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ON THE GENERAL PROBLEM OF CHEMICAL STATICS[1]

BY P. DUHEM

Professor of Theoretical Physics in the Faculty of Sciences at Bordeaux

INTRODUCTION

The present paper is a commentary on and a complement to the celebrated memoir of J. Willard Gibbs: 'On the Equilibrium of Heterogeneous Substances.'[2] All chemists now know, how, in this memoir, the illustrious New Haven professor has deduced from the principles of thermodynamics the equations which represent the states of equilibrium of all chemical systems; all know, under the name of the 'phase rule,' the weighty theorems which he has found through comparing the number of unknown quantities to be determined, with the number of independent equations subsisting among them. The labors of H. W. Bakhuis Roozeboom and of his pupils have illustrated the bearing of the phase rule, in applying it to the discussion of a host of complex chemical reactions; and the special treatises of W. Meyerhoffer[3] and of Wilder D. Bancroft[4] have assembled under it the chief problems of chemical mechanics.

Now, it seems to me that the demonstrations given by certain authors, for the phase rule, leave something to be desired in one

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[1] Translated, from the author's French manuscript, by J. E. Trevor.

[2] Trans. Conn. Acad., 3, 108 and 343 (1875 to 1878).

[3] Die Phasenregel, Leipzig und Wien (1893).

[4] The Phase Rule, Ithaca, N. Y., U. S. A. (1897).

point: they admit, at least implicitly, that the independently variable components of each of the phases of a system are identical with the independently variable components of the system as a whole. But this is not in general the case: it may be that one of the independently variable components of the system is excluded from one of the phases, or it may be that two of the independently variable components can appear in one of the phases only in the fixed ratio of a definite compound. Consider for example a case made classic by the work of Debray, the system made up of the two independently variable components, quicklime and carbon dioxid: here none of the three coexistent phases, in which the system ordinarily appears, admits both of these components; one phase admits no component other than the quicklime, a second no other than the carbon dioxid, while the third contains calcium carbonate alone. Gibbs, however, has shown,[1] in a few lines, how the demonstration of the phase rule can be made wholly general; and it has seemed to me, hereupon, to be desirable to develop, with all possible rigor, this demonstration which he has indicated.

I have sought, furthermore, to add to the propositions discovered by Gibbs certain new theorems having, likewise, wholly general character. These theorems are not deduced solely from the principles of thermodynamics; they rest as well upon two very simple postulates, which are readily verifiable in any realizable case. They are as follows:

I. *When the mass, the temperature and the composition of a fluid are maintained constant, the volume of the fluid will decrease when its pressure is increased; and the reverse;*

II. *When the homogeneity of a mixture of bodies is disturbed, it will tend to be restored by diffusion.*

These postulates, whose character is seen to be essentially physical, suffice to establish important propositions of chemical mechanics, of which in the first instance the following theorems may be cited:—

I. *When the temperature, the pressure, and the masses of*

---

[1] Trans. Conn. Acad., 3, 153.

the independently variable components of a system are given, the composition attained by each of the phases of the system, when equilibrium ensues, is uniquely determined;

2. *If the volume occupied by the system be given, instead of the pressure under which it stands, then not only the composition but also the density of each phase is uniquely determined.*

Capillary action and terms due to friction will be neglected in establishing these propositions; relating, further, only to *true equilibria*, they will fail to apply to real or apparent '*false equilibria*;' it may be said, in fact, that the falsity of these propositions characterizes the false equilibria. To these propositions must be added the two following:

3. *If the temperature of a system, and the pressure under which it stands, be maintained constant, the chemical equilibrium of the system can be only stable or indifferent;*

4. *If the temperature of the system, and the volume which it occupies, be maintained constant, the resulting chemical equilibrium must be, likewise, either stable or indifferent.*

The relation of these propositions to the postulates upon which they rest leads to the remark, which seems to me to have its peculiar importance in natural philosophy, that—

Attributing physical, hydrostatic, stability to a system, excludes the possibility of any instable chemical equilibrium.

PRELIMINARY CHAPTER

THE THERMODYNAMIC POTENTIAL OF A HOMOGENEOUS MIXTURE

1. *The Thermodynamic Potential, for Constant Pressure, of a Mixture of Fluids.*—A homogeneous mixture of the fluids 1, 2, . . ., n, under the constant pressure Π and at the temperature T, admits a total thermodynamic potential $\mathfrak{H}$ which depends upon the masses M_1, M_2, . . ., M_n of the mixed fluids, upon the pressure Π and the temperature T:—

$$\mathfrak{H} = \mathfrak{H}(M_1, M_2, \ldots, M_n, \Pi, T).$$

If under the same pressure Π, at the same temperature T, we mix the masses $\lambda M_1, \lambda M_2, \ldots, \lambda M_n$ of the fluids $1, 2, \ldots, n$, we shall obtain a second mixture, like to the first but with a λ-fold mass; if we neglect the actions exerted by the different parts of a same mixture upon one another, we can attribute to the second mixture a total thermodynamic potential λ-fold that of the first mixture, and shall then have—

$$\mathcal{H}(\lambda M_1, \lambda M_2, \ldots, \lambda M_n, \Pi, T) = \lambda \mathcal{H}(M_1, M_2, \ldots, M_n, \Pi, T).$$

The total thermodynamic potential of a homogeneous mixture of n fluids is a homogeneous function of the first degree of the masses of the n mixed fluids. Writing

$$\frac{\partial \mathcal{H}}{\partial M_1} = F_1, \quad \frac{\partial \mathcal{H}}{\partial M_2} = F_2, \ldots, \frac{\partial \mathcal{H}}{\partial M_n} = F_n, \tag{1}$$

and applying the theorem of Euler to the function $\mathcal{H}$ we find

$$\mathcal{H} = M_1F_1 + M_2F_2 + \ldots + M_nF_n. \tag{2}$$

The functions $F_1, F_2, \ldots, F_n$ are evidently homogeneous functions of the zero degree of the variables $M_1, M_2, \ldots, M_n$; applying the theorem of Euler to each of these functions we find the identities

$$\left.\begin{array}{l} M_1\dfrac{\partial F_1}{\partial M_1} + M_2\dfrac{\partial F_1}{\partial M_2} + \ldots + M_n\dfrac{\partial F_1}{\partial M_n} = 0, \\ M_1\dfrac{\partial F_2}{\partial M_1} + M_2\dfrac{\partial F_2}{\partial M_2} + \ldots + M_n\dfrac{\partial F_2}{\partial M_n} = 0, \\ \ldots \\ M_1\dfrac{\partial F_n}{\partial M_1} + M_2\dfrac{\partial F_n}{\partial M_2} + \ldots + M_n\dfrac{\partial F_n}{\partial M_n} = 0. \end{array}\right\} \tag{3}$$

The definition of the functions $F_1, F_2, \ldots, F_n$, given by equations (1), furnishes the identities

$$\frac{\partial F_i}{\partial M_j} = \frac{\partial F_j}{\partial M_i}$$

through which the equations (3) can be replaced by the equations—

$$\left.\begin{aligned} &M_1\frac{\partial F_1}{\partial M_1}+M_2\frac{\partial F_2}{\partial M_1}+\dots+M_n\frac{\partial F_n}{\partial M_1}=0,\\ &M_1\frac{\partial F_1}{\partial M_2}+M_2\frac{\partial F_2}{\partial M_2}+\dots+M_n\frac{\partial F_n}{\partial M_2}=0,\\ &\dots\\ &M_1\frac{\partial F_1}{\partial M_n}+M_2\frac{\partial F_2}{\partial M_n}+\dots+M_n\frac{\partial F_n}{\partial M_n}=0. \end{aligned}\right\} \qquad (4)$$

2. *Stability of the Physical Equilibrium of a Homogeneous Mixture under Constant Pressure.*—We are to consider a mixture of the n fluids 1, 2, ..., n, at the temperature T, and subject to the action of no exterior force other than a uniform pressure Π; it is clear that at equilibrium this mixture will be homogeneous. Admitting that its equilibrium is a stable one, and that if the homogeneity of the mixture be disturbed it will be restored of necessity by diffusion, we will seek the properties which these circumstances assign to the functions $F_1, F_2, \dots, F_n$.

Supposing the initially homogeneous mixture to be composed of the masses $2M_1, 2M_2, \dots, 2M_n$, of the fluids 1, 2, ..., n, its thermodynamic potential, for the constant pressure Π, is

$$\mathcal{H}(2M_1, 2M_2, \dots, 2M_n, \Pi, T)$$

or, since the function $\mathcal{H}$ is homogeneous and of the first degree with respect to the masses of the mixed fluids,

$$2\mathcal{H}(M_1, M_2, \dots, M_n, \Pi, T).$$

By means of a surface S, let the mixture be divided into two parts A and B, each having the same total mass; each will then contain the masses $M_1, M_2, \dots, M_n$ of the fluids 1, 2, ..., n. Cause the infinitesimal masses $\delta M_1, \delta M_2, \dots, \delta M_n$ of these fluids to pass from the part A to the part B, the pressure and temperature remaining constant. If

$$\frac{\delta M_1}{M_1}=\frac{\delta M_2}{M_2}=\dots=\frac{\delta M_n}{M_n}, \qquad (5)$$

the two parts will retain their original composition, the mixture will remain homogeneous, and its thermodynamic potential for constant pressure will suffer no variation. If, on the other hand, the equations (5) are not satisfied, the mixture will become heterogeneous; this change, however, will be impossible, while the opposite change will be possible but irreversible. The virtual variation in question would accordingly correspond to an increase of the thermodynamic potential for constant pressure.

At the close of this virtual transfer of matter, A will contain the masses $(M_1 - \delta M_1)$, $(M_2 - \delta M_2)$, ..., $(M_n - \delta M_n)$, its thermodynamic potential for the constant pressure Π becoming

$$\mathcal{H}(M_1 - \delta M_1,\ M_2 - \delta M_2,\ \dots,\ M_n - \delta M_n,\ \Pi,\ T).$$

Developing this expression, with consideration of infinitesimals of the second order, and comparing with the equations (1), we find

$$\begin{aligned}
&\mathcal{H}(M_1,\ M_2,\ \dots,\ M_n,\ \Pi,\ T)\\
&-F_1(M_1,\ M_2,\ \dots,\ M_n,\ \Pi,\ T)\delta M_1\\
&-F_2(M_1,\ M_2,\ \dots,\ M_n,\ \Pi,\ T)\delta M_2\\
&-\dots\\
&-F_n(M_1,\ M_2,\ \dots,\ M_n,\ \Pi,\ T)\delta M_n\\
&+\tfrac{1}{2}\left[\frac{\partial F_1}{\partial M_1}(\delta M_1)^2 + \frac{\partial F_2}{\partial M_2}(\delta M_2)^2 + \dots + \frac{\partial F_n}{\partial M_n}(\delta M_n)^2\right.\\
&\qquad\qquad\left. + \sum_{ij}\left(\frac{\partial F_i}{\partial M_j} + \frac{\partial F_j}{\partial M_i}\right)\delta M_i \delta M_j\right],
\end{aligned}$$

where the sign $\sum\limits_{ij}$ denotes a summation over all the possible combinations ij of the indices 1, 2, ..., n, taken two at a time.

The part B contains the masses $(M_1 + \delta M_1)$, $(M_2 + \delta M_2)$, ..., $(M_n + \delta M_n)$; its thermodynamic potential, developed to include infinitesimals of the second order, is

$$\begin{aligned}
&\mathcal{H}(M_1,\ M_2,\ \dots,\ M_n,\ \Pi,\ T)\\
&+F_1(M_1,\ M_2,\ \dots,\ M_n,\ \Pi,\ T)\delta M_1\\
&+F_2(M_1,\ M_2,\ \dots,\ M_n,\ \Pi,\ T)\delta M_2\\
&+\dots\\
&+F_n(M_1,\ M_2,\ \dots,\ M_n,\ \Pi,\ T)\delta M_n
\end{aligned}$$

$$+\frac{1}{2}\left[\frac{\partial F_1}{\partial M_1}(\delta M_1)^2+\frac{\partial F_2}{\partial M_2}(\delta M_2)^2+\cdots+\frac{\partial F_n}{\partial M_n}(\delta M_n)^2 + \sum_{ij}\left(\frac{\partial F_i}{\partial M_j}+\frac{\partial F_j}{\partial M_i}\right)\delta M_i\delta M_j\right].$$

The final thermodynamic potential of the whole mixture thus becomes

$$2\mathfrak{H}(M_1, M_2, \ldots, M_n, \Pi, T)$$
$$+\frac{\partial F_1}{\partial M_1}(\delta M_1)^2+\frac{\partial F_2}{\partial M_2}(\delta M_2)^2+\cdots+\frac{\partial F_n}{\partial M_n}(\delta M_n)^2 + \sum_{ij}\left(\frac{\partial F_i}{\partial M_j}+\frac{\partial F_j}{\partial M_i}\right)\delta M_i\delta M_j,$$

its increase during the virtual transfer reducing to

$$\frac{\partial F_1}{\partial M_1}(\delta M_1)^2+\cdots+\frac{\partial F_n}{\partial M_n}(\delta M_n)^2+\sum_{ij}\left(\frac{\partial F_i}{\partial M_j}+\frac{\partial F_j}{\partial M_i}\right)\delta M_i\delta M_j,$$

whereby we reach the two propositions: When the quantities $\delta M_1, \ldots, \delta M_n$ satisfy equations (5), we have

$$\frac{\partial F_1}{\partial M_1}(\delta M_1)^2+\cdots+\frac{\partial F_n}{\partial M_n}(\delta M_n)^2+\sum_{ij}\left(\frac{\partial F_i}{\partial M_j}+\frac{\partial F_j}{\partial M_i}\right)\delta M_i\delta M_j=0;$$

while, on the other hand, this sum is positive when the quantities $\delta M_1, \ldots, \delta M_n$ do not satisfy equations (5). The first proposition brings nothing new; it is easy to see, in fact, that it follows directly from equations (3).

These two propositions can be cast into a slightly different form—as follows: Let $X_1, X_2, \ldots, X_n$ be any n finite quantities; one can then always put—

$$\delta M_1 = X_1\delta t,\ \delta M_2 = X_2\delta t,\ \ldots, \delta M_n = X_n\delta t,$$

δt being an infinitesimal. If the n quantities $X_1, X_2, \ldots, X_n$ satisfy the equations

$$\frac{X_1}{M_1}=\frac{X_2}{M_2}=\cdots=\frac{X_n}{M_n}, \tag{6}$$

we shall have the equation

$$\frac{\partial F_1}{\partial M_1}X_1^2 + \cdots + \frac{\partial F_n}{\partial M_n}X_n^2 + \sum_{ij}\left(\frac{\partial F_i}{\partial M_j} + \frac{\partial F_j}{\partial M_i}\right)X_iX_j = 0; \qquad (7)$$

if they do not satisfy equations (6) we shall have the inequality

$$\frac{\partial F_1}{\partial M_1}X_1^2 + \cdots + \frac{\partial F_n}{\partial M_n}X_n^2 + \sum_{ij}\left(\frac{\partial F_i}{\partial M_j} + \frac{\partial F_j}{\partial M_i}\right)X_iX_j > 0. \qquad (8)$$

3. *Formulas Relating to a Mixture Maintained at Constant Volume.*—Having considered mixtures supporting a constant pressure, let us now examine a mixture maintained at constant volume. Let V and T denote the volume and the absolute temperature, and $M_1, M_2, \ldots, M_n$ the masses of the several components of the mixture; the inner thermodynamic potential of the system may then be represented by $\mathcal{F}(M_1, M_2, \ldots, M_n, V, T)$. From one of the fundamental relations of the theory of the thermodynamic potential we have

$$\frac{\partial}{\partial V}\mathcal{F}(M_1, M_2, \ldots, M_n, V, T) = -\Pi, \qquad (9)$$

Π being the equilibrium pressure of the system at the volume V. This equation can be solved for V,—

$$V = V(M_1, M_2, \ldots, M_n, \Pi, T), \qquad (10)$$

the volume occupied by the mixture at equilibrium under the pressure Π at the temperature T. If in the expression

$$\mathcal{F}(M_1, M_2, \ldots, M_n, V, T) + \Pi V,$$

we replace V by its value in (10), we shall obtain the function $\mathcal{H}(M_1, M_2, \ldots, M_n, \Pi, T)$. Equation (10) thus transforms the equation

$$\mathcal{H}(M_1, \ldots, M_n, \Pi, T) = \mathcal{F}(M_1, \ldots, M_n, V, T) + \Pi V \qquad (11)$$

into an identity. It results herefrom that we have identically

$$\frac{\partial \mathcal{H}}{\partial M_1} = \frac{\partial \mathcal{F}}{\partial M_1} + \left(\frac{\partial \mathcal{F}}{\partial V} + \Pi\right)\frac{\partial V}{\partial M_1},$$

if we suppose (10) satisfied; but equation (10), in the form (9), causes the last term to disappear from this last equation, whereby follows the first of the equations—

$$\left.\begin{aligned} \frac{\partial \mathcal{H}}{\partial M_1} &= \frac{\partial \mathcal{F}}{\partial M_1}, \\ \frac{\partial \mathcal{H}}{\partial M_2} &= \frac{\partial \mathcal{F}}{\partial M_2}, \\ \cdots& \\ \frac{\partial \mathcal{H}}{\partial M_n} &= \frac{\partial \mathcal{F}}{\partial M_n}. \end{aligned}\right\} \qquad (12)$$

The others may be established similarly.

