Riehlé cement testing machine. Six briquets are made for each run, three briquets being made from each batch of grit and glue. The average breaking strength of the briquets is the so-called "briquet strength" which is taken as a measure of the adhesion between the grit and the glue.

After testing a series, it is common to find one of them has tested 15% or more under the average. It is very difficult to make a perfect set of briquets, because of the rapidity at which it has to be done to prevent setting before the grit is packed into the moulds. This results in imperfect distri-

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[1] Ind. Eng. Chem., 19, 1191 (1927).

bution of the glue and an occasionally very poor briquet. In such a case, I believe it is perfectly justifiable to omit that result, and this has been done throughout the work. That it is a fault of uneven distribution is plainly visible on close examination of the broken briquet, and the use of that value is merely leading to a false conclusion. It cannot be argued that weakness in that briquet would be made up for in strength of the others. Theoretically there would be an added glue content to the others but it would be negligible, whereas one poor briquet would lower the average as much as 30 in many cases. The majority of the briquets tested lie within 5% of the average, although there are some that do not. When one considers the variations in mixing the glue, packing the moulds, and the actual breaking test, this variation seems allowable. There is a chance for error, due to drying at different humidities, for the remaining moisture content will doubtlessly affect the strength of the glue. Inasmuch as the glue is much stronger than the bond between glue and grit, the strength of the glue is not the determining factor. It does not appear likely that the bond would be more than very slightly affected by a slight difference in moisture content. The average drying taking place over a two weeks period is quite uniform and the change taking place the last few days is small. It is true that the glue changes quite rapidly with humidity conditions, but in a briquet this change would involve only the surface. For best possible results the drying should be done at a definite temperature and humidity, but for this work it was deemed sufficiently accurate to hang the briquets in a hood where there is continuous changing of air at room temperatures. It is not advisable to lay the briquets on anything to dry, for uneven drying is thus obtained and the briquets do not dry completely or without warping.

It was early noticed that on adding the water to the glue, some of the glue took up the water rapidly and swelled up in the beaker but did not form a jelly or homogeneous mass. Again the glue took up the water slowly and finally formed a jelly in the beaker. This appeared to be caused by varying sizes of the glue flakes. As it is taken from the bag, it is alternately fine and coarse throughout the mass. It was feared that this non-uniformity would cause a difference in the tests so it was checked up as follows:

A quantity of the glue was passed through a 10-mesh and a 35-mesh sieve. Roughly 1/5 is retained by the coarse sieve, and about 1/10 passes the 35-mesh, the rest is retained by the 35-mesh. Six briquets were made from each grade, using a 36-mesh TJ-treated Norton sharp-fracture alundum. These briquets tested as follows:

Finest glue	864.7	briquet strength
Medium grade	874.0	" "
Coarse grade	859.0	" "

These results show that in spite of the variations in size the glues had adsorbed the water completely by the time that they were mixed with the grit and briquets made from the different grades checked within ± 1%. The different grades showed the above-mentioned characteristics when swelling.

Another purpose of this work is to determine the relation if there be any between the "capillarity" of a grit, as determined by the Norton method, and the attraction between that grit and glue. The method mentioned is carried out thus: there is a rack which holds in an upright position a number of glass tubes, 25 cms. long with an internal diameter of 5–6 mms., the bottom of the tubes rests on a wire screen in a shallow well in which there is a 1 cm. high baffle, behind the tubes is a scale which is graduated from the top of the baffle up. Before use, the tubes are cleaned in cleaning solution and rinsed in distilled water and dried. The tubes are then set up in the rack and the grit whose capillarity is desired is poured in from the top without shaking in any way. Then water between 70° and 80° F. is poured into the well until it overflows the baffle; then start a stop-watch. At the end of the specified time interval for each grit number, reading is made of the height of the water rise directly on the scale behind the tubes. This height in centimeters, expressed as a percentage of the height the water would reach if the grain were of maximum capillarity, constitutes the capillarity of the grain. For the 36 grit, the time period is 3½ minutes, and the maximum capillarity is 10 cms.

Capillarity attraction of abrasive grain is that property of attracting water so that the surfaces of the grain particles are thoroughly wetted. This is very essential to all kinds of abrasive grains that are to be used in conjunction with adhesives. Foreign matter on the grain surface that is repellant to water would result in very poor bonding between the grain particles and the adhesive; therefore the grains must be so prepared that the adhesive will not only spread easily on the surface of the grain particles but also adhere thoroughly after the bond has set.

There is however a doubt as to the worth of this means of determining whether the glue will adhere to the grit or not. Its theory as far as it goes is right, but it goes only as far as water to grain. We have no proof that a grain which is readily wetted by water is also readily wetted by glue. Throughout this work close check will be kept between the two to decide whether capillarity is a direct measure of adhesiveness or not.

A few preliminary tests were made with a sharp-fracture 36 TJ Norton alundum. The quenching treatments were carried out as follows: A muffle furnace was brought up to dull red heat and the grain was put into the furnace in large porcelain crucibles, each holding about 500 grs. of grain. At the end of the time interval, the crucibles were taken out and the glowing grains poured into a liter beaker containing the solution, as fast as was possible to prevent excess cooling. The grit was then throughly washed free from the solute and drained and dried by centrifugal action, then put into a drying oven at 100°–110°C. The boiling treatments were carried out in large evaporators, heated with a bunsen flame. Timing was started when the solution first boiled. Any boiled off water was replaced. Drying is the same as above.

The treatments were:

1. Heat in muffle furnace to dull red heat 1 hour. Quench in 10% sodium silicate. Wash and dry.

2. Heat 1 hour in muffle furnace at dull red heat. Quench in a 3–1 mixture of 10% sodium silicate and sodium hydroxide.

3. Heat 1 hour in muffle furnace at dull red heat. Quench in 10% sodium silicate. Wash. Boil 15 minutes in 10% sodium hydroxide.

4. Boil 15 minutes in 10% sodium hydroxide. Wash. Boil 15 minutes in 10% sodium chromate.

5. Heated 1 hour in muffle furnace. Quenched in 10% sodium hydroxide. Washed. Boiled 15 minutes in 10% sodium chromate. Washed. Dried. Heated to dull red in muffle furnace.

6. Heated 3 hours in muffle furnace at dull red heat. Quenched in 10% sodium hydroxide. Washed. Boiled 15 minutes in 10% sodium chromate.

7. Heated in muffle furnace 1 hour. Quenched in a 5% solution of glue.

8. Grit untreated. 4 drops of glycerol added to the glue solution.

9. Grit untreated. As soon as glue was mixed in, the pan was covered air tight and the whole was heated for five minutes in boiling water. Then the moulds were filled.

10. Control.

TABLE I

No.	Ave. Briquet Strength	Capillarity	No.	Ave. Briquet Strength	Capillarity
1.	642	54%	6.	865	58%
2.	860	63%	7.	627	25%
3.	823	62%	8.	919	——
4.	755	42%	9.	725	——
5.	808	60%	10.	723	59%

These results are given in Table I and Fig. 1. From this we see at a glance that the same capillarities do not mean the same adhesion between the grain and the glue. The silicate-treated grains do check among themselves, but not with the chromate-treated. The chromate-treated do not check with any.

Inasmuch as the TJ is a treated grit, any additional treatment cannot be considered as a means of improving an untreated grain. It is thought that the TJ is a silicate treatment but nothing beyond that can be even guessed at. It is apparent that an alkali-silicate treatment improves it, but so does the alkali-chromate treatment.

Efforts to bring the glue itself into closer contact with the grain, without using other means to clean the grain or change its surface, have little or no effect in increasing the adhesion.

After the preliminary tests on the TJ alundum, similar treatments were tried on the untreated "99" alundum. Due to the different fracture of this grit, the packing is different and 85 grams of glue solution with 400 grams of the grit, gives us a nearly fluid mass. Since the object is not to fill in the air spaces, but merely to coat the grain surfaces with glue, the amount of 20% glue solution was cut down to 80 grams. The results of the first series are given in Table II. The details will be found in Table V.

TABLE II

No.	Capillarity	Briquet Strength	No.	Capillarity	Briquet Strength
1A	53%	859.5	5A.	50%	806.0
2A	36%	620.0	6A.	40%	544.0
3A	27%	504.3	7A.	56%	797.5
4A	29%	417.5			

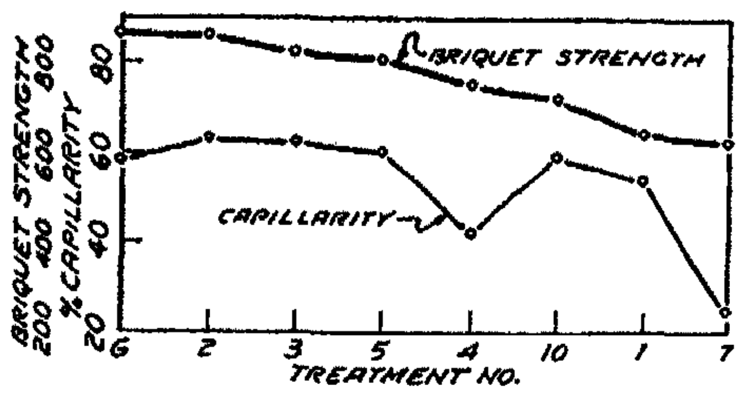

FIG. 1
Briquet Strength-Capillarity

One conclusion can immediately be drawn from these results: chromate treatments do not compare with silicate treatments. Nos. 2A, 3A, 4A, and 5A are all chromate treatments, the others are hydroxide-silicate treatments.

The next series was that in which calcium hydroxide and calcium sulphate were used. Boiling as well as quenching was tried and will be more in the future to determine whether the same results can be obtained at a lower temperature. 8A, 8B, 9A, and 9B are the numbers of these treatments, details also being in Table V. The results are given in Table III.

TABLE III

No.	Capillarity	Briquet Strength
8A	Not det'd.	666.6
8B	" "	453.0
9A	" "	659.0
9B	" "	566.0

These treatments are but a trifle better than the preceding chromate treatments.

It is apparent that the strong alkali and silicate treatments give the grain the surface which is best held by glue. It is then desirable that we know whether the results vary with different sodium hydroxide/sodium silicate ratios. And so a series of treatments by quenching, with varying silicate-hydroxide ratios, was made. The tabulated and graphical results are on following pages. To complete the data, quenching was also done in the 10% solutions of each constituent alone.

The best adhesion is obtained with the grit which was quenched in sodium silicate alone. That quenched in 5-1 mixture of sodium silicate and sodium hydroxide runs a close second. The grit treated with sodium hydroxide alone is very poor, the test increasing in general as the percent of sodium silicate is increased.

Treatments 11A and 12A are the same except that the former was heated 12 hours in the muffle furnace, the latter but one hour. Results are:

No.	Capillarity	Briquet Strength	Hours Treated
11A	61%	840	12
12A	48%	721	1

The difference here may be due to the long heating and it may be that a higher temperature was reached and the grit was hotter when quenched. It is either way a matter of more heat giving higher adhesive properties.

22A treatment is quenching in a mixture of sodium hydroxide and tannic acid. The capillarity is but 15% and the briquet strength 533.

If there is a chemical reaction between the alundum and the alkali, we should get better results using a more concentrated solution. The following results bear out this theory:

No.	Capillarity	Briquet Strength
20A	65%	952
27B	60%	940

The question arises, "Will long boiling give the same results as quenching?" The answer is in Table IV.

TABLE IV

No.	Capillarity	Briquet Strength
30A.	44%	929.5
31A.	58%	1038.3
32A.	49%	942.0
32B.	50%	857.0

The last series of tests include more boiling treatments which show up as well as, and better than, quenching, Table V.

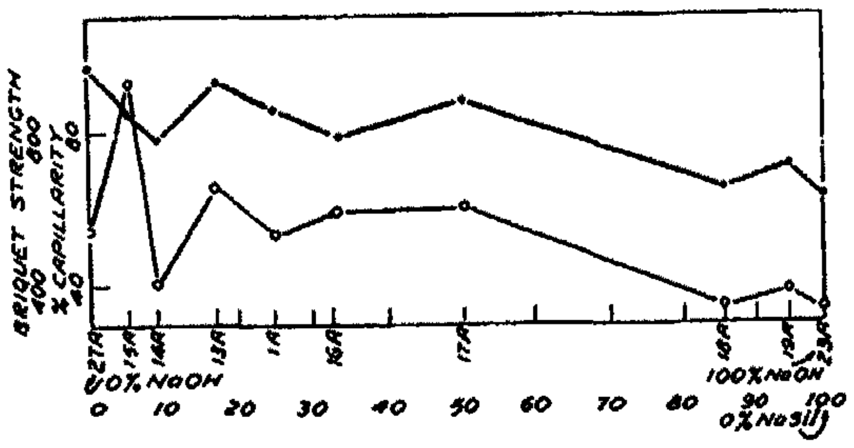

FIG. 2
Variations in NaOH-Na Silicate Ratio

TABLE V

Treatments with 99 Alundum

1A. Heated in muffle furnace one hour. Quenched in a 3-1 mixture of 10% sodium silicate and sodium hydroxide.

2A. Heated one hour in muffle furnace. Quenched in 10% sodium hydroxide. Washed. Boiled 15 minutes in 10% sodium chromate.

3A. Heated three hours in muffle furnace. Quenched in 10% sodium hydroxide. Washed. Boiled 15 minutes in 10% sodium chromate.

4A. Heated three hours in muffle furnace. Quenched in 10% sodium hydroxide. Washed. Boiled 15 minutes in "cleaning solution."

5A. Heated three hours in muffle furnace. Quenched in a 3-1 mixture of 10% sodium silicate and sodium hydroxide. (Dried at 140).

6A. Heated one hour in muffle furnace. Quenched in a 3-1 mixture of 10% sodium hydroxide and sodium chromate.

7A. Heated one hour in muffle furnace. Quenched in a 1-3 mixture of 10% sodium silicate and sodium hydroxide. (Dried at 140).

8A. Heated one hour in muffle furnace. Quenched in a 10% solution of calcium hydroxide.

9A. Heated one hour in muffle furnace. Quenched in a 1-1 mixture of 10% calcium hydroxide and calcium sulphate.

8B. Boiled 15 minutes in 10% calcium hydroxide.

9B. Boiled 15 minutes in a 1-1 mixture of 10% calcium hydroxide and calcium sulphate.

11A. Heated twelve hours in muffle furnace. Quenched in a 3½-2 mixture of 10% sodium silicate and sodium hydroxide.

12A. Heated one hour in muffle furnace. Quenched in a 3½-2 mixture of 10% sodium silicate and sodium hydroxide.

13A. Heated one hour in muffle furnace. Quenched in a 5-1 mixture of 10% sodium silicate and sodium hydroxide.

14A. Heated one hour in muffle furnace. Quenched in a 10-1 mixture of 10% sodium silicate and sodium hydroxide.

15A. Heated one hour in muffle furnace. Quenched in a 20-1 mixture of 10% sodium silicate and sodium hydroxide.

16A. Heated one hour in muffle furnace. Quenched in a 2-1 mixture of 10% sodium silicate and sodium hydroxide.

17A. Heated one hour in muffle furnace. Quenched in a 1-1 mixture of 10% sodium silicate and sodium hydroxide.

18A. Heated one hour in muffle furnace. Quenched in a 1-6 mixture of 10% sodium silicate and sodium hydroxide.

19A. Heated one hour in muffle furnace. Quenched in a 1-20 mixture of 10% sodium silicate and sodium hydroxide.

20A. Heated one hour in muffle furnace. Quenched in 20% sodium hydroxide. Washed. Boiled in 10% sodium silicate 15 minutes.

22A. Heated one hour in muffle furnace. Quenched in a 4-1 mixture of 10% sodium hydroxide and tannic acid.

TABLE V (Continued)

Treatments with 99 Alundum

23A. Heated one hour in muffle furnace. Quenched in 10% sodium hydroxide.
27A. Heated one hour in muffle furnace. Quenched in 10% sodium silicate.
27B. Heated one hour in muffle furnace. Quenched in 20% sodium silicate.
30A. Boiled four hours in 10% sodium silicate.
31A. Boiled four hours in a 5-1 mixture of 10% sodium silicate and sodium hydroxide.
32A. Boiled four hours in 20% sodium hydroxide, drained and boiled 15 minutes in 10% sodium silicate.
32B. Boiled four hours in 20% sodium hydroxide, drained and boiled 45 minutes in 10% sodium silicate.

All these treatments were quenchings in mixtures of 10% sodium hydroxide and 10% sodium silicate. The "% NaOH" is that percent of the total solution which was 10% NaOH solution. The results are shown in Table VI and Fig. 2.

TABLE VI

No. of treatment	Capillarity	Briquet Strength	% NaOH
27A	54%	960 lbs.	0%
15A	92%	849	5%
14A	40%	776	9%
13A	65%	992	16.7%
11A	53%	859½	25%
16A	59%	782	33.3%
17A	60%	873	50%
18A	34%	653	85.7%
19A	38%	705	95%
23A	33%	626	100%

Bookbinders have for many years added glycerine to glue to make it more flexible. This suggested the addition of small amounts of glycerine to the glue used in making briquets to determine whether it affects the strength or the keeping qualities of the glue. To determine the best amount to use, a series was made using 2, 4, and 6 drops of glycerol to each 80 grams of glue solution. Six briquets were made of each. The results were as follows:

2 drops glycerol—Average briquet strength 580½ lbs.
4 " " " " " 568 "
6 " " " " " 573 "
Control, no glycerol—" " " 411 "

Untreated "99" alundum was used in all cases.

It apparently makes little difference which amount is used. Hence a happy medium was taken and 4 drops used for the next runs.

A series of 18 briquets were made using 1A grit. Some of the briquets were tested after two weeks and others were set aside to be tested later. The results on these tests were as follows:

Tested after 14 days—Average strength 847½
Tested after 63 days—Average strength 845½
Control, no glycerol—Average strength 859½

When used on the untreated grit, the glycerol causes a 36% to 42% increase in the breaking strength. This cannot be due to an increase in strength of the glue, for it is known that the glue will readily stand over a thousand in briquet tests. Hence we conclude that it increased the adhesion between the untreated grit and the glue. Before the glue can be adsorbed by the grit, the air film around the grit must be removed, or replaced. The glycerol probably replaces this film better than the straight glue solution and brings the glue in better contact with the grit thus increasing the adhesion between them.

With the silicate treated grit there is no increase in adhesion between grit and glue; that is, the surface of the treated grit is of such a nature that it is wetted as easily by the glue alone as it is by the glycerol. There is a possibility that the adhesion is greater, but that its affect is destroyed by a weakened glue but this seems improbable. Two months time did not affect the glycerol-treated glue so it seems probable that there is no ill effect. Other briquets of this series are to be given six months before testing.

Treatment No. 8 on page 3589 shows the effect of glycerol when working with TJ treated grit, an increase in strength of nearly 37%. The surface of this grain is more readily wetted by the glue and glycerol than by the glue alone.

The following series of runs are made in duplicate and are known as series "E" and "H." The treatments are chosen from those that previously gave best results and are duplicates of each other. There is some question as to the duplicatability of the results obtained. To decide this, these treatments are made separately, one series being done at a time. The briquets are made up likewise and their drying covers a different period, but one of the same length. In order to cut down the variations liable to arise in the quenching procedure as heretofore carried out, the method was changed as follows: the grain was fed from a large funnel through a small orifice into an inclined iron pipe, with an eccentric under one end to insure the grains against stopping in the pipe. The pipe was heated to red heat by three blast lamps, and the hot grit passing out of the pipe drops directly into the quenching bath. The advantages of this method are believed to be more uniformity of heating, and a great saving of time in treating the grit. The temperatures reached are not as high however so the results of the tests are not as high as had been obtained. Since the chief aim is comparison, this does not matter.

These rules were adhered to strictly in making the briquets:

1. All treatments started and finished the same day.
2. No grit left in drying oven over three hours.
3. Drying temperature not over 110°C.
4. All grits thoroughly washed in tap-water.
5. Glue shall soak 25–30 minutes before placing in the boiling water.
6. Water shall be boiling when glue is placed in it.
7. Glue shall be heated exactly 10 minutes in boiling water.
8. Briquets shall be removed from mould as soon as set.
9. Briquets shall dry in the rack 14 days.
10. Six briquets shall be made of each grit.

Details of the treatments are:

1. Boil 4 hours in 10% sodium hydroxide. Wash. Boil 30 minutes in 10% sodium silicate.

2. Boil 4 hours in 10% sodium hydroxide. Wash. Boil 60 minutes in 10% sodium silicate.

3. Boil 4 hours in 20% sodium hydroxide. Wash. Boil 30 minutes in 20% sodium silicate.

4. Boil 4 hours in 20% sodium hydroxide. Wash. Boil 60 minutes in 20% sodium silicate.

5. Boil 4 hours in 10% sodium hydroxide. Wash. Boil 60 minutes in 20% sodium silicate.

6. Quench in 10% sodium hydroxide. Wash. Boil 15 minutes in 10% sodium silicate.

7. Quench in 10% sodium hydroxide. Wash. Boil 60 minutes in 10% sodium silicate.

8. Quench in 20% sodium hydroxide. Wash. Boil 15 minutes in 10% sodium silicate.

9. Quench in 20% sodium hydroxide. Wash. Boil 60 minutes in 10% sodium silicate.

10. Quench in 20% sodium hydroxide. Wash. Boil 15 minutes in 20% sodium silicate.

11. Quench in 20% sodium hydroxide. Wash. Boil 60 minutes in 20% sodium silicate.

12. Quench in a 5–1 mixture of 10% sodium hydroxide and sodium silicate.

13. Quench in a 5–1 mixture of 20% sodium hydroxide and sodium silicate.

The tabulated results for these series are given in Table VII, and the capillarity-briquet strength comparison curves in Figs. 3 and 4.

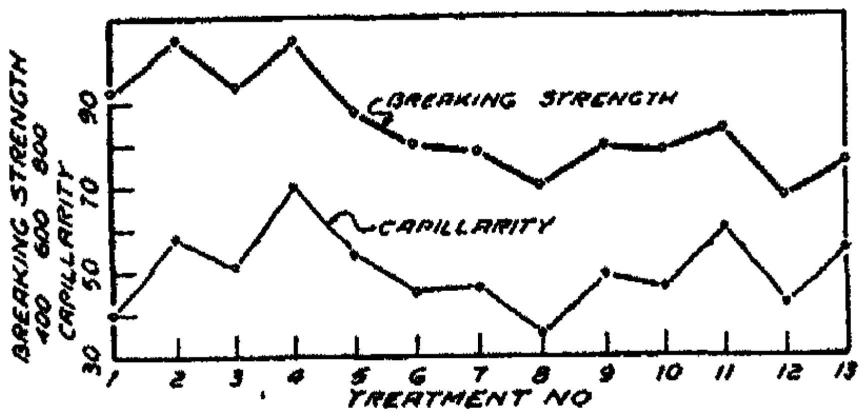

Fig. 3
Capillarity—Briquet Strength Series "E"

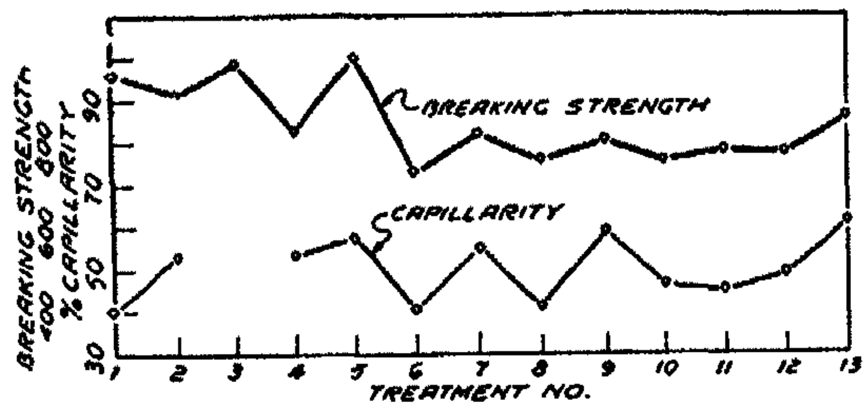

Fig. 4
Capillarity--Briquet Strength Series "H"

Table VII

Results of Series "E" and "H"

Grit No.	Capillarities		Briquet Strength	
	"E"	"H"	"E"	"H"
1	40%	40%	926 lbs.	954 lbs.
2	58	53	1049	910
3	51		930	981
4	70	53	1046.6	820
5	54	57	876	997
6	45	40	800	726
7	46	55	783½	822
8	35	41	700	756½
9	49	59	795½	801
10	46	46	784½	752
11	60	45	832.6	779
12	42	49	673½	773
13	55	61	753½	858

As has been stated, series "E" and "H" are primarily to show whether the results obtained can be consistently duplicated or not. From this standpoint, results are not highly satisfactory. Good checks are obtained in seven cases, very poor checks in four cases. From this we do get some interesting information. The treatments are not the kind that give results regardless of how they are done, but on the contrary are very easily affected by imperfect control of all factors. Among the possible sources of error are variation in concentration of solutions, quenching temperatures, under or over-washing the grain, drying temperatures, and possibly presence of certain substances in the solutions which will effect the results obtained. These factors were all watched during the above runs, but plainly not closely enough. It is known that imperfect washing will lead to a high capillarity and low briquet strength with some treatments, possibly so with all. Too much washing may decrease the effect of the treatment.

In comparing the relative effect of different treatments, I believe we should accept the highest value obtained for each. No treatment can show up better than it actually is, but one slip somewhere might decrease its value considerably. Any result once obtained can be duplicated if the proper conditions are found and followed. The danger lies in underestimating the worth of any treatment, not in overestimating.

In reviewing the treatments tried, we find that no high results are obtained except from a silicate treatment, either with or without sodium hydroxide. With sodium hydroxide, the ratio sodium hydroxide/sodium silicate must be kept small. It makes little difference whether long boiling or quenching from red heat is the method used. Long boiling has the advantage of being less trouble, and the maximum results can be obtained more easily. Where both sodium hydroxide and sodium silicate are used, there seems to be little difference whether they are used separately or together; the single treatment is of course simpler. The concentration has little effect, in general the 20% solutions gave slightly better adhesion to the grit than did the 10%, but this was not always true, nor was there much difference where there was any.

The mechanism of this increased adhesion is merely a good point to theorize on until more is known concerning the surface of the treated grains. Sodium hydroxide will react slowly with aluminum oxide to form a sodium aluminate. This will in turn react with sodium silicate to form a complex sodium aluminum silicate. The treated grit shows no microscopic evidence of etching however, so it is not likely that there is formed a mechanical joint which strengthens the bond. This silicate film is either formed on the grain or is adsorbed by it. This film in turn has a specific attraction, if it may be called that, for the glue solution, is readily wetted by it and forms a very strong bond with it. Since the same result may be had without the use of the strong alkali, it seems quite likely that the whole matter is an adsorption of the silicate film on the surface of the treated grain. There is, as well, a cleansing action, and removal of any grease and air films which may be on the grit. Since these films are definitely replaced by another film, the effect of the treatment is long-lasting. If this grit is allowed to lie around in the open air for a long period of time, it will however lose its adhesive properties slowly, due to dirt and air gradually collecting on the treated surface. Merely heating the grain causes it to have a higher adhesive strength, due to cleansing of the grain. A heated or "burned" grit loses its adhesive properties quickly, since there is nothing to prevent it rapidly taking up air and dirt. The treatment does not give as high an adhesiveness as the silicate treatment, which supports the silicate film theory and its specific attraction for glue.

The author takes this opportunity to thank the director of this research. The kindly suggestions and understanding of Professor Bancroft have made the work and the associations most enjoyable.

Cornell University.

THE RATES OF FORMATION OF THE ACTIVE REDUCTANTS OF SEVERAL SUGARS*

BY MARTIN H. ROEPKE** AND JOHN M. ORT***

Introduction

"Active glucose" and similar terms for other sugars have long been used to designate those comparatively reactive components of the solutions of various sugars which a great mass of chemical and biologic evidence indicates exist.

Since apparently the great bulk of sugar present in solution cannot, under many conditions, be directly involved in the reactions which are the most obvious and which can be studied easily, it has seemed that there must be present a rather small amount of an extraordinarily reactive substance in order to account for the activity found. There is no decisive evidence as to the chemical nature of these substances, and therefore terms such as "active glucose" have had a rather loose and indefinite meaning. Since the sugar molecules may be considerably changed in producing these "active sugars," and since the most important property developed is reducing ability, it would seem that "active reductant" is a more accurate term. It will be used in this sense in the present paper.

In previous work[2] it was shown that at pH 10 a solution of 60 gm. of glucose, plus 100 c.c. of buffer, contained about one part of this active reductant to 250,000 parts of total glucose present, assuming the reductant to be divalent. By the same procedure a somewhat larger amount, although of the same order of magnitude, has since been found to be present at pH 9 for a similar solution. Experiments at pH 8 and pH 7 have indicated that similar small amounts are present under these conditions, although the rate of reaction between reductant and dissolved O_2 (the oxidant used for the electrometric titration) is here too slow, compared to the rate of regeneration of the active reductant from the great mass of sugar in solution, to enable these amounts to be determined accurately by this method.

It is evident that if these small amounts are to play an important part in the mechanism of the oxidation of sugars, whether in vivo or in vitro, they must be comparatively rapidly replaced when oxidized. It was the purpose of the present investigation, therefore, to determine the rates of formation of the active reductants of several of the common reducing sugars.

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* The material for this paper was taken from a thesis submitted by D. Roepke to the Faculty of the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1930. Read before the Division of Organic Chemistry, American Chemical Society, Indianapolis, Indiana, March 30 to April 3, 1931. Submitted for publication August 27, 1931.

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Experimental Procedure and Apparatus

To determine the rate of formation of active reductant, all reducing substances initially present were removed by adding an oxidant in excess of any active reductants present in the solution, although not in excess of the total amount of sugar dissolved. The rate at which the excess oxidant was removed thereafter is equal to the rate of formation of active reductant. In order to be suitable for such determinations the oxidant must satisfy two requirements: (1) It must react very rapidly with the active reductant, so that the latter will be oxidized practically instantaneously the moment it is formed, and (2) the oxidant must not attack the components of the solution other than the steadily forming active reductant (after the initial removal of reducing substances that have accumulated before the oxidant is added). Potassium ferricyanide was found to satisfy these important qualifications; these will be considered more fully later.

This oxidant has the additional advantage of forming with its reduced form a completely reversible, electromotively active oxidation-reduction system. The course of reaction with the active reductants of the sugars can therefore be followed electrometrically, since after the initial period necessary completely to destroy accumulated reductants, the oxidation-potential of a platinum electrode is determined only by the ratio of ferrocyanide to ferricyanide, as long as there is an appreciable quantity of the ferricyanide left in solution. Since this ratio alone is involved, and not the total quantity of ferrocyanide or ferricyanide added, determinations can be made using small or large amounts of this oxidant and, by varying the ratio at the start, they can be made throughout a range of oxidation-reduction intensities.

The apparatus used for the measurements was essentially similar to one already described,[21] but with a capacity for thirty-two simultaneous determinations. When the electrode chambers containing the solution to be studied were lowered into the oil bath of the thermostat they could be shaken to insure rapid mixing of any added reagent, although there was an all-glass connection from the supply of pure nitrogen gas to the liquid in the chambers. This connection was broken when the chambers were raised out of the bath, at the end of the run, for cleaning. Oxygen-free nitrogen was prepared from commercial nitrogen by passing the gas through more than 12 feet of an elaborate gas washing system containing sodium pyrogallol. Tests showed that the nitrogen so obtained was inert to sugar solutions and contained no oxygen nor any carbon monoxide or other reducing gases. Control of temperature was accurate to within 0.05°C.

The electrode chambers, each containing 100 c.c. of buffer solution together with the sugar were fastened to their stoppers and lowered into the oil bath. Nitrogen was bubbled through the solution for at least twenty minutes to remove most of the dissolved oxygen. Then the potassium ferricyanide or a mixture of potassium ferricyanide and potassium ferrocyanide was added by a pipet through a hole in the stopper. A particularly vigorous stream of nitrogen bubbling through the sugar solution during this addition prevented the entrance of air in amounts significant for this work. Potential readings were then taken at intervals of ten to sixty minutes for a number of hours.

The buffers used were either M/15 or M/5 phosphate buffers, as indicated in the data. Determinations of hydrogen-ion concentration were made with the hydrogen electrode at 30°C.; the standard reference electrode was the hydrogen electrode in molar 20th potassium acid phthalate.[1] Hydrogen-ion concentration was maintained nearly constant during a run by intermittent additions of the necessary amounts of alkali.

Due to the "salt effect" it was necessary to determine the E_0 values of the ferrocyanide-ferricyanide system for each different set of experimental conditions. This was done in two ways: electrometrically and colorimetrically. For the first method a mixture of two parts of ferricyanide and one part of ferrocyanide was added to the sugar solution to be studied, and the oxidation potential was observed for a certain time. Between the points of the potential time curve representing one-third reduced and two-thirds reduced, the curve is nearly a straight line if the reduction is proceeding at a constant rate. Hence if the slope of the curve after the reaction has become steady is used to extrapolate back to zero time, the potential of a mixture two-thirds oxidized is obtained and E_0 can be calculated from the well-known equation:

$$E = E_0 - \frac{RT}{NF} \ln \frac{\text{Red}}{\text{Ox}}.$$

The values so obtained check with those determined colorimetrically in the following manner. Pure ferricyanide was added to the sugar solution and when the oxidation potential indicated it has been approximately one-half reduced, the reduction was stopped by acidifying the solution. The ferrocyanide present was then determined by Folin's method[8,9] and from the potential read just prior to the acidification, E_0 was calculated as before.

It was originally intended to check colorimetrically all potentiometric determinations of the rate of formation of the active reductants by observing the time rate of decolorization of various dyes. Preliminary experiments along these lines indicated values of the same order of magnitude as those determined potentiometrically. Wurmser and Geloso have also shown that both electrode and dye give the same indications as to the oxidation-reduction intensities in sugar solutions. In a former work[2] from this laboratory it was also shown that in well-stirred solutions the platinum electrode indicated conditions throughout the entire solution and not just those of a local layer adjacent to the surface of the platinum. For these reasons, and because the electrometric method is more convenient, rapid and accurate, it was used throughout the remainder of the work.

The chemicals used were Merck's anhydrous chemically pure dextrose, Bureau of Standards' dextrose, Eastman's levulose, Pfanstiehl's levulose, lactose, maltose, mannose, and galactose, and Baker's chemically pure potassium ferricyanide and potassium ferrocyanide. The buffers were made from Central Scientific Company's chemically pure sodium hydroxide, and LaMotte's disodium phosphate and potassium acid phosphate for buffers.

Experimental Results and Comments

Since there are acids produced by the reactions between sugars and potassium ferricyanide, it was necessary first of all to determine, in an empirical manner, the amount of alkali to be added during the oxidation-reduction process to keep the hydrogen-ion concentration constant. This was done by titrating the solution with alkali, after the ferricyanide had been reduced, to the hydrogen-ion concentration of the sugar solution before the addition of ferricyanide.

In the reduction of ferricyanide to ferrocyanide as illustrated by the change:

$$K_3Fe(CN)_6 \rightarrow K_4Fe(CN)_6$$

one equivalent of alkali is necessary. Any alkali needed in excess of this one equivalent is used to neutralize the acids produced by oxidation of the sugars. It was found that, for the range of hydrogen-ion concentration studied, the amount of alkali necessary to keep the hydrogen-ion concentration constant varied from 1.15 to 1.30 equivalents of alkali. That is, for example, if 3 c.c. of fifth normal ferricyanide were reduced, the amount of alkali needed would be 1.15 to 1.30 times 3 c.c. of fifth normal hydroxide. At alkalinities around pH 8 or less, the amount of ferricyanide reduced in a reasonable length of time is quite small. The solutions are highly buffered by the phosphate buffer present, so the differences in hydrogen-ion concentration produced by the additions of 1.15 and 1.30 equivalents of alkali is very low; in fact it is within the limits of accuracy of the hydrogen-ion determinations (±0.02 pH). At the higher alkalinities, around pH 9.5 or higher, where the amount of ferricyanide reduced in a given time is much greater, and the solution is not buffered as well, the amount of alkali necessary to keep the hydrogen-ion concentration constant appeared to be between 1.20 and 1.30 equivalents. Therefore, the amount of alkali added for the experimental work which followed was 1.25 equivalents. From the readings of potential which were taken at short intervals of time, the amounts of ferricyanide reduced during those intervals could be calculated, and from this the amounts of alkali to be added at these times were determined.

The oxidation of the aldehyde group of the sugar molecule directly to an acid group would require two equivalents of ferricyanide and would produce one equivalent of an organic acid. This type of oxidation would require 1.5 equivalents of alkali. However, if each molecule of the reducing substance reduces 4 molecules of ferricyanide, and in so doing forms 1 molecule of an organic acid, then the amount of alkali necessary to keep the hydrogen-ion concentration constant would be 1.25 times the amount of ferricyanide reduced. Or if each molecule of reductant requires 6 molecules of ferricyanide for its oxidation and thereby produces 1 molecule of an acid, the alkali required to maintain a constant hydrogen-ion concentration would be 1.16 times the amount of ferricyanide. The optimal amount of alkali to be added as found by experiment (1.25 equivalents) seems to favor the second condition and would suggest that the oxidation of a molecule of the active reducing substance first formed in an alkaline medium requires four equivalents of ferricyanide and results in the formation of 1 molecule of an acid. The difficulties encountered in determining the exact amount of acid formed in solutions that are highly buffered (optimal conditions for the present studies) warrant a more thorough study along this line.