These equations become identities when V is replaced in their second members by its expression (10). Differentiating, with respect to M_j, the identity in the row i, we have

$$\frac{\partial^2 \mathcal{H}}{\partial M_i \partial M_j} = \frac{\partial^2 \mathcal{F}}{\partial M_i \partial M_j} + \frac{\partial^2 \mathcal{F}}{\partial M_i \partial V} \frac{\partial V}{\partial M_j}.$$

Equation (9), on the other hand, becomes an identity when its V is replaced by the expression (10); differentiating it with respect to M_j we find

$$\frac{\partial^2 \mathcal{F}}{\partial V \partial M_j} + \frac{\partial^2 \mathcal{F}}{\partial V^2} . \frac{\partial V}{\partial M_j} = 0;$$

and the last two equations yield the relation

$$\frac{\partial^2 \mathcal{H}}{\partial M_i \partial M_j} = \frac{\partial^2 \mathcal{F}}{\partial M_i \partial M_j} - \frac{\dfrac{\partial^2 \mathcal{F}}{\partial V \partial M_i} \dfrac{\partial^2 \mathcal{F}}{\partial V \partial M_j}}{\dfrac{\partial^2 \mathcal{F}}{\partial V^2}}, \qquad (13)$$

holding for any values of the indices i and j,—provided that V is substituted from the expression (10).

The equations (13) are equivalent to another equation. The quantities X_1, X_2, . . ., X_n being arbitrary, it is clear from (13) that, whatever X_1, X_2, . . ., X_n may be,—

$$\frac{\partial^2 \mathcal{H}}{\partial M_1^2} X_1^2 + \frac{\partial^2 \mathcal{H}}{\partial M_2^2} X_2^2 + \cdots + \frac{\partial^2 \mathcal{H}}{\partial M_n^2} X_n^2 + 2 \sum_{ij} \frac{\partial^2 \mathcal{H}}{\partial M_i \partial M_j} X_i X_j$$

$$= \frac{\partial^2 \mathfrak{F}}{\partial M_1^2} X_1^2 + \frac{\partial^2 \mathfrak{F}}{\partial M_2^2} X_2^2 + \cdots + \frac{\partial^2 \mathfrak{F}}{\partial M_n^2} X_n^2 + 2 \sum_{ij} \frac{\partial^2 \mathfrak{F}}{\partial M_i \partial M_j} X_i X_j$$

$$- \frac{1}{\frac{\partial^2 \mathfrak{F}}{\partial V^2}} \left(\frac{\partial^2 \mathfrak{F}}{\partial V \partial M_1} X_1 + \frac{\partial^2 \mathfrak{F}}{\partial V \partial M_2} X_2 + \cdots + \frac{\partial^2 \mathfrak{F}}{\partial V \partial M_n} X_n \right)^2. \qquad (14)$$

By virtue of equations (1), the first member of (14) is identical with the first members of equation (7) and of the inequality (8).

This equation (14) will serve to establish various important results; let us consider in particular the following problem, whose importance in chemical mechanics will soon appear.—

In a mixture of the masses $M_1, M_2, \ldots, M_n$ of the bodies 1, 2, …, n, having the volume V at the constant temperature T, all the independent variables save the T are supposed to vary by $\delta M_1, \delta M_2, \ldots, \delta M_n, \delta V$; and the second variation $\delta^2 \mathfrak{F}$ of the inner thermodynamic potential

$$\mathfrak{F}\,(M_1, M_2, \ldots, M_n, V, T)$$

is sought. We have—

$$2\delta^2 \mathfrak{F} = \frac{\partial^2 \mathfrak{F}}{\partial M_1^2} (\delta M_1)^2 + \cdots + \frac{\partial^2 \mathfrak{F}}{\partial M_n^2} (\delta M_n)^2 + 2 \sum_{ij} \frac{\partial^2 \mathfrak{F}}{\partial M_i \partial M_j} \delta M_i \delta M_j$$

$$+ 2 \left(\frac{\partial^2 \mathfrak{F}}{\partial M_1 \partial V} \delta M_1 + \cdots + \frac{\partial^2 \mathfrak{F}}{\partial M_n \partial V} \delta M_n \right) \delta V + \frac{\partial^2 \mathfrak{F}}{\partial V^2} (\delta V)^2. \qquad (15)$$

On the other hand, the pressure Π requisite to sustain equilibrium is defined by equation (9), so the variations $\delta M_1, \delta M_2, \ldots, \delta M_n, \delta V$ at constant T condition a variation $\delta \Pi$ such that

$$\frac{\partial^2 \mathfrak{F}}{\partial V \partial M_1} \delta M_1 + \cdots + \frac{\partial^2 \mathfrak{F}}{\partial V \partial M_n} \delta M_n + \frac{\partial^2 \mathfrak{F}}{\partial V^2} \delta V = -\delta \Pi. \qquad (16)$$

Squaring both members of this equation we have

$$(\delta \Pi)^2 = \left(\frac{\partial^2 \mathfrak{F}}{\partial V^2} \right)^2 (\delta V)^2 + \left(\frac{\partial^2 \mathfrak{F}}{\partial V \partial M_1} \delta M_1 + \cdots + \frac{\partial^2 \mathfrak{F}}{\partial V \partial M_n} \delta M_n \right)^2$$

$$+ 2 \left(\frac{\partial^2 \mathfrak{F}}{\partial V \partial M_1} \delta M_1 + \cdots + \frac{\partial^2 \mathfrak{F}}{\partial V \partial M_n} \delta M_n \right) \frac{\partial^2 \mathfrak{F}}{\partial V^2} \delta V,$$

which transforms (15) to

$$2\delta^2\mathfrak{F} = \frac{\partial^2\mathfrak{F}}{\partial M_1^2}(\delta M_1)^2 + \dots + \frac{\partial^2\mathfrak{F}}{\partial M_n^2}(\delta M_n)^2 + 2\sum_{ij}\frac{\partial^2\mathfrak{F}}{\partial M_i\partial M_j}\delta M_i\delta M_j$$

$$-\frac{1}{\frac{\partial^2\mathfrak{F}}{\partial V^2}}\left(\frac{\partial^2\mathfrak{F}}{\partial V\partial M_1}\delta M_1 + \dots + \frac{\partial^2\mathfrak{F}}{\partial V\partial M_n}\delta M_n\right)^2 + \frac{1}{\frac{\partial^2\mathfrak{F}}{\partial V^2}}(\delta\Pi)^2,$$

which equation, with (14), gives

$$2\delta^2\mathfrak{F} = \frac{\partial^2\mathfrak{H}}{\partial M_1^2}(\delta M_1)^2 + \dots + \frac{\partial^2\mathfrak{H}}{\partial M_n^2}(\delta M_n)^2 + 2\sum_{ij}\frac{\partial^2\mathfrak{H}}{\partial M_i\partial M_j}\delta M_i\delta M_j$$

$$+\frac{1}{\frac{\partial^2\mathfrak{F}}{\partial V^2}}(\delta\Pi)^2. \tag{17}$$

The quantity $\partial^2\mathfrak{F}/\partial V^2$ has a very simple meaning: If, maintaining constant the masses $M_1, M_2, \dots, M_n$ and the temperature T, the volume of the mixture be increased by dV, the equilibrium pressure will rise by $d\Pi$ and, according to (9),—

$$d\Pi = -\frac{\partial^2\mathfrak{F}}{\partial V^2}dV.$$

Now, according to the law of the isothermal displacement of equilibrium, $d\Pi$ and dV have opposite signs; under all circumstances therefore,

$$\frac{\partial^2\mathfrak{F}}{\partial V^2} > 0. \tag{18}$$

This equation, combined with equation (17) and the propositions stated at the close of section 2, supply the theorem:—

In order that the quantity $\delta^2\mathfrak{F}$ disappear, it is necessary and sufficient that the isothermal virtual change, to which it relates, satisfy the two following conditions:—

1. *We have*

$$\frac{\delta M_1}{M_1} = \frac{\delta M_2}{M_2} = \dots = \frac{\delta M_n}{M_n}, \tag{19}$$

the mass of the mixture varies, the composition remaining unchanged, during the virtual change;

2. *We have*

$$\delta\Pi = 0, \tag{20}$$

the equilibrium pressure of the mixture remains constant during the change.

If neither of these conditions is satisfied $\delta^2\mathfrak{F}$ *is positive.*

The various propositions established above involve important consequences for chemical statics, which consequences shall now be passed in review.

CHAPTER I

GENERAL THEOREMS OF THE CHEMICAL STATICS OF HOMOGENEOUS SYSTEMS

1. *The General Laws of Chemical Equilibrium in a Homogeneous System under Constant Pressure.*—Let us suppose a homogeneous mixture of the masses $M_1, M_2, \ldots, M_n$ of the substances 1, 2, ..., n, at the pressure Π and the temperature T. Certain reactions may occur in the system, so that at the final state of equilibrium the mixture will contain the masses $\mu_\alpha, \mu_\beta, \ldots, \mu_\lambda$ of certain substances $\alpha, \beta, \ldots, \lambda$, instead of the masses $M_1, M_2, \ldots, M_n$ of the original constituents. Now when the variables $M_1, M_2, \ldots, M_n, \Pi, T$, are given, how are the masses $\mu_\alpha, \mu_\beta, \ldots, \mu_\lambda$ to be determined?

The total mass M_1 of the substance 1 must exist, in one form or another, in the masses $\mu_\alpha, \mu_\beta, \ldots, \mu_\lambda$ of the new constituents: Suppose, for example, that the substance 1 contributes only to the formation of the substances α, β, γ. Suppose α to be made up of the substance 1 combined with one other body; writing p_1 and π_α for the molecular weights of 1 and of α, and m for the number of mols of 1 contained in 1 mol of α, the formation of the mass μ_α of the substance α will require the mass $\frac{mp_1}{\pi_\alpha}\mu_\alpha$ of the body 1.

Suppose, likewise, the bodies β and γ to be formed from two products of the decomposition of 1; these products having the molecular weights p'_1 and p''_1, and existing either independently or in combination with other bodies; and suppose further one mol of β to contain m' mols of the first decomposition-product, and 1 mol of γ to contain m'' mols of the second product. Setting, finally, π_β, π_γ for the molecular weights of β and γ, the formation of the masses μ_α and μ_β of these substances will require a mass $\left(\frac{m'p'_1}{\pi_\beta}\mu_\beta + \frac{m''p''_1}{\pi_\gamma}\mu_\gamma\right)$ of the body 1. We shall then have

$$\frac{mp_1}{\pi_\alpha}\mu_\alpha + \frac{m'p'_1}{\pi_\beta}\mu_\beta + \frac{m''p''_1}{\pi_\gamma}\mu_\gamma = M_1.$$

In general we find in this way n equations—

$$\left.\begin{aligned} A_1\mu_\alpha + B_1\mu_\beta + \dots + L_1\mu_\lambda &= M_1, \\ A_2\mu_\alpha + B_2\mu_\beta + \dots + L_2\mu_\lambda &= M_2, \\ \dots \\ A_n\mu_\alpha + B_n\mu_\beta + \dots + L_n\mu_\lambda &= M_n, \end{aligned}\right\} \tag{1}$$

where A_i, B_i, …, L_i are *purely numerical* constants, which can be calculated from the chemical formulas of the substances 1, 2, …, n, on the one hand, and of α, β, …, λ, on the other.

Let $H(\mu_\alpha, \mu_\beta, \dots, \mu_\lambda, \Pi, T)$ be the thermodynamic potential, for the constant pressure Π at the temperature T, of the mixture containing the masses μ_α, μ_β, …, μ_λ of the bodies α, β, …, λ. For the system to be in equilibrium it is necessary and sufficient that for all infinitesimal variations, under the constant pressure Π at the temperature T, of the masses μ_α, μ_β, …, μ_λ, which are compatible with the conditions (1), the corresponding variation of the function H shall become zero. In other words: *the necessary and sufficient conditions for the equilibrium of the system are obtained by expressing that*

$$\frac{\partial H}{\partial \mu_\alpha}\delta\mu_\alpha + \frac{\partial H}{\partial \mu_\beta}\delta\mu_\beta + \dots + \frac{\partial H}{\partial \mu_\lambda}\delta\mu_\lambda = 0, \tag{2}$$

at the same time that μ_α, μ_β, …, μ_λ *satisfy equations* (1); *and that* $\delta\mu_\alpha$, $\delta\mu_\beta$, …, $\delta\mu_\lambda$ *satisfy the equations*

$$\left.\begin{aligned} A_1\delta\mu_\alpha + B_1\delta\mu_\beta + \dots + L_1\delta\mu_\lambda &= 0, \\ A_2\delta\mu_\alpha + B_2\delta\mu_\beta + \dots + L_2\delta\mu_\lambda &= 0, \\ \dots \\ A_n\delta\mu_\alpha + B_n\delta\mu_\beta + \dots + L_n\delta\mu_\lambda &= 0, \end{aligned}\right\} \tag{3}$$

obtained by differentiating the equations (1), *in which* M_1, M_2, ..., M_n *have assigned values.*

The relations (2) and (3) form a system of $n+1$ linear and homogeneous equations in $\delta\mu_\alpha$, $\delta\mu_\beta$, ..., $\delta\mu_\lambda$; that they may be satisfied simultaneously by a set of values of $\delta\mu_\alpha$, $\delta\mu_\beta$, ..., $\delta\mu_\lambda$, of which one at least is not zero, it is necessary and sufficient that n coefficients K_1, K_2, ..., K_n, exist, independent of $\delta\mu_\alpha$, $\delta\mu_\beta$, ..., $\delta\mu_\lambda$, such that

$$\begin{aligned}
&\left(\frac{\partial H}{\partial\mu_\alpha} + K_1A_1 + K_2A_2 + \dots + K_nA_n\right)\delta\mu_\alpha \\
+ &\left(\frac{\partial H}{\partial\mu_\beta} + K_1B_1 + K_2B_2 + \dots + K_nB_n\right)\delta\mu_\beta \\
+ &\dots \\
+ &\left(\frac{\partial H}{\partial\mu_\lambda} + K_1L_1 + K_2L_2 + \dots + K_nL_n\right)\delta\mu_\lambda = 0,
\end{aligned}$$

whatever be the values of $\delta\mu_\alpha$, $\delta\mu_\beta$, ..., $\delta\mu_\lambda$; this identity may be resolved into the λ equations

$$\left.\begin{aligned}
&\frac{\partial H}{\partial\mu_\alpha} + K_1A_1 + K_2A_2 + \dots + K_nA_n = 0, \\
&\frac{\partial H}{\partial\mu_\beta} + K_1B_1 + K_2B_2 + \dots + K_nB_n = 0, \\
&\dots \\
&\frac{\partial H}{\partial\mu_\lambda} + K_1L_1 + K_2L_2 + \dots + K_nL_n = 0.
\end{aligned}\right\} \quad (4)$$

The n equations (1), together with the λ equations (4), suffice to determine both the λ unknown quantities μ_α, μ_β, ..., μ_λ, and the n auxiliary unknown quantities K_1, K_2, ..., K_n, when one knows the pressure Π, the temperature T, and the masses M_1, M_2, ..., M_n of the components initially composing the system.

According to the theorems derived in the second section of the Preliminary Chapter, if ξ_α, ξ_β, ..., ξ_λ denote any λ quantities, and these quantities satisfy the equations

$$\frac{\xi_\alpha}{\mu_\alpha} = \frac{\xi_\beta}{\mu_\beta} = \dots = \frac{\xi_\lambda}{\mu_\lambda}, \quad (5)$$

we shall have the equation

$$\frac{\partial^2 H}{\partial \mu_\alpha^2}\xi_\alpha^2 + \cdots + \frac{\partial^2 H}{\partial \mu_\lambda^2}\xi_\lambda^2 + 2\sum_{\phi\,\psi}\frac{\partial^2 H}{\partial \mu_\phi \partial \mu_\psi}\xi_\phi\,\xi_\psi = 0; \qquad (6)$$

while, whenever equations (5) are not satisfied, we shall have the inequality

$$\frac{\partial^2 H}{\partial \mu_\alpha^2}\xi_\alpha^2 + \cdots + \frac{\partial^2 H}{\partial \mu_\lambda^2}\xi_\lambda^2 + 2\sum_{\phi\,\psi}\frac{\partial^2 H}{\partial \mu_\phi \partial \mu_\psi}\xi_\phi\,\xi_\psi > 0. \qquad (7)$$

In equation (6), as in the equality (7), the indicated summation is taken over all the possible combinations, without repetition, of the indices α, β, ..., λ, taken two at a time.

These propositions establish that, *for given pressure* Π, *temperature* T, *and masses* M_1, M_2, ..., M_n *of the original constituents of the mixture, the masses* μ_α, μ_β, ..., μ_λ *are uniquely determined.* For, suppose the mixture to be in equilibrium for the system of values

$$\mu_\alpha = m_\alpha, \quad \mu_\beta = m_\beta, \quad \ldots, \quad \mu_\lambda = m_\lambda,$$

and also for the system

$$\mu_\alpha = m'_\alpha, \quad \mu_\beta = m'_\beta, \quad \ldots, \quad \mu_\lambda = m'_\lambda.$$

We must have, because of equations (1),—

$$A_1 m_\alpha + B_1 m_\beta + \cdots + L_1 m_\lambda = M_1,$$
$$A_2 m_\alpha + B_2 m_\beta + \cdots + L_2 m_\lambda = M_2,$$
$$\cdots$$
$$A_n m_\alpha + B_n m_\beta + \cdots + L_n m_\lambda = M_n,$$

and also

$$A_1 m'_\alpha + B_1 m'_\beta + \cdots + L_1 m'_\lambda = M_1,$$
$$A_2 m'_\alpha + B_2 m'_\beta + \cdots + L_2 m'_\lambda = M_2,$$
$$\cdots$$
$$A_n m'_\alpha + B_n m'_\beta + \cdots + L_n m'_\lambda = M_n,$$

equations from which follow—

$$\left.\begin{aligned}
&A_1(m'_\alpha - m_\alpha) + B_1(m'_\beta - m_\beta) + \dots + L_1(m'_\lambda - m_\lambda) = 0,\\
&A_2(m'_\alpha - m_\alpha) + B_2(m'_\beta - m_\beta) + \dots + L_2(m'_\lambda - m_\lambda) = 0,\\
&\dots\\
&A_n(m'_\alpha - m_\alpha) + B_n(m'_\beta - m_\beta) + \dots + L_n(m'_\lambda - m_\lambda) = 0.
\end{aligned}\right\} \quad (8)$$

Moreover, writing for brevity

$$h = H(m_\alpha,\ m_\beta,\ \dots,\ m_\lambda,\ \Pi,\ T),$$

$$h' = H(m'_\alpha,\ m'_\beta,\ \dots,\ m'_\lambda,\ \Pi,\ T),$$

we must have

$$\frac{\partial h}{\partial m_\alpha}\delta\mu_\alpha + \frac{\partial h}{\partial m_\beta}\delta\mu_\beta + \dots + \frac{\partial h}{\partial m_\lambda}\delta\mu_\lambda = 0. \qquad (9)$$

$$\frac{\partial h'}{\partial m'_\alpha}\delta\mu_\alpha + \frac{\partial h'}{\partial m'_\beta}\delta\mu_\beta + \dots + \frac{\partial h'}{\partial m'_\lambda}\delta\mu_\lambda = 0, \qquad (9a)$$

for every set of values of $\delta\mu_\alpha$, $\delta\mu_\beta$, $\dots$, $\delta\mu_\lambda$ that satisfies the equations (3).

Comparing equations (8) with the conditions (3), it appears that the latter are satisfied if we put

$$\begin{aligned}
\delta\mu_\alpha &= \epsilon(m'_\alpha - m_\alpha),\\
\delta\mu_\beta &= \epsilon(m'_\beta - m_\beta),\\
&\dots\\
\delta\mu_\lambda &= \epsilon(m'_\lambda - m_\lambda),
\end{aligned}$$

ϵ being any infinitesimal such that the equations (9) and (9*a*) require

$$(m'_\alpha - m_\alpha)\frac{\partial h}{\partial m_\alpha} + (m'_\beta - m_\beta)\frac{\partial h}{\partial m_\beta} + \dots + (m'_\lambda - m_\lambda)\frac{\partial h}{\partial m_\lambda} = 0, \qquad (10)$$

$$(m'_\alpha - m_\alpha)\frac{\partial h'}{\partial m'_\alpha} + (m'_\beta - m_\beta)\frac{\partial h'}{\partial m'_\beta} + \dots + (m'_\lambda - m_\lambda)\frac{\partial h'}{\partial m'_\lambda} = 0. \qquad (10a)$$

We shall see that if we do not have

$$m'_\alpha - m_\alpha = 0,\quad m'_\beta - m_\beta = 0,\quad \dots,\quad m'_\lambda - m_\lambda = 0, \qquad (11)$$

the equations (10) and (10*a*) are incompatible.

Let us suppose, indeed, that at least one of the equations (11) is not satisfied. Consider a quantity x, variable continuously from 0 to 1, and λ functions of x defined by the equations

$$\left.\begin{aligned} \mu_\alpha(x) &= m_\alpha + (m'_\alpha - m_\alpha)\, x, \\ \mu_\beta(x) &= m_\beta + (m'_\beta - m_\beta)\, x, \\ &\dots \\ \mu_\lambda(x) &= m_\lambda + (m'_\lambda - m_\lambda)\, x. \end{aligned}\right\} \qquad (12)$$

When x varies from 0 to 1, these masses vary from m_α, m_β, ..., m_λ to m'_α, m'_β, ..., m'_λ, each variation being in a unique sense. They remain positive therefore, so one can speak of a mixture formed of the masses $\mu_\alpha(x)$, $\mu_\beta(x)$, ..., $\mu_\lambda(x)$.

The equations (1) and (8) give easily

$$\left.\begin{aligned} A_1\mu_\alpha(x) + B_1\mu_\beta(x) + \dots + L_1\mu_\lambda(x) &= M_1, \\ A_2\mu_\alpha(x) + B_2\mu_\beta(x) + \dots + L_2\mu_\lambda(x) &= M_2, \\ &\dots \\ A_n\mu_\alpha(x) + B_n\mu_\beta(x) + \dots + L_n\mu_\lambda(x) &= M_n, \end{aligned}\right\} \qquad (13)$$

in such wise that, whatever x may be, the mixture of the masses $\mu_\alpha(x)$, $\mu_\beta(x)$, ..., $\mu_\lambda(x)$ can be regarded as obtained by mixing the masses M_1, M_2, ..., M_n. Under the constant pressure Π at the temperature T, the thermodynamic potential of the mixture of $\mu_\alpha(x)$, $\mu_\beta(x)$, ..., $\mu_\lambda(x)$ is

$$H[\mu_\alpha(x), \mu_\beta(x), \dots, \mu_\lambda(x), \Pi, T] = \mathfrak{H}(x), \qquad (14)$$

from which we find

$$\frac{d\mathfrak{H}(x)}{dx} = \frac{\partial H}{\partial \mu_\alpha}\frac{d\mu_\alpha(x)}{dx} + \frac{\partial H}{\partial \mu_\beta}\frac{d\mu_\beta(x)}{dx} + \dots + \frac{\partial H}{\partial \mu_\lambda}\frac{d\mu_\lambda(x)}{dx}$$

or, indeed, because of equations (12),

$$\frac{d\mathfrak{H}(x)}{dx} = (m'_\alpha - m_\alpha)\frac{\partial H}{\partial \mu_\alpha} + (m'_\beta - m_\beta)\frac{\partial H}{\partial \mu_\beta} + \dots + (m'_\lambda - m_\lambda)\frac{\partial H}{\partial \mu_\lambda}. \qquad (15)$$

By reason of this equation (15), the equations (10) and (10*a*) are seen to be equivalent to the proposition, that the equation

$$\frac{d\mathfrak{H}(x)}{dx} = 0$$

has the roots $x = 0$ and $x = 1$. The theorem of Rolle asserts hereupon that there exists at least one quantity θ, lying between 0 and 1, such that

$$\frac{d^2\mathfrak{H}(\theta)}{d\theta^2} = 0.$$

Because of (12) and (15) this equation can be written

$$\left.\begin{aligned}(m'_\alpha - m_\alpha)^2 \frac{\partial^2 H}{\partial \mu_\alpha^2} + (m'_\beta - m_\beta)^2 \frac{\partial^2 H}{\partial \mu_\beta^2} + \cdots + (m'_\lambda - m_\lambda)^2 \frac{\partial^2 H}{\partial \mu_\lambda^2} \\ + 2 \sum_{\phi\,\psi} (m'_\phi - m_\phi)(m'_\psi - m_\psi) \frac{\partial^2 H}{\partial \mu_\phi \partial \mu_\psi} = 0,\end{aligned}\right\} \quad (16)$$

setting, for brevity,

$$\mu_\alpha(\theta) = \mu_\alpha, \quad \mu_\beta(\theta) = \mu_\beta, \quad \ldots, \quad \mu_\lambda(\theta) = \mu_\lambda.$$

Now, according to the proposition recalled by equations (5) and (6), in order that (16) may hold it is necessary and sufficient that

$$\frac{m'_\alpha - m_\alpha}{\mu_\alpha(\theta)} = \frac{m'_\beta - m_\beta}{\mu_\beta(\theta)} = \cdots = \frac{m'_\lambda - m_\lambda}{\mu_\lambda(\theta)}.$$

But these equations, together with equations (8), give the equations

$$\begin{aligned}&A_1\mu_\alpha(\theta) + B_1\mu_\beta(\theta) + \cdots + L_1\mu_\lambda(\theta) = 0,\\ &A_2\mu_\alpha(\theta) + B_2\mu_\beta(\theta) + \cdots + L_2\mu_\lambda(\theta) = 0,\\ &\cdots\\ &A_n\mu_\alpha(\theta) + B_n\mu_\beta(\theta) + \cdots + L_n\mu_\lambda(\theta) = 0,\end{aligned}$$

which are contradictory; for the equations (13), which are true whatever x may be, give

$$\begin{aligned}&A_1\mu_\alpha(\theta) + B_1\mu_\beta(\theta) + \cdots + L_1\mu_\lambda(\theta) = M_1,\\ &A_2\mu_\alpha(\theta) + B_2\mu_\beta(\theta) + \cdots + L_2\mu_\lambda(\theta) = M_2,\\ &\cdots\\ &A_n\mu_\alpha(\theta) + B_n\mu_\beta(\theta) + \cdots + L_n\mu_\lambda(\theta) = M_n.\end{aligned}$$

Rejecting the equations (11) leads therefore to a contradiction—as was asserted. So: *When the pressure* Π, *the temperature* T, *and the masses* $M_1, M_2, \ldots, M_n$ *are given, the masses* $\mu_\alpha, \mu_\beta, \ldots, \mu_\lambda$ *making up the system at equilibrium are uniquely determined.* Or, in other words: *The values of* $\mu_\alpha, \mu_\beta, \ldots, \mu_\lambda$ *which determine the state of equilibrium of the mixture, are uniform functions of* $M_1, M_2, \ldots, M_n, \Pi, T$.

Setting out from this theorem we shall now prove that *the quantities* $\mu_\alpha, \mu_\beta, \ldots, \mu_\lambda$, *which determine the equilibrium composition of the mixture, are homogeneous functions of the first degree of the variables* $M_1, M_2, \ldots, M_n$. For, let it be recalled that the quantities $\mu_\alpha, \mu_\beta, \ldots, \mu_\lambda$ can be characterized by the fact that they satisfy the conditions (1), and that they render the equations (3) and (4) compatible in $\delta\mu_\alpha, \delta\mu_\beta, \ldots, \delta\mu_\lambda$. Suppose, next, that a set of values of $M_1, M_2, \ldots, M_n, \Pi, T$ has been given, and a corresponding set $m_\alpha, m_\beta, \ldots, m_\lambda$ of values of the variables $\mu_\alpha, \mu_\beta, \ldots, \mu_\lambda$ has been found—values such that the foregoing conditions are satisfied. Taking the masses $PM_1, PM_2, \ldots, PM_n$ of the substances, at the constant pressure Π and temperature T, it is evident that the equations (1) will be satisfied if we put

$$\mu_\alpha = Pm_\alpha, \quad \mu_\beta = Pm_\beta, \quad \ldots, \quad \mu_\lambda = Pm_\lambda.$$

Moreover, after this change of the values of $\mu_\alpha, \mu_\beta, \ldots, \mu_\lambda$, the equations (2) and (3) will remain compatible in $\delta\mu_\alpha, \delta\mu_\beta, \ldots, \delta\mu_\lambda$; for the change alters neither the values of the purely numerical constants $A_n, B_n, \ldots, L_n$ nor those of the quantities $\partial H/\partial\mu_\alpha, \partial H/\partial\mu_\beta, \ldots, \partial H/\partial\mu_\lambda$, which we know to be homogeneous functions of the zero degree of the variables $\mu_\alpha, \mu_\beta, \ldots, \mu_\lambda$. Our theorem is thus demonstrated. It can be stated in the form: *Equilibrium will ensue in a like manner in like systems maintained at a given pressure and a given temperature.*

This general study of the equilibria attained in homogeneous mixtures under constant pressures may now be terminated by a demonstration of the proposition that: *At constant temperature and pressure the state of equilibrium of a system is a state of stable equilibrium.* Let

$$\mu_\alpha = m_\alpha, \quad \mu_\beta = m_\beta, \quad \ldots, \quad \mu_\lambda = m_\lambda \tag{17}$$

be the values of μ_α, μ_β, ..., μ_λ corresponding to the equilibrium. The proposition in question is then equivalent to the statement that $H(m_\alpha, m_\beta, \ldots, m_\lambda, \Pi, T)$ is the minimum of all possible values which the function $H(\mu_\alpha, \mu_\beta, \ldots, \mu_\lambda, \Pi, T)$ can assume for the given set of values of $M_1, M_2, \ldots, M_n, \Pi, T$. We know already that the equations (17) are such that equation (2) is satisfied whenever equations (3) are satisfied; it remains, then, to demonstrate that we have

$$\frac{\partial^2 H}{\partial m_\alpha^2}(\delta\mu_\alpha)^2 + \frac{\partial^2 H}{\partial m_\beta^2}(\delta\mu_\beta)^2 + \cdots + \frac{\partial^2 H}{\partial m_\lambda^2}(\delta\mu_\lambda)^2$$
$$+ 2\sum_{\phi\psi}\frac{\partial^2 H}{\partial m_\phi \partial m_\psi}\delta\mu_\phi\delta\mu_\psi > 0$$

whenever $\delta\mu_\alpha$, $\delta\mu_\beta$, ..., $\delta\mu_\lambda$ satisfy equations (3). Furthermore,—referring back to equations (5), (6), and (7),—for this to be the case it is seen to be necessary and sufficient that no set of values of $\delta\mu_\alpha$, $\delta\mu_\beta$, ..., $\delta\mu_\lambda$ exists, satisfying at the same time equations (3) and the equations

$$\frac{\delta\mu_\alpha}{m_\alpha} = \frac{\delta\mu_\beta}{m_\beta} = \cdots = \frac{\delta\mu_\lambda}{m_\lambda}. \tag{18}$$

But this proposition is evident, for if a set of values of $\delta\mu_\alpha$, $\delta\mu_\beta$, ..., $\delta\mu_\lambda$ satisfied simultaneously both (3) and (18) we should have

$$\begin{gathered}
A_1 m_\alpha + B_1 m_\beta + \cdots + L_1 m_\lambda = 0, \\
A_2 m_\alpha + B_2 m_\beta + \cdots + L_2 m_\lambda = 0, \\
\cdots \\
A_n m_\alpha + B_n m_\beta + \cdots + L_n m_\lambda = 0,
\end{gathered}$$

while, from equations (1),—

$$\begin{gathered}
A_1 m_\alpha + B_1 m_\beta + \cdots + L_1 m_\lambda = M_1, \\
A_2 m_\alpha + B_2 m_\beta + \cdots + L_2 m_\lambda = M_2, \\
\cdots \\
A_n m_\alpha + B_n m_\beta + \cdots + L_n m_\lambda = M_n.
\end{gathered}$$

2. *The General Laws of Chemical Equilibrium in a Homogeneous System at Constant Volume.* We will now examine systems maintained at constant volume V, in the same way in

which systems under constant pressure have been treated above; and we shall retain the notation of the foregoing section. Let $f(\mu_\alpha, \mu_\beta, \ldots, \mu_\lambda, V, T)$ denote the inner thermodynamic potential of the system. The values of $\mu_\alpha, \mu_\beta, \ldots, \mu_\lambda$ at equilibrium must satisfy equations (1), and render compatible, in $\delta\mu_\alpha, \delta\mu_\beta, \ldots, \delta\mu_\lambda$, the equations (3) and the equation

$$\frac{\partial f}{\partial \mu_\alpha}\delta\mu_\alpha + \frac{\partial f}{\partial \mu_\beta}\delta\mu_\beta + \cdots + \frac{\partial f}{\partial \mu_\lambda}\delta\mu_\lambda = 0. \tag{19}$$

When the system is in equilibrium there must then exist n quantities $P_1, P_2, \ldots, P_n$ such that

$$\left.\begin{aligned}
&\frac{\partial f}{\partial \mu_\alpha} + P_1A_1 + P_2A_2 + \cdots + P_nA_n = 0,\\
&\frac{\partial f}{\partial \mu_\beta} + P_1B_1 + P_2B_2 + \cdots + P_nB_n = 0,\\
&\cdots\\
&\frac{\partial f}{\partial \mu_\lambda} + P_1L_1 + P_2L_2 + \cdots + P_nL_n = 0.
\end{aligned}\right\} \tag{20}$$

The n equations (1), together with the λ equations (20), determine the λ unknown quantities $\mu_\alpha, \mu_\beta, \ldots, \mu_\lambda$, and the n unknown auxiliary quantities $P_1, P_2, \ldots, P_n$, when the volume V, the temperature T, and the masses $M_1, M_2, \ldots, M_n$ are known.

We shall now show that, when the volume V, *the temperature* T, *and the masses* $M_1, M_2, \ldots, M_n$ *are given, the values assumed at equilibrium by the masses* $\mu_\alpha, \mu_\beta, \ldots, \mu_\lambda$ *are uniquely determined.* Suppose, indeed, that, in the volume V, at the temperature T, the mixture were in equilibrium for the set of values

$$\mu_\alpha = m_\alpha,\ \mu_\beta = m_\beta,\ \ldots,\ \mu_\lambda = m_\lambda$$

and also for the values

$$\mu_\alpha = m'_\alpha,\ \mu_\beta = m'_\beta,\ \ldots,\ \mu_\lambda = m'_\lambda,$$

$M_1, M_2, \ldots, M_n$ having the same values in both cases. We shall see that supposing the equations

$$m'_\alpha = m_\alpha,\ m'_\beta = m_\beta,\ \ldots,\ m'_\lambda = m_\lambda \tag{21}$$

to be false, leads to a contradiction. We should have, in fact, the equations

$$\left.\begin{aligned}
&A_1(m'_\alpha - m_\alpha) + B_1(m'_\beta - m_\beta) + \dots + L_1(m'_\lambda - m_\lambda) = 0,\\
&A_2(m'_\alpha - m_\alpha) + B_2(m'_\beta - m_\beta) + \dots + L_2(m'_\lambda - m_\lambda) = 0,\\
&\dots\\
&A_n(m'_\alpha - m_\alpha) + B_n(m'_\beta - m_\beta) + \dots + L_n(m'_\lambda - m_\lambda) = 0.
\end{aligned}\right\}\quad(8)$$

Writing, for brevity,

$$\phi = f(m_\alpha, m_\beta, \dots, m_\lambda, V, T),$$
$$\phi' = f(m'_\alpha, m'_\beta, \dots, m'_\lambda, V, T),$$

we have, because of equation (19),

$$\frac{\partial\phi}{\partial m_\alpha}\delta\mu_\alpha + \frac{\partial\phi}{\partial m_\beta}\delta\mu_\beta + \dots + \frac{\partial\phi}{\partial m_\lambda}\delta\mu_\lambda = 0,$$
$$\frac{\partial\phi'}{\partial m'_\alpha}\delta\mu_\alpha + \frac{\partial\phi'}{\partial m'_\beta}\delta\mu_\beta + \dots + \frac{\partial\phi'}{\partial m'_\lambda}\delta\mu_\lambda = 0,$$

for every set of values of $\delta\mu_\alpha, \delta\mu_\beta, \dots, \delta\mu_\lambda$ that satisfies (3); or, in particular, because of equations (8), for the set of values—

$$\left.\begin{aligned}
&\delta\mu_\alpha = \epsilon(m'_\alpha - m_\alpha),\\
&\delta\mu_\beta = \epsilon(m'_\beta - m_\beta),\\
&\dots\\
&\delta\mu_\lambda = \epsilon(m'_\lambda - m_\lambda),
\end{aligned}\right\}\quad(22)$$

where ϵ is any infinitesimal. We must then have

$$(m'_\alpha - m_\alpha)\frac{\partial\phi}{\partial m_\alpha} + (m'_\beta - m_\beta)\frac{\partial\phi}{\partial m_\beta} + \dots + (m'_\lambda - m_\lambda)\frac{\partial\phi}{\partial m_\lambda} = 0, \quad (23)$$

$$(m'_\alpha - m_\alpha)\frac{\partial\phi'}{\partial m'_\alpha} + (m'_\beta - m_\beta)\frac{\partial\phi'}{\partial m'_\beta} + \dots + (m'_\lambda - m_\lambda)\frac{\partial\phi'}{\partial m'_\lambda} = 0. \quad (23a)$$

Consider, now, a quantity x, variable continuously from 0 to 1, and the λ functions of x, — $\mu_\alpha(x), \mu_\beta(x), \dots, \mu_\lambda(x)$ — defined by equations (12) and therefore satisfying equations (13).