When the hydrogen-ion is kept constant, as just described, the rate at which the ferricyanide is reduced to ferrocyanide by the alkaline sugar solution is essentially a constant, except for a short time just after the addition of the ferricyanide, during which time adjustments of equilibrium are made, and again during the last few minutes when the last trace of ferricyanide is reduced. If the values for the amount of ferricyanide present at various intervals of time are calculated from the potential readings, and these values are plotted against time, the type of curve obtained is that shown in Fig. 1. The rate at which the ferricyanide is reduced is essentially a constant for a period of nearly five hours and seems to bear no relationship to the amount of ferricyanide present, nor to the oxidation-reduction intensity within the range of this system. This proved always to be the case, even though the amount of ferricyanide added was greatly varied, and also when various mixtures of ferricyanide and ferrocyanide were used.

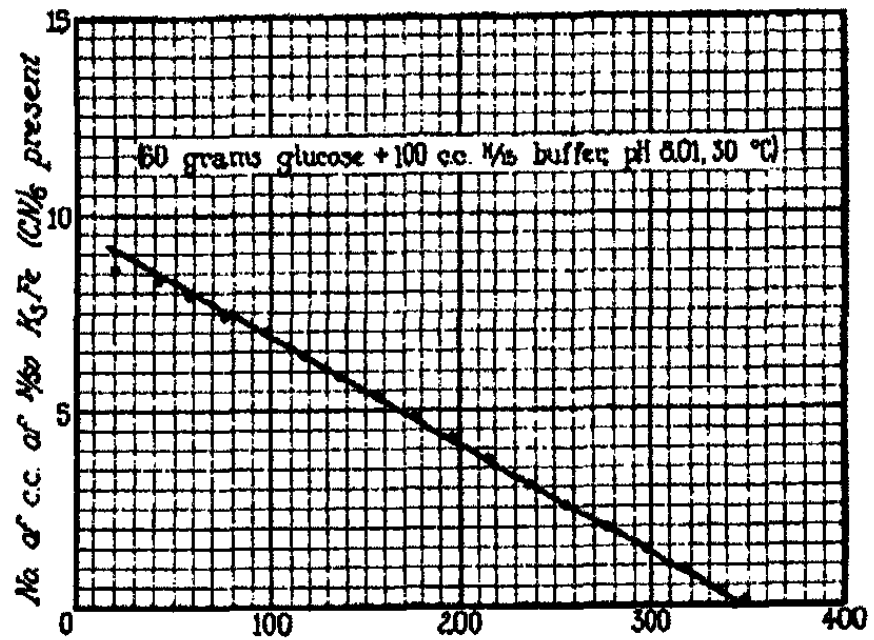

Fig. 1

The rate of formation of the active reductant of glucose is constant.

This indicates that a small amount of a reducing substance is formed steadily from the sugar present, and that this reducing substance is oxidized as rapidly as it is formed. Moreover, the ferricyanide cannot react with any appreciable speed with any of the other components of the sugar solution since the speed of any such side reactions must necessarily fall off with a drop in concentration of the oxidant. Since the ferricyanide is removed at a constant rate throughout a wide range of its concentration, it must oxidize the active reductant practically the instant it appears.

These conditions are in contrast to those of Wurmser and Geloso, who attempted to determine such a rate by the use of methylene blue. Their curve (November, 1929) shows clearly a drop in the rate of oxidation with the fall in concentration of the dye. Rates so determined are consequently lower than those determined by our method would be for the same experimental conditions. That is, methylene blue solutions, unless too concentrated for accurate determinations of small changes during small intervals of time, cannot remove instantly the active reductant as fast as it appears. Consequently a certain concentration of this reductant is built up until the speed of its reaction with the dye becomes enough to prevent a further accumulation. Although this may result in a steady state, with a practically constant speed of oxidation for considerable time thereafter, the fact that such a "constant speed" falls off with the concentration of methylene blue shows that this speed of oxidation is not equal to the speed of formation of active reductant, but is lower. The concentration of active reductant under all such conditions is high enough to support an appreciable reverse reaction in the equilibrium: glucose solution active reductant. That is, the rate of formation equals the rate of oxidation plus the rate of reversal, and it is the speed of reaction between methylene blue and reductant that is being measured and not the rate of formation of reductant.

Wurmser and Geloso's rate of oxidation of glucose (November, 1929) as determined by methylene blue was 7 molecules in thirty-five minutes for each 1,000 molecules of sugar originally present, 3 gm. per cent at a final pH of 10, and at 20° C. This is considerably higher than our rate for this concentration, temperature, and hydrogen-ion concentration. However, their solutions had been previously subjected to an unknown pH of more than 10 and besides had been previously heated to temperatures as high at 84° C. until their limiting potentials had been reached. That is, the Lobry de Bruyn-van Ekenstein changes had taken place. Wurmser and Geloso's systems were therefore quite different from those we were dealing with in fresh glucose solutions. Speaking of velocities of reduction of methylene blue in solutions of glucose similarly prepared they stated (November, 1929), "These velocities are both much greater than the velocity of decoloration of methylene blue by a solution of glucose not heated previously." Moreover, the true velocities of formation of active reductants would be still higher under these conditions than the rates they found for the reduction of methylene blue after destruction of any reductant initially present.

In Fig. 2 are shown curves representing the rates of formation of the active reductant of glucose under different conditions of temperature, concentration of glucose and hydrogen-ion concentration. Because of the wide range in values it seemed best to plot both the rates and hydrogen-ion concentrations as logarithms. The curves as plotted, then, have the same shapes as though all numerical values were plotted directly. The outstanding effect noticed is that of the H^+ or OH^- ions. The dotted lines represent the forty-five degree slope the curves would have if the rates were exactly directly proportional to the OH^- ion concentration. The rates for glucose then increase faster than the hydroxyl ion concentration. The equation satisfying the experimentally determined facts is:

$$\log V = 1.116\,\mathrm{pH} + C$$

where V is the rate of formation of the active reductant and C is a constant.

This constant C varies, of course, with concentration of glucose, concentration of buffer, and temperature. For a solution of 60 gm. of glucose + 100 c.c. of M/15 phosphate and sodium hydroxide buffers at 30° C., C has a value of −8.70.

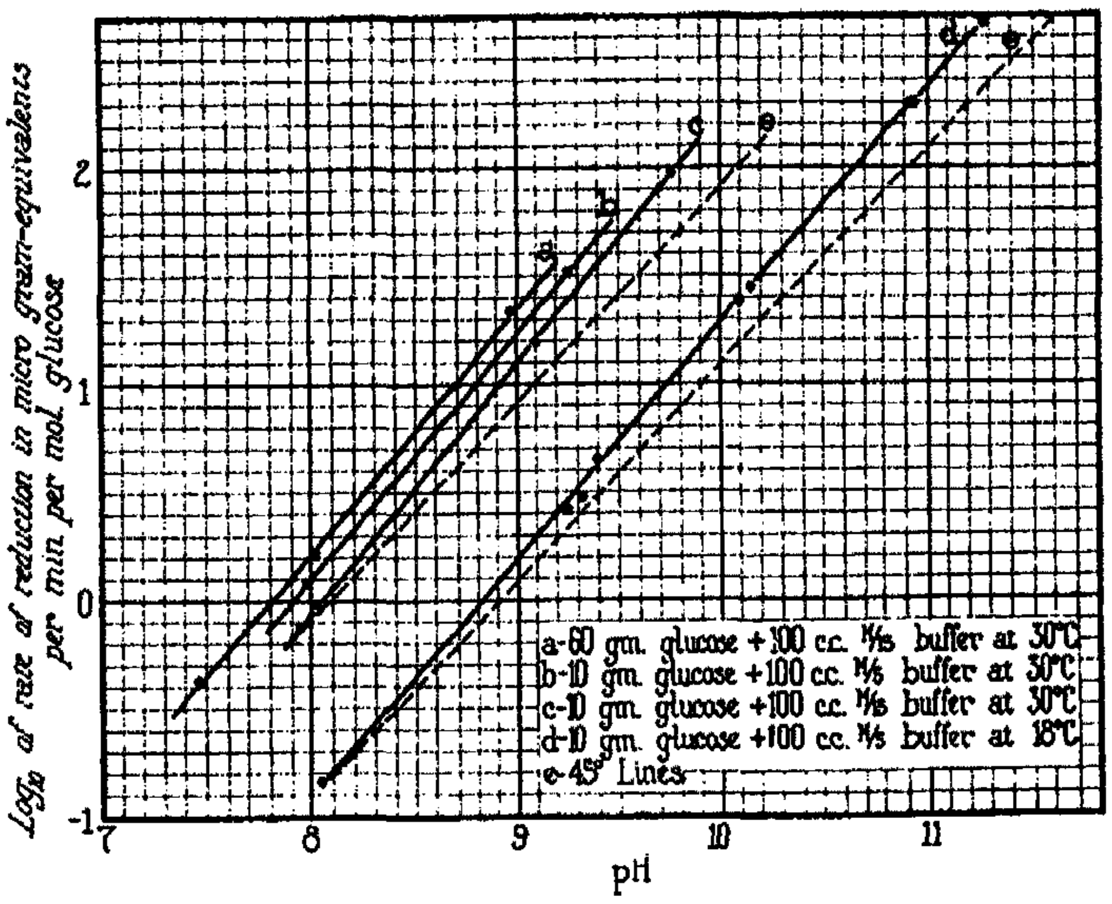

Fig. 2

The rate of formation of the active reductant of glucose is proportional to the OH^- ion concentration.

Wurmser and Geloso (November, 1929), who have been associated also in similar work with Aubel and Genevois quote the rate for the reduction of methylene blue as determined by the latter workers as:

$$\log V = 0.5\,\mathrm{pH} + C_1$$

which gives slower rates of formation of active reductant than those determined by our method under equivalent conditions, for reasons which we have considered.

The fact that the rate of formation of the reducing substance bears such a close relationship to the hydroxyl-ion concentration suggests that the hydroxyl ion is involved either directly in the formation of the active form, or indirectly, by increasing the amount of the glucose ion, since sugars are weak acids, as has been shown by Michaelis and Rona,[21,22] Stearn, and others. In the latter case, the glucose ion would be considered as the precursor of the active form. However, in both cases the rate should increase tenfold for each pH, whereas the actual rate was found to increase somewhat faster. In this connection, slow oxidation of the first oxidation product might be considered as a possible cause for the deviation from the tenfold increase. If this slower secondary oxidation should take place, its speed should be affected by the concentration of the oxidant. As discussed previously, the rate of reduction of the ferricyanide does not seem to be affected by either the concentration of the oxidant or the oxidizing potential within the range of potentials studied. This phenomenon will be discussed again in connection with the rates found for the other sugars studied.

Still other evidence can be found from curves B and C (Fig. 2) that an ion is directly or indirectly involved in the formation of the active reductant. The only difference between the two solutions used for the determination of the rates in these two cases is that one (B) was observed in the presence of M/5 phosphate buffer and the other (C) in the presence of M/15 phosphate buffer. Since the hydrogen electrode indicates the hydrogen-ion activity instead of actual hydrogen-ion concentration, the actual hydrogen-ion concentrations of the two solutions are different, even though the hydrogen-ion activity may be the same as indicated by the hydrogen electrode; ion activity is equal to the actual ion concentration, times the activity coefficient. It is a well known fact that an increase in concentration of salt lowers the activity coefficient of an ion, and therefore, for solutions having different concentrations of an inert salt, the actual concentration of the ion in question would be higher for the solution possessing the higher concentration of salt when the activity of the ions of the two solutions is the same. Now it is the product of the activities of the H^+ and OH^- ions that must be constant under a given set of conditions and not necessarily the product of their concentrations. The activity coefficient of the OH^- ions and glucose ions would of course also be lowered in the more concentrated buffers, making the concentration there higher for an apparently identical hydrogen-ion concentration. Hence the rates of formation of active reductant from sugar, which increase markedly with OH^- ion concentration, are higher in curve B than in curve C.

If the activity coefficients for a monovalent ion present only in traces in the presence of M/15 and M/5 disodium phosphate are calculated by the well-known Debye-Hückel equation,

$$-\log i = 0.5Z_i^2$$

the activity coefficients are found to be 0.597 and 0.410 respectively. The ratio of these coefficients is 1.46 and the ratio of the two rates (curves B and C, Fig. 2) is approximately 1.38. The activity coefficients, as calculated from the Debye-Hückel equation, are only approximate for solutions of electrolytes as concentrated as M/5 sodium phosphate. However, the parallelism between the ratios of the activity coefficients and the rates of formation is close enough to indicate that an ion is directly or indirectly involved in the formation of the active reductant from the common form of glucose.

In order to study the effect of hydrogen-ion concentration on the rate of formation of the active reductant at higher alkalinity, a series of determinations on glucose was carried out at 18° C., at which temperature the rates are much lower than at 30° C., and therefore more accurate determinations at higher values of hydroxyl-ion concentration are possible. The rates obtained are shown in curve D (Fig. 2). The rate of formation of the active reductant then was found to be a linear function of the hydrogen-ion concentration between pH 7.5 and 11.3.

The effect of temperature on the rate of formation of the active reductant from glucose is shown in Fig. 3. The experimental values deviate slightly from a straight line (dotted line). There is no evidence as to whether this slight deviation is an apparent or a real deviation, for the same buffer-glucose mixture was used throughout this series of determinations, the hydrogen-ion concentration of which was determined at 30° C. and the hydrogen-ion concentration of phosphate buffers increases slightly on increasing the temperature.

As is shown in Fig. 3, temperature just as hydrogen-ion concentration, is very important in its effect on the rate of formation of the active reductant. An increase of 22.5° C. increases the rate of formation approximately one hundred fold. That is:

$$\log V = 0.09T + C_2$$

where C_2 is another constant the value of which depends on the various experimental conditions. The equation of Aubel and Gènevois, as given by Wurmser and Geloso is:

$$\log V = 0.06T + C_3.$$

Again, and for the same reasons given before, our values would be higher.

Assuming that the rate of formation obtained by extrapolating the dotted line (Fig. 3) to 100° C. is approximately near the true value, then, all other conditions being constant, the rate of formation at 100° C. is approximately 24,000,000 times higher than at 18° C. The amount of active reductant formed in one minute at 100° C. would require approximately forty-five years for its formation at 18° C., all other conditions remaining constant. Again, assuming that the rates of formation obtained by extrapolation of curve D (Fig. 2) to pH 7.4 and pH 13, are reasonably near the true values, the rate of formation at pH 13 is approximately 1,780,000 times higher than at pH 7.4. Or the amount of active reductant that could be formed at pH 13 in one minute would require approximately 3.3 years for its formation at pH 7.4, all other conditions remaining constant.

These comparisons emphasize the importance of hydrogen-ion concentration and temperature on the activation of glucose. It does not necessarily follow that all of the reactions which glucose undergoes in alkaline solutions are affected to the same extent by hydrogen-ion concentration and temperature as the reaction studied in this research. Also, the comparisons imply that the active reductant is removed by oxidation as rapidly as it is formed.

In view of the fact that the reactive groups present in the maltose and lactose molecules belong to a glucose group in both cases, it was thought that comparison of the rates of formation of the active reductant from these two, and several other, somewhat differently constituted sugars, would give additional information as to the mechanism of the formation of the reducing substance or substances that these various sugars produce in solution. Accordingly, a series of determinations was carried out to determine the effect of *hydrogen-ion concentration on the rates for these sugars*. The results are shown in Fig. 4, the dotted lines again representing a forty-five degree slope.

The curve for levulose is distinctly different from any of the other sugars studied. At pH 7.4 the rate for levulose is approximately one-hundred-fold higher than for glucose. However, above pH 9 the two curves parallel each other, but the rate for levulose is still approximately twenty times that of glucose. In this respect, the activities of the two sugars parallel somewhat their relative activities in biologic systems. The rate of fermentation of levulose is approximately three times higher than that for glucose,[14] and the ease of formation of glycogen from levulose in rats fasted for forty-eight hours is approxmately twice that of glucose.[3]

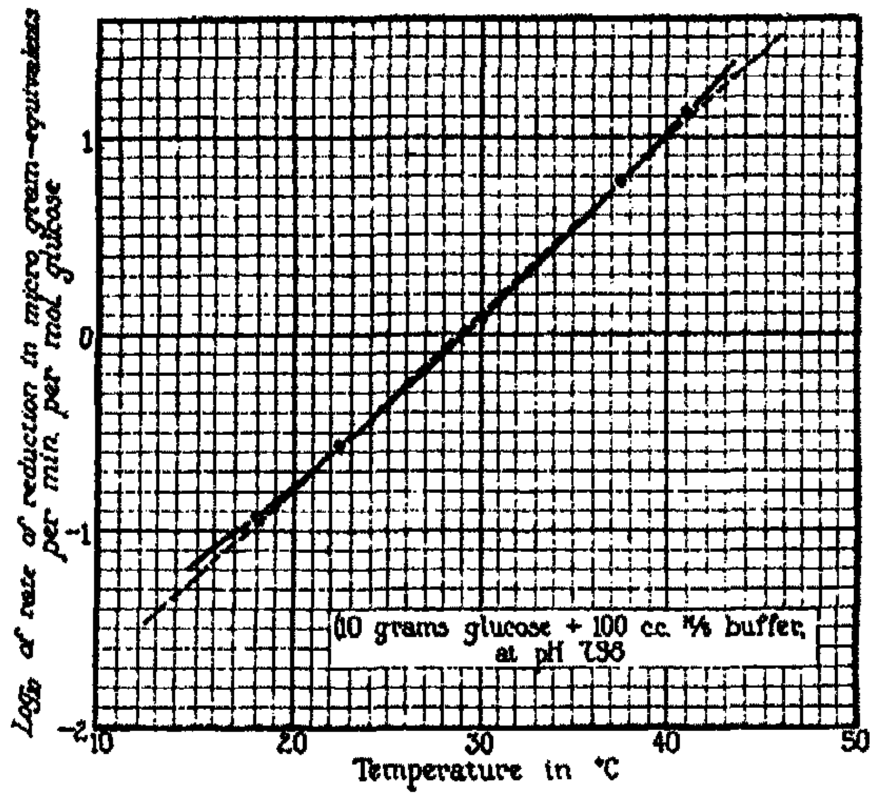

Fig. 3

The rate of formation of the active reductant of glucose increases one-hundred-fold every 22.5° C.

Even though the reducing groups present in maltose and lactose belong to a glucose portion of the disaccharides, the rates at which they reduce ferricyanide are not the same and are also different from that for glucose at the same hydrogen-ion concentration. However, if the rates of formation are compared with the dissociation constants of the sugars as weak acids, as is done in Table 1, there seems to be a definite relation between the dissociation constants and the rates of formation of the respective active reductants. The constant rate of formation of the active reductants seems to be due then to the presence of a constant amount of the salts or the ions of the sugar in question. The concentrations of the salts or ions present in solution over the ranges of hydrogen-ion concentration values studied are low because of the weak acid properties or the low dissociation tendencies of the sugars. The amounts of sugar oxidized in the determinations over the hydrogen-ion concentration ranges used were small compared to the total amount of sugar present. Therefore a constant amount of the salts or ions is present in solution throughout the determination. That these salts or ions, of themselves are not the reducing substances, is evident because of the comparatively slow rates of formation of the reducing substances found experimentally. Ordinary acid-base reactions are, of course, very rapid compared to the rates found in these experiments. If the view that the precursor of the active reductant is the salt or ions of the sugar is correct, then the influence of hydrogen-ion concentration on the activity of alkaline sugar solutions is largely indirect in that it determines the concentration of the precursor of the active forms under the given conditions of concentration of the sugar and so forth.

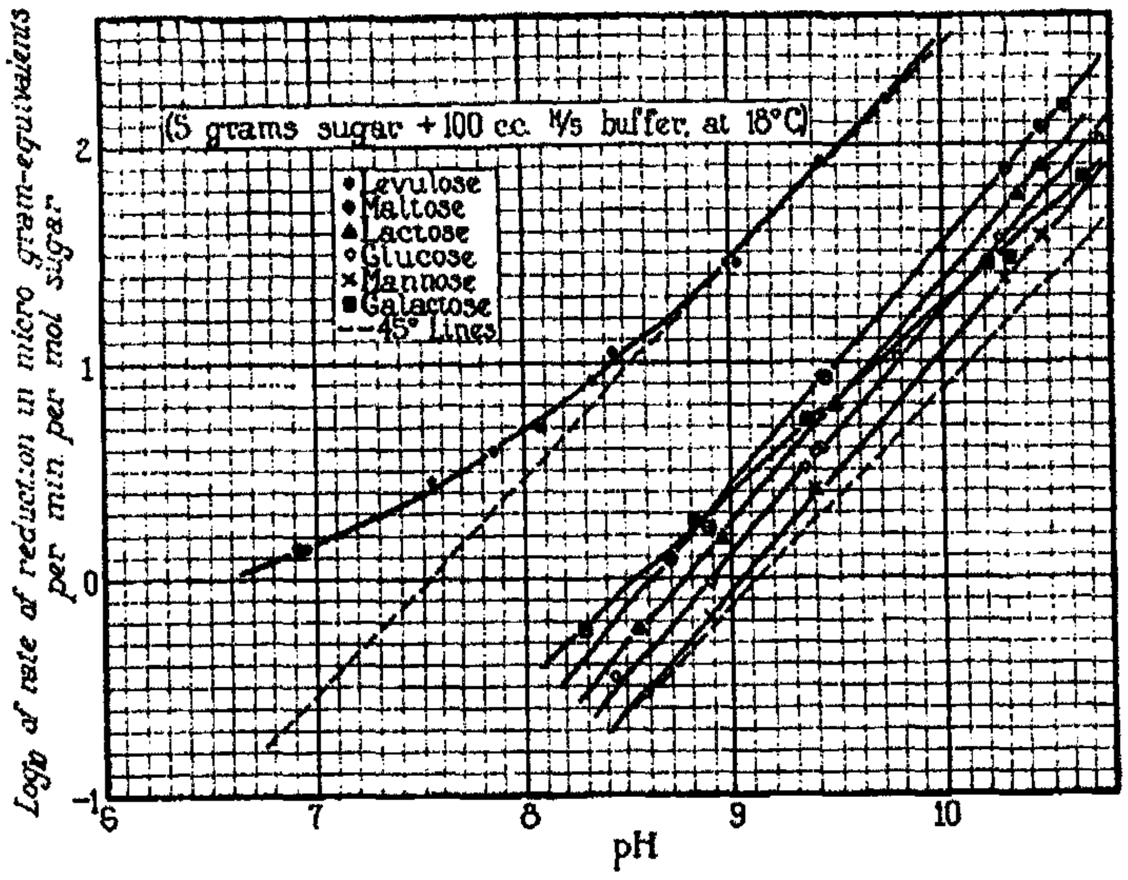

Fig. 4

A comparison of the rates of formation of the active reductants of six sugars of different hydrogen-ion concentrations.

That the first active forms of the sugars from which the transformation or rearrangement reactions begin in solution are the sugar ions or the sugar salt is a belief which has been expressed by Nef, Mathews, Shaffer, Shaffer and Friedemann, von Euler and his associates[5,6] Groot, Michaelis and Rona[21,22] and others. In view of the results of these investigators and those of Evans and his associates, and of Shou and Wurmser it seems probable that the rates of formation of the active reductants found experimentally in this research are measures of the rates of formation of the 1–2 enediol forms of the aldoses studied and 1–2 and 2–3 enediol forms in the case of levulose.

Besides the primary effect of hydrogen-ion concentration which has just been considered there seems also to be a smaller secondary effect of hydrogen-ion concentration on the rate of formation of the active reductant from any given sugar. This is noticed by the differences between the curves for galactose and for levulose below pH 9 from those of mannose and the glucose series (Fig. 4). The effect of hydrogen-ion concentration on galactose is represented by the equation:

$$\log V = 0.86 \text{ pH} + C$$

The angle between the curve for galactose and the forty-five degree line is approximately equal to, but opposite in sign to, the angles between this line and the curves for mannose and for the glucose series. This suggests that there is a secondary effect of hydrogen-ion concentration not related directly to the primary effect.

An interesting fact in this connection is that the important structural difference between galactose and the mannose-glucose series is in the stereo arrangement of the fourth carbon atom which is diametrically opposite in the two cases.

The work of Pryde, Levene and his associates, Haworth and his associates, Irvine, and others has shown that sugars possess a cyclic structure, and that the fourth and fifth carbon atoms are largely those involved in the ring formation. The different ring forms are considered as existing in equilibrium with each other in solution. In his review of "active glucose," Levene expressed the belief that the ring structures are of importance in the activity of sugar solutions. Decreased hydrogen-ion concentration might be considered, then, as causing a shift in the equilibrium from the 1–5 to the less stable 1–4 oxide ring structure in the case of the mannose-glucose series, and have the opposite effect on galactose, due to the fact that the stereo arrangements of the fourth carbon atoms are mirror images of each other in the two cases. However, it is to be remembered that the behavior of maltose and of lactose parallels that of glucose. The unions of the two hexoses present in each of these two disaccharides are made by way of the fourth carbon atom of the reducing hexose which would prevent the fourth carbon atom from entering into any oxide ring formation.

According to dissociation constants for glucose and mannose (Table I) the concentration of the ion precursor of the active form of mannose is nearly twice that for glucose under the same conditions of hydrogen-ion concentration and concentration of sugar. However, the rate of formation of the reducing form from mannose is but 64 per cent of that for glucose (Fig. 4), even though the concentrations of the precursors are in the ratio of approximately 1.7 to 1, respectively. From these relationships it would appear that the glucose ion or salt can rearrange or change to the reducing form 2.5 times more easily than can the mannose ion or salt. In this connection, it may be that the secondary effect of hydrogen-ion concentration mentioned previously is due to changes in hydrogen-ion concentration causing changes in the case of rearrangement of the precursor, or first active form, to the reducing form, and that this effect for galactose is diametrically opposite to that for the mannose-glucose series. This also may explain the peculiar shape of the curve for levulose, if one considers that according to Nef's general theory, levulose may rearrange directly to either the 1–2 or the 2–3 enediol form. The ease of rearrangement to either form of the enediols may each vary as some function of the hydrogen-ion concentration, to give the type of curve found experimentally (Fig. 4). The possibility of secondary and tertiary ionization of these various sugars must also be considered. The secondary effect of hydrogen-ion concentration may perhaps involve these dissociations of the sugars which may have their effect on the rates of formation of the active reductants.

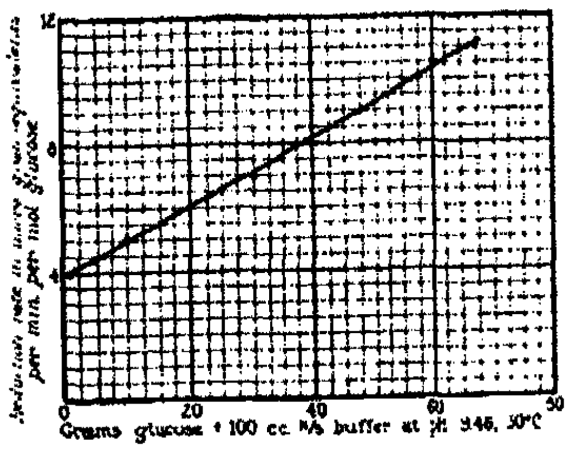

Fig. 5

The rate of formation of the active reductant of glucose is proportional to the concentration of glucose.

The presence of ferrous hydroxide does not increase the rate of formation of the active reductant from glucose. The concentration of iron used was the same as that found by Clifton and Ort to be adequate to cause rapid oxidation of the active reductant by molecular oxygen (0.000025 gm. equivalents in a solution of 60 gm. of glucose plus 100 c.c. buffer). In view of the results found by Spoehr and Smith, and by Palit and Dhar, this indicates that the catalytic action of sodium ferro-pyrophosphate, ferrous hydroxide, cerrous hydroxide, and so forth, on the oxidation of carbohydrates by molecular oxygen is due to catalysis of the reaction between the reductant and oxygen, and not due to an increase in the rate of formation of the reducing substance.

Fig. 5 shows the effect of concentration of glucose, expressed in terms of varying amounts of glucose added to a constant amount of buffer on the rate at which active reductant is formed for each gram mol of glucose present. The ratio of the rates for the highest and lowest concentrations studied (60 gm. and 1 gm., respectively, plus 100 c.c. buffer) is approximately 2.7 to 1. There seems to be no certain answer to the question of why this difference occurs. A probable explanation centers around an apparent or a real increase in the dissociation constant of glucose with increasing hydrogen-ion concentration.

The dissociation constant of a weak acid is represented by the following equation:

$$\frac{[H^+] \times [A^-]}{[HA]} = K$$

where $[H^+]$ is the hydrogen ion concentration, $[A^-]$ the anion concentration, and $[HA]$ the concentration of the undissociated acid. From this it follows that if K and $[H^+]$ are constant the rate of formation of the active reductant, assuming that the glucose ion A^- is its precursor, when calculated as rate per gram mol, should be independent of the concentration of the glucose solution. The increased rate of formation of the reducing form in the solutions of higher glucose concentration may be due either to actual increase in the dissociation constant (K) caused by the glucose changing the nature of the solvent, or an apparent increase in the dissociation constant may be due to the actual hydrogen-ion concentration being lower in the solutions of higher glucose concentration, even though the hydrogen electrode might indicate the two to be the same. A phenomenon of this type has been observed by Michaelis and Rona, who found that the addition of ethyl alcohol (which is considered as a very weak acid) to a solution of sodium hydroxide, in such a quantity as to make the solution 2 normal with respect to ethyl alcohol, did not decrease the hydroxyl-ion concentration, but they found, rather, an increase in the hydroxyl-ion concentration as measured by the hydrogen electrode. This apparent or real increase is equivalent to an increase of 7 per cent in the ionization product of water. Kendall also emphasizes the fact that the part played by the solvent in ionization cannot be ignored. The increase in the dissociation constant of glucose necessary to account for the 2.7 fold increase in the rate of formation of the active reductant over the range of concentrations studied would be represented by a change of from $10^{-12.17}$ to $10^{-11.74}$. Or, from a slightly different point of view, hydration of the sugar molecules which naturally proceeds further in more dilute solutions may produce a hydrated sugar molecule which is more difficult for the OH^- ions to attack. That is, hydrated glucose is a still weaker acid; its ionization constant is lower. The less hydrated molecule of the more concentrated solutions, therefore, would give more ions which probably are the precursors of the active reductant, and hence there is a faster rate of formation of this reductant.

Summary

The rate of formation of the active reductants formed in mildly alkaline aqueous sugar solutions has been determined for glucose, mannose, galactose, levulose, maltose and lactose under accurately controlled conditions of hydrogen-ion concentration and temperature. The effect of hydrogen-ion concentration on the rate of formation of the active reductant from each of the sugars named has been determined. It is represented by the equation:

$$\log V = 1.116 \text{ pH} + C,$$

for the mannose-glucose series, and

$$\log V = 0.86 + C,$$

for galactose.

This rate for glucose is higher than that found by Aubel and Genevois, or

$$\log V = 0.5 \text{ pH} + C.$$

We believe that under the conditions of their experiments the active reductant was not removed as fast as formed, and that consequently their rate is too low.

The relationship between the effect of hydrogen-ion concentration on the rate of formation of the active reductants from the various sugars studied and the dissociation constants of the respective sugars, indicates that the precursor from which the reducing substances are derived is the sugar ion. The effect of electrolytes on the rate of formation of the reducing substances as found experimentally is also in accordance with this view.

Besides the primary effect of hydrogen-ion concentration in regulating the concentration of the ions or salt of the sugar, there is a less pronounced secondary effect of hydrogen-ion concentration on the rate of formation of the reducing forms. This secondary effect of hydrogen-ion concentration on galactose is diametrically opposite to that found for glucose, mannose, maltose and lactose.

The rate of formation of the active reductant from glucose as affected by temperature was studied between 18° and 41° C. An increase in temperature of 22.5°C. increased the rate of formation approximately one-hundred-fold; that is,

$$\log V = 0.09T + C.$$

The equation of Aubel and Génevois was:

$$\log V = 0.06T + C.$$

The effect of concentration of glucose on the rate of formation of the active reductant was studied at concentrations ranging from 1 gm. of glucose to 60 gm. of glucose plus 100 c.c. of buffer. The rate of formation was found to increase approximately as a linear function of the concentration, the rate for each gram mol of glucose increasing 2.7 fold over this range of concentration. This phenomenon is believed to be due to gradual apparent or real increase in the dissociation constant of glucose with increasing concentration.

The rate of formation of the active reductant from glucose is not influenced by the presence of ferrous hydroxide.

The rates of formation of the active reductants as found experimentally in this research are believed to be measures of the rates of formation of the 1-2 enediol forms for the aldoses studied and both the 1-2 and 2-3 enediols in the case of levulose.

TABULATION

Sugar	Ionization constants $\times 10^{-13}$			Ratios of ionization constants Glucose = 1			Ratios of experimentally determined rates of formation of active reductants Glucose = 1
	A*	B**	C***	A*	B**	C***	
Glucose	6.6	6.0	6.8	1	1	1	1
Lactose	6.1	7.6	10.6	0.93	1.26	1.59	1.37
Maltose	18.0	8.5	12.2	2.73	1.42	1.80	2.04
Mannose	10.9		11.6	1.65		1.71	0.68
Galactose	5.2	4.3	4.3	0.79	0.72	0.65	
Levulose	9.0	8.6		1.36	1.43		

A* Michaelis and Rona, 18°C. (1913).
B** Stearn, 23°C. (1931).
C*** Authors, 30°C. (1931).

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THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY CADMIUM IODIDE

BY RALPH U. GOODING AND JAMES H. WALTON

The catalytic decomposition of hydrogen peroxide by soluble iodides was first studied systematically by Walton[1] who found that in neutral solutions of potassium iodide, sodium iodide and ammonium iodide the rate of decomposition of hydrogen peroxide is directly proportional to the concentration of the iodine ions present in the solution. This relationship may be quantitatively expressed as follows:

$$\frac{\text{velocity constant}}{\text{concentration of iodides} \times \text{degree of dissociation}} = 1.46$$

The degree of dissociation was determined from conductivity measurements. In the case of cadmium iodide the above expression gave a value of 1.91, which discrepancy was believed to be due to the complexity of the cadmium iodide molecules. In such a solution conductivity measurements would obviously give no data for iodine ion concentrations.

McBain,[2] who studied the properties of solutions of cadmium iodide, assumes very incomplete dissociation, and the presence of the complex anion CdI_3^- and the partially dissociated cation CdI^+ formed as follows:

$$CdI_2 \rightleftarrows Cd^{++} + 2I^-$$
$$CdI_2 \rightleftarrows CdI^+ + I^-$$
$$3CdI_2 \rightleftarrows Cd^{++} + 2CdI_3^-$$

Using the E.M.F. measurements of cadmium iodide in various concentrations in the cell

$$\begin{array}{c|c|c|c|c} Cd & CdI_2 & \text{KCl} & \text{KCl } Hg_2Cl_2 & Hg \\ & & \text{Sat.} & .1\text{N Solid} & \end{array}$$

McBain[3] determined the concentration of the Cd^{++} ions and from these data together with the E.M.F. measurements made by Getman[4] on the cell

$$Cd \mid CdI_2 \mid AgI \mid Ag$$

calculated the concentration of the iodine ions in the solution. Using the general formulation of migration of Laing and McBain[5] the concentrations of the complex cation CdI^+ and anion CdI_3^- were determined.

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[1] Walton: Z. physik. Chem., 47, 185 (1904).
[2] McBain: Z. Elektrochemie, 11, 215 (1905).
[3] McBain: J. Phys. Chem., 35, 999 (1931).
[4] Getman: J. Phys. Chem., 32, 940 (1928).
[5] Laing and McBain: J. Phys. Chem., 28, 673 (1924).

It was hoped that by using McBain's data[3] for the concentration of iodine ions in cadmium iodide solutions it would be possible to account for the difference in behavior between the catalytic action of cadmium iodide and the action of sodium, potassium and ammonium iodides on hydrogen peroxide.

Experimental

In order to obtain data for the concentrations used by McBain a series of measurements were made on the catalytic effect of various concentrations of cadmium iodide solutions on the decomposition of hydrogen peroxide. The hydrogen peroxide used was Merck's C.P. quality Superoxol which had been distilled from quartz under reduced pressure and preserved in quartz flasks. When the product thus purified was redistilled it gave results similar to that having but one distillation. In order to determine the effect of any volatile acids present on the rate of decomposition the distilled hydrogen peroxide was redistilled from barium carbonate. A sample of this hydrogen peroxide also showed the same rate of decomposition as that which had been distilled but once under reduced pressure. Merck's C.P. quality cadmium iodide, twice recrystallized from conductivity water, was used. Concentrations are expressed in mols of solute per liter of solution.