Consider a mixture of the masses $\mu_\alpha(x)$, $\mu_\beta(x)$, ..., $\mu_\lambda(x)$; in the constant volume V at the temperature T, the thermodynamic potential of this mixture will be

$$f[\mu_\alpha(x), \mu_\beta(x), \ldots, \mu_\lambda(x), \mathrm{V}, \mathrm{T}] = \mathfrak{F}(x), \tag{24}$$

an equation which gives

$$\frac{d\mathfrak{F}(x)}{dx} = \frac{\partial f}{\partial \mu_\alpha}\frac{d\mu_\alpha(x)}{dx} + \frac{\partial f}{\partial \mu_\beta}\frac{d\mu_\beta(x)}{dx} + \cdots + \frac{\partial f}{\partial \mu_\lambda}\frac{d\mu_\lambda(x)}{dx},$$

or, because of equations (12),

$$\frac{d\mathfrak{F}(x)}{dx} = (m'_\alpha - m_\alpha)\frac{\partial f}{\partial \mu_\alpha} + (m'_\beta - m_\beta)\frac{\partial f}{\partial \mu_\beta} + \cdots$$
$$+ (m'_\lambda - m_\lambda)\frac{df}{\partial \mu_\lambda}. \tag{25}$$

Because of this equation (25), the equations (23) and (23*a*) are equivalent to the statement that the equation

$$\frac{d\mathfrak{F}(x)}{dx} = 0$$

has the roots $x = 0$ and $x = 1$. We conclude herefrom, by the theorem of Rolle, that there exists at least one quantity θ, lying between 0 and 1, such that

$$\frac{d^2\mathfrak{F}(\theta)}{d\theta^2} = 0.$$

Because of equations (12) and (25), this equation can be written

$$(m'_\alpha - m_\alpha)^2\frac{\partial^2 f}{\partial \mu_\alpha^2} + (m'_\beta - m_\beta)^2\frac{\partial^2 f}{\partial \mu_\beta^2} + \cdots + (m'_\lambda - m_\lambda)^2\frac{\partial^2 f}{\partial \mu_\lambda^2}$$
$$+ 2\sum_{\phi\psi}\frac{\partial^2 f}{\partial \mu_\phi \partial \mu_\psi}(m'_\phi - m_\phi)(m'_\psi - m_\psi) = 0, \tag{26}$$

setting, for brevity,

$$\mu_\alpha(\theta) = \mu_\alpha, \quad \mu_\beta(\theta) = \mu_\beta, \quad \ldots, \quad \mu_\lambda(\theta) = \mu_\lambda.$$

At constant volume V and temperature T of the mixture of the masses $\mu_\alpha(\theta)$, $\mu_\beta(\theta)$, ..., $\mu_\lambda(\theta)$, let us consider the infinitesimal variation of these masses that is defined by equations (22); to this virtual variation will correspond a second variation $\delta^2 f$ of the inner thermodynamic potential, which second variation is the product of $\epsilon^2/2$ and the first member of equation (26). Let $\delta\Pi$ denote the infinitesimal increment, due to the virtual variation considered, of the pressure of the surrounding walls upon the mixture. According to the proposition proved at the close of the Preliminary Chapter, for equation (26) to hold it is necessary and sufficient that the equation

$$\delta\Pi = 0$$

holds good, as also the equations

$$\frac{m'_\alpha - m_\alpha}{\mu_\alpha(\theta)} = \frac{m'_\beta - m_\beta}{\mu_\beta(\theta)} = \dots = \frac{m'_\lambda - m_\lambda}{\mu_\lambda(\theta)}.$$

But it has been shown in the preceding section that these two equations are incompatible. Our proposition is therefore demonstrated.

We shall next show that: *If the temperature and volume of the system are maintained constant, its state of equilibrium will be a stable state.* Let

$$\mu_\alpha = m_\alpha, \quad \mu_\beta = m_\beta, \quad \dots, \quad \mu_\lambda = m_\lambda \tag{27}$$

be the values of $\mu_\alpha, \mu_\beta, \dots, \mu_\lambda$ corresponding to equilibrium. The proposition in question is equivalent to the assertion that, of all the values that the function $f(\mu_\alpha, \mu_\beta, \dots, \mu_\lambda, V, T)$ can take for given values of $M_1, M_2, \dots, M_n, V, T$, the value $f(m_\alpha, m_\beta, \dots, m_\lambda, V, T)$ is a minimum. We know already that the equations (27) are such that equation (19) is satisfied whenever equations (3) are satisfied; so there remains merely to demonstrate that

$$\begin{aligned}\frac{\partial^2 f}{\partial m_\alpha^2}(\delta\mu_\alpha)^2 + \frac{\partial^2 f}{\partial m_\beta^2}(\delta\mu_\beta)^2 + \dots + \frac{\partial^2 f}{\partial m_\lambda^2}(\delta\mu_\lambda)^2 \\ + 2\sum_{\phi\psi}\frac{\partial^2 f}{\partial m_\phi \partial m_\psi}\delta\mu_\phi\delta\mu_\psi > 0,\end{aligned} \tag{28}$$

whenever $\delta\mu_\alpha, \delta\mu_\beta, \dots, \delta\mu_\lambda$ satisfy equations (3), δV and δT

being zero. Now, because of equation (14) of the preceding chapter, we can write

$$\frac{\partial^2 f}{\partial m_\alpha^2}(\delta\mu_\alpha)^2 + \cdots + \frac{\partial^2 f}{\partial m_\lambda^2}(\delta\mu_\lambda)^2 + 2\sum_{\phi\psi}\frac{\partial^2 f}{\partial m_\phi \partial m_\psi}\delta\mu_\phi\delta\mu_\psi$$

$$= \frac{\partial^2 H}{\partial m_\alpha^2}(\delta\mu_\alpha)^2 + \cdots + \frac{\partial^2 H}{\partial m_\lambda^2}(\delta\mu_\lambda)^2 + 2\sum_{\phi\psi}\frac{\partial^2 H}{\partial m_\phi \partial m_\psi}\delta\mu_\phi\delta\mu_\psi$$

$$+ \frac{1}{\frac{\partial^2 f}{\partial V^2}}\left(\frac{\partial^2 f}{\partial V \partial m_\alpha}\delta\mu_\alpha + \cdots + \frac{\partial^2 f}{\partial V \partial m_\lambda}\delta\mu_\lambda\right)^2. \qquad (29)$$

A demonstration similar to that which terminates the preceding section shows that we cannot have

$$\frac{\delta\mu_\alpha}{m_\alpha} = \frac{\delta\mu_\beta}{m_\beta} = \cdots = \frac{\delta\mu_\lambda}{m_\lambda}$$

so we find, because of equation (17),

$$\frac{\partial^2 H}{\partial m_\alpha^2}(\delta\mu_\alpha)^2 + \cdots + \frac{\partial^2 H}{\partial m_\lambda^2}(\delta\mu_\lambda)^2 + 2\sum_{\phi\psi}\frac{\partial^2 H}{\partial m_\phi \partial m_\psi}\delta\mu_\phi\delta\mu_\psi > 0.$$

On the other hand, equation (18) of the Preliminary Chapter gives

$$\frac{\partial^2 f}{\partial V^2} > 0.$$

These two inequalities, taken together with equation (29), demonstrate the inequality (28), and, therefore, the proposition that was to be established.

CHAPTER II

GENERAL PRINCIPLES OF THE CHEMICAL STATICS OF HETEROGENEOUS SYSTEMS MAINTAINED UNDER A GIVEN PRESSURE

1. *Various Definitions.*—We shall consider a system, at the temperature T, subject to the action of no exterior force other than a normal and uniform pressure Π; we shall, further, neglect all capillary actions, and suppose the system to be composed entirely

of homogeneous masses. It may be that two of these masses have the same composition and state, that an element of one is identical with an equal element of the other; in such cases it shall be said that the two masses belong to the same *phase*. We will suppose the system to comprise several phases in contact with one another, each being made up of one or more homogeneous masses. If none of the various virtual changes that the system can undergo can effect a variation in the nature or mass of the bodies constituting some given phase, we shall then have to do with an *invariable phase*, which will play no part in the chemical statics of the system concerned, and which shall therefore be neglected in the following developments.

The system to be examined shall be supposed to comprise ϕ variable phases, which shall be distinguished by the indices α, β, ..., ϕ; *the number ϕ of the variable phases into which the system separates is one of the numbers that characterize the system, from the point of view of chemical mechanics.*

Let us consider the different simple bodies that enter into the composition of the whole system. The definition of the system involves, in general, certain conditions, which make it impossible to choose arbitrarily the masses of each of these simple bodies: if, for example, two of them, A and B, appear only in the form of a certain definite compound containing both, then knowing the mass of A in the system is sufficient to make known the mass of B. It shall be admitted that c simple or compound bodies can be found, such that: 1, A system of the kind studied can be formed from the arbitrary masses $\mathfrak{M}_1$, $\mathfrak{M}_2$ ..., $\mathfrak{M}_c$; 2, A determinate system of the kind studied corresponds to a set of determinate values of the masses $\mathfrak{M}_1$, $\mathfrak{M}_2$, ..., $\mathfrak{M}_c$ of the bodies 1, 2, ..., c. The bodies 1, 2, ..., c shall be termed the *independent components* of the system.

In certain cases it is possible to choose in different ways the independent components of systems of a given kind; it may be that these systems can be regarded as formed from the independent components 1, 2, ..., c, or from the independent components α, β, ..., γ. This lack of determinateness, however, can not affect the number of the independent components for it may be asserted that: *When the independent components of systems of a given kind can be chosen in two different ways, the number of these components remains the same in both cases.* For, suppose indeed that the systems of a certain kind can be regarded as formed either from the independent components 1, 2, . . ., c, or from the components α, β, . . ., γ. From the masses $\mathfrak{M}_1$, $\mathfrak{M}_2$, . . ., $\mathfrak{M}_c$ of the bodies 1, 2, . . ., c we can then make up a determinate system of the kind considered, and, on the other hand, the system can be regarded as made up of the determinate masses μ_α, μ_β, . . ., μ_γ of the bodies α, β, . . ., γ: to a determinate set of values of $\mathfrak{M}_1$, $\mathfrak{M}_2$, . . ., $\mathfrak{M}_c$ there corresponds therefore a determinate set of values of μ_α, μ_β, . . ., μ_γ, and it can be shown likewise that a determinate set of values of $\mathfrak{M}_1$, $\mathfrak{M}_2$, . . ., $\mathfrak{M}_c$ corresponds to a determinate set of values of μ_α, μ_β, . . ., μ_γ. Let us examine how this reciprocal relation is to be established.

The mass $\mathfrak{M}_1$ must reappear, in one form or another, in the masses μ_α, μ_β, . . ., μ_γ. Among the masses serving to form μ_α there occurs a mass $P_{1\alpha}\mu_\alpha$ supplied by the body 1; the quantity $P_{1\alpha}$ being a purely numerical coefficient, depending upon the chemical composition of the bodies 1 and α. Among the masses

$$\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$$

and the masses

$$\mu_\alpha, \mu_\beta, \ldots, \mu_\gamma$$

there obtain the relations

$$\begin{aligned} P_{1\alpha}\,\mu_\alpha + P_{1\beta}\,\mu_\beta + \cdots + P_{1\gamma}\,\mu_\gamma &= \mathfrak{M}_1, \\ P_{2\alpha}\,\mu_\alpha + P_{2\beta}\,\mu_\beta + \cdots + P_{2\gamma}\,\mu_\gamma &= \mathfrak{M}_2, \\ \cdots \\ P_{c\alpha}\,\mu_\alpha + P_{c\beta}\,\mu_\beta + \cdots + P_{c\gamma}\,\mu_\gamma &= \mathfrak{M}_c, \end{aligned}$$

which are the only relations existing among these masses. For these c relations to require a definite set of values of the γ unknown quantities μ_α, μ_β, . . ., μ_γ to correspond to a definite set of values of $\mathfrak{M}_1$, $\mathfrak{M}_2$, . . ., $\mathfrak{M}_c$, it is necessary that γ be not greater than c. It may be shown likewise that c can not be greater than γ; so it must be that

$$c = \gamma,$$

which proves the proposition stated. So: *the number of independent components of systems of a given kind is definitely fixed. This number c, and the number ϕ of the phases, characterize the system, from the point of view of chemical statics.*

For a definite system formed from the masses $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$ of the independent components $1, 2, \ldots, c$, and separating into the phases $\alpha, \beta, \ldots, \phi$,—the phase α being made up of the masses $M_{1\alpha}, M_{2\alpha}, \ldots, M_{c\alpha}$ of the independent components of the system,—we must have

$$\left.\begin{array}{l} M_{1\alpha} + M_{1\beta} + \cdots + M_{1\phi} = \mathfrak{M}_1, \\ M_{2\alpha} + M_{2\beta} + \cdots + M_{2\phi} = \mathfrak{M}_2, \\ \cdots \\ M_{c\alpha} + M_{c\beta} + \cdots + M_{c\phi} = \mathfrak{M}_c. \end{array}\right\} \qquad (1)$$

From the circumstance that the masses $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$ are arbitrary, it does not follow that the masses $M_{1\alpha}, M_{1\beta}, \ldots, M_{c\phi}$ are all arbitrary. It may be that certain of the independent components do not appear in one of the phases, in α for example; the definition of the system imposes indeed, in general, a certain number of conditions, such as

$$M_{i\lambda} = 0, \quad M_{j\mu} = 0, \ldots, \qquad (2)$$

$i, j, \ldots$ being among the indices $1, 2, \ldots, c$, and $\lambda, \mu, \ldots$ among the indices $\alpha, \beta, \ldots, \phi$,—let p be the number of these conditions (2). Furthermore, even when certain components do appear in the phase α, for example, it may be that their masses are not wholly arbitrary there; it may be that certain of them can appear in the phase α only in the form of certain definite compounds; in other words, *it may be that those independent components of the system that appear in the phase α are not independent components of this phase.*

Let $a_\alpha, b_\alpha, \ldots, k_\alpha$ be the independent components of the phase α, and $m_{a_\alpha}, m_{b_\alpha}, \ldots, m_{k_\alpha}$ the masses, of these components, of which the phase α is made up. Among those of the masses $M_{1\alpha}$, $M_{2\alpha}$, …, $M_{c\alpha}$ that are not necessarily zero, and the masses m_{a_α}, m_{b_α}, …, m_{k_α}, there obtain the relations

$$\left.\begin{array}{l} A_{1a_\alpha} m_{a_\alpha} + A_{1b_\alpha} m_{b_\alpha} + \cdots + A_{1k_\alpha} m_{k_\alpha} = M_{1\alpha}, \\ A_{2a_\alpha} m_{a_\alpha} + A_{2b_\alpha} m_{b_\alpha} + \cdots + A_{2k_\alpha} m_{k_\alpha} = M_{2\alpha}, \\ \cdots \\ A_{ca_\alpha} m_{a_\alpha} + A_{cb_\alpha} m_{b_\alpha} + \cdots + A_{ck_\alpha} m_{k_\alpha} = M_{c\alpha}, \end{array}\right\} \quad (3)$$

the coefficients A being purely numerical coefficients, known when the chemical formulas of the bodies 1, 2, …, ϕ and of the bodies a_α, b_α, …, k_α are known. The number of these equations (3) is equal to the number of the masses $M_{i\alpha}$ that are not constantly zero. Moreover, when one of these masses is constantly zero, the equation

$$0 = M_{i\alpha},$$

which then appears among the equations (2), has in fact the form of equations (3); it can therefore be suppressed in the series of equations (2) and be written among the equations (3). The p equations (2) can thus be suppressed, and ϕ equations like (3) be written for each phase; to the conditions (1) will thus be added $c\phi$ conditions of the type (3).

The coefficients A of equations (3) must therefore be such that these equations involve as consequences—

$$\begin{aligned} & M_{1\alpha} + M_{2\alpha} + \cdots + M_{c\alpha} \\ & = m_{a_\alpha} + m_{b_\alpha} + \cdots + m_{k_\alpha} = \mathfrak{M}_\alpha, \end{aligned} \quad (4)$$

$\mathfrak{M}_\alpha$ denoting the total mass of the phase α. In a virtual change of state of the system, the masses

$$\begin{array}{l} M_{1\alpha}, \quad M_{22}, \quad \ldots, \quad M_{c\alpha}, \quad \ldots, \quad M_{c\phi}, \\ m_{a_\alpha}, \quad m_{b_\alpha}, \quad \ldots, \quad m_{k_\alpha}, \quad \ldots, \quad m_{k_\phi}, \end{array}$$

whose number is

$$c\phi + k_\alpha + k_\beta + \cdots + k_\phi \quad (5)$$

will suffer the variations

$$\left.\begin{array}{l} \delta M_{1\alpha}, \delta M_{2\alpha}, \ldots, \delta M_{c\alpha}, \ldots, \delta M_{c\phi}, \\ \delta m_{a_\alpha}, \delta m_{b_\alpha}, \ldots, \delta m_{k_\alpha}, \ldots, \delta m_{k_\phi}, \end{array}\right\} \quad (6)$$

which are the same in number, and are subject to the

$$c(\phi + 1) \tag{7}$$

relations—

$$\left.\begin{array}{l} \delta M_{1\alpha} + \delta M_{1\beta} + \cdots + \delta M_{1\phi} = 0, \\ \delta M_{2\alpha} + \delta M_{2\beta} + \cdots + \delta M_{2\phi} = 0, \\ \cdots \\ \delta M_{c\alpha} + \delta M_{c\beta} + \cdots + \delta M_{c\phi} = 0, \end{array}\right\} \tag{1a}$$

$$\left.\begin{array}{l} A_{1a_\alpha}\delta m_{a_\alpha} + A_{1b_\alpha}\delta m_{b_\alpha} + \cdots + A_{1k_\alpha}\delta m_{k_\alpha} = \delta M_{1\alpha}, \\ A_{2a_\alpha}\delta m_{a_\alpha} + A_{2b_\alpha}\delta m_{b_\alpha} + \cdots + A_{2k_\alpha}\delta m_{k_\alpha} = \delta M_{2\alpha}, \\ \cdots \\ A_{ca_\alpha}\delta m_{a_\alpha} + A_{cb_\alpha}\delta m_{b_\alpha} + \cdots + A_{ck_\alpha}\delta m_{k_\alpha} = \delta M_{c\alpha}, \\ \cdots \\ A_{ca_\phi}\delta m_{a_\phi} + A_{cb_\phi}\delta m_{b_\phi} + \cdots + A_{ck_\phi}\delta m_{k_\phi} = \delta M_{c\phi}, \end{array}\right\} \tag{3a}$$

obtained by differentiating the conditions (1) and (3), whereby, in the former, the masses $\mathfrak{M}_1$, $\mathfrak{M}_2$, ..., $\mathfrak{M}_c$ are supposed invariable.

2. *On the Indifferent State of a Heterogeneous System.* Let us now examine whether it be possible to produce in a heterogeneous system a virtual change which shall not vary the composition of any phase. For such to be the case it is necessary and sufficient that—

$$\frac{\delta m_{a_\alpha}}{m_{a_\alpha}} = \frac{\delta m_{b_\alpha}}{m_{b_\alpha}} = \cdots = \frac{\delta m_{k_\alpha}}{m_{k_\alpha}} = P_\alpha.$$

The question then becomes: whether it be possible to find ϕ quantities P_α, P_β, ..., P_ϕ such that the equations

$$\begin{array}{l} \delta m_{a_\alpha} = P_\alpha m_{a_\alpha}, \ \delta m_{b_\alpha} = P_\alpha m_{b_\alpha}, \ \ldots, \ \delta m_{k_\alpha} = P_\alpha m_{k_\alpha}, \\ \cdots \\ \delta m_{a_\phi} = P_\phi m_{a_\phi}, \ \delta m_{b_\phi} = P_\phi m_{b_\phi}, \ \ldots, \ \delta m_{k_\phi} = P_\phi m_{k_\phi}, \end{array} \tag{8}$$

correspond to a virtual change in the system. For this to be possible, it is necessary and sufficient that the quantities $\delta M_{1\alpha}$, $\delta M_{2\alpha}$, ..., $\delta M_{c\phi}$, determined by (8) and (3*a*), satisfy the equations

(1*a*); now, equations (3) show that the equations (8) and (3*a*) give—

$$\delta M_{1\alpha} = P_\alpha M_{1\alpha}, \quad \delta M_{2\alpha} = P_\alpha M_{2\alpha}, \quad \ldots, \quad \delta M_{c\alpha} = P_\alpha M_{c\alpha},$$
$$\ldots$$
$$\delta M_{1\phi} = P_\phi M_{1\phi}, \quad \delta M_{2\phi} = P_\phi M_{2\phi}, \quad \ldots, \quad \delta M_{c\phi} = P_\phi M_{c\phi},$$

and it is necessary and sufficient, therefore, that these quantities satisfy the equations (1*a*); so, *it is necessary and sufficient that* ϕ *quantities* P_α, P_β, …, P_ϕ *can be found, which satisfy the* c *linear and homogeneous equations*—

$$\left.\begin{array}{l} M_{1\alpha}P_\alpha + M_{1\beta}P_\beta + \cdots + M_{1\phi}P_\phi = 0, \\ M_{2\alpha}P_\alpha + M_{2\beta}P_\beta + \cdots + M_{2\phi}P_\phi = 0, \\ \cdots \\ M_{c\alpha}P_\alpha + M_{c\beta}P_\beta + \cdots + M_{c\phi}P_\phi = 0. \end{array}\right\} \qquad (9)$$

When these ϕ quantities can be found, one of them, at least, not being zero, it shall be said that *the system is in an indifferent state.*

It appears, in the first place, that if the number ϕ of the phases into which the system separates be greater than the number c of its independent components, the system is, in general, in an indifferent state.

If, on the other hand, ϕ is not greater than c, the system will be only exceptionally in an indifferent state. To express that the state is indifferent, we must express that equations (9) are compatible in P_α, P_β, …, P_ϕ, whereby we are supplied with one or more relations homogeneous in $M_{1\alpha}$, $M_{2\alpha}$, …, $M_{c\alpha}$. Because of equations (3), these relations become homogenous in m_{a_α}, m_{b_α}, …, m_{k_α}; so they remain satisfied when all these masses are multiplied by any same number, or, in other words, when the total mass of the phase α is changed without altering the composition of the phase. It can be shown, likewise, that these relations remain satisfied when the mass of the phase β is changed without altering the composition of this phase; and so on. It can be said, therefore, that—

When two systems have the same independent components *and the same number of phases, the corresponding phases of each having the same nature and composition but different masses, the state of the second system will be indifferent when that of the first is so.*

The consideration of indifferent states will reappear through considerations differing but slightly from the foregoing. Let us examine the following question: Can the masses $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$, of the c independent components of the system appearing in ϕ phases, be arranged in two different ways, such that the system, in its two states, will be made up of phases having the same composition but different masses?

In the first state of the system, let $m_{a_\alpha}, m_{b_\alpha}, \ldots, m_{k_\alpha}, \ldots, m_{k_\phi}$, be the masses making up the different phases; if, by means of the equations (3) and these masses, we form the masses $M_{1\alpha}$, $M_{2\alpha}, \ldots, M_{c\alpha}, \ldots, M_{c\phi}$, the latter will satisfy equations (1).

In the second state of the system, let $m'_{a_\alpha}, m'_{b_\alpha}, \ldots, m'_{k_\alpha}, \ldots, m'_{k_\phi}$ be the masses making up the different phases; for these phases to have the same composition as before it is necessary and sufficient that ϕ quantities $P_\alpha, P_\beta, \ldots, P_\phi$ can be found, such that—

$$\left.\begin{array}{l} m'_{a_\alpha}=(1+P_\alpha)m_{a_\alpha}, m'_{b_\alpha}=(1+P_\alpha)m_{b_\alpha}, \ldots, m'_{k_\alpha}=(1+P_\alpha)m_{k_\alpha}, \\ \ldots \\ m'_{a_\phi}=(1+P_\phi)m_{a_\phi}, m'_{b_\phi}=(1+P_\phi)m_{b_\phi}, \ldots, m'_{k_\phi}=(1+P_\phi)m_{k_\phi}. \end{array}\right\} \quad (10)$$

Moreover, that the second state of the system, like the first, can be formed from the masses $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$, it is necessary and sufficient that the quantities $M'_{1\alpha}, M'_{2\alpha}, \ldots, M'_{c\alpha}, \ldots, M'_{c\phi}$, obtained through replacing $m_{a_\alpha}, m_{b_\alpha}, \ldots, m_{k_\alpha}, \ldots, m_{k_\phi}$, by $m'_{a_\alpha}, m'_{b_\alpha}, \ldots, m'_{k_\alpha}, \ldots, m'_{k_\phi}$ in equations (3), satisfy the equations—analogous to equations (1)—

$$\left.\begin{array}{l} M'_{1\alpha} + M'_{1\beta} + \cdots + M'_{1\phi} = \mathfrak{M}_1, \\ M'_{2\alpha} + M'_{2\beta} + \cdots + M'_{2\phi} = \mathfrak{M}_2, \\ \ldots \\ M'_{c\alpha} + M'_{c\beta} + \cdots + M'_{c\phi} = \mathfrak{M}_c. \end{array}\right\} \quad (1b)$$

But equations (3) and (10) give at once—

$$\left.\begin{array}{l} M'_{1\alpha}=(1+P_\alpha)M_{1\alpha},\ M'_{2\alpha}=(1+P_\alpha)M_{2\alpha},\ \ldots,\ M'_{c\alpha}=(1+P_\alpha)M_{c\alpha}, \\ \ldots \\ M'_{1\phi}=(1+P_\phi)M_{1\phi},\ M'_{2\phi}=(1+P_\phi)M_{2\phi},\ \ldots,\ M'_{c\phi}=(1+P_\phi)M_{c\phi}, \end{array}\right\}$$

whence,—since $M_{1\alpha}$, $M_{2\alpha}$, ..., $M_{c\alpha}$, ..., $M_{c\phi}$ satisfy equations (1), by hypothesis,—in order that equations (1*b*) be satisfied, it is necessary and sufficient that P_α, P_β, ..., P_ϕ satisfy equations (9). So we may say:—

In order that the given masses $\mathfrak{M}_1$, $\mathfrak{M}_2$, ..., $\mathfrak{M}_c$ *of the independent components of a system can form two different sets of* ϕ *phases, in such wise that in these two states the phases shall have the same composition but different masses, it is necessary and sufficient that one of the states be indifferent;*

the theorem demonstrated above shows, moreover, that when one of the states is indifferent the other is so also.

When the quantities P_α, P_β, ..., P_ϕ satisfy equations (9), the same is true of xP_α, xP_β, ..., xP_ϕ, where x is any coefficient. So, if the masses $\mathfrak{M}_1$, $\mathfrak{M}_2$, ..., $\mathfrak{M}_c$ are distributed among the ϕ phases in such wise that the latter are made up of m_{a_α}, m_{b_α}, ..., m_{k_α}, ..., m_{k_ϕ}, and the state so reached is indifferent, the same masses can be distributed among the ϕ phases in such wise as to form the masses

$$\begin{array}{l} m_{a_\alpha}(x)=(1+P_\alpha x)m_{a_\alpha},\ \ldots,\ m_{k_\alpha}(x)=(1+P_\alpha x)m_{k_\alpha}, \\ \ldots \\ m_{a_\phi}(x)=(1+P_\phi x)m_{a_\phi},\ \ldots,\ m_{k_\phi}(x)=(1+P_\phi x)m_{k_\phi}, \end{array}$$

where P_α, P_β, ..., P_ϕ can be determined, but x is an arbitrary quantity. This furnishes the proposition:—

If the masses $\mathfrak{M}_1$, $\mathfrak{M}_2$, ..., $\mathfrak{M}_c$ *can be distributed in* ϕ *phases in such wise that the state of the system is indifferent, they can be distributed in these phases in an infinite number of ways, whereby the composition of each phase remains the same, only its mass suffering change; the result is a continuous series of indifferent states.*

It will appear that the conception of an indifferent state plays an important part in the chemical statics of systems maintained under a given constant pressure.

3. *Conditions of Equilibrium of Heterogeneous Systems under constant Pressure; the Phase Rule.*—We are to consider a system of ϕ phases, $\alpha, \beta, \ldots, \phi$, formed from the independent components $1, 2, \ldots, c$, having the temperature T and supporting the constant pressure Π. Neglecting capillary actions, the thermodynamic potential H of the system can be written

$$H = H_\alpha + H_\beta + \cdots + H_\phi,$$

the functions $H_\alpha, H_\beta, \ldots, H_\phi$ denoting the thermodynamic potentials of the phases $\alpha, \beta, \ldots, \phi$. The function H_α is a homogeneous function of the first degree of the masses $m_{a_\alpha}, m_{b_\alpha}, \ldots, m_{k_\alpha}$, and depends further, of course, upon Π and T. We write—

$$\frac{\partial H_\alpha}{\partial m_{a_\alpha}} = F_{a_\alpha}, \quad \frac{\partial H_\alpha}{\partial m_{b_\alpha}} = F_{b_\alpha}, \quad \ldots, \quad \frac{\partial H_\alpha}{\partial m_{k_\alpha}} = F_{k_\alpha}, \qquad (11)$$

so that, in any virtual change of the system, H_α will suffer a variation

$$\delta H_\alpha = F_{a_\alpha}\delta m_{a_\alpha} + F_{b_\alpha}\delta m_{b_\alpha} + \cdots + F_{k_\alpha}\delta m_{k_\alpha}. \qquad (12)$$

Analogous considerations apply to the phases $\beta, \ldots, \phi$.

Making the supposition that the system contains no vanishing phases, these virtual changes remain subject only to the conditions (1*a*) and (3*a*); they are all revertible[1]. Now, to find the conditions of equilibrium of the system at the temperature T and the pressure Π, we must consider the most general virtual change, of its state, compatible with the conditions (1*a*) and (3*a*), and put equal to zero the corresponding variation δH of the thermodynamic potential. This gives, using equations (10) and (12),—

$$\begin{aligned} & F_{a_\alpha}\delta m_{a_\alpha} + F_{b_\alpha}\delta m_{b_\alpha} + \cdots + F_{k_\alpha}\delta m_{k_\alpha} \\ + & F_{a_\beta}\delta m_{a_\beta} + F_{b_\beta}\delta m_{b_\beta} + \cdots + F_{k_\beta}\delta m_{k_\beta} \\ + & \cdots \\ + & F_{a_\phi}\delta m_{a_\phi} + F_{b_\phi}\delta m_{b_\phi} + \cdots + F_{k_\phi}\delta m_{k_\phi} = 0. \qquad (13) \end{aligned}$$

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[1] ['*Renversables*': Irreversible changes of a system, in both directions, between fixed end states, are 'revertible' processes. See Duhem : *Introduction à la Mécanique chimique*, p. 94 (Gand 1893). J. E. T.]

This equation must be satisfied always when the

$$c(\phi + 1) \tag{7}$$

equations ($1a$) and ($3a$) are satisfied: the number of the variations

$$\delta m_{a_\alpha},\quad \delta m_{b_\alpha},\quad \ldots,\quad \delta m_{k_\alpha},\quad \ldots,\quad \delta m_{k_\phi},$$
$$\delta M_{1\alpha},\quad \delta M_{2\alpha},\quad \ldots,\quad \delta M_{c\alpha},\quad \ldots,\quad \delta M_{c\phi}$$

being

$$c\phi + k_\alpha + k_\beta + \cdots + k_\phi, \tag{5}$$

the necessary and sufficient condition for this to be so is expressed by

$$\begin{aligned} \theta &= c\phi + k_\alpha + k_\beta + \cdots + k_\phi - c(\phi + 1) \\ &= k_\alpha + k_\beta + \cdots + k_\phi - c, \end{aligned} \tag{14}$$

which are linear and homogeneous relations, with purely numerical constant coefficients, among the functions F_{a_α}, F_{b_α}, ..., F_{k_α}, ..., F_{k_ϕ}. They may be written

$$\left.\begin{aligned} &f_1(F_{a_\alpha}, F_{b_\alpha}, \ldots, F_{k_\alpha}, \ldots, F_{k_\phi}) = 0, \\ &f_2(F_{a_\alpha}, F_{b_\alpha}, \ldots, F_{k_\alpha}, \ldots, F_{k_\phi}) = 0, \\ &\ldots \\ &f_\theta(F_{a_\alpha}, F_{b_\alpha}, \ldots, F_{k_\alpha}, \ldots, F_{k_\phi}) = 0, \end{aligned}\right\} \tag{15}$$

which θ equations are the *conditions of equilibrium* of the system.