The rate of decomposition of hydrogen peroxide was determined by measuring the volumes of oxygen evolved in various time intervals. The reaction was carried out in a pyrex flask of 100 cc. capacity connected by glass capillary tubing to a 50 cc. burette. The method of adding the catalyst to the solution and the device used to shake the flask, and thus avoid supersaturation, have been described by Walton.[1] All measurements were made at 25°.

The rates of decomposition of hydrogen peroxide by cadmium iodide were determined for several concentrations. The constants (unimolecular) agree within 3 per cent. Table I summarizes the data obtained with different concentrations of cadmium iodide.

Table I

The decomposition of hydrogen peroxide by various concentrations of cadmium iodide

Mols CdI_2	K	Mols CdI_2	K
.005	.01045	.0643	.0611
.00643	.01287	.100	.0667
.010	.01785	.125	.0764
.020	.0295	.200	.0932
.02735	.0362	.250	.1079
.050	.0531	.500	.1642
.0547	.0535		

Although the decomposition of hydrogen peroxide by potassium iodide has been repeatedly measured, it was thought best to repeat these measurements, and to extend the concentrations of potassium iodide used. The data are summarized in Table II, columns one and four.

A. *The catalytic effect of the iodine ion*

The data obtained are shown in Table II, where the relation between the velocity constant and the concentration of iodine ions has been calculated. The values used for the dissociation of potassium iodide were taken from the International Critical Tables Vol. VI, page 235.

TABLE II

Relation between the speed of decomposition of hydrogen peroxide and iodine ion concentration

KI ($\Lambda_\infty = 149.8$)

Mols KI per liter	Λv	α	K	K/C_{I^-}
.005	144.2	96.3	.00725	1.50
.010	141.9	94.7	.01439	1.52
.020	139.1	92.9	.02920	1.57
.030	137.1	91.5	.04499	1.64
.050	134.1	89.5	.0718	1.60
.100	130.5	87.1	.1410	1.61
			Avg.	1.57

The average value in the last column differs from that determined by Walton[1] but agrees with that determined by Abel.[6] Walton found it to be 1.46 while the average of Abel's determinations give a value of 1.57.

From the data of McBain and the results of our experiments given in Tables I and II, it is now possible to determine whether or not the catalytic decomposition of hydrogen peroxide by cadmium iodide is directly proportional to the iodine ion concentration as in the case of the other iodides.

TABLE III

The composition of cadmium iodide solutions according to McBain and the catalytic decomposition of hydrogen peroxide by cadmium iodide solutions.

Mols CdI_2	I^-	CdI^+	CdI_3^-	K(Obs.)	K_{I^-}(Calc.)	K(Obs.)—K_{I^-}(Calc.)
.005	.0063	—	—	.01045	.00989	.00056
.010	.0103	.0029	—	.01785	.01617	.00168
.020	.0148	.0079	.0011	.0295	.0232	.00627
.050	.0228	.0196	.0064	.0530	.0358	.01728
.100	.0252	.0237	.0153	.0667	.0396	.0271
.200	.0285	.0359	.0350	.0932	.0447	.0485
.500	.0181	.0004	.1769	.1642	.0284	.1358

McBain's data for the concentration of the various ions in cadmium iodide solutions are given in the first four columns of Table III. To calculate the velocity of decomposition of the hydrogen peroxide by the iodine ion in a given

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[6] Abel: Z. Elektrochemie., 14, 598 (1908).

concentration of cadmium iodide it is simply necessary to multiply the iodine ion concentration by the value *1.57*. The results, listed in column 6, plainly do not agree with the observed velocity constants given in column 5. The fact that K observed is greater than K calculated shows that in the decomposition of hydrogen peroxide by cadmium iodide other factors beside the iodine ions are operating to decompose the peroxide. Other ions present in the solution which might act as catalysts in the reaction are Cd^{++}, CdI^+ and CdI_3^-.

In order to determine the effect of the Cd^{++} ion the rates of decomposition of hydrogen peroxide by solutions of cadmium iodide with the addition of various concentrations of Cd^{++} ions, in the form of cadmium chloride, were determined. The addition of .5 gram and 1 gram of cadmium chloride to a .10 molar solution of cadmium iodide had practically no effect on the rate of decomposition, the value K being .0649, .0641 and .0667 respectively for the three solutions, consequently the cadmium ions can be eliminated.

The effect of CdI^+ and CdI_3^- will now be considered. From McBain's data in Table III it will be seen that in 0.01 molar cadmium iodide, iodine ions and CdI^+ ions are present while the concentration of 0.5 molar cadmium iodide contains iodine ions and CdI_3^- ions, with a negligible concentration of CdI^+ ions. Since the catalytic effect of the iodine ion is known it is possible to calculate the effect of the CdI^+ ion for the .01 molar solution. This gives a value of .58 for the effect of the CdI^+ ion. Similarly the effect of the CdI_3^- ion, calculated from the data for a 0.5 molar solution, gives .77 for the effect of that ion, a value very close to one half that for the iodine ion. Using these values it is now possible to calculate the catalytic effect of each ion in the various solutions of cadmium iodide. The data are given in columns 4 and 5 of Table IV. The assumption that the catalytic effect of these ions is directly proportional to the concentration of each ion is seen to be justified. The sum of the values in columns 4 and 5, listed in column 6, which give the combined effects of CdI^+ and CdI_3^- show a very good agreement with the data in column 7.

TABLE IV

The catalytic effect of CdI^+ and CdI_3^- ions

Mols CdI_2	CdI^+	CdI_3^-	K_{CdI^+}	$K_{CdI_3^-}$	Calc. $K_{CdI^+}+K_{CdI_3^-}$	Obs. $K_{CdI^+}+K_{CdI_3^-}$
.010	.0029	—	.00168	—		
.020	.0079	.0011	.00458	.00085	.00543	.00627
.050	.0196	.0064	.01137	.00493	.0163	.0173
.100	.0237	.0153	.01375	.01178	.0255	.0271
.200	.0359	.0350	.02695	.02695	.0477	.0485
.500	.0004	.1769				

These data, therefore, substantiate the work of McBain in that the concentration of each ion he postulates as being present in solutions of cadmium iodide agrees with its catalytic decomposition of hydrogen peroxide. Each specific ion has a definite rate of catalytic action and the remarkable agreement between the concentration of each type of ion in solution, as calculated by McBain from conductance measurements and transport numbers, with the results of the present study can not be attributed to chance. While it has not been proven that the ions present are those postulated by McBain, nevertheless, it has been shown that the effect of the ions in this decomposition can be attributed to the same ions which influence conductance and transference.

B. *The effect of the addition of iodine to solutions of cadmium iodide*

The influence of the addition of iodine on the catalysis of hydrogen peroxide by potassium iodide has been determined by Walton.[1] He found that as the concentration of iodine increased the rate of decomposition decreased. This effect was explained on the theory that potassium iodide is practically completely dissociated and with the addition of iodine, I_3^- ions are formed.

$$K^+ + I^- + I_2 = K^+ + I_3^-$$

The I_3^- ions were found to have practically no effect on the decomposition of hydrogen peroxide. This effect was quantitative since the number of mols of potassium iodide in a solution could be calculated by kinetic measurements as well as by the method of Jakowkin.[7]

Experiments were performed to determine the effect on the decomposition of hydrogen peroxide of solutions of cadmium iodide to which iodine had been added. These results are recorded in Table V.

TABLE V

The decomposition of hydrogen peroxide by solutions of cadmium iodide containing various concentrations of iodine

Mols CdI_2	Mols I_2	K	Mols CdI_2	Mols I_2	K
.01	.0000	.01785	.250	.0000	.1079
.01	.0045	.01316	.250	.00338	.1024
.01	.0075	.01125	.250	.02040	.1051
			.250	.03624	.1035
.125	.0000	.0763			
.125	.015	.0765			
.125	.025	.0740			

These data, Table V, indicate that in solutions of cadmium iodide the addition of iodine has a greater effect on the rate of decomposition of hydrogen peroxide in dilute solutions than it does in concentrated solutions. The velocity constant decreases from .01785, for a solution of .01 molar cadmium iodide to .01316 for a solution of the same concentration of cadmium iodide to which .0045 mol of iodine has been added. In contrast to this, for a .25 molar solution of cadmium iodide the velocity constant is .1079 as compared to .1024 for the same concentration of cadmium iodide to which 0.00338 mol of iodine has been added and .1035 for .03624 mol of iodine added.

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[7] Jakowkin: Z. physik. Chem., 20, 19 (1896).

Bruns[8] has shown that when iodine is added to solutions of cadmium iodide the conductance of the solution is increased. According to his theory this increase is due to the shift in equilibrium between the associated molecules and the simple molecules of cadmium iodide according to the following equation:

$$(CdI_2)_n \rightleftarrows nCdI_2 \rightleftarrows nCd^{++} + 2nI^-$$

This explanation agrees with our results since in a dilute solution there are practically no associated molecules while in a concentrated solution there is a considerable percentage of them. When iodine is added to a dilute solution of cadmium iodide I_3^- ions are formed. When, however, the iodine is added to concentrated solutions, as the I_3^- ions are formed the complex molecules are broken down into simple molecules which can in turn dissociate to give iodine ions.

These results also agree with the work of Van Name and Brown[9] on the distribution of iodine between aqueous solutions of cadmium iodide and carbon bisulfide.

Summary

(1) In the catalytic action of cadmium iodide the Cd^{++} ions have been shown to be without appreciable catalytic effect on the hydrogen peroxide. The active agents in the catalytic decomposition of hydrogen peroxide are I^- ions and the CdI^+ ions and CdI_3^- ions, postulated by McBain. CdI_3^- ions decompose hydrogen peroxide at a rate which is nearly 50% that of the iodine ions. In each case the velocity of decomposition is directly proportional to the concentration of the active ions.

(2) The ionic complexity of cadmium iodide solutions, as determined quantitatively by McBain, has been confirmed by kinetic measurements.

(3) The effect on the decomposition of hydrogen peroxide of solutions of cadmium iodide to which various concentrations of iodine have been added has been determined. The addition of iodine to dilute solutions of cadmium iodide showed large decreases in the velocity constants. The addition of iodine to concentrated solutions of cadmium iodide showed very small decreases in the velocity constants.

Madison, Wisconsin.

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[8] Bruns: Z. Physik, **34**, 751 (1925).

[9] Van Name and Brown: Am. J. Sci., **44**, 105 (1907).

RHYTHMIC SPLITTING OF SILICIC ACID GELS[1]

BY EARL C. H. DAVIES

Introduction.—For several years the author has been interested in the structure of gels, especially that of silicic acid gels. It had been observed that during syneresis they frequently split in planes at about a 45° angle to the axis of the tube. During August of 1930 a few experiments were carried out in different shaped flasks, but no definite conclusions were reached. In April of 1931 my attention was called[2] to a 50 cm length of ordinary glass tubing which had apparently been used for stirring a silicic acid gel mixture, and had been put away full of it. The gel had split in rhythmic waves whose cause seemed worthy of investigation.

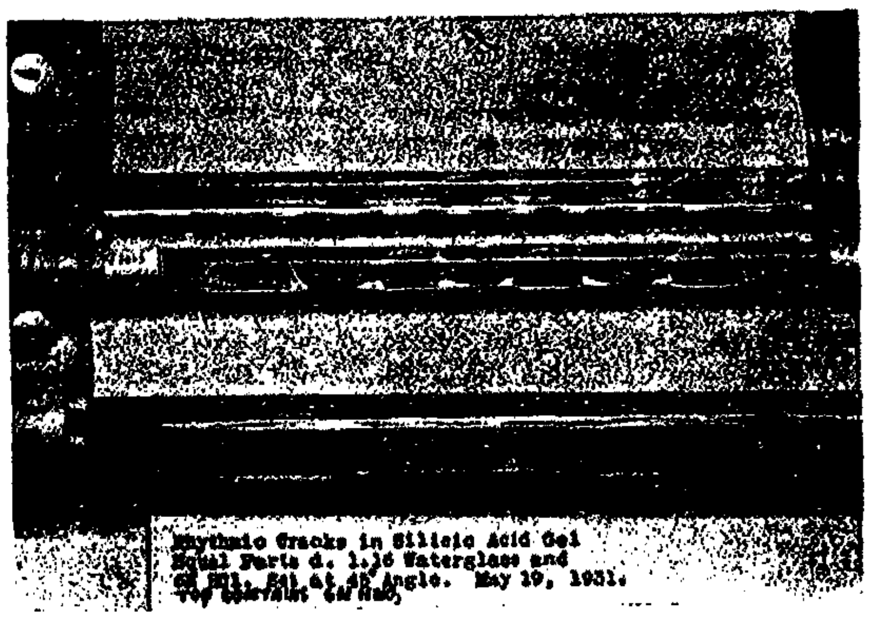

Fig. 1
(Photo by Fred. A. Bisceglia)

Appearance of Rhythmic Splits.—In general shape a rhythmic split (Fig. 1) resembles a sine wave curve, but the waves are about 1.5 times as long as those of a true sine curve. In the large tubes, especially those with diameters of more than about 7 cm, splitting is rapid and the split is filled with water solution resulting from syneresis. When the tube is open at both ends this liquid may be poured out or it may be permitted to slowly evaporate. In either case drying then continues until the wave segments are entirely separated from each other, and finally the gel shrinks and may disintegrate. For smaller tubes splitting is similar, except that in them there is less tendency for the appearance in the split of any solution, and splitting is not so rapid. When first formed, especially in the larger tubes, the cross section of a split

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[1] Presented in September, 1931, at Buffalo, before the Colloid Division of the American Chemical Society.

[2] By Joe H. Balthis, Jr., in this laboratory.

seems to be nearly if not entirely flat, before drying removes some of the water. During drying the curvature of the cross section steadily increases in such a way that it is convex toward the wall it is leaving and concave toward the wall it is approaching.

Three Types of Splitting of Silicic Acid Gels.—Splitting of a silicic acid gel in a tube begins at the open end and progresses toward the closed end. It may take place in one of three ways.

1. The gel may split away from the wall (Fig. 3, left), producing a cylinder which gradually shrinks and in some cases (such as HCl-silicic acid gels) disintegrates. This form of split is quite common for vertical tubes, especially when they are fairly large.

2. The gel may split straight, along the center of the tube, whenever the split starts along a line coinciding with a diameter of the tube. Generally such a split will be a little off center, will be pulled toward the side of the tube and then begin to split rhythmically.

3. The gel will split rhythmically whenever setting and syneresis is accompanied by sufficient contraction to cause any splitting, and providing the initial splitting occurs along some line not coinciding with the inside circumference of the tube or one of its diameters. Rhythmic splitting is general whenever the gel is allowed to set in other than a vertical position, because the split starts at the top off center due to the lack of symmetry of the meniscus. Even with a circular meniscus rhythmic splitting will result if an off-center crack be started with a sharp point or blade.

Experimental

Experiments were carried out with the following objectives.

1. *Acids used for Rhythmic Splitting.*—Since the accidentally discovered rhythmic splits had been produced in a gel of uncertain composition, preliminary experiments were carried out with gels made from d. 1.16 water glass and equal volumes of five different acids varying in strength from 3N to 12N. It was found that rhythmic splitting was obtained with the following acids: hydrochloric, sulfuric, nitric, citric, and acetic. However, acetic was not so good as the others. From standpoint of stability, and uniformity of results sulfuric acid proved best. The gels made with nitric acid were entirely satisfactory in the smaller tubes, but gave some irregularities in the larger ones. The chief trouble with the gels made with hydrochloric acid is that on standing they readily disintegrate, especially at the higher temperatures, giving long, hair-like crystals over the entire gel surface. Citric acid gels are sometimes fairly satisfactory. Each gel consisted of equal parts of the acid and a d. 1.16 commercial water glass. The latter was Philadelphia Quartz Co. "E Brand," except for the HCl gels, which were made with "Rutland" water glass.

Some of these preliminary results are given[3] in Table I.

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[3] This set of gels was prepared and preliminary measurements made by W. N. Dunn, S. R. Brownstein and F. H. Crago. The measurements given here are those made by the author.

TABLE I

Wave Lengths of Splits in Silicic Acid Gels at 38.5°C and at an Angle of 57°

	Diameter average in mm D	Acid in gel	Number of waves counted	Average length each wave in mm L	L/D
	6.966	12 N HCl	5	31.35	4.500
	5.624	12 N H_2SO_4	4	30.9	5.497
	4.781	12 N HAc	1	25.0	5.221
Average			3.3	29.08	5.073
	5.881	6N HCl	13	27.52	4.680
	7.241	6N H_2SO_4	2	34.4	4.764
	5.678	6N HNO_3	9	25.55	4.502
	5.612	6N HAc	5	23.8	4.243
Average	6.103		29	27.82	4.549
	4.947	3N H_2SO_4	1	25.0	5.058
	5.896	3N HNO_3	2	26.5	4.495
	5.890	3N Citric	2	35.0	5.940
Average	5.578		5	28.8	5.164

They show that a wide range of acids may be used to give rhythmic splits. Measurements of tube diameters were made across two diameters at right angles to each other, with a Gaertner micrometer microscope on a sliding stage and giving readings to 0.001 mm. The wave lengths were read to 0.1 mm. Therefore, all readings are quite exact, but still it would be necessary to make many more determinations before one could definitely arrange these acids in order of decreasing wave lengths for the splitting of their silicic acid gels. This has been done for: 6N HCl, 6N H_2SO_4, 6N HNO_3, and 3N HCl.

Beside preliminary experiments, a final run (Table III) was made simultaneously with 50 tubes of gel prepared from each of these acids. The order of decreasing wave lengths of the rhythmic splits in tubes of 3.58 mm diameter is 6N HNO_3 (5.045) > 6N HCl (4.821) > 6N H_2SO_4 (4.631) > 3N HCl (4.567). The values in parentheses are for $\frac{\text{wave length}}{\text{diameter of tubes}}$.

2. *The Influence of Angle of Setting on Rhythmic Splits.*—Since the accidentally discovered rhythmic splits had been produced in a gel contained in a horizontal tube, and since good rhythmic splits have escaped general notice, it seemed possible that the position of the tube during setting might be found important. It is seldom that a tube of gel is allowed to set at other than a vertical position.

Hence, preliminary experiments were carried out with tubes at different angles ranging from horizontal to vertical. These preliminary results are given in Table[4] II. All the tube diameters were measured with the Gaertner micrometer, across two diameters at each end of each tube. The clean tubes were then nearly filled with the gel mixture made from equal parts of the acid and d. 1.16 water glass (Philadelphia Quartz Co. "E Brand"), and closed at one end with a clean rubber tubing and glass rod. Each tube was placed at a definite angle and the gel allowed to set and remain at that angle until splitting had progressed about 30 cm, to the bottom of the tube. Tubes were also run with both ends open (after setting) and with both ends closed. Good rhythmic splits resulted only when the tube was open.

TABLE II

Influence of Angle of Setting and Temperature on Rhythmic Splitting of Silicic Acid Gels (L = wave length, D = diameter of tube in mm)

Angle of setting	L/D for 6N HCl		L/D for 6N H_2SO_4 at 59.4°C	L/D for 6N HNO_3		L/D for 6N Citric 25°C	L/D for 3N HCl 59.4°C	L/D averages	
	at 25°C	at 59.4°C		25°C	59.4°C			at 25°C	59.4°C
0°	4.760	3.819	4.502	4.840	4.336	4.880	none good	4.824	4.219
21°	5.202			5.161		4.837		5.067	
42°	5.402	5.184	4.080	5.006	4.750	4.929	4.275	5.079	4.572
49°		4.813	3.850		4.616		4.507		4.447
57°	5.180			4.980		4.820		4.991	
71°		4.581	3.910		4.612		4.115		4.305
90°	5.524	4.492	4.073	4.658	4.210	4.779	4.205	4.987	4.245
Averages	5.210	4.578	4.083	4.929	4.505	4.829	4.276	4.990	4.360
Average diameter in mm	3.537	6.035	5.949	3.567	5.746	3.552	6.039	3.654	5.942
Number of waves measured	48	29	32	29	42	18	22	95	125
Average length of top wave		28.5	21.6		24.7		24.5	Grand average for top wave at 59.4°C was 23.8 mm	
Average length of bottom wave		28.2	27.0		25.9		28.6	Grand average for bottom wave at 59.4°C was 27.4 mm	

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[4] This set of gels was prepared by E. I. Silk and R. E. Walker. Measurements given are by the author.

Another series of experiments was run by the author with gels similarly made, but at 59.4°C (also in Table II). In this case the tubing was Pyrex, cut in 24 cm lengths, and had two diameters measured with the Gaertner micrometer at each end of each tube. Tubes were filled as before and put at different angles in a Freas electric oven. It was found that such a high temperature was not very satisfactory, especially for gels made with the hydrochloric acid. The averages for 6N HCl, 6N H_2SO_4, and 6N HNO_3 are given in the last column of Table II.

In order to more definitely establish the relationship between angle of setting and wave lengths of rhythmic splits in silicic acid gels a giant run was made using 4 different acids at 5 different angles and at two different temperatures. The acids were 6N HCl, 6N H_2SO_4, 6N HNO_3, and 3N HCl. Angles were 0° (horizontal), 37°, 43°, 70°, and 90° (vertical). Temperatures were 37.8°C ± 1°C and 27.8– 31.8°C. The latter was room temperature as recorded by a maximum-minimum thermomemeter placed near the gels. From the same batch of tubing 20 were selected. They were 155 cm long and all had about the same diameter of 3.6 cm. The exact diameter was obtained from the average length and weight of an approximately 20 cm column of mercury, as measured near each end of each five foot length. Each length was then cut up into 10 equal pieces of 15 cm each and every other section put in one pile. Thus, each five foot length gave two sets of five tubes whose average diameter was taken as that of the uncut tubing. In every case one of these sets of five was used for a given gel at oven temperature, while the other paired set of five tubes was used for room temperature, both sets being placed at the same angle. Similarly, other paired sets of five tubes each were tried at each of four other angles.

In making the actual run, the paired sets of tubes were tied together with rubber bands, thoroughly cleaned with cleaning mixture, washed with plenty of water, and allowed to dry. Each tube was fitted with a short length of pure rubber tubing. Thus, for each of 4 gel mixtures there were 5 bundles of 10 tubes each, and each bundle was further separated by a rubber band into 2 equal bundles of 5 tubes each. A tall, narrow beaker was found, such that when the bundles of tubes were placed into it with rubber ends up, the top of the beaker came to about the height of the glass tubes.

The respective gel mixture was then prepared by stirring d. 1.16 water glass (Philadelphia Quartz Co. "E Brand") into an equal volume of the acid and poured around the tubes contained in the tall beaker. Thus, the tubes filled simultaneously and uniformly. Glass rods, previously provided, were quickly inserted into the rubber, the bundles removed, inverted, and washed with water on the outside, care being taken to have no water enter the open ends. Vigorous jolting brought air bubbles to the top and left a good meniscus in each tube. Every bundle of five tubes was quickly placed at the desired angle in boxes provided for that purpose, and was not further touched until removed to make the readings recorded in Table III.

Experiments carried out at temperatures of about 25°C (Table II), 37.8°C (Table III), and 59.4°C (Table II), and at angles ranging from horizontal to vertical, show that for ordinary temperatures the wave lengths of the rhythmic split in a silicic acid gel is nearly the same for all angles of setting. But, especially for the larger tubes, the angle of setting is important in determining whether the split will be circular along the wall, a straight center split, or a rhythmic split. Averages for 30°C and 37.8°C, for 40 tubes of 3.580 mm diameter and containing gel made from equal parts of d. 1.16 water glass (Philadelphia Quartz Co. "E Brand") and either 6N HCl, 6N H_2SO_4, 6N HNO_3, or 3N HCl, showed the following wave length for each angle: at 0° angle 17.02 mm, at 37° angle 16.97 mm, at 43° angle 17.14 mm, at 70° angle 17.03 mm, and at 90° angle 17.01 mm.

TABLE III

Influence on Rhythmic Splits of: Angle of Setting, Temperature, and Composition of Gel (Average D = 3.580 mm)

	Average L/D for 4 gels		Average for all Angles for Respective Gels			Total Length of Splits After 5 Days	
Angle	At 30°C	At 37.8°C	Gel Contains	L/D At 30°C	L/D At 37.8°C	At 30°C	At 37.8°C
0°	4.79	4.72	6N HNO_3	4.99	5.13	71 mm	125 mm
37	4.78	4.70	6N HCl	4.92	4.72	117	133
43	4.71	4.87	6N H_2SO_4	4.62	4.65	62	99
70	4.78	4.74	3N HCl	4.52	4.55	54	84
90	4.76	4.79					
Grand Averages	4.76	4.76		4.76	4.76	76	110

3. *The Influence of Tube Diameter on the Wave Lengths of the Rhythmic Splits in Silicic Acid Gels.*—Since the accidentally discovered rhythmic splits had been produced in a relatively small tube it seemed desirable to see how these wave lengths would vary with the diameter of the tube. Preliminary results (Table I) showed that the wave lengths of the splits varied directly with the tube diameters. This is also readily seen in Fig. 1 and was qualitatively demonstrated by allowing a silicic acid gel to set in tubes drawn into cone shapes.

In order to definitely establish the relationship between the wave length of the rhythmic split and the tube diameter, experiments were carried out in an electric Freas oven at an average temperature of 37.8°C ± 1°C. Two runs were made with a total of 51 tubes, ranging in diameter from 0.338 mm to 15.516 mm and about 30 cm in length. The four gels were made, with d. 1.16 water glass and equal volumes of the respective acid, including 6N HCl, 6N H_2SO_4, 6N HNO_3, and 3N HCl. At the density used the "E Brand" (Philadelphia Quartz Co.) had a normality of 1.479, using phenolphthalein as indicator. According to the manufacturer "E Brand" is specially clarified and has about the composition 29.0% SiO_2, 8.9% Na_2O, 62.1% H_2O, and d. 41° Baumé (1.394 in C. G. S.).

In each run tubes were so selected that for each diameter used there would be four tubes of nearly the same diameter, and generally cut from the same piece of tubing. Each one of these 4 tubes was used for one of the 4 kinds of gel, so that each result given in Table IV is an average for the 4 kinds of gel. Every tube was measured across two diameters, at each end, using the Gaertner micrometer. The diameter given in column 1 is the average for 4 tubes. The capillary tubes, of less than 1 mm diameter, were made by drawing out larger tubing, and their diameters were measured after the gel had split. The capillary tubes were broken at each end of the zone containing the waves to be measured, and averages for the two ends taken as the diameters. All these gels were set at a 43° angle to the horizontal, and allowed to remain in the oven without further disturbance until final readings were made. One set remained for 9 days, the other for 12 days.

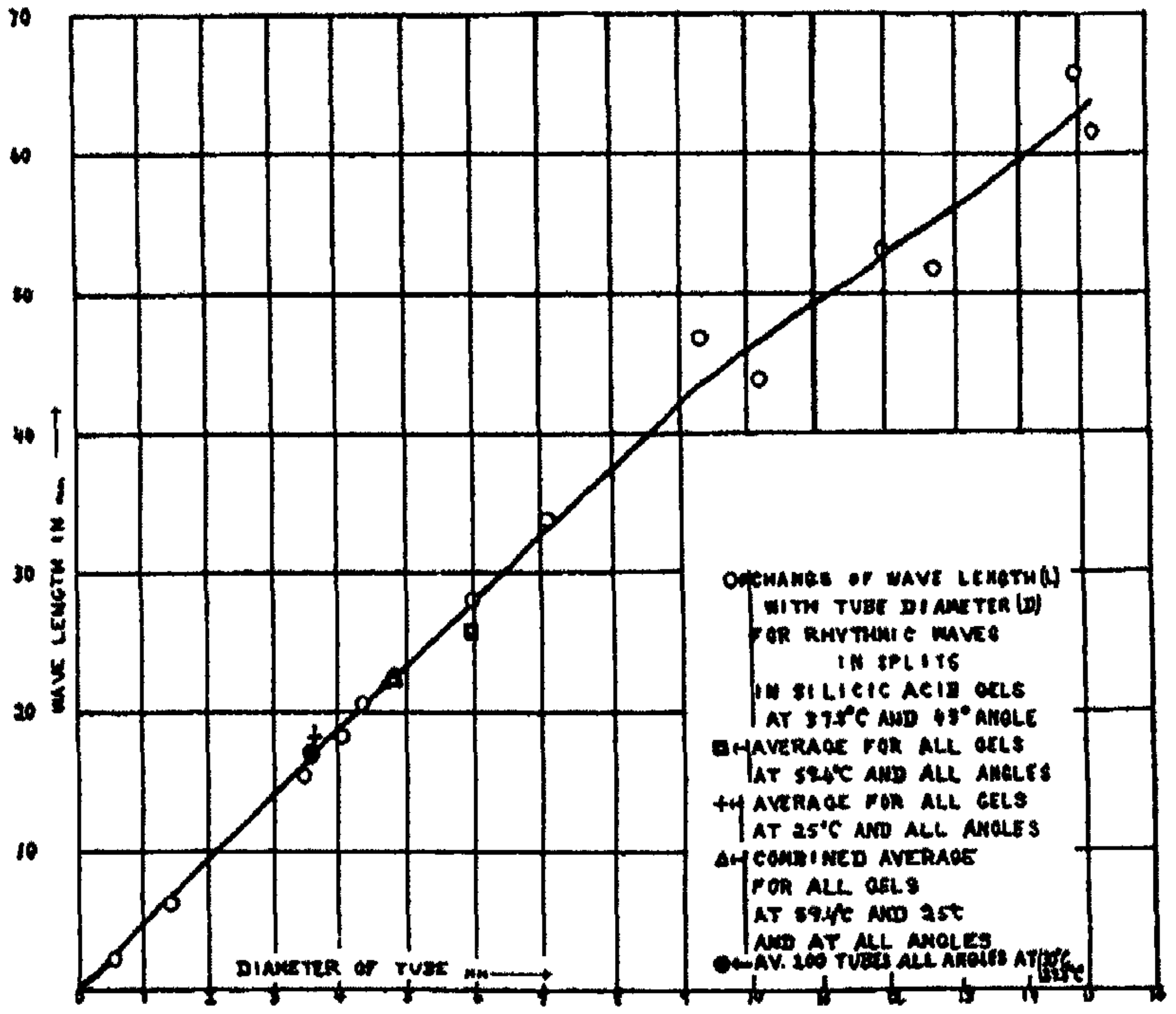

Fig. 2

In addition to obtaining the average wave length (L) for each tube of diameter D, measurements were made of the distance to which splitting had progressed. It will be observed that with the 9 day gels the larger tubes still contained some solution at the bottom ends of the splits (column 3), while there was no solution visible in the splits of tubes smaller than about 6 mm diameter. In column 5 is given the average lengths of the first good waves at the top of the gels, while column 6 contains the average lengths of waves farther down, at the average distances shown in column 7. It will be observed that, except in the larger tubes, there is very little change in wave length with depth. This is in contrast with gels run at 59.4°C, where the average length of top waves was 23.8 mm, while that for the bottom waves was 27.4 mm. In the last column is given $\frac{\text{wave length}}{\text{tube diameter}}$. The average wave length for the 4 gels at each of the 13 average diameters is plotted in Fig. 2, where the curve is based solely upon the results recorded in Table IV. However, on this same graph has been shown: the average (Table II) for all gels at 59.4°C (□) and all angles, the average (Table II) for all gels at 59.4°C (+) and all angles, the combined average (Table II) for all gels at 25°C and 25°C (△) and at all angles, and the average (Table III) for 200 tubes at 30°C or 37.8°C (●) and at all angles between the horizontal and vertical positions.

TABLE IV

Average Wave Lengths of Rhythmic Splits in 4 Silicic Acid Gels at 37.8° C and 43° Angle

Diameter Average in mm	Total Lengths of Splits mm		Time Days	Variation of Wave Length With Distance From Top			Average Length Each Wave (L) mm	L/D
	Air Filled	Solution Filled		L at top	L at	distance from top of		
4.378	143.9	none	9	20.7	20.6	109 mm	20.70	4.729
5.969	178.7	4	9	28.3	28.9	122	28.11	4.711
9.314	185.6	76.9+	9	43.8	43.8	147	46.90	4.676
11.967	169	92	9	55.0	53.8	89	53.05	4.439
14.97	147	136	9	62.7	67.1	113	65.73	4.395
0.507			12				2.256	4.491
1.416	148.9	none	12				6.241	4.396
3.440	180.5	"	12				15.50	4.521
4.053	190.0	"	12				18.26	4.505
7.077	203+		12				33.82	4.777
10.195	181.4	12+	12				43.84	4.299
12.673	182	74+	12				51.74	4.416
15.218	185	62+	12				61.52	3.998

Influence of Temperature on the Wave Lengths of Rhythmic Splits in Silicic Acid Gels.—Experiments carried out at temperatures of about 25°C, 30°C, 37.8°C, and 59.4°C, and at angles ranging from horizontal to vertical, show that for ordinary temperatures the decrease of wave length with increase of temperature will be slight and for most purposes negligible. At 30°C (Table III) in 100 tubes of average diameter 3.58 mm the average wave length was 17.04 mm, while at 37.8°C in 100 paired tubes of exactly the same diameter the average wave length of the same gels was 16.99 mm. Based upon the less comprehensive results (Table II) for gels made from 6N HCl and 6N HNO_3, in different diameter tubes, but figured for tubes of this same diameter, wave lengths would be 18.15 at about 25°C and 16.28 mm at 59.4°C. These latter results may not be compared with those at 30°C and 37.8°C because they involve only 2 of the 4 gels, but they do show that for a large increase of temperature there is an appreciable decrease in wave length of the rhythmic split.

Influence of Tube Wall on Rhythmic Splits in Silicic Acid Gels.—In order to study the influence of the tube wall on rhythmic splits, 6NHCl – d. 1.16 water glass was used. All tubes were cleaned with chromic acid cleaning mixture and thoroughly washed. Some were then allowed to dry in air, while others were dried with alcohol and ether. One of the latter tubes was wet inside with Nujol (a heavy, pure, paraffin oil), another with a dilute solution (about 0.01%) of abietic acid in ether, and another tube was left in the dry condition. These 5 foot tubes, nearly 5 mm in diameter, were then filled with the gel mixture and allowed to lie in the horizontal position for several weeks. It was found that all the tubes gave similar rhythmic splits, except that in the tube wet with Nujol splitting was very greatly delayed, perhaps due to slower evaporation, and was not very regular. These experiments showed that for good, rhythmic splits it is essential that the gel adheres well to the walls, but that otherwise there is probably no connection between the composition of the walls and the formation of rhythmic splits. This is also borne out by the fact that tubes of Pyrex and of other softer glasses seem to give rhythmic splits equally well.

Rate of Formation of Rhythmic Splits in Silicic Acid Gels.—Using a microscope with polarizing condenser and micrometer eyepiece I watched and, with a stopwatch, timed the splitting in a 3N HCl – d. 1.16 water glass gel. The tube was of Pyrex, of about 4 mm diameter, at 28°C, and the splitting was occurring 38 mm from the end of the tube. The rate was 0.0148 mm per minute, 0.888 mm per hour, or 21.31 mm per day. After heating to about 55°C the rate of splitting increased to 0.0789 mm per minute, or 113.6 mm per day. At the higher temperature a preliminary, solution filled split, preceded the air filled crack, while at the lower temperature splitting and drying were apparently taking place at the same rate.

At 30°C (Table III) in tubes of 3.58 mm diameter, during 5 days, gels made from d. 1.16 water glass and equal volumes of the following acids split to the distance shown below:

6N HCl 116.6 mm, 6N HNO_3 70.7 mm, 6N H_2SO_4 61.5 mm, 3N HCl 53.8 mm.

The corresponding distances for 37.8°C were:

6N HCl 133.3 mm, 6N HNO_3 124.9 mm, 6N H_2SO_4 98.5 mm, 3N HCl 83.6 mm. These results not only show that the rate of splitting increases with temperature, but also that it varies greatly with the acid used in making the gel.

Also at 37.8°C and with the same 4 gels but in tubes of different diameters (Table IV) it was found that gels split faster in large than in small tubes, due principally to the fact that in tubes of more than about 6 mm diameter the air filled split is preceded by a solution filled split, whereas in the smaller tubes splitting and evaporation seem to be occurring at the same rate. At room temperature a 6N HCl — d. 1.16 water glass gel in tubes of 7.718 mm and 12.330 mm diameter, in horizontal position, split 150 cm, the entire length of the tubes, in less than 1 day, while in smaller tubes of 4.2 mm diameter it split from 18 to 32 cm in 25 days.

Laboratory Directions for Demonstration of Rhythmic Splitting in Silicic Acid Gels.—Use about 20 cm lengths of ordinary glass tubing such as used for connections. Clean, dry, and nearly fill them with a gel mixture made by stirring 6N H_2SO_4 into an equal volume of d. 1.16 water glass. After filling, close each tube at one end with a rubber tube and glass rod. Jar the tube until any air bubbles come to the top, leaving a good meniscus. Put away open and at about a 45° angle. Observe over a period of 2 weeks.