Denoting, according to equation (4) and its analogues, the total masses of the phases α, β, ..., ϕ by $\mathfrak{M}_\alpha$, $\mathfrak{M}_\beta$, ..., $\mathfrak{M}_\phi$, we shall now, for the purpose of determining the state of equilibrium of the system, introduce the $k_\alpha + k_\beta + \ldots + k_\phi$ variables

$$\left.\begin{aligned} &Y_{a_\alpha} = \frac{m_{a_\alpha}}{\mathfrak{M}_\alpha},\ Y_{b_\alpha} = \frac{m_{b_\alpha}}{\mathfrak{M}_\alpha},\ \ldots,\ Y_{k_\alpha} = \frac{m_{k_\alpha}}{\mathfrak{M}_\alpha}, \\ &\ldots \\ &Y_{a_\phi} = \frac{m_{a_\phi}}{\mathfrak{M}_\phi},\ Y_{b_\phi} = \frac{m_{b_\phi}}{\mathfrak{M}_\phi},\ \ldots,\ Y_{k_\phi} = \frac{m_{k_\phi}}{\mathfrak{M}_\phi}, \end{aligned}\right\} \tag{16}$$

which ratios must satisfy the ϕ relations

$$\left.\begin{aligned} &\Upsilon_{a_\alpha}+\Upsilon_{b_\alpha}+\cdots+\Upsilon_{k_\alpha}=1,\\ &\Upsilon_{a_\beta}+\Upsilon_{b_\beta}+\cdots+\Upsilon_{k_\beta}=1,\\ &\cdots\\ &\Upsilon_{a_\phi}+\Upsilon_{b_\phi}+\cdots+\Upsilon_{k_\phi}=1, \end{aligned}\right\} \tag{17}$$

which follow from (4) and (16). The variables $T_{a_\alpha}, T_{b_\alpha}, \ldots, T_{k_\alpha}$ define the composition of the phase α, though not at all its total mass $\mathfrak{M}_\alpha$. The consideration of these new variables has an especial interest because the functions $F_{a_\alpha}, F_{b_\alpha}, \ldots, F_{k_\alpha}$ are homogeneous functions of the first degree of $m_{a_\alpha}, m_{b_\alpha}, \ldots, m_{k_\alpha}$, besides depending upon Π and T; they are, in other words, functions of the variables

$$\Upsilon_{a_\alpha}, \Upsilon_{b_\alpha}, \ldots, \Upsilon_{k_\alpha}, \Pi, T.$$

The function $f_i(F_{a_\alpha}, F_{b_\alpha}, \ldots, F_{k_\alpha}, \ldots, F_{k_\phi})$ becomes thus a function $\psi_i(T_{a_\alpha}, T_{b_\alpha}, \ldots, T_{k_\alpha}, \ldots, T_{k_\phi}, \Pi, T)$, which transforms equations (15) to—

$$\left.\begin{aligned} &\psi_1(\Upsilon_{a_\alpha}, \Upsilon_{b_\alpha}, \ldots, \Upsilon_{k_\alpha}, \ldots, \Upsilon_{k_\phi}, \Pi, T)=0,\\ &\psi_2(\Upsilon_{a_\alpha}, \Upsilon_{b_\alpha}, \ldots, \Upsilon_{k_\alpha}, \ldots, \Upsilon_{k_\phi}, \Pi, T)=0,\\ &\cdots\\ &\psi_\theta(\Upsilon_{a_\alpha}, \Upsilon_{b_\alpha}, \ldots, \Upsilon_{k_\alpha}, \ldots, \Upsilon_{k_\phi}, \Pi, T)=0. \end{aligned}\right\} \tag{18}$$

So, among the

$$k_\alpha+k_\beta+\cdots+k_\phi+2 \tag{19}$$

variables

$$\Upsilon_{a_\alpha}, \Upsilon_{b_\alpha}, \ldots, \Upsilon_{k_\alpha}, \ldots, \Upsilon_{k_\phi}, \Pi, T \tag{20}$$

there hold the relations (17) and (18), —whose number is $\theta+\phi$, or, indeed, because of (14),

$$k_\alpha+k_\beta+\cdots+k_\phi+\phi-c. \tag{21}$$

These relations involve neither the masses $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$ of the independent components of the system, nor the total masses $\mathfrak{M}_\alpha, \mathfrak{M}_\beta, \ldots, \mathfrak{M}_\phi$ of its several phases.

Consider, now, the $c\phi$ new variables

$$R_{1\alpha}, R_{2\alpha}, \ldots, R_{c\alpha}, \ldots, R_{c\phi}, \tag{22}$$

related to those introduced above, through the equations

$$\left.\begin{array}{l} A_{1a_\alpha}Y_{a_\alpha} + A_{1b_\alpha}Y_{b_\alpha} + \cdots + A_{1k_\alpha}Y_{k_\alpha} = R_{1\alpha}, \\ \cdots \\ A_{ca_\alpha}Y_{a_\alpha} + A_{cb_\alpha}Y_{b_\alpha} + \cdots + A_{ck_\alpha}Y_{k_\alpha} = R_{c\alpha}, \\ \cdots \\ A_{ca_\phi}Y_{a_\phi} + A_{cb_\phi}Y_{b_\phi} + \cdots + A_{ck_\phi}Y_{k_\phi} = R_{c\phi}, \end{array}\right\} \tag{23}$$

which equations, when compared with equations (3) and equations (16), yield

$$\left.\begin{array}{l} R_{1\alpha} = \dfrac{M_{1\alpha}}{\mathfrak{M}_\alpha}, \; R_{2\alpha} = \dfrac{M_{2\alpha}}{\mathfrak{M}_\alpha}, \; \ldots, \; R_{c\alpha} = \dfrac{M_{c\alpha}}{\mathfrak{M}_\alpha}, \\ \cdots \\ R_{1\phi} = \dfrac{M_{1\phi}}{\mathfrak{M}_\phi}, \; R_{2\phi} = \dfrac{M_{2\phi}}{\mathfrak{M}_\phi}, \; \ldots, \; R_{c\phi} = \dfrac{M_{c\phi}}{\mathfrak{M}_\phi}. \end{array}\right\} \tag{24}$$

Comparison of these equations with (1) shows that the $c\phi$ variables

$$R_{1\alpha}, R_{2\alpha}, \ldots, R_{c\alpha}, \ldots, R_{c\phi}$$

must satisfy the c relations

$$\begin{array}{l} \mathfrak{M}_\alpha R_{1\alpha} + \mathfrak{M}_\beta R_{1\beta} + \cdots + \mathfrak{M}_\phi R_{1\phi} = \mathfrak{M}_1, \\ \mathfrak{M}_\alpha R_{2\alpha} + \mathfrak{M}_\beta R_{2\beta} + \cdots + \mathfrak{M}_\phi R_{2\phi} = \mathfrak{M}_2, \\ \cdots \\ \mathfrak{M}_\alpha R_{c\alpha} + \mathfrak{M}_\beta R_{c\beta} + \cdots + \mathfrak{M}_\phi R_{c\phi} = \mathfrak{M}_c, \end{array} \tag{25}$$

which, alone, depend upon the masses $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$ of the independent components from which the system is produced, and the total masses $\mathfrak{M}_\alpha, \mathfrak{M}_\beta, \ldots, \mathfrak{M}_\phi$ of its several phases. The solution of our problem now depends essentially upon the *variance* of the system, as the excess of the number (19) over the number (21) has been termed by J. E. Trevor; this excess is

$$v = c + 2 - \phi. \tag{26}$$

If the number v be negative, it will, in general, be impossible to find values of the $k_\alpha + k_\beta + \cdots + k_\phi + 2$ variables (20) which will satisfy the $k_\alpha + k_\beta + \cdots + k_\phi + \phi - c$ equations (17) and (18). So, in general: *a system with negative variance cannot be in a state of equilibrium at any temperature, under any pressure.* Such a system will undergo change until one or more of its phases shall have disappeared.

(1). We will now consider a system for which

$$v = 0,$$

that is to say—according to the nomenclature of Trevor—an *invariant system.* For such a system, the number (21) of the equations (17) and (18) is equal to the number (19) of the variables (20); these variables are, therefore, in general, determined independently of any information concerning the masses $\mathfrak{M}_1$, $\mathfrak{M}_2, \ldots, \mathfrak{M}_c$ of the independent components of which the system is made up.—

The equilibrium values of the temperature, the pressure, and the composition of each phase of an invariant system are, in general, entirely determinate; and they are independent of the masses of the components constituting the system.

The variables $T_{a_\alpha}, T_{b_\alpha}, \ldots, T_{k_\alpha}, \ldots, T_{k_\phi}$ once determined, the variables $R_{1\alpha}, R_{2\alpha}, \ldots, R_{c\alpha}, \ldots, R_{c\phi}$ become uniquely determined by equations (23); but the masses $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$ of the independent components being supposed given, to determine the ϕ masses $\mathfrak{M}_\alpha, \mathfrak{M}_\beta, \ldots, \mathfrak{M}_\phi$ of the different phases we have only the $c = \phi - 2$ equations (25). So:—

The masses of the independent components of an invariant system do not suffice to fix the mass of each phase at equilibrium: the masses of any two of the phases can, in general, be chosen arbitrarily; this, then, determines the masses of the others.

This proposition confirms what we knew already: that the state of an invariant system is indifferent.

(2). In the case of a *univariant system*, for which

$$v = 1,$$

the number (21) of the equations (17) and (18) is less by one than the number (19) of the variables (20). Wherefore—

Under an arbitrarily given pressure Π, *a univariant system is in equilibrium at a determinate temperature* (*the 'transformation-temperature' under the given pressure*), *and with an equally determinate composition of each phase; neither the temperature nor the composition depends upon the masses of the independent components of the system.*

At an arbitrarily given temperature T, *the equilibrium will ensue at a determinate pressure* Π (*the 'transformation-pressure' at the given temperature*), *and with an equally determinate composition of each phase; neither the pressure nor the composition depends upon the masses of the independent components of the system.*

The variables $T_{a_a}, T_{b_a}, \ldots, T_{k_a}, \ldots, T_{k_\phi}$, once determined, the variables $R_{1a}, R_{2a}, \ldots, R_{ca}, \ldots, R_{c\phi}$ become uniquely determined by equations (23); but, the masses $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$ of the independent components being supposed given, to determine the ϕ masses $\mathfrak{M}_\alpha, \mathfrak{M}_\beta, \ldots, \mathfrak{M}_\phi$ of the different phases, we have only the $c = \phi - 1$ equations (25). So:—

The masses of the independent components of a univariant system, together with one of the two quantities Π *and* T, *do not suffice to fix the mass of each phase at equilibrium: the mass of one of the phases can, in general, be chosen arbitrarily; this, then, determines the masses of the others.*

We know already that the state of a univariant system is indifferent.

(3). In a bivariant system, for which

$$v = 2,$$

the number (21) of the equations (17) and (18) is less by two than the number (19) of the variables (20); when the pressure Π and the temperature T are arbitrarily given, therefore, the *remaining* variables in (20) become determinate.—

The state of a bivariant system is, in general, determinate when the temperature and pressure are arbitrarily given; the *equilibrium-composition of the several phases is then determinate, and is independent of the masses of the independent components of the system.*

The variables Υ_{a_α}, Υ_{b_α}, ..., Υ_{k_α}, ..., Υ_{k_ϕ} once determined, the variables $R_{1\alpha}$, $R_{2\alpha}$, ..., $R_{c\alpha}$, ..., $R_{c\phi}$ become uniquely determined by equations (23); but the masses $\mathfrak{M}_1$, $\mathfrak{M}_2$, ..., $\mathfrak{M}_c$ of the independent components being supposed given, to determine the ϕ masses $\mathfrak{M}_\alpha$, $\mathfrak{M}_\beta$, ..., $\mathfrak{M}_\phi$ of the different phases, we have the $c = \phi$ linear equations (23); So:—

Assigned values of the temperature, the pressure, and the masses of the independent components of a bivariant system, determine the mass of each of the phases at equilibrium.

This proposition, however, is subject to exception. For, the $c = \phi$ equations (25) cease to determine the masses $\mathfrak{M}_\alpha$, $\mathfrak{M}_\beta$, ..., $\mathfrak{M}_\phi$ when

$$\begin{vmatrix} R_{1\alpha} & R_{1\beta} & \cdots & R_{1\phi} \\ R_{2\alpha} & R_{2\beta} & \cdots & R_{2\phi} \\ \cdots \\ R_{c\alpha} & R_{c\beta} & \cdots & R_{c\phi} \end{vmatrix} = 0. \qquad (27)$$

It is involved in this condition that the state of the system is indifferent; for, taking equations (24) into account, and suppressing the factor

$$\frac{1}{\mathfrak{M}_\alpha \ \mathfrak{M}_\beta \ \ldots \ \mathfrak{M}_\phi},$$

which cannot be zero, the condition (27) becomes—

$$\begin{vmatrix} M_{1\alpha} & M_{1\beta} & \cdots & M_{1\phi} \\ M_{2\alpha} & M_{2\beta} & \cdots & M_{2\phi} \\ \cdots \\ M_{c\alpha} & M_{c\beta} & \cdots & M_{c\phi} \end{vmatrix} = 0,$$

expressing that the equations (9) are compatible in P_α, P_β, ..., P_ϕ.

Through equations (23), the condition (27) becomes a relation among the $k_\alpha + k_\beta + \cdots + k_\phi$ variables $\Upsilon_{a_\alpha}, \Upsilon_{b_\alpha}, \ldots, \Upsilon_{k_\alpha}, \ldots, \Upsilon_{k_\phi}$. Eliminating these variables from the equations (27) and the conditions of equilibrium (17) and (18), whose number here is $k_\alpha + k_\beta + \cdots + k_\phi$, leaves a relation between the variables Π and T only, a relation independent of the masses $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$. Whence—

The condition, that the state of equilibrium of a bivariant system be an indifferent state, is expressed by a relation between the temperature and pressure,—a relation in which the masses of the independent components of the system do not appear.

If, for example, the bivariant system considered be made up of the aqueous solution of an anhydrous salt, in contact with a solid hydrate of the salt, the state of equilibrium of the system will be indifferent when the temperature is the temperature of aqueous fusion of the hydrate at the pressure which obtains.

(4). For polyvariant systems, for which v is greater than 2,—

$$v = 2 + p,$$

whence, because of (26),—

$$c = \phi + p. \tag{28}$$

The ϕ masses $\mathfrak{M}_\alpha, \mathfrak{M}_\beta, \ldots, \mathfrak{M}_\phi$ of the different phases must satisfy the c equations (25); which will be possible, in general, only if p of these equations follow from the $\phi = c - p$ others,—a condition which is expressed by p relations among the quantities $R_{1\alpha}, R_{2\alpha}, \ldots, R_{c\alpha}, \ldots, R_{c\phi}$, and the masses of the c independent components, or, what amounts to the same thing, because of equations (23), among the quantities $\Upsilon_{a_\alpha}, \Upsilon_{b_\alpha}, \ldots, \Upsilon_{k_\alpha}, \ldots \Upsilon_{k_\phi}$ and the masses of the independent components. These relations shall be denoted by

$$\left.\begin{array}{l} \delta_1(\Upsilon_{a_\alpha}, \Upsilon_{b_\alpha}, \ldots, \Upsilon_{k_\phi}, \mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c) = 0, \\ \delta_2(\Upsilon_{a_\alpha}, \Upsilon_{b_\alpha}, \ldots, \Upsilon_{k_\phi}, \mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c) = 0, \\ \ldots \\ \delta_p(\Upsilon_{a_\alpha}, \Upsilon_{b_\alpha}, \ldots, \Upsilon_{k_\phi}, \mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c) = 0. \end{array}\right\} \tag{29}$$

Among the $k_\alpha + k_\beta + \ldots + k_\phi$ quantities

$$\Upsilon_{a_\alpha}, \Upsilon_{b_\alpha}, \ldots, \Upsilon_{k_\alpha}, \ldots, \Upsilon_{k_\phi}$$

and the quantities

$$\Pi, T, \mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$$

there obtain the relations (17) and (18), the number (21) of which, because of equation (28), becomes—

$$k_\alpha + k_\beta + \cdots + k_\phi - p,$$

and also the p relations (29); that is to say—

$$k_\alpha + k_\beta + \cdots + k_\phi$$

relations altogether. The quantities

$$\Upsilon_{a_\alpha}, \Upsilon_{b_\alpha}, \ldots, \Upsilon_{k_\alpha}, \ldots, \Upsilon_{k_\phi}$$

are then, in general, determinate when the values of the quantities

$$\Pi, T, \mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$$

are given. Therefore—

To determine the equilibrium-composition of each of the phases of a polyvariant system, it is, in general, necessary and sufficient to know not only the temperature and pressure, but also the masses of the independent components of which the system is made up.

The equations (29) reduce the c equations (25) to $c - p = \phi$ distinct equations, which determine the masses $\mathfrak{M}_\alpha$, $\mathfrak{M}_\beta$, $\ldots$, $\mathfrak{M}_\phi$,—the masses $\mathfrak{M}_1$, $\mathfrak{M}_2$, $\ldots$, $\mathfrak{M}_c$ being given, and the quantities Υ_{a_α}, Υ_{b_α}, $\ldots$, Υ_{k_α}, $\ldots$, Υ_{k_ϕ} being made determinate in the way just pointed out. Wherefore—

The masses of the different phases of a polyvariant system are, in general, determinate, when the temperature, the pressure, and the masses of the independent components of the system are known.

Thus are rigorously established the various propositions contained in the Phase Rule of J. Willard Gibbs.

[*To be concluded*]

FRACTIONAL CRYSTALLIZATION

BY C. A. SOCH

It is often desired to separate a mixture of two salts getting both pure. By fractional crystallization from a solution at constant temperature it is rarely possible to effect a complete separation. Let us suppose the simplest case, in which the salts form no compounds and no solid solutions. For each temperature there will be a definite concentration for the solution in equilibrium with the two salts as solid phases. If the original solution or mixture contained relatively more of either salt than the monovariant system that excess can be recovered. Since the relative proportions of the two salts in the saturated solution usually varies with the temperature it is possible, by repeated crystallization at two different temperatures, to obtain a complete separation. Theoretically this would require an infinite number of operations and it becomes desirable to have some definite statement of the general conditions governing such conditions that one may be able to form some idea of the least number of operations in which a given percentage separation can be obtained. Since working at high temperatures presents certain experimental difficulties it is also important to be able to estimate how much one is losing in efficiency by working at 50°, let us say, instead of at 100°. The present paper is intended to fill some of these gaps in our knowledge of this subject. It was also deemed advisable to study the effect of partial precipitation with alcohol since it would certainly be possible to change the relative concentrations of the two salts in this way and there are no data illustrating this point.

Ordinary ninety-five percent alcohol was treated with anhydrous copper sulfate until a test portion did not color the salt even after standing some time. The alcohol was then filtered from the copper sulfate and distilled from metallic sodium, taking precautions to prevent absorption of moisture from the atmosphere. The distilled product was preserved in a glass-stoppered bottle. The salts used, potassium chlorid, potassium nitrate, sodium chlorid and sodium nitrate, were freed from their impurities—KCl and NaCl from sulfates, KNO_3 and $NaNO_3$ from chlorids—by repeated crystallization. After each crystallization the mother-liquor was decanted and the crystals sucked dry with the water-pump. The ordinary distilled water of the laboratory was used both in this work and in the solubility determinations. In each case, after purification, the salt was dried thoroughly in an air bath, pulverized and put in a glass-stoppered bottle.

Solubility determinations were made at 25° and at 80° in pure water and at 25° in forty percent aqueous alcohol. The salt pairs were potassium chlorid and potassium nitrate, potassium chlorid and sodium chlorid, potassium nitrate and sodium chlorid, sodium nitrate and sodium chlorid. Potassium nitrate and sodium nitrate were not taken owing to the difficulty in analyzing the solutions while potassium chlorid and sodium nitrate are the instable pair.