Results for Gelatin Gels.—Short lengths of ordinary glass tubes were filled[6] with 5%, 10%, 15%, and 20% gelatin, and the tubes allowed to remain for about 2 months in an electric refrigerator, at an angle of about 14° to the horizontal position. All the tubes were open, and part of them were in a dessicator over P_2O_5 which was renewed at the end of 2 weeks. In the latter tubes there was some tendency for the formation of rhythmic splits, but it was very slow and not at all satisfactory.

Theoretical Explanation of Rhythmic Splitting in Silicic Acid Gels.—For a true sine curve $L_s = 2\pi r$,

where L_s is the wave length, and r is the radius of curvature. For the case of rhythmic splits in cylindrical tubes, r would be the radius of the tube. Hence, for a true sine wave split we would have

$$L_s = 2\pi r = \pi D = 3.1416\ D = C,$$

where D is the diameter of the tube, and C is its inside circumference

Experimentally, for good rhythmic splits in tubes of 3.58 mm diameter, for the 4 gels studied, and at 37.8°C (Table IV)

$$L_o = 4.76\ D,$$

where L_o is the observed length of a rhythmic split, and D is the diameter of the tube. Therefore, it follows that

$$\frac{L_o}{D} \div \frac{L_s}{D} = \frac{4.76}{3.142} = 1.514.$$

Thus, at ordinary temperatures the observed wave length of the rhythmic split in the usual silicic acid gel is about 1.5 times that of a true sine curve. For large tubes this value becomes about 1.4. Its exact value will vary with the composition of the gel and to some extent will depend upon the temperature. This stretching out of the waves is due to the effect of the longitudinal pull superimposed upon that from each of the two walls adjacent and opposite to the split.

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[6] By Guss Hall and W. H. Carr.

In Fig. 3 I have made a scale drawing, of a 6N H_2SO_4 – d. 1.16 water glass gel, which had been in a Pyrex tube of 11.93 mm diameter, at a 43° angle and at 37.8° C for 9 days. It is evident that B is the high point of the gel, and, therefore, the place which would first dry and crack. The split went directly beneath the meniscus toward E and along the tube wall toward H. As syneresis, accompanied by contraction progresses, it is evident that the gel would be pulled away from the wall BH. Consider the split at any point C, nearer to wall BH than to EF. It is apparent that the pull at C will be very nearly proportional to the area of the triangle ECF, where CF is tangent to the curve of splitting at C. On the opposite side of the split, at I, the pull will be due to gel at the right of a line tangent to the curve at I. Next, consider the split when it has reached D. The pull toward the left will now be proportional to the area of the triangle EDG, which is relatively small, while the pull of the contracting gel on the opposite side of D will be relatively large. Thus, the triangle on the left gets smaller until the split has reached the point K, nearest the wall. After passing K the conditions will be similar to those at C, except that the pull toward the left will be toward wall HL, and will, after passing K, be at once relatively large, becoming less and less until the split has reached the opposite wall. Thus, the split progresses wave after wave.

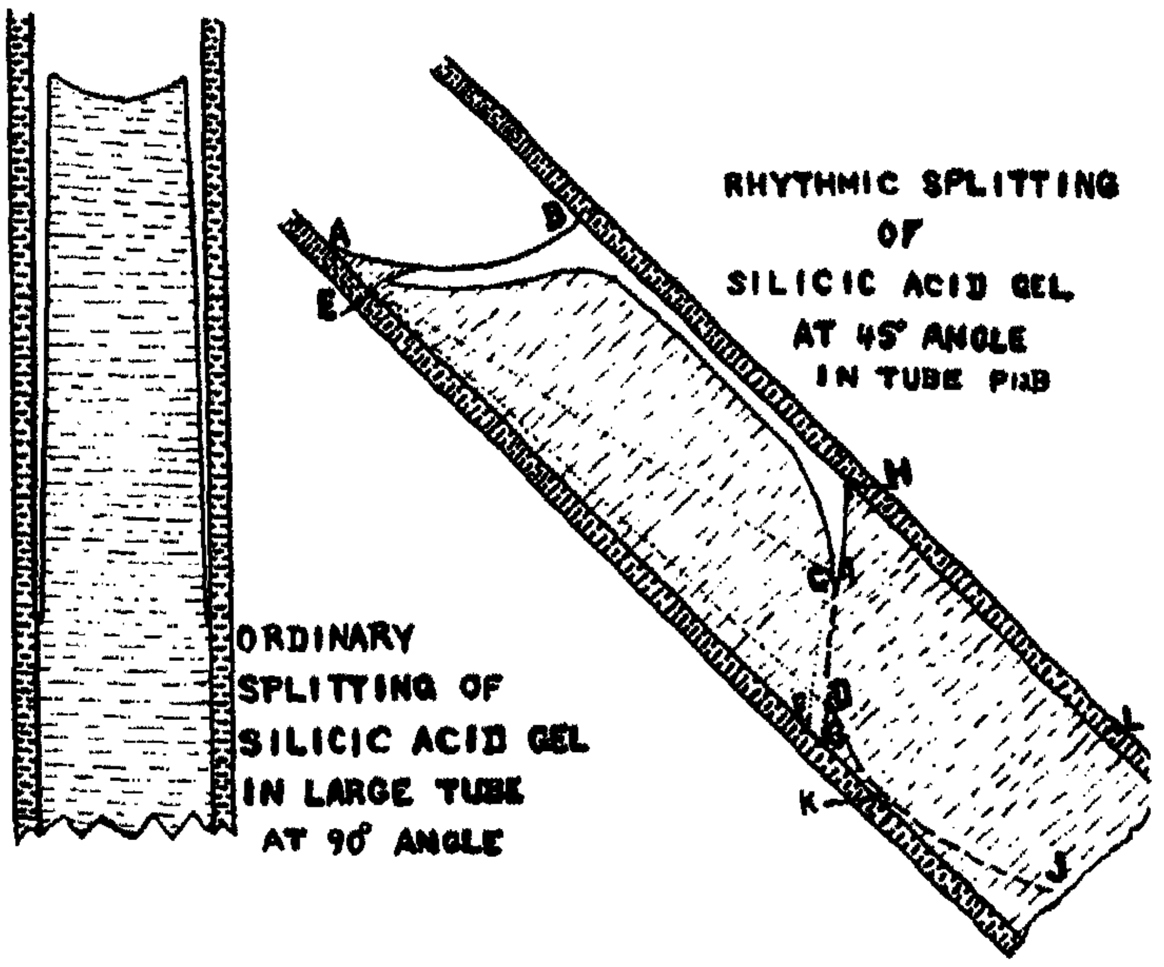

Fig. 3

When, during syneresis, a gel splits away from the wall (Fig. 3, left) it is simply because the split starts symmetrically at the top edge of the meniscus, due to the symmetrical cup shape of the latter, resulting in the top edge drying first. As the gel contracts the pull at the split is uniformly down and in-ward, so that there are no opposing forces to cause rhythmic splitting. With a 6N HCl — d. 1.16 water glass gel I have shown, by a series of experiments in test tubes, that this is a normal split for such a gel in a vertical tube of reasonably wide diameter. However, rhythmic splitting resulted whenever the gel meniscus was pricked with a needle or sharp blade. These holes were made about two hours after the gel mixture had been made. Theoretically, it should be possible to artificially make a hole or split in the exact center of the meniscus in such a way that the split would go down the center of the gel, but it is rather difficult to artificially make such a split.

However, center splits are fairly common in silicic acid gels. They result whenever the split at the surface begins in the exact center of the tube. As syneresis proceeds, with its resulting contraction, the forces acting toward opposite walls will be equal, and the split will go straight down the tube. Occasionally a center split will go 10 to 20 cm, but usually it is not so long, because the split is generally closer to one side than to the other, gradually producing more and more pronounced waves due to the play of rhythmically balanced forces.

Irregularities in rhythmic splits may be caused by foreign particles, such as pieces of solid matter and especially by bubbles of gas. Cross striations, sometimes observed in the splitting of silicic acid gels, seem to be due to temperature changes. They break the smooth surface of the wave into little steps, reminding one of ripples on a water surface.

Reasons why Rhythmic Splitting has escaped General Notice.—It may at first seem remarkable that rhythmic splitting has previously escaped general notice, but this is easily understood when one recalls the conditions for good rhythmic splits, which are as follows.

1. Tubes of gel should be allowed to set at some other than the usual vertical position.
2. Tubes should be left open, whereas they are generally closed.
3. Narrow tubes give better results than larger ones, whereas gels are generally allowed to set in test tubes or bottles.
4. Rhythmic splitting in small tubes requires that the gel stand for some time.
5. It would not be observed when the gels are covered with a water solution, as is done for diffusion experiments.

Summary.—Silicic acid gel will split rhythmically whenever setting and syneresis is accompanied by sufficient contraction to cause any splitting, and providing the initial splitting occurs along some line not coinciding with the inside circumference of the tube or one of its diameters. Rhythmic splitting is general whenever the gel is allowed to set in other than the vertical position, because the split starts at the top off center due to the lack of symmetry of the meniscus. Even with a circular meniscus rhythmic splitting will result if an off center crack be started with a sharp point or blade, or if the tube be of small diameter.

As the result of the accurate measurements of about 2000 wave lengths of rhythmic splits in over 400 tubes of known diameters, it has been found that for the particular gels studied

$$L_o = \text{about } 4.76\ D,$$

where L_o is the observed wave length of the rhythmic split and D is the diameter of the tube. Since, for a true sine wave curve

$$L = 3.1416\ D,$$

it turns out that the observed wave length of a rhythmic split is about 1.5 times that of a true sine curve.

Experiments carried out at temperatures of about 25°C, 30°C, 37.8° C, and 59.4°C, and at angles ranging from horizontal to vertical, show that for ordinary temperatures the decrease of wave length with increase of temperature is slight and for most purposes negligible, while the rate of splitting increases with temperature and is especially rapid for the tubes of larger diameters. The wave length is nearly the same for all angles of setting, but, especially for the larger tubes, the angle of setting is important in determining whether the split will be circular along the wall, a straight center split, or a rhythmic split.

The rhythmic splits were obtained with gels made by mixing equal parts of d. 1.16 water glass and one of the following acids: 12 N HCl, 12 N H_2SO_4, 12 N HAc, 6 N HCl, 6N H_2SO_4, 6N HNO_3, 6N HAc, 3N HCl, 3N H_2SO_4, 3N HNO_3, and 3 N citric acid. Tubes ranged in diameter from 0.338 mm to 15.516 mm and up to 155 mm in length. Between 30°C and 37.8°C the order of decreasing wave lengths of the rhythmic splits in tubes of 3.58 mm diameter is 6N HNO_3 (5.045) > 6N HCl (4.821) > 6N H_2SO_4 (4.631) > 3N HCl (4.567). The values in parentheses are for $\frac{\text{wave length}}{\text{diameter of tubes}}$ for averages at these 2 temperatures at all angles between the horizontal and vertical position.

A photograph of rhythmic splits is shown. A drawing of a meniscus and split makes it possible to explain the rhythmic play of forces at work during the gel contraction, and responsible for the continuously changing direction of splitting, resulting in the rhythmic waves.

Chemistry Department,
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Morgantown, W. Va.
July 30, 1931.

STUDIES ON HYDRAZINE: THE PHOTO-CHEMICAL OXIDATION OF HYDRAZINE BY FERRICYANIDE*

BY E. C. GILBERT

The velocity of the oxidation of hydrazine by ferricyanide has been previously studied.[1] In alkaline solution the reaction proceeds very rapidly but in the presence of acid it runs with measurable velocity. Stoichiometrically the reaction is

$$N_2H_5^+ + 4Fe(CN)_6^{---} + 5\ OH^- \rightarrow N_2 + 4\ Fe(CN)_6^{----} + 5\ H_2O$$

Kinetically, however, in the presence of a 1 M buffer solution the reaction is of first order with respect to each reactant, i.e.,

$$dx/dt = K\cdot \text{Conc.}_{N_2H_5^+} \cdot \text{Conc.}_{Fe(CN)_6^{---}} \cdot \text{Conc.}_{OH^-}$$

where "x" = mols of nitrogen formed in time "t". Certain difficulties encountered in the previous work indicated that the reaction was sensitive to light and the present investigation bears this out, the velocity being considerably increased by visible light.

Experimental

Materials.—Hydrazine sulfate and hydrazine monoperchlorate were recrystallized and their purity checked by the iodate method.[2] Potassium ferricyanide was recrystallized from conductivity water. Baker's "C.P." disodium phosphate was used to buffer the solutions slightly.

Apparatus.—The velocity of the reaction was followed by measuring the volume of nitrogen evolved. A test tube 5 cm. in diameter was provided with a stirrer operating through a mercury seal, an inlet tube for reagents, and an outlet tube for nitrogen, the latter being collected over mercury in a graduated 10 cc. gas pipette with leveling tube. The apparatus was placed in a constant temperature bath provided with a plate glass window. The temperature was maintained at 25° ± 0.05.

Procedure.—When studying the dark reaction the laboratory was darkened and the reaction test tube surrounded by a black bottle. When studying the light reaction two 200 watt nitrogen-filled Mazda lamps were placed outside the bath at a distance of fifteen cm. from the reaction vessel, the light passing through the plate glass window. The reagents were brought to the temperature of the bath and forty cc. of ferricyanide, twenty cc. of 0.2 M disodium phosphate, and forty cc. of hydrazine sulfate introduced into the test tube in the order named, and the stirrer started. Some nitrogen is lost by this method of introducing the reagents and the results are therefore to be considered

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* Contribution from the Department of Chemistry, Oregon State College.

[1] Gilbert: Z. physik. Chem., **142A**, 139 (1929).

[2] Bray and Cuy: J. Am. Chem. Soc., **46**, 858 (1924).

qualitative in nature. By adjusting the leveling tube more or less continuously the pressure was maintained close to atmospheric and no difficulty was experienced with the mercury seal. The volume could not be adjusted more accurately than 0.05 cc. so no correction was made for changes in barometric pressure. The rate of stirring was constant throughout at about 250 r.p.m. and the volume of reagents and position of lamps was the same in all runs.

Results

Three series of runs were made, duplicates being easily obtained with the exception of the case when hydrazine was present in double proportion in the light. These were more erratic and it is thought that there may have been some oxidation of hydrazine by oxygen in the reagents. The results are shown in Fig. 1.

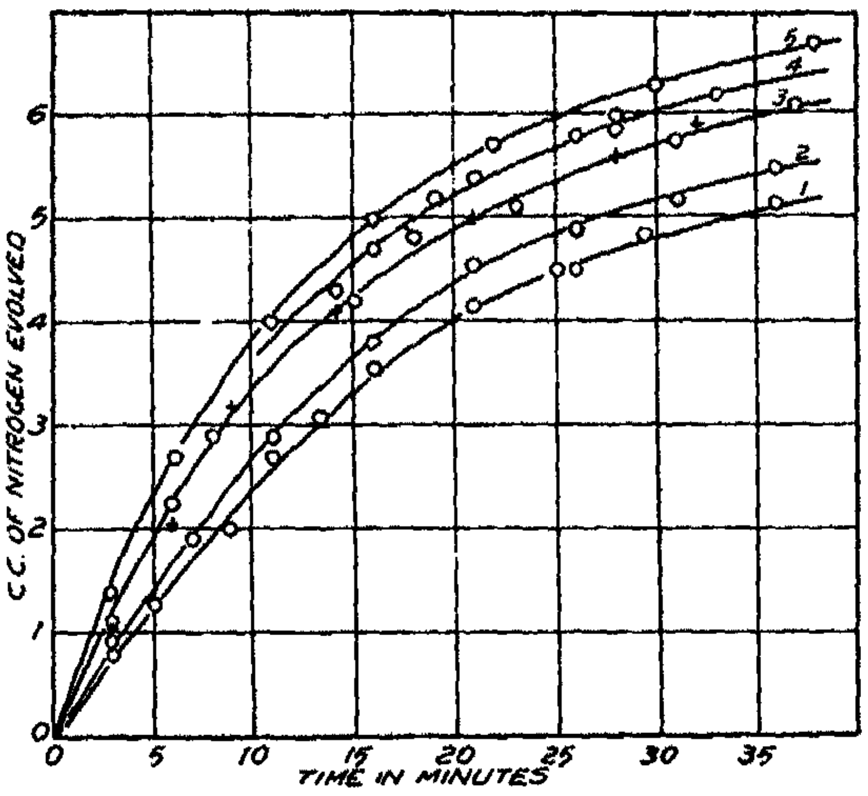

Fig. 1.

Velocity of Oxidation of Hydrazine by Ferricyanide, at 25°.

Curve 1. Dark reaction; Hydrazine and ferricyanide in stoichiometric proportions, 1:4
Curve 2. Light reaction; Hydrazine and ferricyanide 1:4.
Curve 3. Dark reaction; Circles, ferricyanide doubled; Crosses, hydrazine doubled.
Curve 4. Light reaction; Hydrazine doubled.
Curve 5. Light reaction; Ferricyanide doubled.

In the first series stoichiometric proportions of hydrazine and ferricyanide were used, i.e., forty cc. of 0.01 M hydrazine sulfate and forty cc. of 0.04 M potassium ferricyanide, together with twenty cc. of 0.2 M disodium phosphate. It should be noted that the hydrazine sulfate dissociates completely in solution giving one equivalent of free H^+ per mol, thus resulting in this case in the addition of the equivalent of forty cc. of 0.01 N acid. For each mol of hydrazine oxidized, five mols of hydroxyl ions are used up so the reaction slows down very rapidly. In the previous work[1] a very concentrated buffer

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[1] Gilbert: loc. cit.

Experimental Data

Velocity of Oxidation of Hydrazine by Ferricyanide

Series I

40 cc. 0.01 M $N_2H_5^+$; 40 cc. 0.04 M $Fe(CN)_6^{---}$; 20 cc. 0.2 M Na_2HPO_4

Time in minutes	Dark Reaction, Curve 1 Cc's N_2 evolved	Time in minutes	Light Reaction, Curve 2 Cc's N_2 evolved
3	0.80	3	0.90
5	1.55	7	1.90
9	2.50	11	2.50
13	3.10	16	3.80
17	3.85	21	4.55
21	4.20	26	4.90
25	4.50	31	5.20
29	4.85	36	5.50

Series II

40 cc. 0.01 M $N_2H_5^+$; 40 cc. 0.08 M $Fe(CN)_6^{---}$; 20 cc. 0.2 M Na_2HPO_4

Time in minutes	Dark Reaction, Curve 3 Cc's. N_2 evolved	Time in minutes	Light Reaction, Curve 5 Cc's N_2 evolved
3	1.10	3	1.40
6	2.25	6	2.70
8	2.90	11	4.00
15	4.20	16	5.00
23	5.10	22	5.70
31	5.75	30	6.30
37	6.10	38	6.70

Series III

40 cc. 0.02 M $N_2H_5^+$; 40 cc. 0.04 M $Fe(CN)_6^{---}$; 20 cc. 0.2 M Na_2HPO_4

Time in minutes	Dark Reaction, Curve 3 Cc's N_2 evolved	Time in minutes	Light Reaction, Curve 4 Cc's N_2 evolved
3	1.05	3	1.10
6	2.05	7	2.80
9	3.10	11	3.95
14	4.10	16	4.70
21	5.00	21	5.40
28	5.60	26	5.80
32	5.90	33	6.20

solution was used to minimize this loss of hydroxyl ion and so simplify the kinetics. This was unnecessary in the present work.

At points on the curves where equal amounts of nitrogen have been evolved the hydroxyl ion concentration is also the same. A calculation of the bimolecular velocity constant at the time when four cc. of nitrogen have been evolved gives for the dark reaction k = 2.15 and for the light reaction k = 2.34, concentration being expressed in mols per liter. This corresponds to about a ten percent increase for this weak illumination.

In the second series the concentration of ferricyanide was doubled. (Hydrazine 0.01 M; ferricyanide, 0.08 M). The acceleration due to radiation was considerably greater. This would indicate that the effective radiation is that absorbed by the ferricyanide ion which begins to absorb strongly in the neighborhood of 4550 Å. In the third series the concentration of hydrazine was doubled. (Hydrazine 0.02 M; ferricyanide, 0.04 M). This was done without altering the acidity by using the neutral monoperchlorate as the source of one half of the hydrazine. It will be noted that the curve for the dark reaction with double hydrazine is identical with that for double ferricyanide in agreement with the previous work.[1] The acceleration due to light is, however, less than that for double ferricyanide corroborating the assumption that the effective radiation is that absorbed by the ferricyanide. This does not preclude the possibility that radiation in the ultra violet will also prove effective.

It is hoped at a later date to make a quantitative study of the reaction.

Summary

The oxidation of hydrazine by ferricyanide is accelerated by visible radiation.

The effective radiation is apparently that absorbed by the ferricyanide.

The increase in velocity is of the order of ten percent with relatively weak illumination.

Corvallis, Oregon,
July 27, 1931.

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[1] Gilbert: loc. cit.

QUANTITATIVE ANALYSIS OF ALLOYS BY X-RAY SPECTROSCOPY

BY C. E. EDDY AND T. H. LABY

In a recent paper Terrey and Barrett[1] have given an account of quantitative analysis carried out by the method of X-ray emission spectra. It is our experience that correct analyses can be made with this method provided certain conditions are fulfilled, and we wish therefore to offer some comments regarding their experiments as we think that their conclusions may prejudice the X-ray emission method of quantitative analysis.

The X-ray tube.—The target of their X-ray tube was inadequately cooled owing to the high thermal resistance of the path between the focal spot and the cooling water. This resulted in the vaporisation of zinc from a brass target and no doubt was the source of many of their difficulties, including the change in atomic concentration of their target. The overheating of the target would further contribute to the very long exposures they found necessary. With a path of low thermal resistance, alloy targets with melting points as low as 160°C. have been used without volatilisation even with tube energies of one kilowatt.[2] Amalgams can be used in hot-filament type X-ray tubes if the cooling system is properly designed.[3] It is true that substances volatile at room temperatures and non-metallic substances (i.e., substances with low thermal conductivities) have so far proved difficult or impossible to use as the target of an X-ray tube, but no difficulty should be experienced with alloys of high melting point.

The measurement of exposures.—In quantitative analysis it is necessary to measure the exposures (which are proportional to (voltage)^n $\times$ tube current $\times$ exposure time) with the accuracy desired in the analysis. In practice the voltage should be kept constant throughout, and it is preferable to keep the current constant in order to avoid the serious difficulties of measuring the average value of a varying current. The authors used an induction coil to excite their X-ray tube. Of high tension generators the induction coil is the least suitable for quantitative X-ray work both on account of the wave-form of the potential which it generates and of its irregularity of operation. The applied voltage was measured with a spark gap, which has the the defect that it only indicates when the voltage exceeds the value fixed by the length of the gap, and the mean R.M.S. value for the whole exposure cannot be inferred with certainty. An electrostatic kilovoltmeter is much to be preferred to a spark gap as it gives a continuous record of the R.M.S. value throughout the exposure. With the poor regulation given by an induc-

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[1] Terrey and Barrett: J. Phys. Chem., **35**, 1156 (1931).

[2] Eddy and Laby: Proc. Roy. Soc., **127**, 32 (1930); (afterwards referred to as I).

[3] Eddy and Turner: Proc. Roy. Soc., **111**, 119 (1926).

tion coil, changes in the tube current due to the evolution of gas from a hot target would be accompanied by large changes in the applied voltage, and the condition of constant voltage could not be maintained.

The photographic method of measuring line intensities.—Terrey and Barrett state that "all photographic methods used in the determination of the intensities of X-ray spectral lines are, on account of the shape of the blackening curve, liable to introduce error." It should be pointed out that this statement ignores the development in recent years of an accurate technique for the photographic measurement of spectral line intensities. It is possibly of value to recall the history of this. With the development of quantum theories, intensity relationships in optical spectra became predictable, and photographic methods of measurement were developed to confirm these predictions. The Physical Laboratory of the University of Utrecht has made notable contributions[1] to this subject and the results obtained are accepted universally and are in agreement with theory. The photographic action of X-rays was investigated here in 1919[2] and photographic methods have been applied in this and other laboratories[3] to the measurement of X-ray line intensities; the method yields results reproducible to about 1% and in agreement with those obtained by both the ionisation and counting methods and with theory.[4] There can be no doubt now as to the accuracy and convenience of the photographic method, in which the shape of the blackening curve can be readily determined.

Terrey and Barrett found by the wedge method, which they used in many of their experiments, that the ratio of the intensity of the K α_1 line to that of the K α_2 line had a value of one or less. It is well known that the value of this ratio is 2 for the doublets they measured. It is evident that the intensities they obtained using the wedge method are unreliable and to an extent which vitiates their conclusions based on this method of measurement. The accuracy of the measurements made with the ionisation chamber cannot be checked in this way, as the α_2 and α_1 lines were not measured separately.

A possible explanation of the incorrect values which they found for the intensities of the lines is that the spectrometer crystal was not rocked uniformly and symmetrically in a wide sweep about the mean position of the two lines whose intensities were to be compared. If this essential condition is not satisfied, serious errors will occur in the measurement of the ratio.[5]

The effect of absorption.—Terrey and Barrett in their treatment of the effect of absorption of radiation in the target state: "This absorption effect will occur whenever there are present on the anticathode two elements such that the characteristic radiation of one falls within the absorption region of the other." "From these figures (see p. 1158) it is seen that the K $\alpha_{2.1}$ line of silver falls within the absorption region of copper." "Copper and silver

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[1] See Dorgelo: Physik. Z., 26, 756 (1925).

[2] Miss Allen and Laby: Proc. Roy. Soc. Vict., 31, 421 (1919); Glocker and Traube: Physik. Z., 22, 345 (1921); Bouwers: Z. Physik, 14, 374 (1923); Dissertation, Utrecht (1924).

[3] Rogers: Proc. Phys. Soc., 43, 59 (1931); Webster: 41, 181 (1929); I, p. 26.

[4] See the papers of Duane and co-workers, Siegbahn and co-workers, Allison and Armstrong, H. C. Webster, and others; or Siegbahn: "Spectroscopy of X-rays," p. 97.

[5] I, p. 31.

therefore afford a very good example of this absorption effect." "In the case of the copper-zinc alloys no absorption of the K $\alpha_{2,1}$ line of zinc occurs."

As will be seen from the table of absorption coefficients given below, the last of these statements is incorrect and the first three are inexact in their quantitative implications.[1] To illustrate the effect of absorption, the authors take a silver-copper alloy as a "very good example" of a target for which the K lines of silver would be absorbed in the copper, and they take brass as an example in which there is "no absorption" of the zinc Kα doublet. Actually the zinc lines would be more strongly absorbed than the silver lines. Although the absorbed silver radiation would give rise to fluorescent copper radiation, the effect of this would be more than offset by the very great absorption of the copper rays in silver.

It is true that the effect of absorption in the target material is all-important in quantitative analysis by X-ray spectroscopy, and this has been investigated and discussed by several workers.[2]

Radiation	Wave length	Absorber	Absorption coefficient
Silver K α	0.5 Å	Copper	27 gm^{-1} cm^2
Zinc K α	1.4 Å	Copper	43 gm^{-1} cm^2
Copper α	1.5 Å	Silver	160 gm^{-1} cm^2

The abrupt discontinuity in Graph 1 shown by Terrey and Barrett cannot be explained by "assuming that the number of copper atoms present are insufficient to absorb the optimum quantity of emitted silver radiation" as the absorption is proportional to the number of copper atoms present.

Theoretical discussion. The fourth equation on p. 1157 and the second on page 1158 of the theoretical discussion are incorrect (probably as a result of printers' errors), but it is not clear why a value of 4.35 should be substituted for the constant K to obtain the results given in the last column of Table IV. From these results it would appear that the authors obtained values from the photographic method in closer agreement with those of chemical analysis than from the ionisation method.

There seems to be no reason why the expression $\frac{I_1}{I_2} \propto \frac{C_1}{C_2}$ for elements of nearly equal atomic number should become $\frac{I_1}{I_2} \propto \frac{C_1}{C_1 + C_2}$ for elements of widely different atomic number.

Results of previous workers. Several workers[3] have shown that, with alloys of elements of nearly equal atomic number, the quantity of an element can be determined from a direct comparison of line intensities. Recently[4] we have investigated a number of alloys of elements of nearly equal atomic number, with widely varying concentrations, and the results obtained by X-ray and other methods are given below.

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[1] For a treatment of X-ray absorption see Siegbahn: "Spectroscopy of X-rays," p. 6, or Compton: "X-rays and Electrons," p. 6.

[2] Hevesy, Bohm, and Faessler: Z. Physik, **63**, 74 (1930); Glocker and Schrieber: Ann. Physik, **85**, 1089 (1928); Schrieber: Z. Physik, **58**, 619 (1929).

[3] See I, p. 24.

[4] I, o. 35.

Alloy	X-ray analysis	Mean	Chemical analysis or synthesis
Cu in Zn	73.11		
	73.17		
	73.15		
	73.20	73.16	73.00% Cu.
Cu in Zn	1.11		
	1.10		
	1.14		
	1.17	1.13	1.12% Cu.
Cu in Zn	0.114		
	0.113		
	0.124		
	0.116	0.117	0.112% Cu.
Sn in Cd	71.1		
	71.2		
	70.9		
	71.3	71.1	70.8% Sn.
Pb in Bi	60.1		
	60.6		
	60.1		
	60.1	60.2	60.45% Pb.
Zn in ZnCuSn	12.1		
	12.1		
	12.2		
	12.2	12.2	12.21% Zn.

It will be seen that the agreement is particularly good when it is remembered that the discrepancies include the errors arising in the photographic measurements of intensity as well as in the determination of the amount of the element by chemical methods or by synthesis.

Methods of quantitative analysis have also been developed for mixtures of elements of widely different atomic number. Coster, Hevesy, Nishina and others[1] have carried out determinations of the hafnium content of a large number of zirconium minerals, and we have analysed a number of lead-zinc alloys with a lead content varying from 0.1 to 0.005%.[2]

Natural Philosophy Laboratory,
University of Melbourne,
August 15, 1931.

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[1] Coster and Nishina: Chem. News, **30**, 149 (1925); Hevesy: "Recherches sur les propriétés du Hafnium."

[2] I, p. 39.

5639

THE THEORY OF GASEOUS EXPLOSIONS AND THE OXIDATION OF HYDROGEN SULPHIDE

BY H. W. THOMPSON

H. A. Taylor and E. M. Livingston have recently described in this Journal[1] an investigation upon the oxidation of hydrogen sulphide, in which their observations are discussed with special reference to the theory of reaction chains and of gaseous explosions as developed by Semënov. Since a rather serious theoretical error has been introduced into this and another paper by H. A. Taylor and his collaborators,[2] and one regarding which there would appear to be some misunderstanding in the current literature, it seems desirable to point out the necessary correction. Further, although much of the interpretation of their results in the oxidation of hydrogen sulphide suggested by Taylor and Livingston is thereby invalidated, it seems possible with the emendation mentioned and in the light of other facts to understand their results in a much more satisfactory way.

The theory of the process of combustion was recently studied mathematically by Semënov.[3] Briefly, two kinds of gaseous explosion were differentiated; in the one, activation of the molecules in the so-called "classical Arrhenius" manner led to the production of so much heat energy that conduction of the latter to the surroundings via the vessel walls became inadequate to prevent inflammation; in the second, the products of an elementary process caused, by virtue of their excess energy or chemical character, the establishment of branching reaction chains and in consequence an extremely rapid complete combustion ensued—a condition synonymous with explosion. These two types were respectively referred to as "thermal" and "chain" explosions.

The conditions determining the production of branched chains and in particular the manner in which α, the probability that one elementary process shall induce another subsequent one, varies with pressure, were examined fully by Semënov, and the theory has since been well-established by the discovery of such chain explosions in which small changes of pressure of the reacting gases cause abrupt alterations in the velocity of chemical change.[4] The details of these phenomena and the difficulties at present existing in their interpretation may be found elsewhere.[5]

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[1] Taylor and Livingston: J. Phys. Chem., 2676 (1931).

[2] Taylor and Riblett: J. Phys. Chem., 2667 (1931).

[3] Semënov: Z. Physik, **48**, 571 (1928).

[4] Semënov: Z. Physik, **46** 109 (1927); Z. physik. Chem., **B1**, 192 (1928); Thompson and Hinshelwood: Proc. Roy. Soc. **119A**, 591 (1929); **124A**, 219 (1930); Kopp, Kowalsky, Sagulin and Semënov: Z. physik. Chem., **B6**, 307 (1930); Thompson: Z. physik. Chem., **B10**, 273 (1930).

[5] Hinshelwood and Garstang: Proc. Roy. Soc., **130A**, 640 (1931); Alyea: J. Am. Chem. Soc., **53**, 1324 (1931); Kowalsky: Z. physik. Chem., **B11**, 56 (1930).

For the "thermal" explosions the essential result of Semënov's treatment was that there exists a critical pressure for any temperature and for a given composition of the reacting gas-mixture, below which ignition will not occur; and the relation between this minimum pressure p and the absolute temperature T is

$$\log p/T = A/T + B \tag{1}$$

It is unnecessary to repeat the derivation of this relationship as described by Semënov. Two quantities A and B are introduced into it as constants. In reality A is closely related to the heat of activation of the process (which as already stated is treated in the "classical Arrhenius" way). In fact $E = 9.9A$ and B depends upon the composition of the mixture, upon the vessel dimensions and its nature, and upon the presence of inert gases. An examination of the validity of relation (1) for any explosive mixture should accordingly as a first approximation serve to indicate whether a "thermal" explosion is involved or not, although it has already been shown that other evidence is also necessary.

Sagulin,[6] in Semënov's laboratory has tested the theory by examination of the critical explosion pressures of many mixtures in this way, employing the above equation and in each case plotting log p/T as a function of 1/T. He estimated the value of the quantity A—being the slope of his plots—for each explosive mixture and in discussing its connection with the several energies of activation measured by different means, he indicated the degree to which these processes could be regarded as chain or thermal explosions, respectively.

Taylor and Livingston have apparently misunderstood the essential result of Semënov's theory and employ the relation

$$\log p = A/T + B \tag{2}$$

instead of that already given. They plot log p as a function of 1/T and thus evaluate A, for the purpose of discovering its connection with the estimated heat of activation of the process.

This procedure is clearly in error. But the authors' mistake may originate in a form of approximation used by Semënov himself in at least two other publications.[7] In each of these Semënov refers to the good agreement with equation (2) discovered by Sagulin (loc. cit.). This repeated error was originally thought to be sufficiently casual as not to require especial mention, but as its consequences appear to be *misleading* it may be pointed out now. It should be observed that the linearity of any log p/1/T plot is hardly disturbed by its conversion into a log p/T/1/T plot; the considerable numerical error in A remains, however, and in any subsequent calculation involving A may become magnified.

Converting the diagram (Fig. 1) given by Taylor and Livingston to represent the relation between log p and 1/T in different vessels and with different percentage mixtures, so as to exhibit log p/T as a function of 1/T, the following diagram is obtained.

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[6] Sagulin: Z. physik. Chem., **B1**, 275 (1928).

[7] Semënov: Chem. Reviews, **4**, 347 (1929); Z. physik. Chem., **B2**, 161 (1929).

In this figure only five of the six series given by Taylor and Livingston are used since plot 3 on their diagram (3%) shows only one point on the line drawn.

The mean value of A read off from the amended figure is approximately 2050. B varies of course for the different mixtures as in the original diagram of Taylor and Livingston.

Assuming that the entirely satisfactory linearity of the plots of log p/T against 1/T indicates the occurrence of a "thermal" explosion, the heat of activation of the principal process would according to theory be 9.9 × 2050 i.e. approximately 20300 cals. This value is much lower than that suggested by Taylor and Livingston on the basis of their data, and they would accordingly again conclude that the explosion could not be thermal.

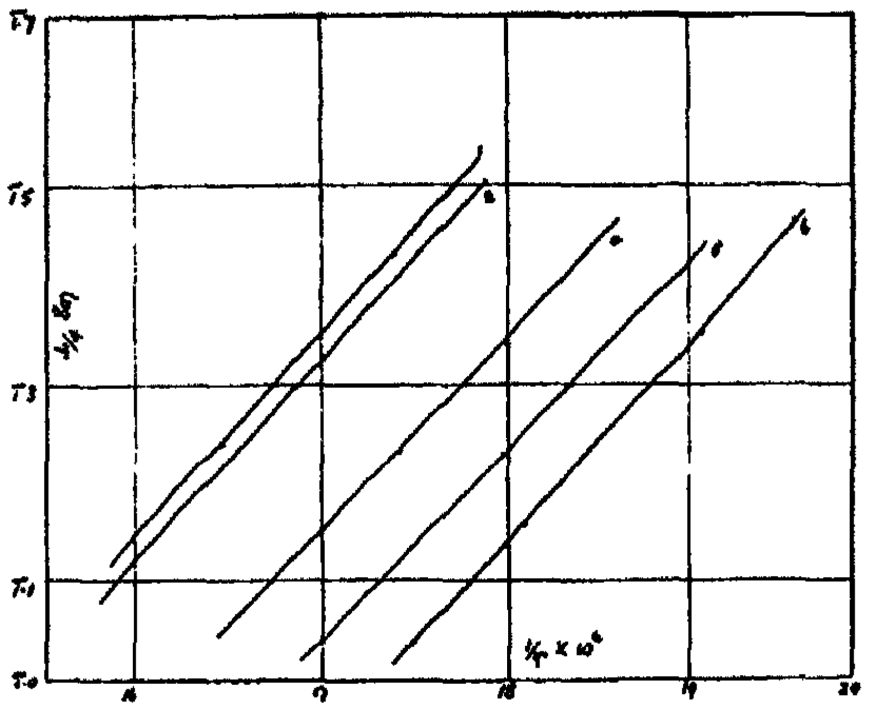

FIG. 1

Whilst agreeing with the essential result, that the reaction between hydrogen sulphide and oxygen is a chain reaction of some kind, many serious objections can be raised to the line of reasoning and arguments used by Taylor and Livingston. Some of these are summarized critically below.