Bottles of about 30 cc with rubber stoppers were used for holding the solutions. Both bottles and stoppers were always cleaned carefully and dried. In all measurements an excess of each salt was weighed out roughly into the several bottles and then the desired amount of solvent added, twenty cubic centimeters with forty percent alcohol and fifteen with pure water. The forty percent alcohol was made by weighing out carefully the required amount of absolute alcohol and water. The two were mixed thoroughly and distributed at once among the several bottles, which were immediately closed tightly with rubber stoppers. To ensure complete saturation the bottles were first suspended for three hours in water kept just above thirty degrees. This bath was allowed to cool slowly and when it reached 28° the bottles were transferred to a constant temperature bath and there kept at 25° for about twenty-four hours. The bottles were shaken vigorously at intervals. The water in the bath was kept stirred up by a Witt stirrer run by a Raabe turbine. One bottle at a time was taken from the bath and since the temperature of the room was but little below that of the bath no precaution was taken to prevent precipitation beyond that of pipetting off the solutions as rapidly as possible. Weighed amounts of the solutions were evaporated to dryness according to the method described by Trevor[1]. Each residue was dissolved in water and made up to one hundred cubic centimeters. The total amount of chlorid was determined by titration with a decinormal solution of silver nitrate using potassium bichromate as an indicator. In each titration 20 cc of the 100 cc solution were used. The amounts of the nitrates are equal to the differences between the residues and the total chlorids. In the determinations at 80° it was not found necessary to keep the solutions in the bath more than eight hours. No pipette was used and the solutions were transferred directly to tared bottles warmed to 80°. Before weighing, these evaporating tubes were allowed to cool. The residues were dissolved in water and made up to five hundred cubic centimeters of which twent-yfive were taken for titration. The results obtained are given in Tables I–III. In Table I, under the heading "alcohol", are given the grams of salt in one hundred grams of aqueous alcohol; under water are the grams of salt in one hundred grams of water. Since the aqueous alcohol was sixty percent water by weight, these values are ten-sixths of the values given under "alcohol". Below the concentrations of the salt pairs are given the ratios of these concentrations. To save space the data in Tables II and III are arranged horizontally instead of vertically. The concentrations are grams of salts per hundred grams of water. The values are the mean of two independent determinations and the probable error is about one percent. The values at 80° agree only fairly with those of Étard[2]; the data for sodium and potassium chlorids accord well with the results of Precht and Wittgen[3]. The displacement of the equilibrium

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[1] Zeit. phys. Chem. 7, 468 (1891).
[2] Ann. Chim. Phys. (7) 3, 275 (1894).
[3] Ber. chem. Ges. Berlin, 14, 1667 (1881).

by addition of alcohol is in no case as large as the change produced by difference of temperature.

TABLE I

Aqueous alcohol at 25°

	Alcohol	Water		Alcohol	Water
KCl	10.06	16.77	KNO_3	13.74	22.90
KNO_3	5.29	8.82	NaCl	15.78	26.30
Ratio	1.90		Ratio	0.87	
$NaNO_3$	22.78	37.97	NaCl	12.28	20.47
NaCl	10.17	16.93	KCl	5.87	9.78
Ratio	2.24		Ratio	2.09	

TABLE II

Water at 25°

KCl	KNO_3	Ratio	KNO_3	NaCl	Ratio
34.12	22.58	1.51	41.14	38.53	1.07
$NaNO_3$	NaCl	Ratio	NaCl	KCl	Ratio
43.66	26.58	1.64	29.05	17.1	1.70

TABLE III

Water at 80°

KCl	KNO_3	Ratio	KNO_3	NaCl	Ratio
40.20	117.5	0.361	168.8	39.81	4.14
$NaNO_3$	NaCl	Ratio	NaCl	KCl	Ratio
121.6	17.62	6.90	26.5	31.0	0.855

In considering the theoretical side of the question of fractional crystallization[1], it will be better to begin with the case where we have water as solvent and work at different temperatures, taking up later the complications introduced by the alcohol. Let A and B be the amounts of the two salts in any given quantity of water at the temperature T when the solution is saturated with respect to both salts. Let A_1 and B_1 be the corresponding values at the temperature T_1. Let $A/B = x$ and $A_1/B_1 = y$ and we will assume temporarily that $x > y$. If we

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[1] I am indebted to Professor Bancroft for the theoretical treatment.

pass from the temperature T to T_1, subtracting or adding enough water to keep the second salt from dissolving or precipitating, the concentration of the second salt has thus been changed from B to B_1, the absolute amount in solution being the same. Since the amount of the first salt is still A grams some must precipitate and equilibrium will be reached when the amount in solution is By grams. Since $B = A/x$ by definition, the final amount of the first salt in solution will be $A\frac{y}{x}$ grams. If we bring the system back to the temperature T adding or subtracting enough water to keep the first salt from precipitating or dissolving, we shall have a solution supersaturated with respect to the second salt and, by the same process of reasoning, we find that the amount of the second salt left in solution will be $B\frac{y}{x}$ grams. We have now come back to the original position except that the total amount of solution is less than before and we have certain amounts of the two salts in the pure state. Since the only change in the solution is a decrease in the absolute mass of the phase, it is clear that repeating the double operation will give a similar result. This can be put in a general form. If we start at the temperature T with a solution saturated with respect to both salts and pass to the temperature T_1 allowing only one salt to crystallize and pass back to the temperature T allowing only the other salt to separate, the total amounts of the two salts remaining in solution after n cycles will be

$$A\left(\frac{y}{x}\right)^n \text{ and } B\left(\frac{y}{x}\right)^n$$

where we define the double operation as a cycle. In deducing this formula it is not assumed that T_1 is higher than T nor vice-versa. It is assumed, however, that $x > y$. If we make the contrary assumption that $x < y$ the general form of the equation remains the same but we shall have for the amounts left in solution after n cycles

$$A\left(\frac{x}{y}\right)^n \text{ and } B\left(\frac{x}{y}\right)^n.$$

If we let X = the ratio of x and y where X is always less than unity we may write for the amounts in grams left in solution:

$$AX^n \text{ and } BX^n$$

and for the amounts in grams obtained pure—

$$A(1 - X^n) \text{ and } B(1 - X^n). \qquad (1)$$

Expression I is the theoretical statement of the results to be obtained by fractional crystallization at two temperatures. Practically the yield would always fall short of the value calculated from the formula, owing to the impossibility of getting rid of all the mother-liquor without washing with pure water and thus dissolving some of the salt. Another source of error lies in the fact that one would always stop a little short of the point at which the solution is saturated with respect to both salts. The formula is of value in two ways. A comparison of the actual with the theoretical yield shows the degree of accuracy with which the separation is being effected. If we desire a given percentage separation we can deduce from the formula the minimum number of cycles necessary to effect this and we shall at least know that more will be needed, how many more depending on the accuracy of the work. To take a practical example it follows from my data for NaCl and KCl at 25° and 80° that very nearly half the total salts are obtained pure at each cycle. Five cycles would therefore give nearly ninety-seven percent separation. With sodium chlorid and sodium nitrate on the other hand, three cycles would give over ninety-eight and one-half percent separation, assuming absolute accuracy of work. It should be noticed that if, as is usually the case, water is distilled off on passing to the higher temperature, water must be added when coming back to the lower temperature. Knowing the total amounts of the two salts in solution at any time and the solubilities at the two temperatures it is a simple matter to figure out the amount of water to be added or subtracted each time. The progress of fractional crystallization at two temperatures is one which should always be checked quantitatively at each step and the saving in time will compensate a hundred-fold for the extra trouble involved.

If we add alcohol to a solution saturated with respect to two salts, there will be a change in the relative concentrations of the two salts and also in the absolute concentrations. We have therefore to consider the precipitated mixture of salts and the amounts remaining dissolved in the aqueous alcohol. We will suppose that the aqueous alcohol is then evaporated. The two mixtures of the two salts can each be treated with water. If carried out properly the result will be two aqueous solutions saturated with respect to the two salts, crystals of one of the salts remaining pure at the bottom of one solution and crystals of the other salt at the bottom of the other solution. The crystals can be separated by filtration, the solutions mixed and the round is complete. We will therefore define as a cycle, the partial precipitation by alcohol, distillation of the aqueous alcohol, and treating the residues with water. Let A and B be the amounts of the two salts in any given quantity of pure water, A_1 and B_1 the amounts in the same quantity of water to which a definite amount of alcohol has been added. If $A/B = x$, $A_1/B_1 = y_1$, and $A/A_1 = z$ it can be shown that the amounts left in solution after n cycles will be

$$A\left(\frac{xz + y_1 - x}{xz}\right)^n \text{ and } B\left(\frac{xz + y_1 - x}{xz}\right)^n \text{ if } x > y$$

or

$$A\left(\frac{y_1z + x - y_1}{y_1z}\right)^n \text{ and } B\left(\frac{y_1z + x - y_1}{y_1z}\right)^n \text{ if } x < y.$$

Letting Y = the term inside the bracket we have for the amounts left in solution after n cycles:

$$AY^n \text{ and } BY^n$$

and for the amounts obtained pure

$$A(1 - Y^n) \text{ and } B(1 - Y^n) \qquad (11)$$

Expressions I and II have the same form, differing only by the difference between X and Y. At the first glance it is clear that the difference between x and y_1 must be very much greater than the difference between x and y for the second expression to compare favorably in results with the first, even supposing that the two cycles involved the same amount of work. For KCl and NaCl it was found that nearly one-half the total amount of salt was purified at each cycle when crystallizing between 25° and 80°. For the same salts at 25° and using forty percent alcohol, a little more than one-thirteenth can be purified per cycle. With sodium chlorid and sodium nitrate the difference is even greater, the rate being about three-fourths per cycle for the two temperatures and one-fourteenth for the alcohol method. It seems probable that precipitation with alcohol could be employed profitably in very few cases, possibly when potassium iodid was one of the salts.

Cornell University

DISTRIBUTION OF MERCURIC CHLORID BETWEEN TOLUENE AND WATER

BY OLIVER W. BROWN

Three measurements by Skinner[1] seem to show that a fairly constant distribution ratio is obtained when mercuric chlorid is added to mixtures of ether and water. It seemed desirable to see whether the same general relations held true when other organic liquids were substituted for ether and I have therefore made some measurements with toluene and water. The toluene was purified by distillation, the water was the ordinary distilled water of the laboratory. Ten cubic centimeters of each solvent were placed in test-tubes and varying amounts of mercuric chlorid added. The test-tubes were corked securely, shaken from time to time and allowed to come to equilibrium at constant temperature. Five cubic centimeters of each of the liquid layers were then pipetted off and the amount of mercuric chlorid in each was determined by running in an excess of potassium iodid solution and titrating back with normal mercuric chlorid. It was found necessary to make a correction of 0.2 cc for each 5 cc of toluene owing to the solubility of mercuric iodid in toluene. The amount of this correction was determined by preliminary experiments with known solutions. It was found that no appreciable error was introduced by adding a small or a large excess of potassium iodid. In analyzing the toluene solutions one ought to add quantities of water varying with the amount of salt in solution. This, of course, is not very practicable and the difficulty was avoided by adding always a large excess of water. In Table I are the experimental data. Under C_1 are grams of mercuric chlorid in five cubic centimeters of the aque-

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[1] Jour. Chem. Soc. 61, 342 (1892).

ous solutions and under C_2 the corresponding values for the toluene solutions. The last solution was saturated.

TABLE I

Temperature 24°

C_1	C_2	C_1/C_2	$C_1^{1.1}/C_2$
0.0221	0.00135	16.4	11.2
0.0366	0.00244	15.0	10.8
0.0390	0.00271	14.4	10.4
0.0596	0.00406	14.6	11.1
0.0908	0.00650	13.9	11.0
0.1883	0.0146	12.9	10.9
0.1877	0.0149	12.6	10.6
0.3344	0.0264	12.7	11.3

The ratio of the concentrations is not constant, the concentrations in the water phase not increasing quite so rapidly as those in the toluene phase. A variation of three percent in the ratio is quite within the probable experimental error; but that would account only for the fluctuations in two successive figures and would not change the general trend of the results. On the other hand the ratio $C_1^{1.1}/C_2$ seems to be constant. According to the Nernst theory this means that there is a slight dissociation in the aqueous solution. Unfortunately one cannot draw any conclusions in regard to the dissociation of mercuric chlorid either from Grotrian's[1] conductivity measurements or from Beckmann's[2] boiling-point studies. It is therefore impossible to determine, at the present time, whether the ratio of the concentration of the undissolved salt in the two phases is constant.

Cornell University

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[1] Wied. Ann. **18**, 177 (1883).

[2] Zeit. phys. Chem. **6**, 437 (1890).

NEW BOOKS

Vorlesungen ueber die Principe der Mechanik. *By Ludwig Boltzmann. Part I; octavo; pp. x and 241. Leipzig: J. A. Barth, 1897. Price: paper 6 marks.*—The volume before us is Part I of a treatise on dynamics, to be completed in three parts, and it discusses those principles only, which, while containing variations of the coordinates and their time derivatives, do not call for time integrations.

In reading Boltzmann one is strongly reminded of Bertrand; both are wont to show an irrepressible fondness for style and epigram, and the reader partakes of poetry and mathematics intermixed. The tone of Boltzmann's present volume, however, is rather defiant. There is much growling with an eye fixed on recent energetics. Boltzmann proposes to return to the classic mechanics of the old masters. He does not do this with a pretense that it alone is destined to survive, but with the object of setting up the splendid accomplishments of the old atomistic mechanics as a model or criterion for all other schools and doctrines. "*Hic Rhodus, hic salta,*" cries he. Boltzmann accordingly treats dynamics as a necessarily imperfect mathematical reproduction of natural phenomena. His aim is to give a clear, simple, and accurate *picture*, free from vague conceptions, and available for calculation. To make his logical structure coincide as nearly as possible with observed facts, certain hypotheses have to be introduced arbitrarily at the outset, and it is to these that his first chapter is devoted. Boltzmann here mercilessly lays bare the shortcomings of his subject. Seven hypotheses are marshalled successively before the reader, without apology and in broad daylight, to be looked at from all points of view: for, in its utmost development, his dynamics can only be an admirable counterfeit of nature, more nearly perfect than any doctrine that has yet been devised, but never to be made absolutely true, least of all by pronouncing a credo over the premises.

With these reservations clearly in mind, the remainder of the book is a logical outcome of the first chapter. Chapter II treats of the dynamics of a particle; Chapter III of the principles of energy, center of mass, and areas. Chapter IV contains a very searching examination of the principle of virtual displacements, both for rest and for motion; and this is followed by extensive examples of the application of these principles to rigid bodies in Chapter V. Chapter VI, finally, gives a critical review of the preceding chapter, and Boltzmann here makes a more general use of Gauss's principle of minimum constraint than is customary in treatises on dynamics. A comparison between the latter and the principle of virtual displacements is worked out, and, with the aid of an example due to J. Willard Gibbs, Gauss's principle is shown to lead to definite solutions, even when the other principle fails.

Although Boltzmann in this treatise returns to classic methods, it is not to be supposed that his lectures are old-fashioned. Indeed, the book is particularly suggestive from the modern point of view. The beginning of each important paragraph is apt to be straightforward reading between familiar equations; but as the subject advances the reader unconsciously finds his gait very much more deliberate. It would be impossible for a man, who like Boltzmann is so fully abreast with the progress of modern science, to write otherwise. Thus, in the treatment of harmonic motion, beginning as early as page 53 of the book, the derivation of the differential equations is followed by a discussion of Lissajous's curves, with remarks on correlative planetary perturbations. Thereupon damped oscillations are taken up in detail, including the method of multiplication and of recoil, the theory of the resonator and, by implication, alternating currents with resistance, self induction, and capacity. Again, in treating orbital motion, the discussion is not limited to Newton's and Kepler's laws, but orbits due to complex laws of force are very fully considered. After perusing the book one is surprised to find so much of dynamics crowded into so few pages. A knowledge of differential equations is of course presupposed; but the book is nowhere abstruse, nor is there mathematical finessing of the modern kind. All the methods are analytic. Unfortunately there is a dearth of figures, and the reader is frequently called on to exercise his imagination. Concise verbal reasoning, to the exclusion of formal methods, now so attractive to English physicists, but in the reviewer's experience an abomination to the reader, is only sparingly used. Verbal mathematics doubtless succeed admirably with men of genius, particularly as an afterthought with the answer already in sight. With humbler minds, however, the time for scorning equational mathematics is wont to be an arrival too late to be awaited without discomfort or even despair.

A book by Boltzmann on so fundamental a subject as dynamics will be welcomed by everybody: but to those who like the reviewer have been brought up on the dynamics of an originally French inspiration, and who found themselves rather left in the lurch when Duhamel's treatise went out of print, Boltzmann's lectures will prove a veritable boon. *Carl Barus*

Manual of Qualitative Chemical Analysis. *By C. Remigius Fresenius. Authorized translation by Horace L. Wells. Octavo; pp. xvii and 748. New York: John Wiley and Sons, 1897. Price: cloth $5.00, postpaid.*—It is now fourteen years since the appearance of the last American translation of this standard work; in the interval such additions and improvements have been introduced into the successive German editions that "it has been necessary to rewrite a large part of the matter and reset the type for the whole work." The book is arranged on much the same plan as its companion volume, the author's indispensable 'Quantitative Analysis;' 128 pages being devoted to apparatus and reagents, 291 to the 'deportment of bodies with reagents' and the remainder of the work to a systematic course in qualitative analysis, with special methods for the examination of silicates, natural waters and soils, and for toxicological analysis. The example set by so experienced a teacher in omitting all abbreviated 'analytical tables,' might be followed with great advantage to their students by the numerous compilers in this country of 'Introductions to Qualitative Analysis.'