This reaction has been studied very recently in two other laboratories independently. Thompson and Kelland[8] on the one hand have shown that in glass vessels below about 220°C the process is primarily not the same as that which proceeds above this temperature. At the lower temperatures, surface effects and subsidiary reactions come into play, but at the higher temperatures up to those of ignition a chain reaction is most important, the chains being shortened by decrease in the vessel size. Their propagation is favoured by excess of oxygen in the mixture and made more difficult by an increase in the hydrogen sulphide concentration. On account of the latter fact the "total order" of the reaction appears low. These observers also noted and to some extent examined the induction period which preceded the reaction. The

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[8] Thompson and Kelland: J. Chem. Soc., 1931, 1809.

pressure decrease accompanying the complete interaction was somewhat greater than would correspond to the equation

$$2H_2S + 3O_2 = 2H_2O + 2SO_2$$

An estimate of the degree of concordance with the Semënov relationship (1) discussed above disclosed a value of 2400 for A in vessels 3.2 cm. in diameter.

The experimental procedure of Taylor and Livingston, and the results thereby obtained, agree to a considerable extent with those described by Thompson and Kelland. They too noticed an erratic nature of the process which was accompanied by deposits of sulphur, and did not proceed strictly according to the above equation. Further, the fact that with a high concentration of hydrogen sulphide explosion did not occur until 390°C would indicate an inhibiting effect of this substance.

Taylor and Livingston however give as principal examples of the measurable reaction several series at 200-210°C, at which temperatures the induction periods are long and irregular, and above all when the reaction is largely a surface process. The minimum explosion temperature recorded by them is 228°C. At this and higher temperatures and higher pressures the gas reaction which occurs has a fundamentally different nature from that which proceeds at the lower ones mentioned. Accordingly the estimate made by Taylor and Livingston of the heat of activation of the process at 200-210°C cannot be valid for the process determining the explosion. That their abnormally high value of 47,000 cals. be obtained for a low order and partially surface reaction is to some extent understandable since the error involved in considering a 6 mm. pressure change would, by virtue of the variable induction periods alone, in general be very great.

The amended value of the quantity A taken from the results of Taylor and Livingston on the explosive reaction is 2050 i.e. a heat of activation of approximately 20,300 cals. The value obtained by Thompson and Kelland in this way was 9,9 × 2400 = 23,800 cals. Whilst the agreement is not perfect these figures are sufficiently close to the value of 18,000 cals. estimated by Thompson and Kelland from the temperature coefficient to be interesting. The degree of divergence might indeed be taken as an indication of short reaction chains. As however has already been affirmed any such coincidence of theory and practice is in this case not entirely conclusive. For this reason it was pointed out that more precise data are required.

By virtue of these arguments the contention that a primary dissociation of the hydrogen sulphide is a first step in its oxidation is considerably weakened; and indeed the experimental evidence on the effect of ultraviolet light upon the system at room temperatures offered by Taylor and Livingston would apparently speak against such a mechanism since no oxidation occurred despite dissociation of the hydrogen sulphide. The influence of ultraviolet light upon the system at temperatures above or about 200°C has been studied here, and the results promise to assist in the interpretation of the reaction as a whole.

Farkas[9] has simultaneously described experiments in which he confirms the retarding effect of narrowing the reaction vessel, the course of the reaction, the nature of the induction period, and also indications of the respective influences of oxygen and hydrogen sulphide described by Thompson and Kelland. Farkas has not studied the rapid measurable reaction which according to Thompson and Kelland (and presumably Taylor and Livingston) passes continuously into explosion; and he regards the whole process as another case of those "limit" phenomena developed by Hinshelwood and by Semënov.[4] In view of the complete study of this measurable process already described (Thompson and Kelland loc. cit.), as well as of subsequent experiments, it is impossible to accept the conclusion of Farkas in this form. Since according to his data the quantity A varies in different vessels, though otherwise rather for the sake of analogy, Farkas concludes that the chains probably start upon the vessel wall. The validity of this conclusion will however be discussed in more detail in a later paper embodying further experiments nearing completion in this laboratory, in which the reaction is studied in pyrex and quartz vessels, and in which the effect of steam and inhibitors on the reaction has been examined.

Summary

Attention is drawn to an error in a paper by Taylor and Livingston and its bearing upon the mechanism of the combustion of hydrogen sulphide is discussed.

The Old Chemistry Department,
The University Museum,
Oxford,
September 14, 1931.

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[9] Farkas: Z. Elektrochemie, 37, 670 (1931).

THE CRYSTAL STRUCTURE OF COPPER ELECTRODEPOSITED IN THE PRESENCE OF GELATINE

BY H. KERSTEN*

Introduction

Electrodeposited metals are usually more microcrystalline when the baths from which they are deposited contain colloids. In the case of copper plated from an acid bath containing gelatine it has been shown[1] that some of the gelatine is deposited with the copper. Fig. 1 shows that such copper is more brittle than that obtained from the same bath without the addition of gelatine. The two kinds of copper shown were plated on stainless steel (to which most electrodeposits adhere poorly) and partly stripped to show the difference in brittleness.

Fig. 1
Left, copper without gelatine.
Right, copper with gelatine.

In view of these differences in physical properties one might expect a difference in the crystal structure of the deposits. Trillat[2] examined such samples by means of x-rays and found apparent, but not conclusive, evidence for a difference in the length D, Fig. 2, of the edge of the unit crystal lattice for the two kinds of copper.

This paper describes a new determination which shows that any difference in the length of the unit lattice for the two kinds of copper must be less than 0.01 Ångström.

Experimental

The x-rays were supplied by a Siegbahn-Hadding type of x-ray tube having a copper target. A special camera shown in Fig. 3 was constructed, in which the x-rays passed through the slits in the ends of the tube A and struck the samples B and C nearly at a tangent. These samples were electroplated on gold-plated brass tubes so that if any x-rays were diffracted by the under metal this fact could be noticed in the picture because the distance D of Fig. 2 for gold is much different from that of copper. The samples B and C were of the same outside diameter and fitted snugly over the pin D. This made the distance from the slit to the film the same for both samples. The

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* Dept. of Physics, University of Cincinnati, Cincinnati, Ohio.

[1] Müller and Bahntje: Z. Elektrochemie, 12, 317 (1906).

[2] Trillat: Rev. Métallurgie, 25, 286 (1928).

film was enclosed in a paper envelope and held on the circumference of the hoops E by a rubber band. Next to the film was placed a piece of 0.02 mm nickel foil which acted as a filter giving approximately monochromatic beams. The place where the two samples joined was aligned with the partition F which prevented the diffracted beams from one of the samples crossing over to the part of the film which was intended to receive the beams from the other sample. An enlarged photograph, taken with this camera, is shown in Fig. 4.

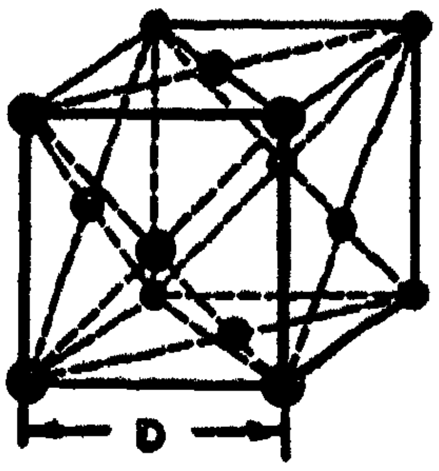

FIG. 2
Unit crystal lattice of copper.

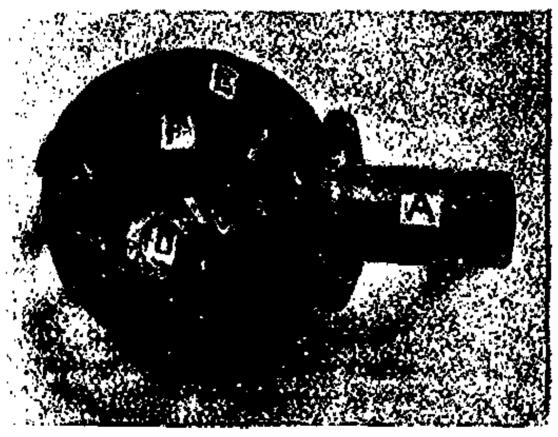

FIG. 3
Special x-ray camera

The plating baths used had the following composition:

Water	1 liter
Copper sulphate crystals	200 gm.
Concentrated sulphuric acid	30 gm.

FIG. 4
Enlarged photograph taken with the camera shown in Fig. 3. Upper part, copper containing gelatine. Lower part, copper not containing gelatine.

The other bath had the same composition except that it contained 100 gm of gelatine. The baths were connected in series and since the cathodes had the same area, the current density was 2 amp per dm^2 for each sample. The temperature was kept constant at 25°C by placing the beakers containing the electrolyte in a water-bath. A sufficiently thick deposit was obtained in one hour.

Theoretical

To show that the difference in the length of the edge of the unit lattice must be less than 0.01 Å for the two kinds of copper, Bragg's law is used:

$$n\lambda = 2\,k\,D\sin\Theta,$$

where:

n = order of the reflection (1, 2, 3, etc.),

λ = wave length of the x-ray beam,

k = a factor which when multiplied by D gives the distance between corresponding planes (for the 111 planes $k = 0.577$),

D = length of the unit crystal edge (Fig. 2),

Θ = angle between the incident x-ray beam and the diffracting plane.

From this, Θ is computed for the various planes which may cause diffraction, assuming the distance D for copper to be its usual value of 3.61Å, as well as 3.60 and 3.50Å. The theoretical positions of the lines thus determined are plotted in Fig. 5 from the computed values given in Table I.

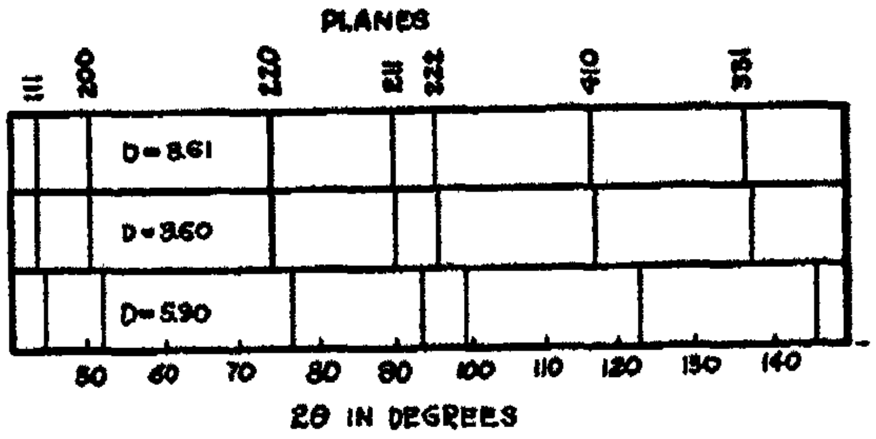

Fig. 5
Theoretical positions of the lines for various values of D.

Table I

Values of 2Θ for various values of D

Planes	2Θ for D = 3.61	3.60	3.50
111	43° 16′	43° 24′	44° 42′
200	50° 24′	50° 32′	52° 6′
220	74° 2′	74° 16′	76° 46′
311	89° 50′	90° 6′	93° 28′
222	95° 2′	95° 21′	99° 2′
400	116° 46′	117° 16′	122° 52′
331	136° 14′	137° 2′	146° 20′

In the computations, λ was taken as 1.537Å.

From the table and from Fig. 5 it is evident that the greatest difference in the positions of the lines occurs on the right-hand end. Turning to Fig. 4, the difference between the positions of the 331 lines is not as great as that between the same lines in Fig. 5 for D = 3.61 and D = 3.60 Å. Hence we conclude that any difference in the unit crystal lattice edge is less than 0.01Å.

THE LIMITING LAW FOR TRANSFERENCE NUMBERS

BY MALCOLM DOLE

Scatchard[1] and Jones and Dole[2] have recently published empirical equations connecting the transference numbers of strong electrolytes with the concentration, but as yet, apparently, no one has attempted to give these equations any theoretical basis. Indeed, on the basis of the old Kohlrausch conception of constant ion mobility the transference numbers would be constant and independent of the concentration,—an idea which would discourage any effort to determine the relationship between transference numbers and the concentration.

The more modern views regarding the change of ion mobility with the concentration as brought to final mathematical perfection in the work of Debye and Hückel[3] and of Onsager[4] offer a possible source of explanation for the transference number variation with the concentration since according to the "theory of complete dissociation" the ion mobilities are not independent of the concentration but depend very definitely upon the ionic constitution of the solution. At great dilution the ion mobilities, or on the assumption of complete dissociation the ion conductances are given by the Debye equation

$$\Lambda_i = \Lambda_i^{\infty} - a_i\sqrt{c} \tag{1}$$

In equation (1) Λ_i is the ionic conductance of the *i*th ion at the concentration c, Λ_i^{∞} is the ionic conductance at infinite dilution and a_i is a constant which may be calculated according to the equation of Onsager or which may be estimated from the experimental data. The transference number, t, of the positive ion of the salt PN, for example, is given by the equation (by definition)

$$t_p = \frac{\Lambda_p}{\Lambda_p + \Lambda_n} \tag{2}$$

Substituting the values of the ionic conductances as given by the Debye equation (1) into equation (2) we obtain an equation between the transference number and the concentration as follows:

$$t_p = \frac{A}{\sqrt{c} - D} + B \tag{3}$$

In equation (3) A, D and B are all constants, independent of the concentration. They are given by the following equations:

$$A = \frac{a_p\Lambda_n^{\infty} - \Lambda_p^{\infty} a_n}{(a_p + a_n)^2} \tag{4}$$

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[1] G. Scatchard: J. Am. Chem. Soc., **47**, 696 (1925).

[2] G. Jones and M. Dole: J. Am. Chem. Soc., **51**, 1073 (1929).

[3] P. Debye and E. Hückel: Physik Z., **24**, 185, 305 (1923).

[4] L. Onsager: Physik Z., **28**, 277 (1927).

$$B = + \frac{a_p}{a_p + a_n} \tag{5}$$

$$D = \frac{A_p^\infty + A_n^\infty}{a_p + a_n} \tag{6}$$

Equation (3) is the limiting law for transference numbers.

Scatchard's equation for the transference numbers is

$$t_p = t_p^\infty + k\sqrt{c} \tag{7}$$

Equation (3) may be expressed in a series as follows:

$$t_p = B - \frac{A}{D} - \frac{A\sqrt{c}}{D^2} - \frac{Ac}{D^3} \ldots \tag{8}$$

By dropping off all terms beyond $\frac{A\sqrt{c}}{D^2}$, Scatchard's equation (7) is obtained inasmuch as

$$B - \frac{A}{D} = t_p^\infty \tag{9}$$

This analysis indicates that Scatchard's equation is an approximate form of the theoretical limiting law.

Jones and Dole's transference equation which they somewhat accidentally discovered is

$$t_p = \frac{M}{\sqrt{c} + N} + R \tag{10}$$

By referring to equation (3), it is readily seen that Jones and Dole's equation has *exactly the same form as the limiting law.* This seems rather remarkable inasmuch as the Jones and Dole equation is valid for all salts as yet studied up to the high concentration of one normal whereas the limiting law is theoretically valid only for very dilute solutions. However an examination of the constants shows that in the two cases they are quite different; for example, the limiting law gives for B the value + 0.5, the analogous constant, R, in the Jones and Dole equation has the value − 1. At very small concentrations the two functions for the transference numbers will coincide since at zero concentration,

$$M/N + R \text{ must equal } B - A/D$$

In conclusion we may remark that the Debye theory gives by far the most satisfactory explanation of the transference number variation with the concentration.

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REACTIONS OF HYDROCARBONS IN THE GLOW DISCHARGE*

BY ERNEST G. LINDER AND ARDITH P. DAVIS

Although the reactions in electrical discharge of a large number of hydrocarbons have already been studied by others, the experimental conditions of these various investigations have differed widely, and hence it is not possible to obtain much information from the literature concerning the relative behavior of this class of compounds under similar experimental circumstances. It was the purpose of the research described in this article to study such relative behavior, and to find if there exist any simple relations between molecular structure and the nature of the reactions.

Fifty-seven different hydrocarbons were investigated. No attempt was made to work out completely the chemical reactions of each substance in the discharge, such an undertaking being a tremendous task, since the determination of the reactions of even a single hydrocarbon is a long and difficult problem which has been solved satisfactorily in only a few cases. Instead, a standard method of procedure was developed and applied to each substance, and, although this did not give complete information regarding the reactions, it gave sufficient to reveal a number of interesting relations.

Of the various types of electrical discharges in gases available for this work, the glow discharge (between metal electrodes, with D. C. current, at a few millimeters gas pressure) was selected, because it was believed to be better understood and more controllable than any of the others. A considerable amount of work, preliminary to the present research, was done by one of us, on the theory of chemical reactions in such a discharge, in order that the data might be better interpreted. Some of this has already been published elsewhere,[1,2] but it is now given in more complete form below.

Theory of Chemical Action in the Glow Discharge

Aside from the difficulty of working out the chemical reactions occurring in gaseous electrical discharges, the principal obstacle to a satisfactory theory has been the lack of a means (either experimental or theoretical) of determining the rate of formation of activated molecules. Even at present this remains a serious obstacle, but recent work has gone far towards its removal, so that it is now possible to form a picture of the principal phenomena, which is quite satisfactory in all its essential details. The present state of knowledge in regard to the fundamental elementary processes occurring in gas discharges has been well summarized by Compton and Langmuir,[3] while theories dealing with the glow discharge itself, which are of particular significance in connection with the rate of formation of active molecules, have been developed by H. A. Wilson,[4] Güntherschulze,[5] Compton and Morse,[6] Morse,[7] and Linder.[2,8]

The glow discharge may be divided into the following parts, starting from the cathode: (1) cathode glow, (2) Crookes dark space, (3) negative glow,

(4) Faraday dark space, (5) positive column, and (6) anode glow. The cathode glow usually appears as a layer of velvety light covering the surface of the cathode. It is a region of high positive ion density, and the luminosity is probably due to excitation of molecules by positive ion impact. The Crookes dark space is the region across which most of the potential drop of the discharge takes place, and where a large fraction of the energy dissipation occurs. It will be discussed more fully below. The negative glow is usually the most luminous region of the discharge. The positive ion and electron densities are greatest here, as is very likely also the density of excited molecules. The Faraday dark space resembles the Crookes dark space, but the energy dissipation is much less. The positive column is a region of almost uniform ion density and energy, unless it is striated, in which case the ion density and energy vary with the striations. However, in no cases are the electron energies comparable with those in the Crookes dark space, nor the positive ion and electron densities nearly as large as those of the negative glow, being only about one hundredth of the latter. The anode glow usually appears as a thin layer of light covering the anode surface. Here the electron energy is a little higher than in the positive column, and the light emission is likely due to electron impacts against molecules.

In discussing chemical action, only three of the above regions need be considered, namely, the Crookes dark space, the negative glow, and the positive column. The energy dissipation in the other regions is so small that the chemical action occurring in them is probably not large. Even in the positive column the reaction is usually negligible, since the energy dissipation per unit volume is small. The reaction in this region would become important only in long discharge tubes, where the positive column would have a large volume, since when the distance between the electrodes is increased, the positive column increases in length, the other regions of the discharge remaining practically unchanged in almost every way. Brewer and his co-workers,[9] and Linder,[2] have shown experimentally that most of the chemical action occurs in the Crookes dark space and negative glow, in tubes of the usual dimensions, such as that used in the present work. Therefore, only these two regions will be considered in the following discussion.

The principal phenomena of the dark space[10] and negative glow are represented in Fig. 1. C is the cathode surface, the dark space extends from C to E, E is the dividing line between the dark space and the negative glow. The negative glow occupies the region from E to F. The lines E and F are not sharply defined in the actual discharge, but are made sharp in the drawing for the sake of simplicity and clarity. We shall consider the entire potential drop as existing between C and E, its value at any point being given by the parabolic curve V, in accordance with Aston's result.[11] In the negative glow, i.e., the region EF, the potential is constant, as represented by the horizontal line, and the region is therefore field-free.

Suppose that an electron is generated at the point a on the cathode surface. Under the action of the electrical field, it will travel away from C, gaining kinetic energy from the field as it advances. Such an electron will make impacts with molecules. These impacts may be divided into three classes: (1) Elastic impacts, i.e., those which involve no (or at most only small) energy changes of either the electron or the molecule concerned, and whose only effect is a possible change of the direction of motion of the electron and molecule, such as is represented at the points marked e. (2) Ionizing impacts, such as those represented by the points i. These always result in the production of a new electron, and a positive ion. (3) Exciting impacts, i.e., those which raise the molecule to a higher quantum state. Dissociating impacts are not included in this list, since dissociation is now regarded as the result of ionization or excitation.

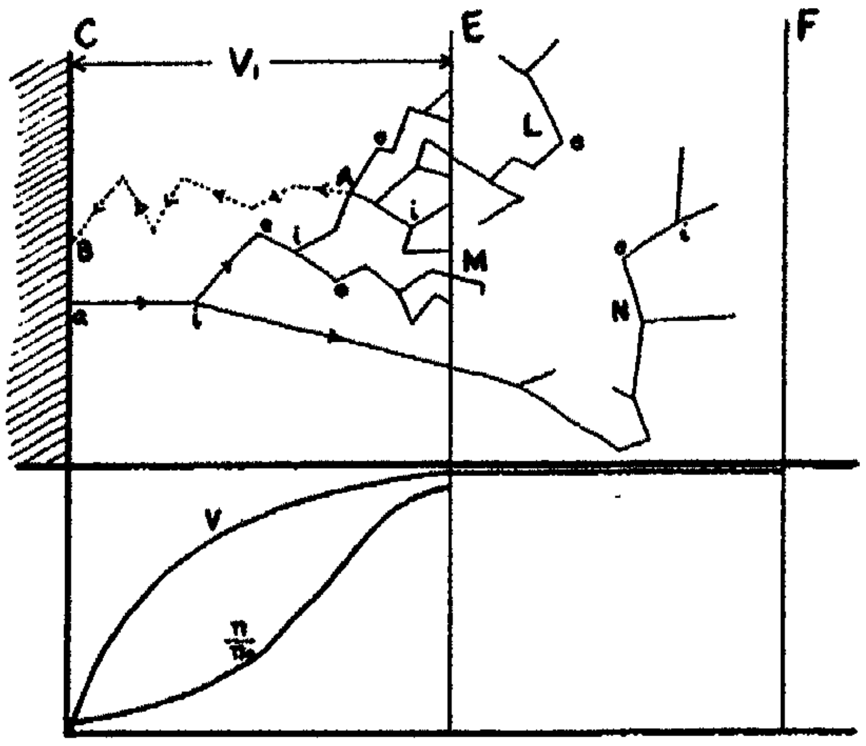

FIG. 1
Representation of Ionization Phenomena in Crookes Dark Space and Negative Glow

As a consequence of ionizing impacts, each electron that leaves the cathode (primary electron) generates a large number of new electrons (secondary electrons), before it reaches E. This is shown by the branching line in Fig. 1. Each fork (such as i) represents an ionizing impact and the consequent production of a new electron, which, in turn, advances and itself produces other new electrons. Thus the number of electrons increases exponentially with distance from the cathode. Townsend[12] has given an equation to represent this increase,

$$\alpha = pC\,e^{\frac{-pCD}{X}},$$

where α is the number of ionizing collisions per centimeter of advance, p is the gas pressure, X is the field strength, and C and D are semi-empirical constants, which have been determined by Townsend for a number of gases. A slight modification of the equation to adopt it to such non-uniform fields as are found in the dark space, has been given by Compton and Morse.[6]

The elastic and exciting collisions, of course, play no part in this exponential increase of ionization, except that they rob the electron of energy which might otherwise be used in producing ions.

It has been found that each primary electron is responsible for the formation of roughly 50 to 100 secondary electrons before reaching E.[3,6] If n represents the total number of electrons produced by n_0 primary electrons, the ratio n/n_0 increases as shown by the curve in Fig. 1. Obviously most of the electrons are generated close to E, and therefore fall through only a small potential drop before reaching E. The average electron energy is therefore low (in a discharge in water vapor it is about 0.15 V_1, expressed in volts, where V_1 is the total cathode potential drop.).

After the electrons reach E, they continue advancing into the negative glow (in Fig. 1 most of the paths are not drawn beyond E for the sake of clarity). Here they continue to make impacts until their energy supply is exhausted. Of course, they can gain no additional energy, since the negative glow is field-free. Path N represents that of an electron generated quite far back in the dark space and travelling all the way to E without making impacts, and consequently having high energy. Such electrons make more than the average number of collisions in the negative glow before their energy supply is exhausted. On the other hand, path M represents the opposite extreme, i.e., that of an electron of such low energy, that it makes no ionizing impacts, only elastic ones. L represents an average path. The number of activating impacts in the negative glow probably decreases asymptotically with increasing distance from E, somewhat as does the luminosity in that region.[13] No attempt has been made to have more than rough quantitative accuracy in the figure, it being desired to present only a qualitative idea at present.

We shall now consider for a moment the various kinds of active molecules formed by electron impacts in the dark space and negative glow. These may be divided into two classes, corresponding to the second and third kinds of impacts mentioned above, (1) positive ions, and (2) excited molecules. We shall consider first the relation of the discharge current to these.

Each positive ion formed in the dark space moves towards the cathode under the action of the electric field. A typical path is illustrated by the dotted line AB in Fig. 1, the ion being generated at A by an electron impact. The impacting electron and the new secondary electron produced, move on toward E, while the positive ion formed, moves back toward C. This ion, being much larger than an electron, especially in the case of large hydrocarbon molecules, such as are being considered here, makes new impacts. However, due to its small mean free path, the ion does not gain enough energy between collision to produce many ionized molecules. Hence the path of the positive ion is generally not branched, as is that of the electron.

It is clear that the number of positive ions reaching C per second is equal to the number of ionizing impacts made in the dark space per second. (This assumes no recombinations of ions and no ionization by positive ion impact, but these are known to be few in number in the dark space.) Since each electron that leaves the cathode produces many positive ions, the number of positive ions reaching C must be much greater than the number of electrons leaving (usually 50 to 100 times greater), therefore the current at C is predominantly a positive ion current. The discharge current is a measure of the positive ion current to C (disregarding the small number of electrons leaving C).

At E however, the current is mostly an electron current. The density of positive ions here is about equal to that of the electrons, but the latter carry most of the current by virtue of their greater mobility. Hence the discharge current is a measure also of the rate at which electrons cross E.

The discharge current is therefore a measure of three rates: (1) the rate at which ionizing impacts are made in the dark space, (2) the rate at which positive ions reach C, and (3) the rate at which electrons cross E. There is obviously no necessary relation between the discharge current and the rate of formation of positive ions in the negative glow, or the rate of formation of excited molecules in any region of the discharge.

The determination of the mechanisms of the reactions of the active molecules formed in the discharge, is a distinct problem for each individual compound, and indeed, for each type of activated molecule for each compound. However, it is possible to make some general remarks which apply to all.

Under the usual conditions of the glow discharge, such as those described below, the concentration of positive ions in the discharge is much smaller than that of normal molecules,[2] hence most of the collisions of the positive ions will be with normal molecules. The density of excited molecules has not been well determined, but there is reason to believe that in most cases it is comparable with that of the positive ions.[14] Consequently most of the collisions of the activated molecules will be with normal molecules, and the number of collisions of active molecules with other active molecules will be negligible. Therefore it would be expected that among the important primary reactions would be those taking place by the interaction of an activated molecule and a normal one. In fact, many reactions reported in the literature have been explained by such interaction,[15, 16, 17, 18] for example, the formation in the discharge, of dihydrodiphenyl from benzene as reported by Mignonac and de Saint-Aunay,[15]

$$C_6H_6 + C_6H_6' \rightarrow C_{12}H_{12}. \qquad (1)$$

Of course, an activated molecule may react with more than one normal molecule. This appears to occur for example, in the case of unsaturated hydrocarbons. But such a combination of three or more molecules does not occur simultaneously, except in rare cases, and strictly should therefore be regarded as a primary reaction (involving two molecules) followed by one or more secondary reactions, as the case may be.

Another type of primary reaction which should be important in many cases is the activation of a single molecule by electron impact followed by its dissociation. Many reactions of this type have been observed,[19] for example,

$$H_2O^+ \rightarrow H + OH^+ \qquad (2)$$

as reported by Barton and Bartlett.[20]

Of course, in most cases the final products do not represent the results solely of primary reactions, but also of a number of secondary reactions, since in many cases the products of the primary reactions are in an active state, e.g., OH^+ in reaction (2) above, and act as the initiators of further reactions almost immediately. It usually requires special methods to isolate the primary products, as for example, the positive ray mass spectograph, or, a discharge tube immersed in liquid air so that the primary products are frozen out before they can react further.

Activated molecules formed in the discharge may be divided into three classes: (1) positive ions formed in the dark space, (2) positive ions formed in the negative glow, and (3) excited molecules. The typical behavior of these three types is illustrated in Fig. 2.

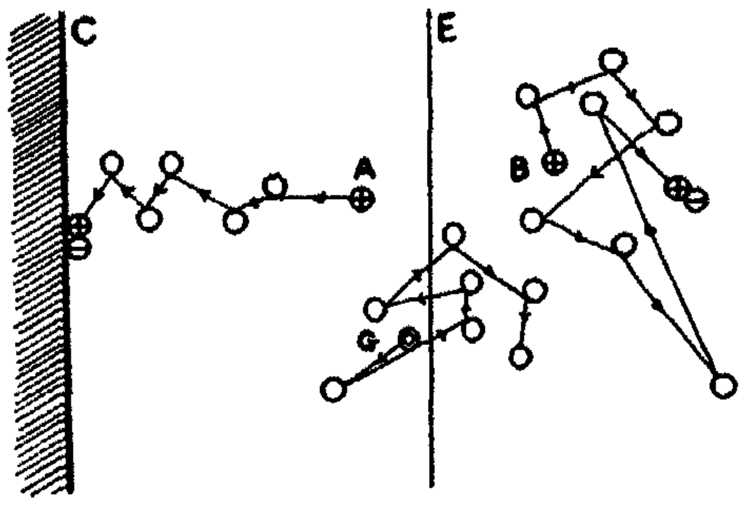

Fig. 2
Typical Behavior of Ions and Excited Molecules

Positive ions formed in the dark space, such as A Fig. 2, travel toward the cathode, making collisions with neutral molecules on the way. Reactions may take place at any of these collisions, or perhaps clusters may form, the ion picking up neutral molecules as it advances, as proposed by Lind.[21] However, it is doubtful that the final neutral reaction products are actually formed until the ion reaches the cathode and is neutralized.

Positive ions formed in the negative glow are not acted upon by any field, and hence move in a random manner, such as is illustrated by the ion B in Fig. 2. Actually there is a small field causing them to drift toward the wall, where some are neutralized. Others are neutralized in the gas phase. The reactions they initiate are probably the same as those initiated by ions in the dark space, but these ions or clusters likely travel farther before neutralization. Furthermore, the positive ions formed in the dark space may participate in surface reactions on the cathode surface, since they are practically all neutralized there, whereas large numbers of the ions formed in the negative glow are neutralized in the gas phase, and hence can play no part in such reactions.

Excited molecules, whether formed in the dark space or negative glow, are not acted upon by electric fields, since they are uncharged, hence they move in a random manner, as shown by molecule G in the figure. Such an excited molecule may either react, or may return to its normal state. The return to the normal state may be accomplished by the transfer of the excitation energy to another molecule in a collision, or by the emission of a light quantum. The light quantum may pass out of the discharge, or may be absorbed by another molecule, producing another excited molecule. In fact such a quantum may be passed on from one molecule to another until it is finally lost from the discharge or participates in a reaction.

Nothing much more of a general nature can be said regarding these various types of activated molecules, since their detailed behavior is probably different for each different compound, and each type of activation.

The rate of reaction in the glow discharge has been found by a number of workers[1, 2, 9, 22, 23] to be almost directly proportional to the discharge current. Linder[2] has shown however, that a probably more correct relation is

$$dq/dt = kWI, \qquad (3)$$

where k is a constant determined by the kind of hydrocarbon, W is the average energy absorbed from the field by the electrons generated in the dark space, and I is the discharge current. W may not vary much as I is changed, so that frequently there is almost direct proportionality between dq/dt and I, in fact, in the normal discharge, W remains constant. In the abnormal discharge, however, an increase in I causes an increase in W, so that the rate of reaction per unit current increases as the current increases. This is due to the fact that the electrons have greater energy and hence produce more activated molecules.[24]

Over a gas pressure range of at least 0.5 to 10 mm, the rate and nature of the reaction is almost independent of the pressure for any given compound.[1, 9, 22, 23] Increasing the pressure reduces the length of the mean free path of the electrons, but the width of the dark space also decreases, the cathode potential drop remaining constant. The result is that each electron makes the same number of collisions as before, and the reaction is unaffected.

The theory presented in this section provides a fairly satisfactory, although still incomplete, theoretical basis for the interpretation of the chemical action in the glow discharge. It will be applied to the experimental data below.

Discharge Apparatus

At the beginning of the investigation many attempts were made to build a satisfactory apparatus using a hot tungsten filament as a source of electrons, and accelerating them by applying a potential between this and a neighboring grid. Such an apparatus would have the great advantage that the number and energy of the bombarding electrons could be varied independently of each other. However, an insuperable difficulty was encountered in trying to eliminate or correct for the thermal decomposition caused by the hot filament. The principal difficulty is that although the amount of thermal decomposition

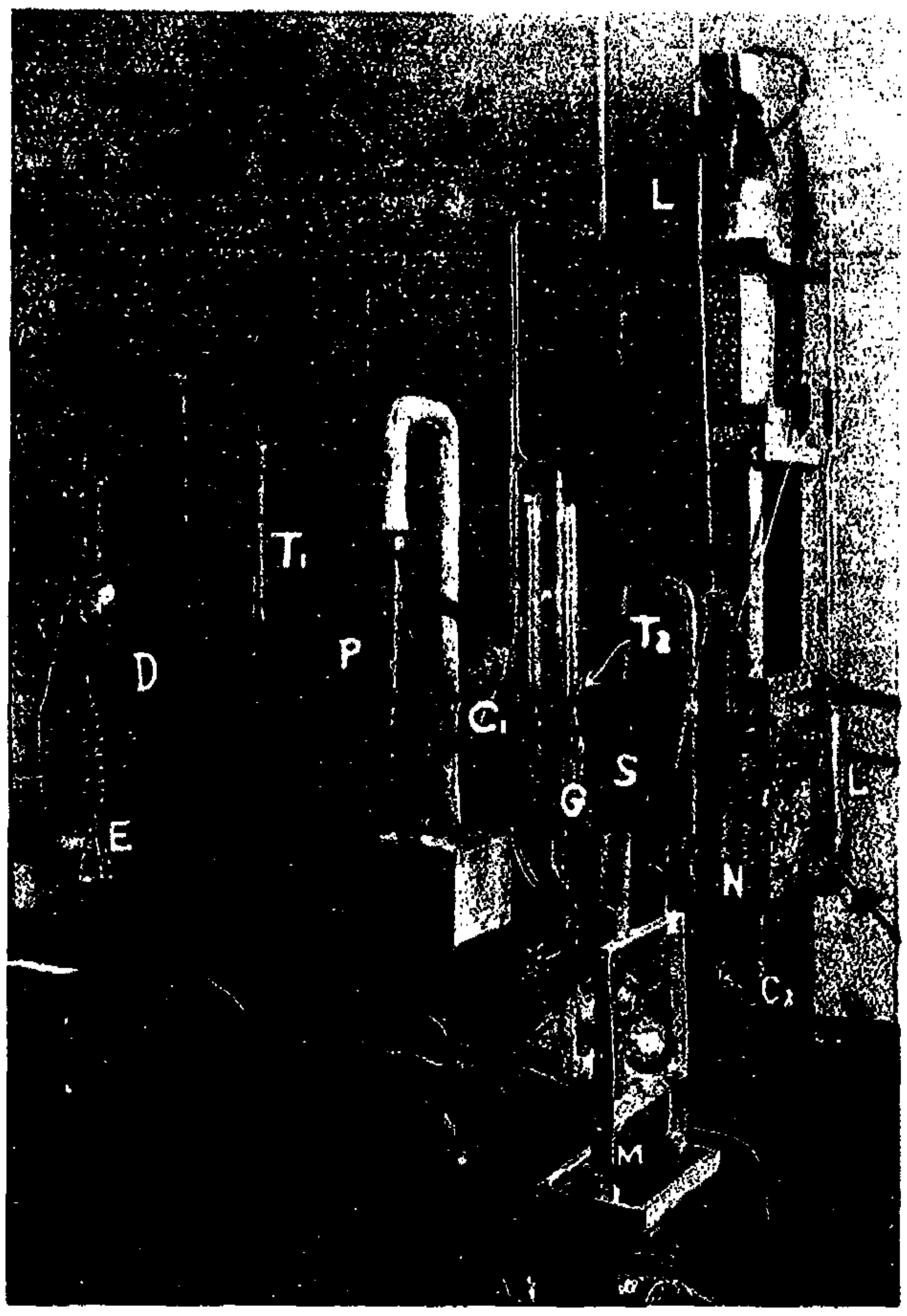

Fig. 3
Discharge apparatus

can be measured when no potential is applied between the filament and grid, it is probably different in amount when the potential is on, because of the attraction of positive ions to the filament, and hence can not be corrected for.

Attempts to develop such an apparatus were finally abandoned in favor of a glow discharge where such a correction is not necessary. The essential parts of the apparatus are shown in Figs. 3 and 4. The hydrocarbon, in solid or liquid form, was contained in the glass bulb E, whence it evaporated and flowed through the discharge chamber D, and then into the trap T_1 where it condensed. The non-condensing gases passed through the trap, and were pumped by the mercury condensation pump P, through a second trap T_2, into the storage bottle S. The rate of pressure increase in S was measured by means of a McLeod gauge G. Samples of gas for analysis were removed by a Toepler pump L.

All runs were made at a pressure such that the width of the Crookes dark space was from about 1 to 3 mm. corresponding to pressures of from about 0.5 to 10 mm. of mercury. A more exact fixation of the pressure was unnecessary in view of the small effect due to pressure changes. In cases where the vapor pressure of the compound at room temperature was sufficiently high, the pressure was regulated by immersing E in a cooling bath of a suitable temperature, but in cases where it was below 0.5 mm, that part of the apparatus surrounded by the dashed line in Fig. 4, was enclosed in an oven and raised to a temperature sufficient to give the desired pressure.

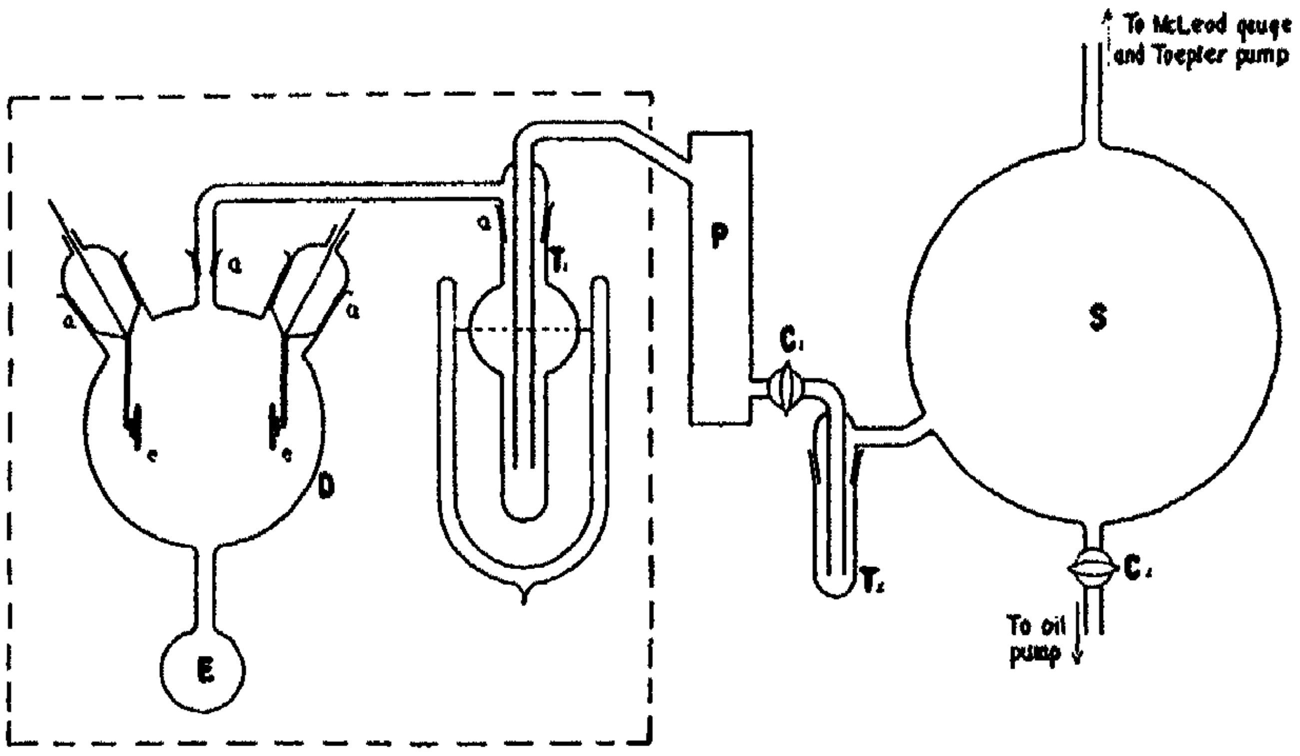

FIG. 4
Schematic sketch of discharge apparatus

In some instances temperatures around 150°C were necessary. In these cases the ground joints a, could not be sealed with any of the ordinary waxes, but it was found that suitable seals could be made by melting sugar into the joints and wrapping cooling coils around them. The joints could then be kept hot enough to avoid too great a lowering of the vapor pressure in D, and yet sufficiently cool so that they remained vacuum tight.

The discharge tube D, was of about 2 liters capacity. The electrodes e, were aluminum disks about 2.5 cm. in diameter. They were spaced 8.5 cm. apart. The leads to them were of heavy tungsten wire, glass covered. The larger ground joints enabled the electrodes to be removed easily for cleaning. The glass spiral shown between E and D in Fig. 3, was not used in any of the work reported here.

The trap T_1 was made with a bulb as shown, so as to prevent clogging by solid substances condensing at the surface line of the cooling solution. Trap T_2 was used only in work with high vapor pressure compounds, whose vapors were not completely stopped by the first trap, and which interfered with the correct functioning of the McLeod gauge if allowed to enter S. It was cooled with the same refrigerant as was used on trap T_1.

In nearly all cases the refrigerant on the traps was a carbon dioxide-ether slush. In a few cases of high molecular weight compounds, ice water was used, but in all instances, the gas samples for analysis were passed through a coiled glass tube N, immersed in carbon dioxide and ether, after being raised to atmospheric pressure by the Toepler pump. Thus, in every case, the gas sample analyzed, contained only those gases not condensible at −77°C, at atmospheric pressure.

The current for the discharge was supplied by a transformer, and rectified by a single kenotron. Its pulsating nature was unimportant, as was shown by tests on a discharge in water vapor, the results of which agreed with those reported by Linder[2] for a smooth direct current. The voltages varied over a range of about 500 to 1000 volts.

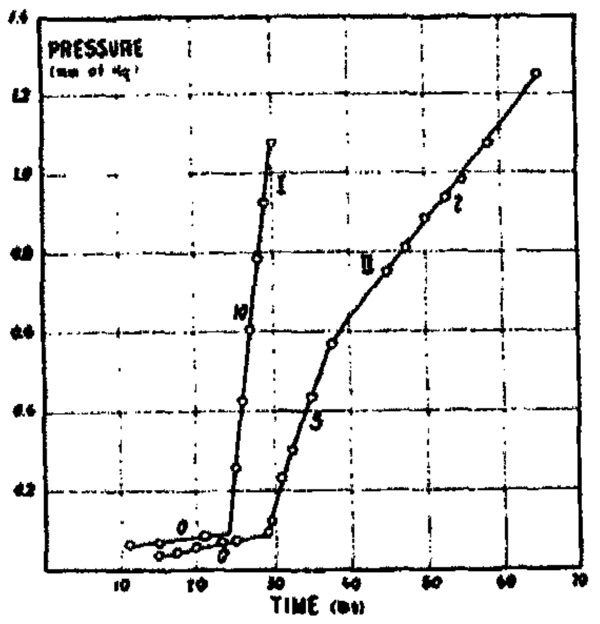

Fig. 5

Typical curves showing rate of pressure increase with time. I. Retene, at 0 and 10 ma. II. Styrene, at 0, 5 and 2 ma.

The principal differences between the method used here and those usually employed in the study of reactions in electrical discharge, is that the gas passes through the discharge only once, and at a low pressure and high rate of flow. Thus, more advanced and complicated secondary reactions probably do not occur to as great an extent as they do when the sample of gas is allowed to remain in the apparatus, or is circulated repeatedly during the time of the discharge.

Procedure

After inserting the hydrocarbon into the bulb E, and sealing the joints a, the system was always tested for air leaks or evolution of gases absorbed in the hydrocarbon. Only the solid hydrocarbons were found to give off appreciable quantities of absorbed gas, and melting them while in the bulb E at low pressure, was found sufficient to cause these gases to be liberated at once. The discharge was started only after the McLeod gauge showed no, or only a small, rate of pressure increase in S, and measurements of this rate of increase, if any, were made at the beginning so that it could be corrected for; for example, see the parts of the curves marked o in Fig. 5.

Upon starting the discharge, the temperature of E, or of the oven, was adjusted so that the width of the dark space was from one to three millimeters. Measurements were then made of the rate of pressure increase in S for discharge currents of 2, 5 and 10 ma., except in the case n-decane, dodecane and n-tetradecane, which were tested over a range of only 0 to 2.5 ma.[1] Typical curves are shown in Fig. 5, in which the pressure in S is plotted against time for various currents. From such curves as these the time rate of pressure increase dp/dt, was determined by measuring the slope.

TABLE I

Rates of Gas Production

(cc/sec/ma × 10^4)

Compound	dq/dt	Compound	dq/dt
n-pentane	60	cyclohexene	105
n-hexane	99	p-diphenylbenzene	51
n-heptane	101	m-diphenylbenzene	41
n-octane	105	o-diphenylbenzene	52
n-decane	113	diphenyl	43
dodecane	133	di-iso-butylene	139
n-tetradecane	145	dipentene	114
n-docosane	155	pinene	101
benzene	25	di-iso-amyl	118
toluene	52	limonene	112
o-xylene	35	p-diethylbenzene	69
m-xylene	47	m-diethylbenzene	71
p-xylene	63	p-cymene	66
mesitylene	71	p-menthane	71
durene	62	styrene	45
hexamethylbenzene	79	2.2.4-trimethylpentane	97
hexaethylbenzene	83	l-heptene	115
n-butylbenzene	81	dibenzyl	49
sec-butylbenzene	80	2.2.3-trimethylbutene	97
tert-butylbenzene	66	methylnaphthalene	62
n-propylbenzene	71	octylene	105
iso-propylbenzene	58	triphenylmethane	42
ethylbenzene	64	anthracene	35
naphthalene	39	stilbene	57
dihydronaphthalene	72	acenaphthene	50
tetrahydronaphthalene	71	retene	56
dekahydronaphthalene	103	phenanthrene	37
cyclohexane	86		
methylcyclohexane	93		
l-methylcyclohexene	105		

When sufficient data had been obtained to determine dp/dt at 2, 5 and 10 ma., a long run at 10 ma. was made for the purpose of obtaining sufficient gas for analysis. This gas was pumped from S by the Toepler pump L, and then passed through the coil N, immersed in carbon dioxide and ether, into the pipette M. The gas analysis is described in a later section.

The solid products of the reactions formed principally on the cathode, but also in smaller amounts on the anode and walls of the discharge tube.

They were removed at the conclusion of the run, by scraping the various parts, then washed and weighed. No attempt has yet been made to investigate liquid products, but their formation was observed in many cases.

Molecular Structure and the Rate of Gas Evolution

Fairly definite and consistent relationships have been found between the structure of the molecule and the rate at which gas is evolved in the discharge, when the current is held constant. The rate at which gas is produced dq/dt for all compounds investigated, is given in Table I. These rates seem to follow two empirical rules, which may be stated as follows:

(1) In a series of similar compounds of increasing molecular weight (e.g., the normal paraffins) the rate of gas evolution increases with the molecular weight.

(2) In a series of similar compounds of the same molecular weight (e.g., o-, m-, and p-xylene) the rate of gas evolution increases with decreasing centralization.

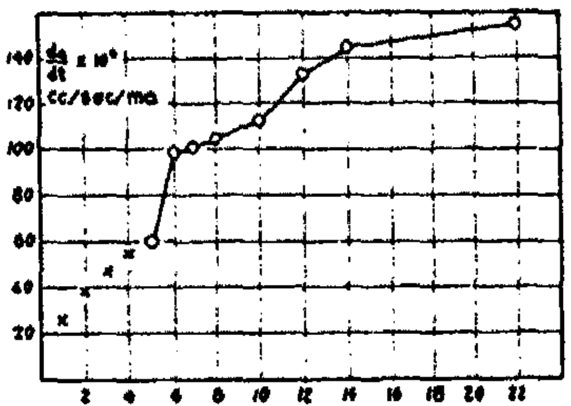

FIG. 6

Rates of gas production for the normal paraffins

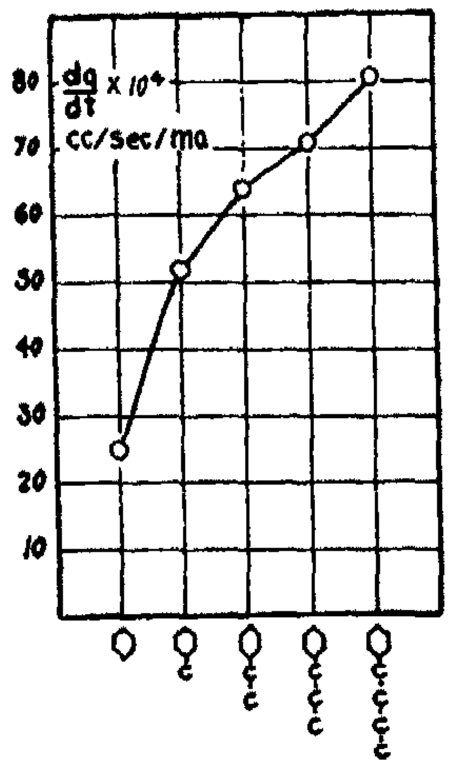

FIG. 7

Rates of gas production for the mono-substituted benzene series:—benzene, toluene, ethylbenzene, n-propylbenzene, and n-butylbenzene.

There is more evidence for the first of these rules than for the second, many isomeric compounds not being available. Also there are some exceptions to both rules.

Some of the more striking results, showing the increase in rate of gas production with molecular size, are graphed in Figs. 6 to 10, which are, for the most part, self-explanatory. The diagrammatic representations of molecular structure, given along the horizontal axes, are somewhat conventionalized.

The data represented by crosses in Fig. 6 will be discussed later. The somewhat large jump between the rate for n-pentane and n-hexane is likely due to the different method of determining dq/dt for n-pentane, necessitated by its high vapor pressure. Its vapor could not be completely stopped by the traps T_1 and T_2, and its interference with the action of the McLeod gauge made the determination of dq/dt unreliable by the use of that instrument; hence its rate was determined by pumping out the gas sample from S and measuring its volume at atmospheric pressure in a burette. The points for n-hexane, n-heptane, n-octane all seem to lie a little too high; this may well be due to the presence of small amounts of their vapors in the gauge. This seems true especially in view of the fact that before the addition of trap T_2 to the apparatus the points for n-hexane and n-heptane lay still much higher[1] than is shown in Fig. 6.

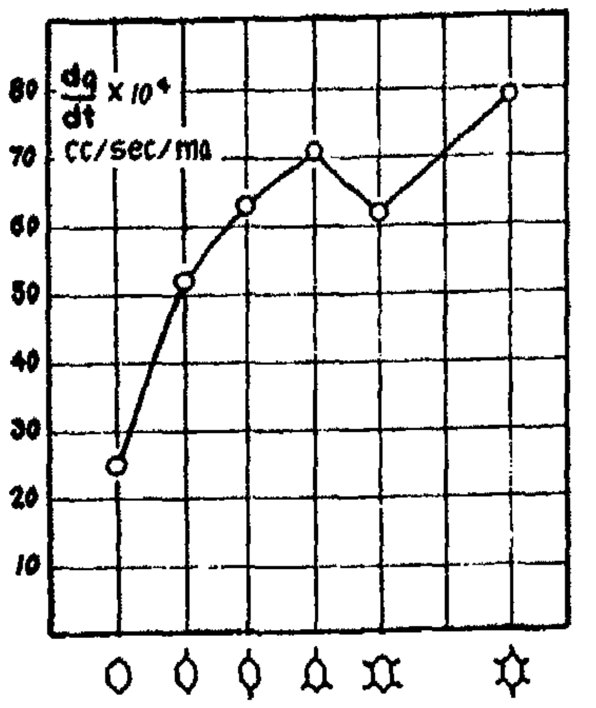

Fig. 8

Rates of gas production for the methyl-substituted benzene series:—benzene, toluene, p-xylene, mesitylene, durene, and hexamethylbenzene.

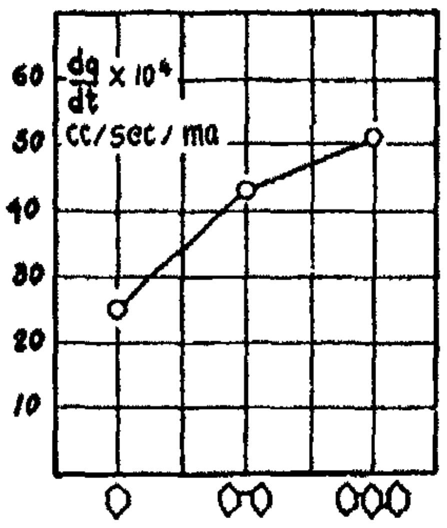

Fig. 9

Rates of gas production for benzene, diphenyl, and p-diphenylbenzene.

Durene seems to be an exception, as is evident from Fig. 8, and also tetrahydronaphthalene, as it may be seen from Fig. 10. In the latter case, however, the departure is probably no greater than the experimental error.

Typical series showing the effects of varying the centralization of the molecule are given in Fig. 11. The o-, m-, and p-diphenylbenzenes do not appear to obey the centralization rule. Other comparisons are listed in Table II.

In addition to size and centralization, saturation also seems to play a part, for example, the rates for n-hexane, cyclohexane and benzene are 0.0099, 0.0086 and 0.0025 cc/sec/ma, respectively, differences which seem too large to be accounted for solely by the small changes in molecular weight. Styrene and ethylbenzene offer another example. However, the data on this point are meager, and in some cases the presence of a double bond seems to have no effect, as in the case of n-octane and octylene. Sometimes even the opposite effect is observed, as for n-heptane and 1-heptene, but the measurements on these compounds are not very reliable due to their high vapor pressure and the consequent probable presence of their vapors in the McLeod gauge, as has been mentioned before.

Parallelism with Knock Rating. There is a striking parallelism between the rate of gas production and the knock rating as given by Lovell, Campbell

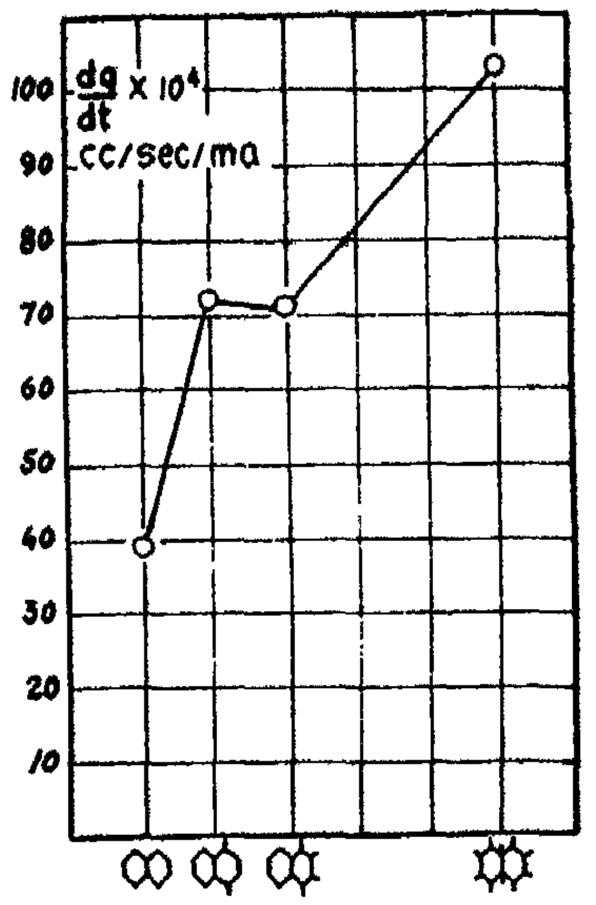

FIG. 10

Rates of gas production for naphthalene, dihydronaphthalene, tetrahydronaphthalene and dekahydronaphthalene.

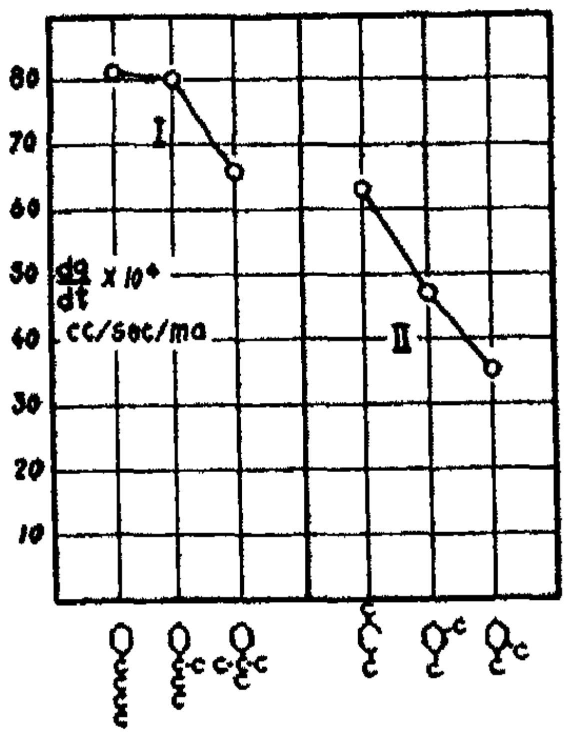

FIG. 11

Series showing effect of centralization on rate of gas production. I. n-butylbenzene, sec-butylbenzene, and tert-butylbenzene. II. p-xylene, m-xylene, and o-xylene.

TABLE II

Some Comparisons between Structure and Rate of Gas Production

Compound	dq/dt (cc/sec/ma × 10⁴)
benzene	25
hexamethylbenzene	79
hexaethylbenzene	83
naphthalene	39
diphenyl	43
acenaphthene	50
stilbene	57
anthracene	35
phenanthrene	37
triphenylmethane	42
p-diphenylbenzene	51
retene	56

and Boyd.[25] These investigators have measured the knock ratings of twenty-seven paraffin hydrocarbons. Definite relations have been found between molecular structure and the tendency to knock. The statement is made that "in a homologous series the tendency to knock increases with the increasing length of the carbon chain, and in an isomeric series the tendency to knock usually decreases as the number of side chains is increased." This is substantially a statement of the two rules enunciated above, governing the rate of gas production in the glow discharge.

Discussion of Relations between Structure and Rate of Gas Evolution. A satisfactory explanation of these results probably requires not only a knowledge of the general features of the glow discharge, such as have been described above, but also information on the fundamental elementary processes of ionization and excitation for the individual hydrocarbons. So far as the authors are aware, no work has ever been done on the critical potentials, probabilities of ionization and excitation, or modes of dissociation by electron impact, of any of the substances dealt with in this article, and until some such work has been carried out, a complete explanation is probably out of the question.

However, in the light of the theory presented above, some idea of the significance of the comparisons in behavior can be obtained. In the first place, it is essential to understand what can be used as a basis of comparison. The most satisfactory would probably be the bombardment of each hydrocarbon by an equal number of equal-energy electrons. This is what was attempted in the apparatus employing the hot filament mentioned above. In the glow discharge this condition cannot be realized, since the electrons have a wide distribution of energies. Furthermore, this energy distribution is not known, nor even the average energy. This latter quantity can be calculated,[2] but the necessary data are not available in the present instances. Therefore, only the number of bombarding electrons is known (the discharge current is a measure of that, as explained above), the average energy (W in equation (3)) being undetermined. Hence the observed variations in the rates of gas production given in this article, may be due to changes in k or W, or both, in equation (3).

It is quite certain that W does change from one hydrocarbon to another, increasing in general with increasing molecular weight. Güntherschulze[26] gives an empirical equation for the cathode potential drop,

$$V = (0.245\,M+4)V_1\alpha, \tag{4}$$

where M is the molecular weight, V_1 the ionization potential, and α a factor depending on the effectiveness of the collisions ("Stossverlust und Wirksamkeit der Stösse"). Although this equation has been shown to hold only for some mono- and diatomic gases, there is no reason to believe it invalid for gases having larger molecules. As a matter of fact, the total voltage across the discharge tube in the experiments reported here was observed to increase with molecular size in general, but due to the great unsteadiness of the voltage, and its dependence upon pressure, these measurements are not recorded here. (The fluctuations in the total voltage were in all probability due to changing conditions in the positive column and on the electrode surfaces, and not to changes in the cathode potential drop, which is the part of the total voltage drop concerned in the chemical action. Otherwise it is difficult to see how such straight lines, representing the relation between dp/dt and time, as those of Fig. 5, could have been obtained).

The changes in the cathode potential drop can be attributed directly to molecular properties, as is suggested by equation (4). The quantum theory lends further support to this, for as the molecular size increases, the number of possible quantum states also increases, and hence the probability that an electron impact will produce an ion rather than an excited molecule, decreases. In other words, the more complex the molecule, the more the opportunities for an electron in an impact to expend its energy in other ways than ionization. Hence, to produce ions at a given constant rate in the dark space, i.e., to have a constant discharge current for each of a series of compounds, requires the expenditure of more energy in the cases of the more complex molecules, since in those cases a smaller percent of the total energy goes to produce ions, and a larger percent toward producing excited molecules.

The rate of reaction depends on the rate of formation of both ions and excited molecules, i.e.,

$$dq/dt = aN + bM,$$

where N is the rate of formation of ions, M the rate of formation of excited molecules, and a and b are constants. The rate of reaction per ion can therefore be written,

$$\frac{dq/dt}{N} = a + bM/N. \tag{5}$$

Hence it should increase as the ratio of excited molecules to ions M/N increases, as is probably the case as we pass from less complex to more complex molecules.

In the case of the data given here on the effect of molecular size, for example in Figs. 6 to 10, the rate of reaction is expressed in terms of gas evolution in cc/sec/ma. This should be proportional to the quantity $\frac{dq/dt}{N}$ in equation (5). Of course, the total number of positive ions formed per second N is not measured, but only those formed in the dark space. However, we shall make the plausible assumption that the ratio of the number formed in the dark space to those formed elsewhere is constant in any series of similar compounds, e.g., the normal paraffins. It follows then that the relations between molecular size and rate of gas evolution may be attributed to variations of a, b and M/N. However, since a and b probably do not vary greatly in a series of similar compounds, most of the change is likely due to changes in M/N. Hence we conclude that *the increase with molecular size in rate of gas evolution per unit current is probably due to the increasing ability of the larger molecules to absorb energy in other ways than by ionization*, i.e., to their larger number of degrees of freedom.[27]

Solid Products

The rates of formation of the solid products are given in Table III. The accuracy of these measurements was not high, because only small quantities were produced (0.1 to 0.5 gm.), and although most of it formed on the cathode, some was deposited in a thin skin over the inside surface of the discharge tube and could not be entirely removed for weighing.

The solid was wax-like in consistency, sometimes brittle. It was dark brown or black in color, and had the appearance of having a high carbon content, although a few preliminary combustion analyses have not borne this out.

The solid weighed was that portion which remained after washings in carbon tetrachloride, benzene and ether, except in a few cases where the amount of solid formed was so small that it had to be determined by weighing the electrodes before and after the run. In these cases the solid was not washed at all.

The rate of formation of this solid for each hydrocarbon is plotted in Fig. 12, against the hydrogen to carbon ratio of the original hydrocarbon from which it was formed. Although the points are scattered, the graph shows a distinct increase in the rate of formation with decrease in the hydrogen to carbon ratio. This is in agreement with the results of Lind,[28] who found that larger ion clusters form in the case of unsaturates than in the case of saturates.

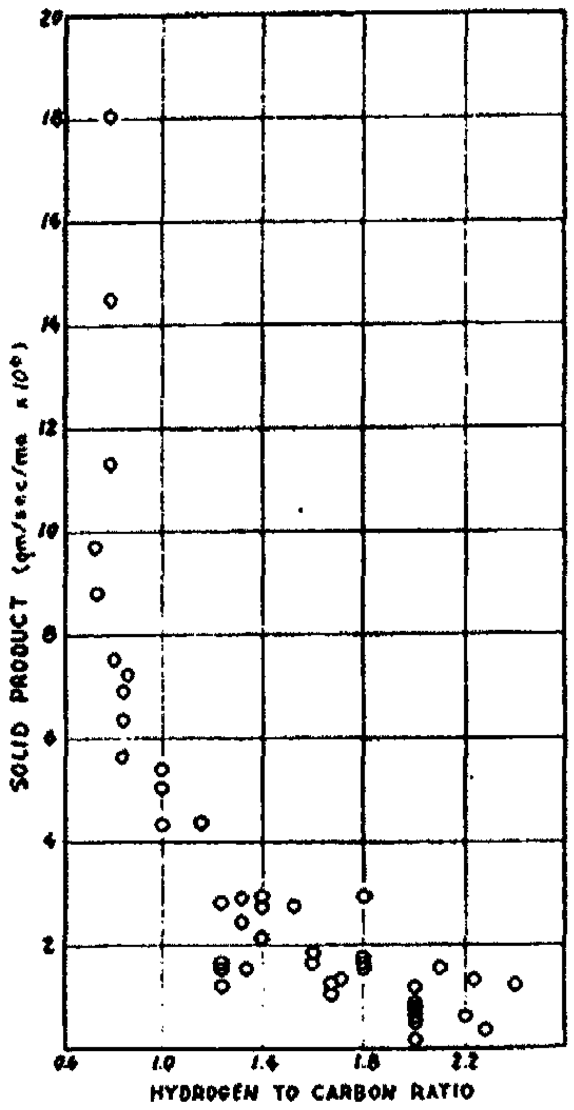

FIG. 12

Data on the formation of insoluble solids from hydrocarbons

Gas Analyses

The complete data on the gas analyses are given in Table IV. These gases were produced in the discharge at a current of 10 ma, and a pressure from 0.5 to 10 mm, and passed, before analysis, through a coiled glass tube immersed in a dry ice-ether mixture.

The analysis apparatus was similar to the one designed by Shepherd[29] at the Bureau of Standards, and embodied the following special features:

1) The balance point of the manometer was obtained by electrical contact. This method was suggested by Gregg[30] and its accuracy determined by Weaver and Ledig.[31] It has been found very satisfactory.

2) A burette illuminator was made by placing a small electric light bulb behind a sheet of tracing cloth. A reflector, made of wood and painted on the inside with aluminum paint, was placed behind the light. This enabled the burette to be read accurately.

TABLE III

Data on Formation of Solids
H/C, hydrogen to carbon ratio; W, rate of solid formation
(gm/sec ma × 10^6)

Compound	H/C	W	Compound	H/C	W
toluene	1.16	4.39	p-diethylbenzene	1.80	1.77
o-xylene	1.24	1.69	m-diethylbenzene	1.80	2.94
p-xylene	1.24	1.37	p-cymene	1.40	2.09
mesitylene	1.32	2.43	p-methane	2.00	0.90
n-butylbenzene	1.40	2.91	styrene	1.00	4.32
sec-butylbenzene	1.40	2.13	2.2.4-trimethylpentane	2.24	1.32
tert-butylbenzene	1.40	2.73	l-heptene	2.00	0.77
ethylbenzene	1.24	2.82	2.2.3-trimethylbutene	2.00	0.58
n-propylbenzene	1.32	2.90	dibenzyl	1.00	5.04
iso-propylbenzene	1.34	1.53	dekahydronaphthalene	1.80	1.52
hexamethylbenzene	1.52	2.76	dihydronaphthalene	1.00	5.40
cyclohexane	2.00	0.51	cyclohexene	1.67	1.06
n-heptane	2.28	0.35	l-methylcyclohexene	1.71	1.36
n-pentane	2.40	1.21	octylene	2.00	0.80
di-iso-butylene	2.00	1.19	naphthalene	0.80	7.51
methylcyclohexane	2.00	0.19	triphenylmethane	0.84	6.91
dipentene	1.60	1.66	hexaethylbenzene	1.67	1.29
pinene	1.60	1.88	p-diphenylbenzene	0.78	14.50
di-iso-amyl	2.20	0.62	m-diphenylbenzene	0.78	18.10
limonene	1.80	1.62	o-diphenylbenzene	0.78	11.60
n-docosane	2.10	1.54	anthracene	0.72	9.70
retene	1.00	5.08	phenanthrene	0.72	8.82
acenaphthene	0.83	6.39	stilbene	0.86	7.24
diphenyl	0.83	5.65			

3) A stopcock with two bores, one a two-millimeter, and the other a constricted bore, was placed in the mercury line at the bottom of the burette. This permitted easy regulation of the mercury level.

4) Capillary T-stopcocks, with large barrels, were used in the distributor. The bore of the capillary tubing was from 1.5 to 2.0 millimeters. Capillary stopcocks with small barrels were tried and found to be unreliable, because of leaks.

5) The water jacket was made large enough to accommodate the burette, compensator and manometer.

6) Dennis-Friedrichs pipettes were used for absorptions.

TABLE IV

Summary of Gas Analyses

Compound	Hydrogen	Acetylenes	Ethylenes	Paraffins
n-pentane	60.2%	10.0%	17.7%	12.1%
n-heptane	46.0	9.7	26.9	17.5
n-octane	48.9	13.8	16.6	20.8
n-docosane	55.7	11.2	25.7	7.4
benzene	46.0	40.5	4.4	9.2
toluene	54.8	29.0	3.0	13.7
o-xylene	60.2	16.0	7.8	16.0
m-xylene	52.2	25.1	6.8	15.8
p-xylene	73.0	11.6	6.3	9.1
mesitylene	55.1	18.9	7.4	18.7
hexamethylbenzene	54.7	11.4	13.1	20.9
hexaethylbenzene	37.8	20.6	17.8	23.8
n-butylbenzene	56.4	9.6	18.0	16.1
sec-butylbenzene	50.6	16.8	16.6	16.2
tert-butylbenzene	45.5	18.8	11.9	23.8
n-propylbenzene	43.0	12.8	27.0	17.2
iso-propylbenzene	51.8	14.4	12.1	21.6
ethylbenzene	50.7	19.6	12.4	17.3
naphthalene	42.8	32.2	23.3	1.7
dihydronaphthalene	54.8	23.4	19.7	2.1
tetrahydronaphthalene	57.0	17.0	20.0	6.0
dekahydronaphthalene	52.5	12.8	30.0	4.7
cyclohexane	46.0	13.2	32.1	8.7
methylcyclohexane	47.0	12.6	26.6	13.8
l-methylcyclohexene	40.8	12.6	31.1	15.5
cyclohexene	48.7	16.5	30.0	4.8
diphenyl	43.2	37.4	17.3	2.1
di-iso-butylene	57.3	11.0	13.8	17.9
dipentene	48.4	11.5	27.0	13.1
pinene	53.7	16.2	18.2	12.0
di-iso-amyl	56.6	15.1	15.5	12.9
limonene	58.4	14.9	18.0	8.7
p-diethylbenzene	36.0	11.4	25.7	27.0
m-diethylbenzene	49.8	14.1	16.9	19.2
p-cymene	46.2	12.0	16.6	25.2

TABLE IV (Continued)

Summary of Gas Analyses

Compound	Hydrogen	Acetylenes	Ethylenes	Paraffins
p-menthane	52.5%	1.4%	28.1%	18.0%
styrene	45.7	18.8	30.7	4.7
2.2.4-trimethylpentane	53.2	3.5	27.1	16.2
octylene	38.7	14.0	36.4	10.9
triphenylmethane	50.1	27.3	21.8	0.8
l-heptene	36.3	24.1	25.4	12.3
retene	39.8	21.1	15.0	24.1
2.2.3-trimethylbutene	37.9	7.9	26.9	27.3
anthracene	44.9	36.2	18.2	0.7
stilbene	46.8	44.8	6.8	1.6
acenaphthene	60.8	24.5	13.3	1.4
phenanthrene	45.8	21.9	28.0	4.3

7) The combustion pipette was constructed as described by Shepherd. It has given service that is entirely satisfactory.

8) A copper oxide tube was used for combustion of hydrogen. It was heated by means of a small electric furnace made from a porcelain porous cup. Connection with the copper oxide tube was made by means of two stopcocks placed in the distributor with the outlets pointing upward.

Shepherd describes the method for exact analysis and also for what he calls technical analysis. The laborious procedure necessary for exact analysis was not followed because gas samples collected under conditions as near identical as possible were found to vary more than the error would be in technical analysis. The error in our analyses was not more than three or four tenths of a percent of the whole sample on each constituent.

Ethylenes and acetylenes were absorbed together in fuming sulphuric acid. Oxygen was absorbed in alkaline pyrogallol. Hydrogen was determined by combustion over copper oxide heated to about 270°C. After these determinations had been carried out the gas that remained consisted of paraffins and nitrogen. The volume of paraffins was determined by combustion in the hot platinum wire pipette. Acetylene was determined in a separate sample of gas.[32] The acetylene was allowed to react with ammoniacal cuprous chloride. The copper acetylide was filtered off, washed with dilute ammonia and dissolved in hot dilute hydrochloric acid. Bromine water was then added to oxidize the copper to the cupric condition. The solution was then evaporated to a thick syrup or to dryness. The copper was then determined by the potassium iodide titration method as described in Scott's Standard Methods of Analysis. Dennis and Nichols[33] say that acetylene is "best determined by leading it through an ammoniacal cuprous chloride solution, a reddish brown precipitate being thrown down.... The acetylene may be determined by taking advantage of the fact that the moist precipitate contains carbon and copper in the atomic proportions of 1:1."

As is evident from Table IV, the composition of the gas evolved from the various hydrocarbons has been found not to vary over a wide range. Furthermore, no evident relations have been found between gas composition and the molecular structure of the original hydrocarbon.

The presence of large amounts of unsaturates in most of the gases is of interest in view of the fact that Lind and Glockler[14] report their absence in gases collected from discharges in hydrocarbons in a Siemens ozonizer. However, these latter runs were of a duration of eight and a half hours, and a flow method was not used. In a run of eighty minutes duration they found small amounts of ethylene and acetylene. Hence, they conclude that unsaturates are formed in the early stages of the reaction, but later used up. The work reported here supports this view, since probably not many secondary reactions occur, and if unsaturates are formed in the first few reactions they should be present in the gas collected, as was found to be the case.

Additivity of Rate of Gas Evolution

There is some evidence that the rate of gas evolution in the discharge is an additive property of the molecule. For example, the points indicated by crosses in Fig. 6, were obtained by subtracting the rate for benzene from those for toluene, ethylbenzene, n-propylbenzene, and n-butylbenzene. The data thus obtained lie on the normal paraffin curve close to the positions that apparently would be occupied by methane, ethane, propane and butane. Also in the case of Figs. 7 and 8, it is apparent that the rates for p-xylene and ethylbenzene are nearly the same, as are also those for n-propylbenzene and mesitylene, suggesting that the carbon groups have the same effect regardless of their arrangement around the benzene ring, providing that they are not too close together. The comparison does not hold good for the higher members of these series, possibly because centralization or crowding, begins to play a part. Such additivity as is suggested here, would be in harmony with the theory proposed above to explain the increase in rate of gas evolution with molecular size, if the number of possible quantum states of a molecule were the sum of the states of its separate parts.

Sources of Compounds and Accuracy of Data

As was stated in the introduction, the purpose of this research was not to study in detail the reactions of individual hydrocarbons, but to make a survey of the entire class of compounds with the idea of finding any outstanding relations which might exist between molecular structure and the nature of the reactions. For this reason, and also because of the prohibitive amount of work and time that would otherwise be required, no great pains were taken in order that each datum be of high accuracy. Consequently, the greatest value of the work lies not in individual figures, but in comparison between numbers of data, each in itself not necessarily highly accurate.

The hydrocarbons used were obtained from the Eastman Kodak Company, with exceptions as follows: acenaphthene, diphenyl, cyclohexane, anthracene, and triphenylmethane were manufactured by the Kahlbaum Chemische Fabrik, Berlin; l-heptene, and 2.2.3-trimethylbutene were supplied by Dr. T. A. Boyd of the General Motors Laboratory, Detroit; methylnaphthalene was supplied by Dr. S. P. Miller of The Barrett Company, New York, and ethylbenzene and n-docosane were prepared by the Department of Organic Chemistry of Cornell University. We wish to take this opportunity to thank all those who helped us in obtaining some of these compounds.

In determining the rates of gas evolution, one run each was made at current values of 2, 5, and 10 ma, (with the exception of the three paraffins mentioned above) and the value of dq/dt at each of these currents obtained. An average dq/dt was then determined by plotting these and drawing the best straight line through the three points. Most of these data are reproducible to within about 10 percent.

The accuracy of the weighings of the solid product is less, owing to the aforementioned difficulty of collecting it, and also to variations in the washing procedure necessitated by differences in the solubilities of the original hydrocarbons which had to be removed.

Only one gas analysis was made of the gases evolved from each hydrocarbon, except when accidents or doubtful results necessitated repetitions. However, considerable work was done in developing the analysis apparatus and procedure, so that the results are probably quite reliable. The method should be accurate to within two or three tenths of a percent.

The formation of solid products on the electrodes, principally the cathode, leads to some ambiguity in the interpretation of the data on gas evolution, since the solid is subjected to continuous bombardment by positive ions and electrons. Thus, complicated and advanced secondary reactions resulting in gas emission, may take place on the electrode surfaces. The gas emission would then not be entirely due to primary or early secondary reactions. However, there is some reason to believe that these solid deposits are a minor factor, at least in so far as the effects on rate of gas production is concerned. In a previous paper[1] it was reported that runs of a duration of 80 minutes showed no departure from the linear relation between pressure and time, as shown in Fig. 5, in spite of the fact that at the beginning of the run the electrodes were clean, whereas at the end they were coated with a heavy layer of solid. Furthermore, McLennan, Perrin, and Ireton[35] have bombarded with cathode rays a similar solid product formed from acetylene, and found no evidence of gas evolution. Runs with an electrodeless discharge are being contemplated, which should clear up this point.

Summary

A theory of chemical action in the glow discharge is presented.

An apparatus for subjecting hydrocarbons in the gaseous phase to the glow discharge, and collecting the reaction products, is described. Data on fifty-seven hydrocarbons are given.

It has been found that in a series of similar compounds of increasing molecular weight (e.g., the normal paraffins) the rate of gas evolution per unit current increases with the molecular weight; whereas in a series of the same molecular weight, (e.g., o-, m-, and p-xylene), it increases with decreasing centralization.

The increase in the rate of gas evolution with molecular size is attributed to the increasing ability of the larger molecules to absorb energy in other ways than by ionization, i.e., to their larger number of degrees of freedom.

The amount of insoluble solid formed has been found to increase generally with decrease in the hydrogen to carbon ratio of the original hydrocarbon.

Analyses are given of the gases evolved in the glow discharge for forty-seven hydrocarbons.

Acknowledgment

In conclusion the authors wish to express their appreciation to those of the Departments of Physics and Chemistry of Cornell University who were helpful in this work, and to Professor Vladimir Karapetoff, who is in general charge of the above-mentioned research program at Cornell on the fundamentals of the disintegration of organic electrical insulation. They wish especially to thank the President of the Detroit Edison Company, Mr. Alex Dow, and the Chief of Research, Mr. C. F. Hirshfeld, for the financial support which made the above-described work possible, and for permission to publish the results.

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References and Footnotes

[*] The work described in this article is a part of an investigation of the fundamentals of the disintegration of organic dielectrics being carried out at Cornell University. It is supported by a fund provided by the Detroit Edison Company.

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[32] In this acetylene analysis the assumption was made that acetylene itself was the only member of the series present. This is quite plausible since the gases were passed through a coil immersed in a carbon dioxide ether slush, the temperature of which was −77°C., whereas the boiling point of the second member of the acetylene series C_3H_4 is −27.5°C.

[33] Dennis and Nichols: "Gas Analysis," 265 (1929). This method was not used however, in the cases of toluene, mesitylene, n-octane, benzene, m-xylene and o-xylene, the acetylenes for these substances being determined by absorption in ammoniacal silver nitrate solution, and ethylenes by absorption in bromine water.

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A STUDY OF THE SODA-ALUM SYSTEM

BY J. T. DOBBINS AND R. M. BYRD

Soda-alum was discovered by Gehlen[1] in 1815. This discovery was confirmed by the work of Zellner[2] and other early investigators. The existence, however, of soda-alum has been questioned by several experimenters, one of whom was Ostwald, who claims that the potassium in ordinary alum may be replaced by rubidium or caesium but not by sodium or lithium. The work of more recent investigators, Auge,[3] Smith,[4] Wadmore,[5] Leffman and Strock,[6] and others has proved conclusively the existance of this compound. The general method employed by these investigators for the preparation of soda-alum was to put together solutions of sodium sulphate and aluminum sulphate in equivalent quantities and concentrate it by heating. The literature does not afford any information as to the limits of concentration between which soda-alum may be prepared, and it appears that little attention was paid to the temperature other than to say that the alum may not be prepared above 30°C. There is also some dispute as to the behavior of soda-alum at ordinary temperatures. Some investigators claim that it does not effloresce at ordinary temperatures, while others contend that it does. Therefore, this investigation was undertaken to see if soda-alum could be prepared at ordinary temperatures, 25°C. being selected, and between what limits of concentration this takes place.

Experimental

Preparation of System: Sodium Sulphate-Aluminum Sulphate-Water

A series of solutions was prepared of varying concentrations with respect to aluminum sulphate, and with sodium sulphate present in excess. Another series of solutions of varying concentrations of sodium sulphate, and with aluminum sulphate present in excess was prepared. These solutions were placed in a constant temperature bath, which was correct to 0.01°C., at 25°C. and allowed to come to equilibrium. After equilibrium had been reached, about 25 grams of the liquid phase, and about 25 grams of the wet residue were weighed out and diluted to a definite volume, from which aliquots were taken for analysis.

Aluminum was determined by a method developed in this laboratory by Dobbins and Sanders,[7] the sodium determined volumetrically by a method developed by Dobbins and Byrd,[8] the sulphates determined gravimetrically by precipitating them as $BaSO_4$, and the water determined by difference.

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[1] Personal communication to Joseph N. Fuchs; Schweiggers Journal, 18, 377.
[2] Schweigger's Journal, 18, 344 (1816).
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[7] Excerpt from Doctoral Dissertation University of N. C. (1931).
[8] Excerpt from Doctoral Dissertation University of N. C. (1931).

In order to ascertain if any appreciable hydrolysis had taken place, in which case it would have been necessary to treat the system as a four component instead of a three component system, a complete analysis was made on several of the samples. By arbitrarily assuming the experimental values of sodium to be correct and calculating their equivalent of sulphate, then calculating the a aluminum sulphate equivalent to the remaining sulphate, the extent of variation of the calculated values of aluminum sulphate from the experimentally determined values could be found. If hydrolysis had taken place, the calculated values for aluminum sulphate would be higher than the experimental values. These results are listed in Table I.

TABLE I

Determination of Hydrolysis of $Al_2(SO_4)_3$

Na_2SO_4 assumed to be correct	$Al_2(SO_4)_3$ by difference	$Al_2(SO_4)_3$ Experimental
0.00%	28.98%	29.29%
2.27	27.27	27.64
3.92	26.45	26.68
6.29	23.04	23.07
10.74	18.26	18.66
16.55	14.25	14.59
18.89	12.84	12.80

TABLE II

Percentage composition of liquid and of residue in system: Sodium sulphate-aluminum sulphate-water at 25°C.

Liquid			Residue		
Na_2SO_4	$Al_2(SO_4)_3$	H_2O	Na_2SO_4	$Al_2(SO_4)_3$	H_2O
0.00	29.29	70.71	0.00	52.78	47.22
2.27	27.64	70.09	1.41	38.54	60.05
3.92	26.68	69.40	1.64	41.71	56.65
6.29	23.07	70.64	11.50	31.10	57.40
10.74	18.66	70.60	14.18	32.98	52.84
13.70	16.24	70.06			
15.44	15.10	69.46	15.30	23.47	61.23
16.30	14.63	69.02			
16.55	14.59	68.86			
18.89	12.80	68.31	19.37	24.75	55.84
18.90	12.28	68.82	40.94	1.63	57.43
19.06	9.18	71.76	39.91	1.54	58.55
19.62	7.28	73.10	40.56	1.08	58.36
19.85	6.83	73.32			
20.13	4.93	74.04			
20.84	2.11	77.05			
21.55	0.00	78.45	44.10	0.00	55.90

The data listed in Table I show that the extent of hydrolysis was insignificant and we were able to treat this as a three component system.

The results of the analysis of the liquid phase and the wet residue are recorded in Table II.

The percentage by weight of anhydrous sodium sulphate and aluminum sulphate as tabulated in Table II are plotted in the conventional way on a triangular diagram. The curve for the liquid phase has two transition points, one giving a very short segment AB on the aluminum sulphate side, a much longer segment BC in the middle, and a fairly long segment CD on the sodium sulphate side. The breaks in the curve at B and at C indicate, of course, that a compound has been formed between the sodium sulphate and the aluminum sulphate.

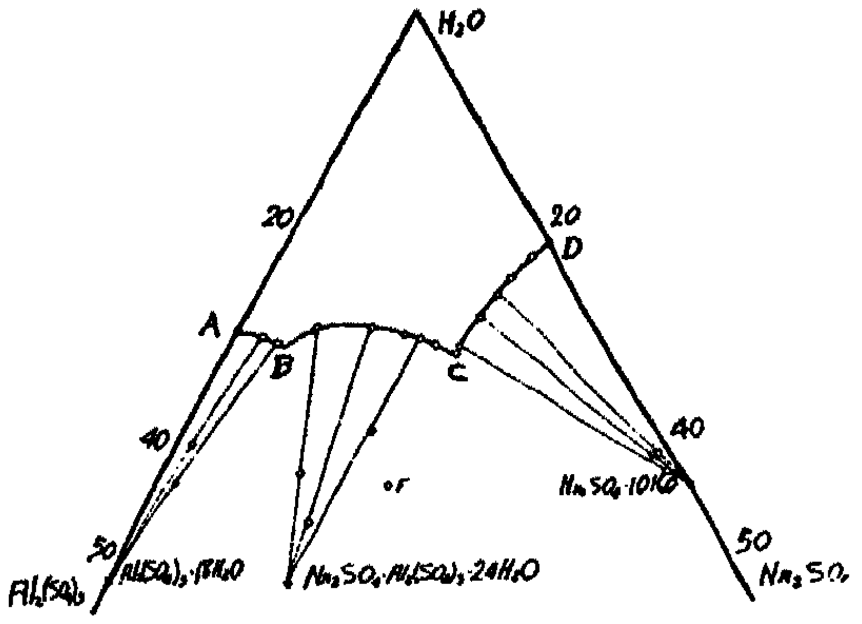

FIG. 1

Solubility of $Na_2SO_4.10H_2O$ and $Al_2(SO_4)_3.18H_2O$ in H_2O at 25° C

In order to determine what compounds exist in contact with the solutions represented by these three curves, samples of the wet residue were analyzed and the results plotted on the triangular diagram. The tie lines drawn from points on segment AB through the corresponding points of the solid phase, intersect at a common point, which represents the composition of hydrated aluminum sulphate of composition $Al_2(SO_4)_3.18H_2O$. Likewise the tie lines drawn from points on the liquid phase segment CD through the corresponding solid phase points, intersect at a common point, which represents the composition of the solid in that field, the compound being hydrated sodium sulphate of composition $Na_2SO_4.10H_2O$.

The compound of primary interest in this system is the one in equilibrium with the solution represented by segment BC. In order to establish the identity of this compound, several samples of the wet residue corresponding to vital points on the liquid phase curve were analyzed and the tie lines drawn. The point of intersection of these lines corresponds exactly to the percentage composition calculated for soda-alum or Na_2SO_4-$Al_2(SO_4)_3.24H_2O$. The composition of this compound was the principal point of contention, and the analysis of it shows conclusively that it is soda-alum.

The point B on the triangular diagram is evidently very near the transition point for the field of soda-alum and hydrated aluminum sulphate, as the tie lines on either side of it pass through the point of composition of hydrated aluminum sulphate on one side and soda-alum on the other. On the other hand, point C is the transition point for the field of soda-alum and hydrated sodium sulphate. This is shown by the analysis of the solid phase which is represented by the point F. At the composition represented by point C, soda-alum and hydrated sodium sulphate exist together in contact with the same solution.

The apparent limits of formation of soda-alum at 25°C. lie between points B and C on the liquid phase curve. Consequently, soda-alum may be prepared at this temperature by taking concentrations which lie between these limits.

It is obvious from Fig. 1 that a straight line joining the point representing solid soda-alum and the apex representing pure water, would cut the curve representing solutions in equilibrium with the solid alum, *i.e.* the components other than water would have the same ratio in both liquid and solid phase. Hence, evaporation at 25°C. of a solution of soda-alum will yield soda-alum without decomposition.

It was found, in the course of this study, that a white, apparently amorphous mass was first formed which later was transformed into small crystals of soda-alum. These crystals grew into larger ones, the growth taking place from the top of the solid layer downward. This peculiar behavior was observed by Spence,[9] and others. Also it was observed that a rather appreciable efflorescence took place in these crystals. This was one of the outstanding points of dispute by some of the other investigators. This point is in agree-agreement with results observed by Leffman and Strock.[10]

Summary

1. A study of the system: Sodium sulphate-aluminum sulphate-water has been made.

2. Soda-alum may be prepared at 25°C. between limits of concentration represented by segment BC on the triangular diagram.

3. Soda-alum effloresces quite readily at room temperature when exposed to the air.

4. Soda-alum can be obtained by evaporating at 25°C. an aqueous solution containing from 5 percent Na_2SO_4 and 26 percent $Al_2(SO_4)_3$ to 19 percent Na_2SO_4 and 8 percent $Al_2(SO_4)_3$.

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[9] Chem. News, 22, 181 (1870).

[10] Am. J. Phar., 100, 474-478 (1928).

THE ELECTROMETRIC TITRATION OF COPPER SALTS BY SODIUM HYDROXIDE*

BY RALPH ALONZO BEEBE

In a previous investigation,[1] the electrometric titration of copper sulphate, chloride and nitrate, using the quinhydrone electrode, was used as a means of estimating the composition of the precipitates formed under various conditions of precipitation. The application of the method to the trichloracetate, acetate, and chlorate is described in this paper.

Preparation of Solutions: A solution of sodium hydroxide (0.4018 normal), free from carbon dioxide, was prepared by the method of Cornog.[2] This solution was used in all the titrations.

Copper trichloracetate (0.4808 normal) was made by the action of trichloracetic acid on a slight excess of basic copper carbonate.[3] After standing several hours the excess carbonate was removed by filtration. An excess of trichloracetic acid was then added to prevent hydrolysis of the copper salt solution. Allowance for this excess was made by taking into account the position of the first break in the titration curves as is shown in Fig. 1.[4]

Copper chlorate (0.3985 normal) was prepared by adding barium chlorate in slight excess to a solution of copper sulphate, and removing the precipitated barium sulphate by filtration.[5]

Copper acetate, 0.4043 normal, was made by dissolving the c.p. salt in water and adding a measured excess of acetic acid to prevent hydrolysis.

All the copper solutions were standardized by adding potassium iodide and titrating the liberated iodine against standard thiosulphate solution using starch indicator. A test showed that potassium chlorate liberated no iodine from a potassium iodide solution. The iodimetric method was therefore assumed to be applicable to copper chlorate.

Copper Trichloracetate

Two methods of titration were employed.

Method A. (*Direct Titration.*) The alkali was added by small increments, allowing about five minutes after each addition for the solution and precipi-

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* Contribution from the Moore Laboratory of Chemistry, Amherst College.

[1] Hopkins and Beebe: J. Phys. Chem., **34**, 570 (1930).

[2] J. Cornog: J. Am. Chem. Soc., **43**, 2573 (1921).

[3] Bateman and Conrad: J. Am. Chem. Soc., **37**, 2555 (1915).

[4] Müller and Müller: Z. anal. Chem., **73**, 47 (1928).

[5] No excess acid was added to the copper chlorate. However, two solutions, one freshly prepared, and the other six months old showed no measurable difference in the titration curves, although some basic salt had precipitated from the latter.

tate to approach equilibrium, before reading the potentiometer.[1] Approximately fifty minutes was required to complete a titration.

In curves 1, 2, 3, and 4 in Fig. 1, obtained by this method for solutions of initial concentration 0.01, 0.03, 0.1, 0.4 normal respectively, the moles of sodium hydroxide per mole of copper salt are plotted against the pH of the solutions. Approximately 1.6 moles of alkali are required for complete precipitation in each case. The alkali requirement was very slightly greater for the more dilute solutions but the difference was too small to be shown on the graph.[2]

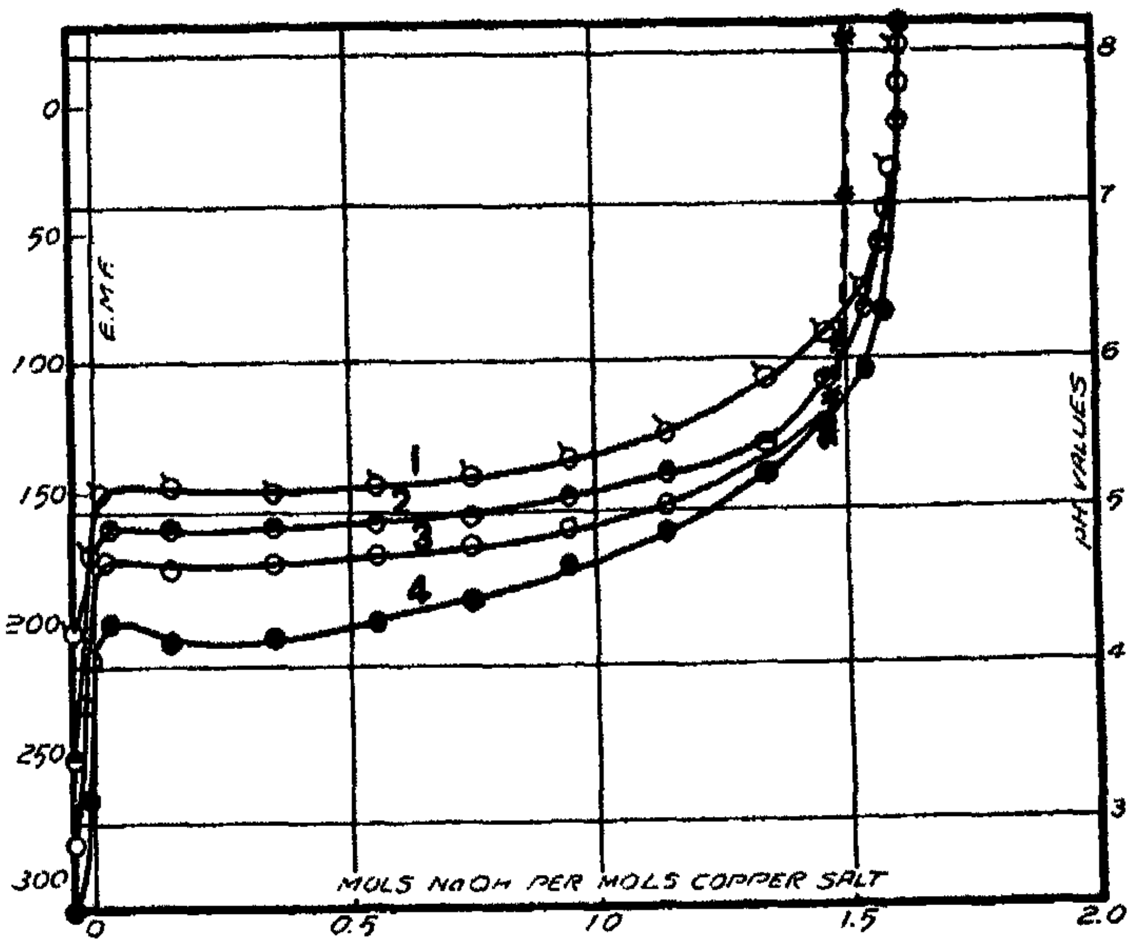

Fig. 1

Copper Trichloracetate. (Curves 1-4, Method A).—1, 0.01 N.; 2, 0.03 N.; 3, 0.1 N.; 4, 0.4 N.; 5, Typical end-point by Method B, (Delayed Titration) for 0.4 N. solution.

Method B. (*Delayed Titration.*) Since it was suspected that curves 1–4 resulted from the precipitation of a mixture of copper hydroxide and the 1:3 basic salt, not in equilibrium, a method of titration was devised to insure that sufficient time should be given to reach equilibrium conditions as nearly as possible. The alkali was added to several samples of copper salt solution in quantities just under 1.5 moles per mole of copper salt. These samples, of different initial concentrations of copper salt, were allowed to stand for varying lengths of time, some with constant stirring, some with occasional

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[1] Even with this time allowance, it was apparent that equilibrium was not completely established because there was a slow drift toward a lower pH indicating the slow disappearance of hydroxyl ions from the solution.

[2] As was shown in the previous paper (loc. cit.), a requirement of 2.0 moles of alkali would indicate the precipitation of the copper in the form of the hydroxide; but 1.5 moles would correspond to the precipitation of the 1:3 basic salt, [Cu(CCl$_3$COO)$_2$ in this case].

shaking, before the titrations were completed electrometrically. The precipitate was bluish white in color after standing and settled readily after shaking. A pH value of 8 was arbitrarily chosen as the end point of the titrations; but, as may be seen in Curve 5, Fig. 1, a deviation of several tenths of a pH above or below this value make no measurable difference in the volume of alkali as read from the curve since the latter is practically vertical throughout the region of pH 6.5 to 8.5.

In Table I are listed the results for the samples which were titrated. The alkali required was decreased when time was allowed to reach equilibrium. All the end-points are closely concordant and in excellent agreement with the theoretical requirement of 1.50 moles corresponding to the precipitation of the 1:3 basic salt. That the time of standing and amount of stirring had no effect indicates that all samples had reached equilibrium.

TABLE I

Alkali required to precipitate Copper Ions from Solution
(1.50 moles required for 1:3 basic salt)

Number of Sample	Salt used	Normality	Time of Standing	Treatment	Moles NaOH added initially	Total moles NaOH
1	Trichlor-	0.48	20 hours	constant stirring	1.461	1.493
2	acetate	0.48	20 hours	occasional shaking	1.461	1.502
3	"	0.40	20 hours	constant stirring	1.461	1.505
4	"	0.40	20 hours	occasional shaking	1.341	1.497
5	"	0.40	20 hours	" "	1.381	1.497
6	"	0.40	12 days	" "	1.345	1.495
7	"	0.10	20 hours	" "	1.480	1.500
8	"	0.10	8 days	" "	1.446	1.494
9	"	0.075	20 hours	" "	1.453	1.497
10	"	0.075	8 days	" "	1.453	1.492
11	"	0.05	20 hours	" "	1.455	1.503
12	"	0.05	8 days	" "	1.460	1.500
						1.498 (Av.)
20	chlorate	0.40	20 hours	" "	1.333	1.586
21	"	0.40	4 days	" "	1.434	1.593
22	"	0.40	9 days	" "	1.384	1.590
23	"	0.10	20 hours	constant stirring	1.333	1.633
24	"	0.10	20 hours	occasional shaking	1.475	1.634
25	"	0.10	20 hours	" "	1.490	1.636
26	"	0.05	20 hours	" "	1.466	1.682
27	"	0.05	20 hours	" "	1.536	1.698

Copper Chlorate

Titrations were carried out by methods A and B as described in the case of the trichloracetate. With the chlorate the E.M.F. readings showed almost no drift, and as a result, the horizontal portions of the curves 1–3 obtained by method A shown in Fig. 2 were more easily reproducible than were the corresponding portions of the trichloracetate curves. Curves 1–3 have breaks in the region between 1.5 and 2.0 moles of alkali. It is worthy of note that the initial concentration of the copper chlorate has a marked effect on the position of the break, a larger amount of alkali being required for the more dilute solutions. A 1:3 basic copper chlorate has been reported by Sabatier.[1] It is probable that the precipitate obtained under the conditions described above is a mixture of this 1:3 basic salt and copper hydroxide.

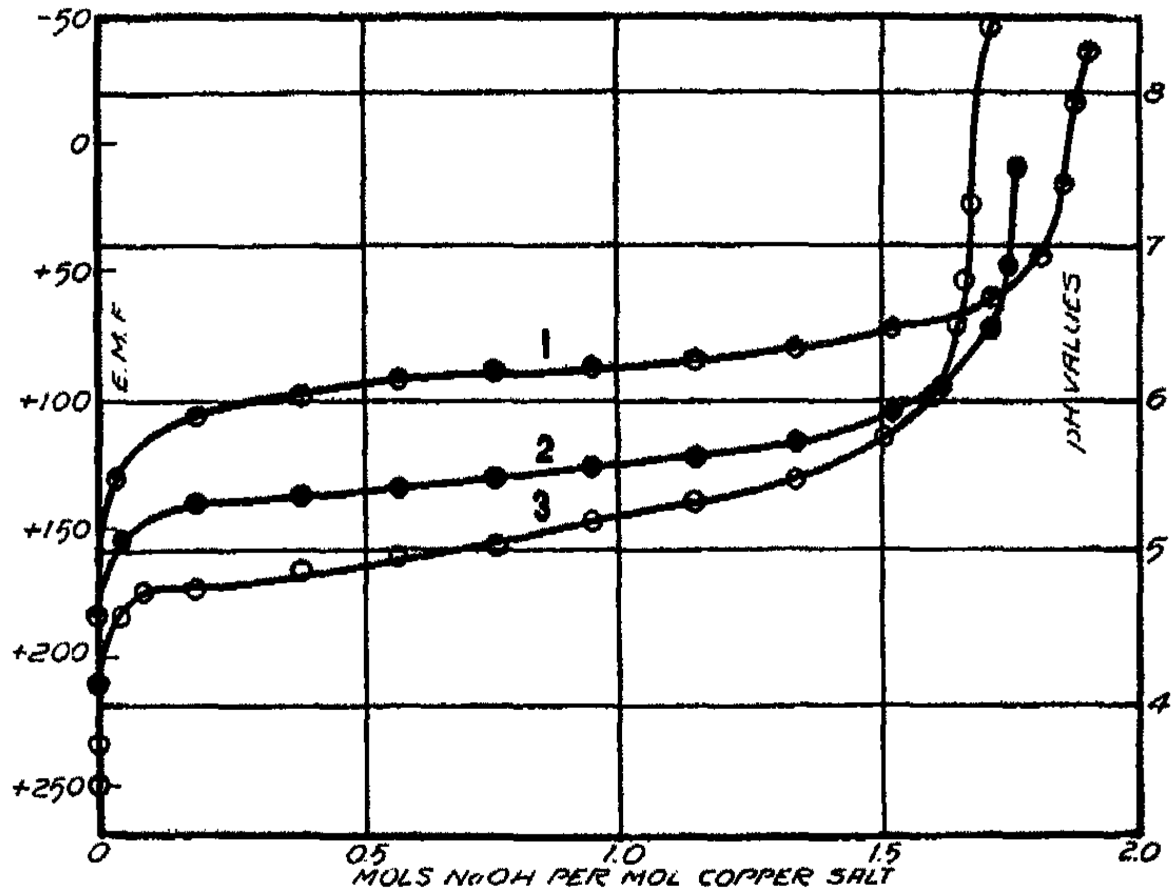

Fig. 2

Copper Chlorate (Direct Titration). 1, 0.01 N.; 2. 0.10 N.; 3, 0.4 N.

An attempt to get more definite evidence for the presence of the 1:3 salt by using Method B was not successful. Less alkali was required for this delayed titration than for the direct titration by method A. For example, the 0.4 normal solution required approximately 1.7 moles by method A (see Fig. 2), and 1.59 moles by method B (see Table I). However, the amounts required for different dilutions were not in agreement and even in the case of the most concentrated solution, considerable more than 1.5 moles was used. Hence no conclusion can be drawn from these data about a definite basic salt.

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[1] Sabatier: Compt. rend., 125, 104 (1897).

Copper Acetate

The occurrence of an inflection at about 1.75 moles in Curve A, Fig. 3, obtained by method A for 0.4 normal copper acetate indicates that the precipitate is even more basic in nature than was the one from a copper chlorate solution of the same concentration. The gradual slope of the inflection was evidently due to the partial decomposition of the basic acetate at first precipitated. Britton has cited a similar case in the precipitation of magnesium by alkali.[1] Titrations by method B showed that there was a demonstrable though rather small diminution in the amount of alkali required if compared to method A.

Slow Titration: Since methods A and B gave unsatisfactory information about the composition of the precipitate, a third method of titration was tried. To equal samples of the copper acetate solution (0.4 N) were added quantities of alkali varying from about 0.1 mole up to 2.0 moles per mole of copper salt. From these samples, kept at 30°C for many days, portions were removed from time to time to determine their pH. Care was taken to shake well before removal of a given portion to insure no change in the relative amounts of solution and precipitate. This method gave the same results as would an extremely slow titration in which several days or weeks were allowed for establishing equilibrium after each addition of the alkali. It was suspected that, by this rather tedious type of titration, some inflection might be found corresponding to the precipitation of a basic copper acetate.

The rather unexpected results of the slow titration, though difficult to interpret, seemed sufficiently striking to be worthy of reporting. They are shown in Fig. 3. The experimental work necessary for the data of Fig. 3 was repeated three separate times, so there can be no question about the existence of the phenomena involved.

Compared to curve A obtained by direct titration, it is seen that there has been a decrease in pH all along the curve after standing one day (Curve 1). Up to about 1.25 moles the amount of this decrease in the first day is relatively small and is negligible after that time. Beyond 1.5 moles the decrease is great. Moreover, a maximum occurs in the curve just above 1.5 moles producing the anomalous effect that a solution to which more base has been added is actually more acidic. This maximum gradually flattens out with time as shown in Curve 4 taken after 49 days. Readings taken after 118 days (not shown on the chart) differed very little from Curve 5. It was not practicable to carry the experiment beyond that point. The final sharp inflection of the curves corresponds quantitatively to the precipitation of copper hydroxide.[2]

Similar results were obtained from copper chlorate and copper sulphate by this method of extremely slow titration. In both cases up to the 1.5 moles point the pH values changed little upon standing, but changed greatly between 1.5 and 2.0 moles of alkali. In this region, the solutions were at first

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[1] H. T. S. Britton: "Hydrogen Ions," p. 255.

[2] A new method by Shiptalskii, Katzen and Klyachko, [J. Russ. Phys.-Chem. Soc., 61, 1497 (1929)], for the estimation of acetic acid in neutral and basic copper acetates has been based on the precipitation of copper oxide from hot solutions of copper acetate by sodium hydroxide. From hot solutions the dehydration would occur much more rapidly.

strongly basic, but changed to a pH of 5–7 when allowed time. In the case of the chlorate a sharp maximum occurred just above the 1.5 moles mark. With the sulphate, the curve suddenly changed direction at the 1.5 moles point becoming almost horizontal.

Although the significance of these curves is not obvious, the presence of the maxima is apparently connected in some way with the dehydration of the precipitated copper hydroxide or basic salt which could be detected by the blackening of the precipitate. There was no blackening of the precipitates in Curve A. On standing, however, those precipitates from the solution to which the greater amounts of alkali had been added gradually darkened, and as time went on the precipitates from samples to which less alkali had been added began to turn dark. The maximum in curves 1–4 gradually moved to the left with time; it was observed that the blackening of the precipitates roughly kept pace with the maximum, precipitates from samples represented by points to the right of the maxima being darkened and those by points to the left remaining blue in color. The appearance of the maxima near the 1.5 moles point suggests the presence of the 1:3 basic copper acetate. So far as the author is aware, no such salt has been reported although basic acetates of composition 2:1, 1:1, and 1:2 have been described.[1]

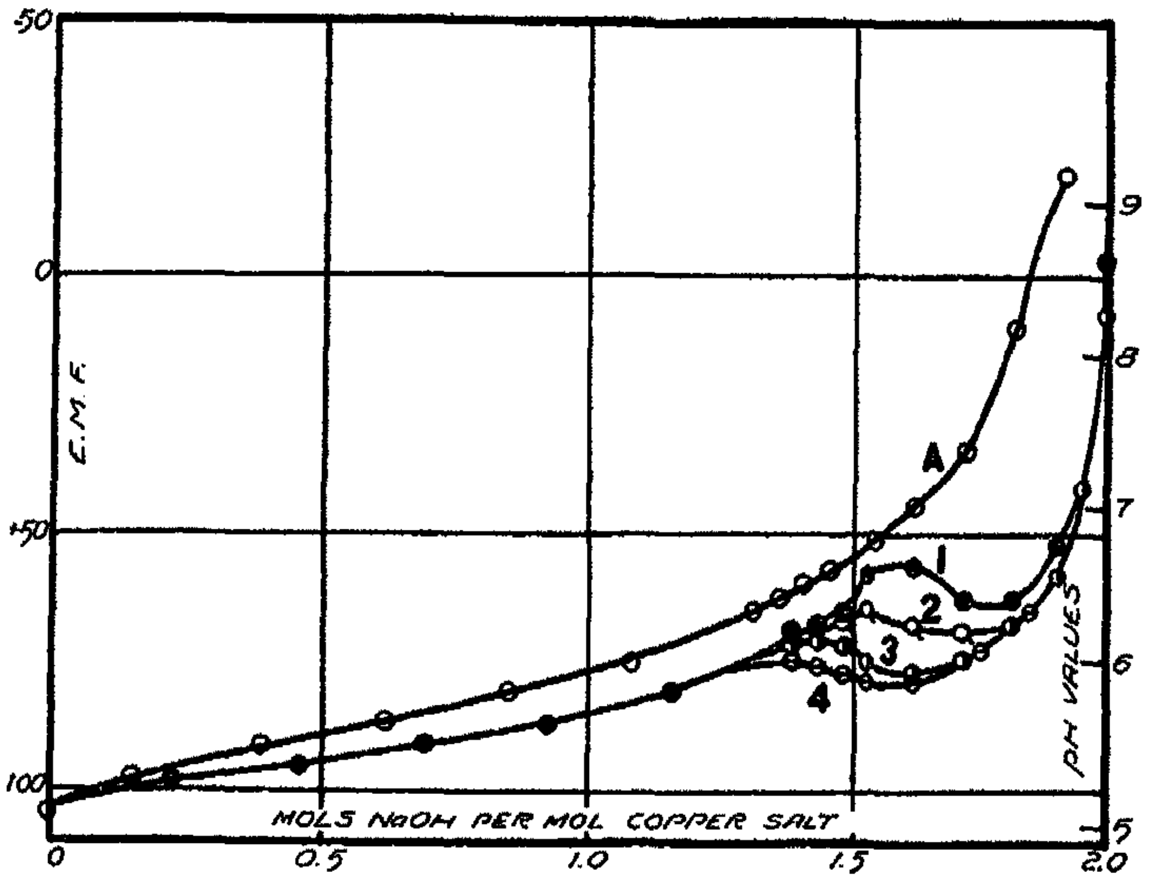

Fig. 3

Copper Acetate. A—Direct titration. (1-4—Slow titration). 1, 1 day; 2, 4 days; 3, 21 days; 4, 49 days.

General Discussion

From the results of this paper and the previous paper by Hopkins and Beebe,[2] it is apparent that under favorable conditions a definite 1:3 basic salt

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[1] Iof, Kobrin and Klyachko: Zhur. Prikladnoi Khim., 3, 336 (1930).

[2] loc. cit.

is precipitated from solutions of copper sulphate, chloride, nitrate, and trichloracetate by addition of alkali, and that less stable basic salts, probably of 1:3 composition, are likewise precipitated from solutions of copper chlorate and acetate, although the evidence for the composition of the latter is not to be considered conclusive. Certain generalizations can be drawn from the data at hand.

All the basic salts are unstable in presence of excess alkali, probably reacting to form copper hydroxide. The order of this instability varies with the different salts, basic copper acetate being the least stable. The latter is so unstable that even in the direct titration it reacts rapidly with hydroxyl ions at relatively low concentrations with the result that the inflection in the titration curve is gradual and almost two moles of alkali, corresponding to the precipitation of copper hydroxide, are required to make the solution alkaline. (See Curve A, Fig. 3). Basic copper chloride, on the other hand, is so stable that it is necessary to reach a relatively high concentration of hydroxyl ions before appreciable rapid decomposition of the basic salt occurs, with the result that a sharp inflection is found at the 1.5 moles point.

The tendency toward decomposition of the basic salt is apparently increased by dilution. This is most noticeable in the case of the nitrate and chlorate and is easily explained by the increased tendency toward hydrolysis of the basic salt in more dilute solution. A comparison of the direct titration curves for copper nitrate and copper chlorate, shows that the basic nitrate is the more stable of the two since for solutions of the same initial concentration, say 0.1 normal, more alkali is required in the case of the chlorate.

On standing in the presence of excess copper salt solution, copper hydroxide tends to react to form the 1:3 basic salt, as shown experimentally by the results of method B in this paper and of the so-called "effect of prolonged stirring," in the previous paper. Here it is found that cupric chloride and sulphate react most readily with copper hydroxide to form the basic salt, and cupric acetate least readily.

By comparison of the relative tendencies of the copper salts to react with copper hydroxide and of the basic salts to be hydrolyzed or to react with excess hydroxyl ions, the basic salts of copper which have been studied may be listed in the following order of stability: chloride > sulphate > trichloracetate > nitrate > chlorate > acetate.[1]

Summary

1. Electrometric titration curves are shown for copper trichloracetate, acetate, and chlorate with sodium hydroxide.

2. Evidence is presented for the formation of a definite 1:3 basic copper trichloracetate, $Cu(CCl_3COO)_2.3\ Cu(OH)_2.xH_2O$ not previously reported.

3. The order of stability of the basic salts of copper thus far studied is chloride > sulphate > trichloracetate > nitrate > chlorate > acetate.

The author's thanks are due to Howard Jones and Stewart Seass who checked a part of the experimental work reported in this paper.

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[1] The position of the sulphate relative to the chloride is rather uncertain owing to the complicating tendency to form a 1:2 basic copper sulphate.

NEW BOOKS

Science in Action. *By Edward R. Weidlein and William A. Hamor. 23 × 15 cm; pp. viii + 310. New York: McGraw-Hill Book Company, 1931. Price: $3.00.* "In essence, the work is an attempt at an explanation of scientific management in the industries—management that is compatible with both correct business administration and sound scientism and is in opposition to empiricism. We do not regard scientific management merely as the sentinel of technology: we look upon such management as the field-marshal of the industries and upon industrial research as the intelligence department of this industrial leader. We have not made any special effort to write anything strictly new or distinctly original. In our desire to prepare a reliably informative and easily readable book of definite type, we have drawn freely upon all available sources of fact and are therefore greatly indebted to the views presented to the eye from many peaks in the mountainous literature of science and technology," p. vi.

The book is divided into six parts, entitled: the past and present conditions of industrial research; science and human welfare; science in the industries; science, the pilot of technology; scientific management and rationalization; industrial-research methods and men.

"It has been found at Mellon Institute that the weight of solids per 1,000 cubic feet of air is about twice as great in smoky weather as in clear weather. It has been concluded from research conducted there that the presence of dust or smoke particles in the atmosphere by decreasing the transmissibility for light and heat, tends to raise the minimum temperature, lower the daily range of temperature, and, in the case of a very dense cloud, to diminish the maximum temperature. The presence of smoke and dust in the air is believed to increase the probability of the formation and maintenance of fog, and the tarry substances from smoke make city fogs more opaque and hence more persistent than country fogs, thereby reducing the hours of sunshine. Both the direct and diffuse solar radiations that filter through a city smoke cloud are very low in the hygienically valuable ultraviolet radiation," p. 75.

"The subject of sleep is receiving thorough attention by the Simmons Investigation at Mellon Institute. H. M. Johnson and the other scientists engaged in this research tell us that, during sleep, something seems to be made or stored in the cells of the body, the reserve supply of which is very small. The maintenance of nourishment and growth in children, the repair of bodily tissues destroyed in the course of the day's activities in persons of all ages, the repair of waste occasioned by disease, and the establishment of immunity, or defense against disease, require adequate sleep for their accomplishment. It has been found that the consequences of sleep-starvation very closely resemble the results of partial deprivation of air, of want of food, and of intoxication by narcotics, such as alcohol.

"In the modern city we cannot control the lights, the noises, or even the temperature, and hence we must seek our rest under external conditions that are not at all favorable. On the other hand, as the demands of work, business, and society become more exacting, the need of adequate attention to sleep and rest is steadily increased. Several cities are inquiring into the practicability of minimizing unnecessary noise. But a noise that disturbs the sleep of one person at a given time may actually enhance the sleep of another; and even the first person, by changing his attentional habits, may come to use it as a means of intensifying his sleep. Deaf people as a class do not rest more quietly than normal people," p. 76.

"Chemistry has given many innovations to packing-house technology. For example, it has made the smoke of hickory bark available in liquid form, so that sausages or other meat products, instead of being 'smoked' for several days or weeks, are very quickly preserved by immersion in this 'condensed smoke,' which is prepared by distilling wood. The chemical principles of this form of preservation are the same by both methods. Another interesting discovery in the meat-packing industry relates to the pickling process. It was formerly thought that, when hams and bacon were pickled by saltpeter, the latter effected the preservation of the meat. Research has revealed, however, that the essential preservative is not the saltpeter itself, but a small amount of sodium or potassium nitrite, which is formed from saltpeter by the action of bacteria. Consequently sodium nitrite is now being used instead of saltpeter in amounts not exceeding 200 parts per million in the finished product. This new process is cheaper and more easily controlled than the original procedure," p. 85.

"There seems to be a natural law that regulates the advance of science. Where only observation can be made, the growth of knowledge creeps; but where experiment can be carried on, knowledge leaps forward. The influence of this law is especially evident in the history of medicine, wherein it is apparent from recorded fact that real medical progress comes from the growth of accurate knowledge as it is gleaned in the laboratories of science. The observation and description of diseases by physicians over many centuries led to little actual advancement. The experimental method, completely and generally followed only in the last several generations, has induced more progress in each decade of its application than all earlier work. This method has headed medicine towards the stage of an exact science," p. 87.

"A statement that is frequently seen in print is that, during the last quarter of a century, from ten to twelve years have been added to the average expectancy of life. This statement is statistically correct, but is generally misunderstood. It does not mean that ten years have been added to the expectancy of life at all ages, but that ten years have been added to the average expectancy, which is very different, indeed. This increase in the average expectancy of life is due almost entirely to a greatly diminished mortality rate during the first few years of life, so that many more individuals live to adult age. There has been practically no increase in life expectancy of those fifty years of age or over," p. 97.

"Scientists are trying to speed up plant growth by chemical treatment. In recent years, in fact, the use of certain organic chemicals as plant stimulants has attracted much attention. It has been found, for example, that the gaseous hydrocarbon ethylene, produced from natural gas, will change the color of citrus fruit from green to yellow. As a result of this work, carload lots of oranges, lemons, and grapefruit can be easily treated to give the color desired for table use. One cubic foot of ethylene per 1,000 cubic feet of space is used commercially. It is said that the treatment does not have a deleterious effect on edible portions of the fruit and that it apparently acts by stimulating life activity. The green color of the stalks and leaves of celery can be removed by blanching with ethylene. This gas also hastens the growth of tomatoes and accelerates the ripening of bananas," p. 106.

"It has been estimated that chemistry has thus added over $10 to the value of the crop for every bale of cotton grown. Cottonseed and its byproducts are now contributing about $275,000,000 annually to the national welfare through the aid of the oil miller and refiner and the chemist. David Wesson, the leading authority in this field, predicts that the value of the cottonseed crop will ascend to $500,000,000 a year when processes for obtaining more oil from seed and for making products of the residue are put into general practice," p. 110.

"If additional proof is needed of the economic value of scientific research in sugar technology, it may be found in the achievements of a western sugar company in the recovery of first-grade sugar from molasses of an inferior grade. The best price obtainable from cattle-feed mixers and yeast manufacturers for this molasses was about $10 a ton. As the annual output by the largest of our beet-sugar companies, itself constituting about 48 per cent of our total beet-sugar production, is 45,000 tons of molasses that is 46 per cent sugar, it is obvious that the prize held out was of attractive magnitude. That the problem has been solved is demonstrated by the fact that the company is now salvaging about three-fourths of the sugar originally held by this 'discard' molasses, the salvaged sugar being sufficiently pure to be used in making fondant, for cream centers of confections. Of the residual products the mother liquor offers possibilities for further recoveries of salts and amines that are usable industrially, and the final molasses residue—about 9 per cent of the original mass—yields that most interesting sugar, raffinose. A characteristic of the latter is its ability to retard the crystallization of sugar solutions, which makes it of interest to the candy manufacturer. It now sells for $160 a pound; and we are told that if sufficient demand for it were to render quantity production feasible, the price would drop to approximately $3 a pound. The work of the research department has therefore justified itself handsomely. From each hundredweight of the original substance, worth 50 cents, there is being reclaimed 35 pounds of sugar, worth $1.75, to which is to be added the income from potassium salts and amines, and the even more valuable raffinose," p. 112.

"A waste utilization of more popular interest has been reported from one of the large Hollywood motion-picture laboratories, which has lately turned its tanks of old developing solutions into a silver mine yielding $6,000 a month. The emulsion on undeveloped film consists largely of silver, combined with bromine as silver bromide. When developed, the silver bromide that has been exposed to light changes to metallic silver. In the fixing bath, the unchanged silver bromide is dissolved out, leaving clear spaces where the film was in darkness. Every pound of silver bromide contains over nine ounces of silver. Though miles of film are run through the solutions weekly, and they contain large quantities of silver, they were formerly thrown into the sewer when their power was exhausted. Now, by a simple chemical process, the silver is recovered and sold to the U. S. Mint at San Francisco. Old film is also burned to win back the silver, and sometimes yields as much as $1,000 worth of silver in a month in addition. One million feet of waste movie film is said to yield 800 ounces of silver," p. 158.

"One of the recent scientific discoveries is a fish-scale substitute for making pearl Celluloid. It has the characteristics of fish-scale at about one twenty-fifth of the cost," p. 168.

"For many years emulsion makers had observed that certain gelatins were satisfactory and others were unsatisfactory for photographic use. A few years ago it was found that an extract could be prepared from a good gelatin which, on addition to a relatively inert gelatin, made it photographically active. An extensive investigation was then begun by the Kodak Company's manufacturing department. The entire process of gelatin manufacture was subjected to a thorough analysis. Hides, bones, cereal preparations, and many other substances were examined. Finally it was shown conclusively that a derivative of mustard oil, called *allyl thiocarbamide*, was the sensitizing substance. Its presence in minute concentrations of 1 part in 1,000,000 to 1 part in 300,000 was shown to be the cause of the suitability of certain gelatins for use in photographic emulsions," p. 169.

In 1916 Erwin O. Freund established at Mellon Institute of Industrial Research a fellowship, the purpose of which was to produce a synthetic casing. "Freund was engaged in the sausage-casing business and early saw the need of a synthetic product that would at first supplement, and ultimately replace, the only partly satisfactory animal containers. This fellowship was in almost continuous operation for ten years. Freund's faith in scientific research was of a most unusual type, as was shown by his persistence even after very unpromising results had been obtained over a period of several years. Even in the face of apparently certain failure of the investigations, Freund 'knew it could be done and the right chemical combination would do it.' His patience and confidence in research did not go unrewarded, for at the end of the tenth year a casing that met the requirements was produced by W. F. Henderson and H. E. Dietrich, the fellowship incumbents," p. 173.

"Triethanolamine is another interesting member of this family. It resembles ammonia somewhat, but is highboiling, not volatile, practically odorless, and slightly viscous. It forms neutral soaps with the fatty acids which are equal in many respects to sodium and potassium soaps and superior to them for certain purposes where neutrality is essential. Triethanolamine soap is a strong emulsifying agent and efficient spot remover. But triethanolamine *per se* is equally as important as its soaps, being useful in the dyeing industry as a solvent for such colors as indigo and vat and sulfur dyes. Monoethanolamine, a similar compound, is being employed for dehairing hides and for degumming silk," p. 191.

"The soap consumption of our country has been lifted by the introduction of such specialties as 'flakes,' 'beads,' and 'snow.' Soaps are being used in 'breaking' oil-field emulsions; common salt is sold to improve whitewash; sulfur is marketed as a fertilizer; mercury is employed in turbine-boilers to generate power; water glass is used to prevent corrosion in hot-water supply systems; corn starch is utilized to protect calcium phosphate from moisture in phosphate baking powders; and licorice is a constituent of fire-extinguishing froths, which it stabilizes. With the facts supplied by biological research, yeast and citrus fruits are no longer merely things to employ in cooking—they are now sold as aids in the promotion of health. Irradiated yeast, dried milk, farina, and margarin have lately been introduced," p. 209.

"Industrial-research laboratories are chiefly staffed by scientists of the analytic group. The directors of these laboratories therefore must depend mostly on the investigational power of well-trained, ordinary men, or mediocrists. Only rarely are they able to invoke the aid of scientists who can provide new ideas, because these specialists are extremely hard to get.

"We now come to this group of the very fortunate few in whom the value of the idea surpasses all questions of method. Theirs are the intellects which are so endowed as to perceive and grasp the subtile relations which exist but of which the average mind is not aware. An idea arises in such a great mind which 'may be a sort of intuitive anticipation of successful research.' From these few, and from these only, may we expect great and strikingly original contributions to science and technology. That they must use the methods common to all investigators in establishing the truth of their ideas is, of course, understood, but the place of method in their lives is secondary to the idea.

"The mental differences between men are tenfold greater than their bodily differences. It is principally in mind that individuals differ, and the real boundaries between men are not varieties of speech or color but varieties of mind," p. 287.

Wilder D. Bancroft.

Lehrbuch der chemischen Physik. *By Arnold Eucken. 23 × 16 cm; pp. xvi + 1037. Leipzig: Akademische Verlagsgesellschaft, 1930. Price: 54 marks; bound 56 marks.* This is the third edition of the author's "Grundriss der physikalischen Chemie" with a new title. The author points out that in the last five years chemistry has developed in the direction of pure physics to such an extent that a change in the title appeared desirable.

The book is divided into two parts: the chemical-physical phenomena from the standpoint of the theory of heat; and the structure of matter. In the first part the next subdivisions are: general fundamentals of the theory of heat, simple systems (pure substances), and complex systems (mixtures and solutions). Under structure of matter the three subheads are atoms, molecules, and crystals.

"One characteristic feature of the pure theory of heat consists in its being divided into two sharply differentiated fields which differ fundamentally in their method of attacking a problem though not very much in regard to the problems to be solved.

"The first method, which we are wont to call the thermodynamic method, depends on a formulation of two very general laws or principles, which rest on a broad empirical foundation and which may be considered as absolutely accurate over a very wide range. These are the law of the conservation of energy (the first law of thermodynamics) and the principle of Carnot and Clausius (the second law of thermodynamics). By combining the consequences of these principles with phenomena showing empirical regularities, it is possible to deduce new relations, very frequently ones which are difficult to deduce experimentally. The advantages of this method, whose importance for practical purposes can scarcely be over-estimated, lies in the absolute trustworthiness of the results. Of importance is also the possibility of developing a definite technique whereby the expert can solve numerous problems almost automatically. On the other hand the thermodynamic attack has the disadvantage of not giving any deep insight into the concrete mechanism of the processes and therefore fails with many problems to solve them completely.

"The complement to the thermodynamic method is the kinetic method. It is true that one as a rule leaves temporarily the firm foundation of experience and tries by means of hypotheses and more concrete or more general mental models to account for and to correlate the directly observed special processes. The process is very easy to understand. The results are somewhat less certain than those of the thermodynamic method because of the use of hypotheses; but the degree of uncertainty varies very much from case to case. If one introduces a hypothesis *ad hoc* in order to account for a single phenomenon, one would naturally ascribe but a small degree of probability to it because of the possibility that other hypotheses might serve equally well. If, however, a single hypothesis accounts for a relatively large number of phenomena both qualitatively and quantitatively, it is improbable that one can find a second hypothesis which can compete with it. A hypothesis loses more of its originally uncertain character, the greater the number of phenomena which it can explain and comes in time more closely to being an unquestioned, although only indirectly accessible, empirical law. Fortunately it is in exactly this way that the actual (more general) basic assumptions of the kinetic theory have received their justification in the last decades," p. 5.

The Nernst heat theorem is stated as follows, p. 57: "For reactions between solids and liquids, that A-curve is the right one which is absolutely horizontal at the absolute zero." "While the Nernst heat theorem is not absolutely accurate even for condensed systems and cannot therefore be put in the same class with the first two laws of thermodynamics, its practical usefulness is not decreased thereby," p. 59. "The inadequacy of the classical theory of heat is particularly evident if one considers a diamond in an atmosphere of hydrogen or helium at 20° abs. If one supplies heat energy to the system, it will be taken up only by the gas molecules, because the atomic heat of the diamond is practically zero." p. 141.

Bridgman's data on ethyl ether show that there is no possibility of defending the assumption by Tumlirz and Tammann that at very high pressures liquids pass into an ideal limiting state, p. 182. The accuracy of the assumption by Mathias of a rectilinear diameter for liquid and vapor is so great that one can determine the critical volume more accurately in this way than by direct measurement," p. 214.

The "inversion point" for iron at about 770° is not sharp and even with the purest materials the heat effect is noticed over a temperature range and not at a single temperature. "On the basis of these facts there can be no phase change in the sense of the phase rule at the A_2 point because the essential condition for discontinuity is lacking. As a matter of fact Westgren examined the structure of iron by means of X-rays and found no change in the crystal structure on passing through that point, while such a change must have occurred if there had been a real phase change of a one-component system since it is impossible in a one-component system to imagine two different phases with the same molecular structure. The heat effect on passing through the A_2-point therefore has no significance for the phase rule. It represents merely an anomaly in the atomic heat which has nothing to do with a phase change." p. 318.

The author says, p. 326, that the experiments to determine the degree of solvation of the ions have led to values which differ widely among themselves. On p. 334, the author points out that a necessary condition for Nernst's distribution law to hold is that the substance in question behaves like an ideal gas in both phases at the concentrations studied. This limitation makes it impossible to work over a range in which there can occur any marked increase in miscibility of the two hypothetically non-miscible liquids.

The author evidently belongs to the Nernst school and not to the Ostwald school, because he calls methyl orange, very properly, a weak base, p. 399. Owing to the abnormally high molecular lowering of the freezing-point with cylohexanol as solvent, the variations from the theoretical are quite different for lithium chloride in cyclohexanol from lithium chloride in water, p. 408. On p. 457, it is clearly implied by Fig. 91a that one must treat a dissolved solid as a liquid, though this is not mentioned specifically. On p. 460 the author states that the water in a twenty percent calcium chloride solution may be considered as being under a pressure of one thousand atmospheres. When charcoal is activated by steam at 800°, its power of adsorbing organic substances is increased enormously; but there is relatively little change in its capacity to adsorb argon, p. 473.

Thiosulphate ion is oxidized by hydrogen peroxide to tetrathionate in presence of iodine ion and to sulphate in presence of molybdic acid, p. 603. Hückel considers that the reaction velocity constant is a function of the molecular dipole moment of the solvent. The author accounts for the decomposition of phosgene being a function of the square root of the conconcentration of the chlorine, p. 607, by postulating the reactions: $COCl_2 + Cl \longrightarrow Cl_3 + CO$, $Cl_3 \longrightarrow Cl_2 + Cl$, $2Cl \longrightarrow Cl_2$. On p. 624 is the statement that certain reactions, such as the formation of hydrogen sulphide seem, to occur according to different mechanisms at different temperatures. In so far as there are heterogeneous reactions, it is probable that there is a difference in the type of adsorption, as postulated by H. S. Taylor in the June number of the Journal of the American Chemical Society.

"Beutler and Josephy showed that under certain circumstances the chemiluminescence of mercury causes the emission of lines whose energy of excitation is considerable, sometimes twice as large as the energy becoming free in the single elementary reactions. One must therefore postulate the coupling of the energies made available by at least two reactions," p. 747.

The conditions for the formation of a chemical compound seem quite simple, p. 917. "The formation of a molecule always occurs if the electrons of the two single atoms are able by combining to form a more stable configuration." "An atom has as many free valences as it has electrons which do not belong to a doublet group," p. 919.

According to Heitler and London, "the phase-waves of the two hydrogen atoms are decisive for the behavior of the electrons, as elsewhere in wave mechanics. To give a better picture let us consider their oscillations with reference to the oscillations of two pendulums. If the pendulums are infinitely far apart, each swings without disturbing the frequency of the other. If they are brought closer together we assume that a mutual coupling takes place in consequence of the electrostatic forces. The system now constitutes a double pendulum, the theory of which is discussed in detail in mechanics. The feature of it, essential to this particular case, is that the two pendulums, when coupled, throw each other out even when the natural frequencies are identical, and there are then present two frequencies, one of which is in general larger and the other smaller than the original frequencies. If we apply this conception to the phase waves of the two electrons, we deduce the existence of two frequencies," p. 938.

On p. 943, we have the empirical generalization that formation of double molecules or association to larger complexes is tied up to the presence of dipole moments. Water, acetone, and the alcohols, have relatively large dipole moments.

In strongly polar crystals, the lattices must be built up either of atoms or of ions. The following facts show that we are dealing with ions. "The thermal frequencies of the elementary components of the salts can be detected electromagnetically by the so-called residual rays, which is only conceivable in case of ionization. Experiment confirms quantitatively the calculation of the so-called lattice energy on the assumption of complete ionization. The intensity of the Röntgen rays scattered (and absorbed) by the atoms depends upon the number of electrons in the outer ring. . . . In the case of lithium fluoride Debye and Scherrer have shown that the reflected intensities are consistent with the assumption that the lattice components are ions," p. 963.

While there is a great deal to be said for the assumption that inside a metal there is a relatively larger number of electrons which are detached from atoms and practically free to move, the author considers it probable "that the assumption is not accurate that the electrons inside a metal are completely free. We must therefore take into account an always present, more or less strong, coupling with the atoms, somewhat in the way postulated by Bloch," p. 1001.

There are a great many good things in this book, which the reviewer expects to utilize in his lectures, such as the data: for the Ramsay and Young rule, p. 232; for the change of melting-point with pressure, p. 238; for the dissociation constant of nitrous oxide, p. 269; for the percentage dissociation of calcium into ions and electrons, p. 301; for the molecular lowering of the freezing-point, p. 344; for the variation of the dissociation constant of water with the temperature, p. 378; for the heats of neutralization of acids and bases, p. 380; for the heats of adsorption of gases by charcoal, p. 471; for the solvation of some ions, p. 542. There are also many helpful cuts: the change of atomic heats with temperature,

p. 128; the change of dissociation with K_p/p, p. 268; the change of the dissociation constant of iodine with the temperature, p. 281; the change of dissociation of iodine vapor with temperature and pressure, p. 298; the activities of succinic acid in presence of alkali halides, p. 451; the reaction velocity curves for the formation and decomposition of hydriodic acid, p. 596; and the change of rate of decomposition of hydriodic acid with the temperature, p. 599.

While there are many good points about this book, there are also many passages which the reviewer believes should have been worded differently. A debatable point is the use of the term Loschmidt number, p. 71, instead of the more usual Avogadro number. On p. 176 the author says that because of the van der Waals forces the concentration of a gas will be lower in contact with the containing vessel than in the mass of the gas. The author has overlooked adsorption. Actually, the adsorption gradient is the reverse of what he assumes. On p. 182 the author says: "One consequence of the surface tension of ordinary glass is the phenomenon that the zero point of a thermometer rises in the course of time. The thermometer bulb contracts for the same reason that a soap-bubble does." In the discussion of Trouton's law, p. 129, there is no mention of Hildebrand's work, though Harteck is cited in a foot-note.

On p. 317 the author says that it is wrong to speak of a liquid phase and a vapor phase, because one passes continuously into the other above the critical temperature. On p. 330 is the statement that Morse's introduction of weight concentration instead of volume concentration in osmotic pressure calculations was purely empirical. That is true so far as Morse is concerned; but van't Hoff had been perfectly clear that the volume occupied by the solvent was the important thing and not the volume occupied by the solution. As van't Hoff said, these do not differ appreciably in the case of very dilute solutions. On p. 358 the author says that it is very hard now to understand why Kohlrausch's law of the independent migration of the ions did not lead at once to the theory of electrolytic dissociation. This shows a curious inability to recognize other people's view-points. Kohlrausch formulated his law in 1873. When Arrhenius came out with the theory of electrolytic dissociation over ten years later, his view was not hailed with delight by the physicists. If it had not been for van't Hoff's explanation of the results of Pfeffer and Raoult, and for the marvellous skill of Ostwald as an expounder, the acceptance of the Arrhenius theory might have been delayed a long time. It was perfectly easy to see in 1873 that electrolytic dissociation, as we now understand it, was a possible explanation of Kohlrausch's results. It was impossible to see that it was a probable explanation, let alone the explanation.

On p. 368 is the statement that practically the only disturbing factor in dilute solutions of strong electrolytes is the mutual action of the ions. This is a probable assumption but it has never been proved and should not be stated as a fact. On p. 373 is the statement that hydrochloric acid must be practically completely dissociated up to about four-normal because the partial pressure of hydrogen chloride is practically zero in more dilute solutions. This is a possible explanation of the facts; but we should get the same result if the undissociated hydrochloric acid were practically completely hydrated. In the same way silver perchlorate would not pass appreciably from the water to the benzene layer if the undissociated silver perchlorate were practically completely hydrated, as it may be. A man who poses as an exponent of exact theory should not fail to mention such possible sources of error. If he can prove that they are non-existent, so much the better; but one has the feeling that this was the silence of ignorance.

So far as the reviewer knows there is no justification for postulating that double salts exist only in the solid form, p. 391. All that people have claimed hitherto is that they are broken down in solution sufficiently to give the ion reactions of the single salts, whereas potassium silver cyanide, for instance, does not give the ordinary reactions for silver as ion.

Diagrams for partial pressures of consolute liquids are given on pp. 426-427; but no real attempt is made to show the significance of the variations from the ideal form. On p. 445 we have a paragraph on the general treatment of non-ideal mixtures and solutions by the use of activity coefficients, where the activity coefficient is, as usual, the factor which makes the concentration agree with the requirements of the equation one wishes to use.

On p. 519, the single, potential differences as determined by Billiter and others are eliminated as having no bearing. Over-voltage is considered to be due, p. 584, either to monatomic hydrogen at the cathode or to supersaturation with molecular cathode. Similarly passivity is said to be due, p. 586, either to adsorbed monatomic oxygen or to an oxide film. He does not even point out that passive iron cannot be due to an adsorbed gas film because one cannot make a permanent break in an adsorbed gas film.

The name of Grotthuss is mis-spelled on p. 718. An optical sensitizer in a photographic plate is said not to take part in the reaction and to sensitize the plate for the light which it transmits, three mistakes in seven lines. On p. 745 phosphorescence and fluorescence are considered to be fundamentally different from the colors of salt flames, because heating is not necessary. As a matter of fact the colors of salts in a Bunsen burner are due to chemiluminescence and are not temperature effects in the ordinary usage of the term.

It is perhaps superfluous to add that the reviewer has not found any place in the book where the question is raised whether the properties of polymerized water molecules may differ from those of less polymerized water molecules except in the matter of density. We know experimentally that white phosphorus is quite different from the stable form; but we stop there. *Wilder D. Bancroft.*

Lakes and Pigments. *By A. W. C. Harrison. 21 × 14 cm; pp. xvi + 274. London: Leonard Hill, 1930. Price 15 shillings.* In the general preface, H. B. Cronshaw, the general editor says: "The present work belongs to a series of handbooks published under the general title of The Modern Chemical Industries Series. The aim of these books is to give a clear straight-forward description—written from a technical standpoint—of present-day manufacturing operations and their scientific control."

Approximately the first fifth of the book is devoted to factory design and equipment, and the second to analytical and testing methods. The next division discusses Inorganic Pigments including chromate pigments, cyanide blues, chromate greens and other precipitated metallic pigments. The fourth division includes pigment dyestuffs and dye-coupling as well as pigments produced by dry blending in the edge runner mill. The final division includes chapters on bases, precipitants, lake colours from basic dyestuffs, lakes from xanthene derivatives, "Fanal" and "Brillfast" colours, lakes from soluble acid dyes, "Reflex" lakes, alizarin and madder lakes, and lakes from natural dyestuffs.

"The object, then, of this book is to fill a distinct gap between manufacturers' publications and the chemical textbooks, and offer the skilled chemist or technical man a reliable practical work of reference, from which he can compare and confirm his own knowledge and theories, and pick out additional practical hints from the experience of others. The book is intended, above all, to serve as a textbook for the junior chemist or technical man, to whom it should prove useful in furnishing actual details of work and enabling him to foresee and provide for many small difficulties which are encountered in the actual working of processes." p. 2.

It is a bit confusing to have the author adopt as his definition of Lake: "Any coloured substance, produced by the precipitation of an organic dyestuff, more or less translucent, insoluble in the particular vehicle in which it is to be used, and non-bleeding in water." This permits him to include a heading for lakes from soluble azo dyes and to define its thus: "This classification is adopted to describe those lakes which are produced from clear dye solutions by simple precipitation with a metallic salt, this being in the majority of cases barium chloride, although in a number of cases calcium chloride and occasionally aluminum, lead or chromium salts are used," p. 215. The colored substance resulting from the use of barium chloride is not what most people call a lake and must certainly differ from that formed by aluminum salt with the same acid dye.

The book as a whole is decidedly empirical in character and about as near as the author gets to any theory of the reactions which he describes is found in his treatment of the alizarin lakes. "The alizarins belong to the 'mordant dyestuff' class, and they owe this property to the presence of two hydroxyl groups in the 1:2 positions of the anthraquinone molecule.

"These are capable of forming with aluminum and calcium a very complex inner salt which is of great stability. Although many theories have been advanced as to the composition of Alizarin lakes, the subject is still a matter of controversy.

"Liechti and Suida give the formula as $Al_2O_3 \cdot CaO(C_{14}H_6O_4)_3H_2O$. Apart from aluminum and calcium, turkey red oil appears to perform a more than purely physical function and to enter into actual chemical combination with the alizarin."

Throughout the book are many formulas and methods of procedure for the preparation of large numbers of important colored substances. The book should prove of interest to those engaged in research in this field or to those actively engaged in "The Manufacture of Lakes and Precipitated Pigments," which is the full title. *Herbert L. Davis.*

Der Smekal-Raman Effekt. *By K. W. F. Kohlrausch. 22 × 14 cm; pp. viii + 392. Berlin: Julius Springer, 1931. Price: 32 marks.* It is now over three and a half years since this effect was announced and few fields of physical enquiry have been so extensively studied by so many observers in such a limited time. At the present time taking the whole of scientific literature there is probably an average of three papers per week on this subject. Many of these publications are of experimental and routine observations, yielding numerical data for a variety of chemical substances. Some of this work will doubtless prove unreliable when familiarity with this effect brings a more leisured type of investigation to study it, and the incentives of priority and novelty have been displaced. The vast accumulation of data clearly calls for sifting and analysis. In this book Professor Kohlrausch has rendered investigators a great service. He has developed the whole subject from the beginning in a text-book style, dealing with both the theoretical and experimental sides of the subject. He has also collected together the experimental data and summarized it as far as possible. Finally, he has provided a bibliography of more than 400 of the principal papers on the subject. There is also a good name and subject index. The general arrangement of the book is briefly as follows. Chapter I introduces the historical background against which this new phenomenon of light-scattering is best appreciated. The experimental technique is dealt with very adequately, and for substances in various physical states. Chapter III deals with characteristic rotation frequencies derived through the Raman effect. There follow a variety of important matters associated with the nature of the scattered radiations, their breadth, intensity, polarisation, etc., and a discussion of the factors modifying Raman spectra. The effect in relation to molecular structure is then systematically discussed for molecules of two, three, four, five, and more than five atoms. A number of interesting physico-chemical problems are considered in a later chapter. Finally the theoretical basis of light scattering are presented.

The whole book is well arranged and well produced, and merits nothing but praise. As a pioneer work in this particular field its value to both physicist and chemist needs no emphasis. We have but one criticism to offer viz., that the price of the book is particularly high. Its costliness may place it beyond the reach of many who would wish to have it.

R. C. Johnson.

Errata

V. K. La Mer, T. H. Gronwall and Lotti J. Greiff: J. Phys. Chem., 35, 2245 (1931). Not all the errors were corrected, p. 3103.

P. 2251 eq. (18′) should read $Y^*_3(x) = \frac{1}{x^6}\int_0^x x^5 X_3^*(x)\,dx$.

P. 2256 eqs. (3) (4) and (5). Insert 10^2 before $[\frac{1}{2}X_2(x) - Y_2(x)]$
and 10^3 before $[\frac{1}{2}X_3^*(x) - 2\,Y_3^*(x)]$.

P. 2283 Eq. (18). Insert 10^3 before $[\frac{1}{2}X_3(x) - 2Y_3(x)]$.

P. 2271 Eq. (10). Insert 10^2 before $[\frac{1}{2}X_2(x) - 2Y_2(x)]$ and 10^3 before $\frac{1}{2}X_3^*(x) - 3Y_3^*(x)]$ and before $[\frac{1}{2}X_3(x) - 3Y_3(x)]$.

P. 2283 Eq. (18). In the third term $Y_2(x)$ should read $10^2Y_2(x)$. In the sixth term $Y_1^*(x)$ should read $10^3\,Y_3^*(x)$.

P. 2284 Eq. (19). In the seventh term $Y_3(x)$ should read $10^3\,Y_3(x)$.

Wilder D. Bancroft: J. Phys. Chem., 35, 3160 (1931). In Table IV, p. 3171 and Fig. 4, p. 3173 change 30.9° to 39.9°.

L. J. Gillespie and John H. Perry: J. Phys. Chem., 35, 3370 (1931). Lines 28 and 37, the figure 0.95 should read 0.095.

NAME INDEX

To Papers

NAME INDEX

To New Books

SUBJECT INDEX

Exclusive of New Books