As time goes on, it becomes increasingly difficult to realize the condition under which the earlier work in chemical analysis was carried on; but the author's detailed description of methods for preparing and purifying reagents and filter-paper, and his illustrations of primitive forms of apparatus, suggest vividly certain features of the period before chemical factories and scientific glass-blowing establishments came into existence; while his retention (until the later editions) of the old system of equivalents, and of the dualistic method of writing formulas, reminds one forcibly how far the practice of the art has outstripped the theory.

In his system of laboratory instruction, Fresenius's aim has been to teach his pupils to carry out accurate analyses with the simple apparatus that served their master when originating or perfecting the methods employed; his Manuals of Qualitative and Quantitative Analysis, embodying the results of fifty-five years of experience, form a lasting monument to their distinguished author's life work—now completed. *W. Lash Miller*

Elements of Theoretical Physics. *By C. Christiansen. Translated by W. F. Magie, 16×23 cm; pp. xii and 339. New York: The Macmillan Co., 1897. Price: cloth $3.25.*—The aim of Christiansen's treatise is to supply a concise account of the essential features of physical theory. The book presents successively the topics of motion, elasticity, the equilibrium and motion of fluids, internal friction, capillarity, electric and magnetic theory, light, thermodynamics, and the conduction of heat. The arrangement is a natural, almost a historical one; and the author assembles under each head just enough material to enable his readers to get a clear idea of the different subjects treated.

Workers in physical chemistry have great need of such a book: their work being essentially an application of physical theories and methods to chemical operations, they must needs have a good idea of the content and significance of physical theory. Thermodynamics, for example, with its manifold chemical applications, rests upon the theory of the potential in mechanics; electrostatics furnishes fundamental conceptions of electrochemistry; the relation of the chemical nature of bodies to their surface tension, to their internal friction, to their absorption of electric waves, to their conductivity for heat, and to their influence upon the refraction, dispersion, and rotation of light, are outstanding problems brought to physical chemistry by theoretical physics; heat-conductivity, further, is related to the migration-velocities of ions, and its laws have given form to the theory of diffusion; and it is the physical theory of thermodynamics, more than anything else, that has made physical chemistry what it is to-day. The terse form of the present book, with its almost exclusive attention to essentials, makes it well adapted for use as a physicochemical reference book; though its usefulness in this respect would be greater if it gave more frequent references to the original literature. Its mechanistic standpoint is to be regretted; the adoption of this irrational point of view is, in particular, one reason why the chapter on thermodynamics is the least satisfactory part of the whole volume; other reasons are that the author does not explain what the term 'heat' denotes, nor what is meant by the 'temperature' of the thermodynamic equations.

The English translation is clear and readable, and the volume is well printed. Undue annoyance, however, is caused the reader by too frequent printing of fractional expressions in parentheses in single lines. Minor errors are rare, yet the proof-reader has passed both 'van der Waal's equation' and 'van der Waals' equation' in several places. The book is distinctly a valuable contribution to the general literature of physics: it should be in every college library, and in the hands of everyone who is taking physical chemistry seriously.

J. E. Trevor

Die Fortschritte der Physik *im Jahre 1896, dargestellt von der physikalischen Gesellschaft zu Berlin. 52d year; Part I, Physics of Matter; edited by Richard Börnstein. 16 × 23 cm; pp. lxx and 476. Braunschweig: F. Vieweg & Sohn, 1897. Price: paper 30 marks.*—We take especial pleasure in calling attention to the appearance of the *Fortschritte der Physik* for the year 1896. It cannot be emphasized too strongly that for the purpose of gaining a general idea of the present shape of any particular topic in physics or in physical chemistry (and almost all branches of physics are special topics in physical chemistry), or for the purpose of getting ready access to the complete literature of any such topic, this comprehensive series of carefully edited abstracts has become of the utmost value. That such is the case has long been recognized by the professional physicists; and now in the reorganization of chemistry, whereby chemical processes are being studied in *all* their phases, and their study is thereby becoming physics, the devotees of this modern expanded discipline find the magnificent literary auxiliary of the physicist ready to satisfy one of their most serious needs.

The physicochemical interest of the present part of the current number of the *Fortschritte* is considerable: we find 82 pages devoted to physical chemistry proper, 6 pages to capillarity, 50 to solutions, and 19 and 7 to diffusion and to absorption and adsorption respectively, — to say nothing of the general interest attaching to the sections summarizing the current work on such matters as density, viscosity, crystallography, and energetics. Research relating to light, thermochemistry and thermodynanics, and to electrochemistry is to be considered in the succeeding numbers.

Since a subject can be well learned only through study of its original sources, the *Fortschritte der Physik* must be regarded as the ideal perennial textbook of the subjects which are embraced in its plan: its past volumes are indispensable for exhaustive research in special topics, and its current volumes serve to supply a terse account of the work done year by year. The mechanical execution of the book is the well-known admirable one of the Vieweg publishing house.

J. E. Trevor

Elements of Electrochemistry. *By Robert Lüpke. Translated from the second German edition by M. M. Pattison Muir. Octavo; pp. xvi and 223. Philadelphia: J. B. Lippincott Co., 1897.*—This book does not pretend to be in any sense a scientific treatise on electrochemistry. The author has tried to give a condensed readable account of the subject, together with a series of simple experiments illustrating the main points. In the latter aim he has been successful. The experimental part of the book is worthy of all praise and is really the feature of the book. The sketch of the modern theories is pleasantly written but not quite satisfactory. One gets a feeling—perhaps unjustifiedly—that the author is not really familiar with the original articles; but that his knowledge is obtained rather from a study of the text-books of Ostwald and of Nernst.

The English version is unmistakably a translation. To cite a single instance, "intensity of fixation" may be a literal rendering of *Haftintensität* but it is not a happy one. In places, the translator has emphasized shortcomings in the text by ill-timed references. From the German edition one would get the impression that the reacting weight of the liquid solvent enters into the formula for the change of vapor pressure with the concentration, and the translator thereupon cites a paper by Poynting. *Wilder D. Bancroft*

Les Fours électriques et leurs Applications. *By A. Minet. 12 × 19 cm; pp. 178: (Encyclopédie des Aide-Mémoire.) Paris: Gauthier-Villars & Fils. 1897. Price: paper 2.50 francs, cloth 3.00 francs.*—This little volume contains a number of scientific and technical facts gleaned from the field of electric heating. In the four parts of the book the author discusses the theory and practice of electric heating; the arc, and electric light carbons; electric furnaces; calcium carbid and acetylene. The reviewer would like to see full references given even in books like this one. *Wilder D. Bancroft.*

Les Constantes physico-chimiques. *By D. Sidersky. 12 × 19 cm; pp. 207; (Encyclopédie des Aide-Mémoire). Paris: Gauthier-Villars & Fils, 1897. Price: paper 2.50 francs, cloth 3.00 francs.*—In this volume the author has brought together such of the physico-chemical constants as refer to density, fusion, vaporization, critical states, viscosity, capillarity, refraction, calorimetry and photometry. Under fusion and vaporization the Beckmann freezing-point and boiling-point methods are considered. The book is not a mere compilation of data, for the author discusses many of the methods in some detail. Whether this be an advantage, is a point that is open to discussion.

Wilder D. Bancroft

Metallic Alloys. *By W. T. Brannt. Second Edition; octavo; pp. xxvii and 527. Philadelphia: H. C. Baird & Co., 1897. Price: cloth $4.50.* —The book is intended exclusively for workers in metals; but the man of science can find much interesting matter scattered through the volume in the form of tables and of occasional comments. Perhaps the most interesting of these latter are the few pages on the behavior of alloys in the presence of acids. It is easy to account for the alloys which are more readily attacked than the pure metals, but what is to be said about alloys containing much gold and little silver, from which it is difficult if not impossible to dissolve the silver and leave the gold? While these are probably cases of solid solutions this has never been established directly. The density of alloys where no compounds are formed, is another interesting point which has defied theoretical treatment.

The author takes up the properties of metals and alloys in general, and then discusses the special alloys of copper, tin, zinc, nickel, aluminum, lead, cadmium, bismuth, silver, gold, platinum, and mercury. Next come chapters on solders and on the analysis of alloys, while in the appendix there is some very interesting information on the coloring of alloys and the recovery of waste metals. The book can be recommended to all who are interested in miscellaneous data. *Wilder D. Bancroft*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of Journal articles that bear upon any phase of Physical Chemistry

General

The genesis of Dalton's atomic theory. Second paper. *H. Debus. Zeit. phys. Chem.* **24**, *325* (*1897*). Half of this long article (27 pages) is devoted to an account of the evolution of Dalton's ideas, as the author understands them; the remainder to a somewhat fiercely worded reply to Roscoe and Harden (1, 736). The latter's "New View of the Genesis of Dalton's Atomic Theory" is based on the interesting discovery of Dalton's laboratory note-book: Debus however will make no use of the note-book, remarking that in general a chemist's laboratory note-book ought not to be used as a source of history. "This remark I commend to Messrs. Roscoe and Harden's kind consideration." *W. L. M.*

The velocity of reacting chlorin molecules. *M. Cantor. Wied. Ann.* **62**, *482* (*1897*). If a sheet of copper, protected on one side by glass, be suspended in a jar of chlorin, the gas will be absorbed at the surface of the copper and a partial vacuum created, into which, obviously, both copper and chlorin tend to move. The author has carried out experiments of this nature, in which the copper was affixed to the arms of a torsion balance, and he regards his results as "proving that the particles of an apparently stationary gas possess a very noticeable velocity;" and consequently as "supplying an experimental proof of the fundamental assumption of the kinetic theory." The "average velocity of the chlorin molecules which react with the copper" is calculated to be about 70 meters per second. *W. L. M.*

On a tubular electric furnace. *D. Helbig. Rend. Accad. Lincei*, (*5*), 6, *I*, *314* (*1897*). A carbon tube is placed inside an iron jacket, enough of the intervening space being filled with magnesia to prevent the iron from being affected. With 250 amperes and 40 volts, a piece of Bayeux porcelain was softened in six minutes. The author claims to be able to keep a very constant temperature with the apparatus. *W. D. B.*

New mercury pump with no cocks and no movable joints. *H. Henriet. Comptes rendus*, **125**, *22* (*1897*). The essential feature is the replacement of the stop-cocks by columns of mercury. *W. D. B.*

One-Component Systems

Limits of the solid state. *G. Tammann. Wied. Ann.* **62**, *280*, (*1897*). The author considers the boundary curves for one component as consisting of a curve for liquid and vapor extending from the critical point to the absolute zero. This line is intersected at two points by a closed curve. The portion of this curve above the line for liquid and vapor represents the equilibrium between solid and liquid; the portion below the line is the curve for solid and vapor. [This distinction is not made in the text, the author having overlooked the equilibrium between solid and vapor.] From this it follows that the solid phase can only exist in a closed field and that there must be two temperatures at which a given solid phase can exist in equilibrium with liquid and vapor. These two triple points seem to have been realized by Pictet with chloroform, melting at —68.5° and —81°, and by Lehmann with crystallized selenium, melting at 96° and 217°. While liquid and vapor are thus the stable monovariant system at very low temperatures, it is not implied thereby that the liquid phase is very mobile at such temperatures. The author considers as solids only such substances as are crystalline and treats amorphous and vitreous masses as supercooled liquids. This seems reasonable because it is known that a substance can pass from the state of a mobile liquid to that of a vitreous solid without discontinuity.

The advantages of this new point of view are that it is now possible to classify amorphous substances, which have no true melting-point, and that Pictet's observations with chloroform are no longer hopelessly unintelligible. It is much to be regretted, however, that the author did not see fit to discuss the bearing of his views upon Ostwald's recently established distinction between metastable and labile states. While it does not follow that either point of view is entirely wrong, both can not be of unlimited application. It is very important to get a clear understanding of the conditions making it possible or impossible to obtain a solidified liquid. This does not seem to have been fully appreciated by the author, although he gives some measurements on the rate of crystallization. *W. D. B.*

On the reproduction of the diamond. *Q. Majorana. Rend. Accad. Lincei,* (*5*) 6, *II*, *141* (*1897*). A piece of carbon was heated by the electric arc and put under great pressure, while still hot, by the explosion of gunpowder. The mass was changed to graphite in which the author found traces of crystals having the properties of the diamond. *W. D. B.*

On some recent laws respecting the molecular volumes of liquids. *R. Nasini. Rend. Accad. Lincei,* (*5*) 6, *II*, *175*, *199* (*1897*). This is an exhaustive, critical discussion of Traube's papers on the molecular volumes of liquids. The inconsistencies in the assumptions and the inaccuracies in the results are brought out with great clearness. The paper amounts practically to a brief monograph on the subject and is a valuable contribution to science. *W. D. B.*

Avogadro's law and the liquid state. *U. Dühring. Wied. Ann.* 62, *204* (*1897*). The author, not J. Traube, was the first to apply "The improved Avogadro-Boyle-Gay-Lussac's law" to liquids and solids. Traube's law, that the 'heat-pressure' of different liquids, under the same conditions of temperature and external pressure, are identical, is based on "insufficient and arbitrarily selected data." *W. L. M.*

On the specific heat of gases. *Fourth Paper. S. Lussana. Nuovo Cimento,* (*4*) **6**, *81* (*1897*). Regnault concluded from his experiments that the specific heat of air is independent of the density. The author has repeated these measurements, working under higher pressures, and finds that, as the mean pressure changes from twenty to one hundred and ten atmospheres, the specific heat C_p increases from 0.2591 to 0.3583. The lowest of these values is higher than any obtained by Regnault. While the absolute values are not final, the author states that there is no question as to the general course of the phenomena. *W. D. B.*

Optical inversion of camphor. *F. S. Kipping and W. J. Pope. Jour. Chem. Soc.* 71, *956* (*1897*). Two optically active modifications of camphor-sulfonic chlorid have been isolated. Both melt at 135° and are very similar in appearance, but mixtures of the two melt at a lower temperature than the components. *W. D. B.*

Derivatives of camphoric acid. Part II. Optically inactive derivatives. *F. S. Kipping and W. J. Pope. Jour. Chem. Soc.* 71, *962* (*1897*). The optically active compounds formed from π-bromo- and π-chloro-camphoric acid have already been studied and the authors have now made the corresponding inactive compounds. A comparison of the two sets brings out some rather curious phenomena. The melting-points of the active and inactive anhydrides are identical, while the inactive acids melt at least fifteen degrees below the corresponding active modifications. On the other hand the active and inactive trans-π-camphanic acids have identical melting-points, and the inactive form consists of a mixture of the dextrorotatory and laevorotatory acids. The same is true of the cis-π-camphanic acid. *W. D. B.*

Resistances and specific heats of some oxids and sulfids of iron. *A. Abt. Wied. Ann.* **62**, *474* (*1897*). A study of some Hungarian iron and nickel ores. The conductivities of various samples of magnetite from the same mine showed great variations, apparently due to the silica present. The specific heat of the magnetite was very nearly that of pure Fe_3O_4, while haematite differed in this respect but little from pure Fe_2O_3. *W. D. B.*

Permeation of hot platinum by gases. *W. W. Randall. Am. Chem. Jour.* 19, *682* (*1897*). Hydrogen was purified by filtering it through a platinum septum, after it had been shown that oxygen, nitrogen and methane are kept back. The hydrogen thus formed showed the "compound" spectrum with the oscillatory discharge. This is not in agreement with the results of Trowbridge and Richards. *W. D. B.*

On the action of the ozonizer on gases. *E. Villari. Rend. Accad. Lincei,* **6**, *I, 343; Nuovo Cimento,* (*4*) 5, *459;* **6**, *113* (*1897*). The passage of the electric spark through air, hydrogen, or oxygen gives these gases temporarily the power to discharge an electroscope. The silent discharge of the ozonizer not only has not this effect but destroys the effect produced by the passage of the spark. *W. D. B.*

Two-Component Systems

Application of the phase rule to the investigation of organic addition-products, II. *B. Kuriloff. Zeit. phys. Chem.* 23, *673* (*1897*). See review in this Journal, 1, 683.

1. β-Naphthol (N) and picric acid (P) unite in equimolecular quantities to form a crystalline compound (D), which melts at 157° C. The melting-point is lowered by addition of either of the components, P or N; the author has made determinations in each direction as far as the quadruple points NDL and PDL; *i. e.*, the temperature at which the solids N and D (or P and D) are in equilibrium with a liquid phase L at atmospheric pressure. The curve (axes Ox = temperature, Oy = mol. percent. of P in L) is similar in form to that representing the solubility of $CaCl_2.6H_2O$ in water.

2. The corresponding addition-product (D) of picric acid (P) and benzene (B) melts at 84.3° C.; but while addition of (B) lowers the melting-point (measurements as far as the point DBL), addition of P apparently causes the melting-point to rise. Examination of the solid phase, however, proved it to consist of P, not D; the temperature 84.3° C. must consequently be regarded not only as the melting-point of D but also as the quadruple point (cryohydric point, transformation point) DPL. This is the first instance in which a fusion and transformation point have been found to fall together.

3. β-Naphthol and benzene form no double compound. The author has determined the course of the solubility curve of N in B, from the melting-point of the former to the point NBL. *W. L. M.*

On the temperature for the maximum density of some solutions of aqueous methyl alcohol. *P. Moretto. Nuovo Cimento,* (*4*) 6, *198* (*1897*). The temperature was determined by Despretz's method from the rate of cooling and heating. The temperature rises with addition of methyl alcohol to water, reaching a maximum of 4.736° with a one percent solution and then decreasing. *W. D. B.*

Experimental researches with a new and accurate areometer on the density of liquids and on capillary action. *A. Sandrucci. Nuovo Cimento,* (*4*) 6, *25* (*1897*). A description and discussion of an elaborate areometer intended to give density measurements accurate to the third and possibly the fourth place of decimals. From experiments on solutions the author draws the interesting conclusion that soluble vapors, such as ammonia, often increase the surface tension of water. *W. D. B.*

On the solubility of supercooled liquids. *L. Bruner. Zeit. phys. Chem.* 23, *542* (*1897*). With hydrocinnammic acid and water the author has succeeded in following the curve for two liquid phases and vapor as far as 19°, the nonvariant system with two liquid phases occurring at 38°. *W. D. B.*

The so-called hydrates of isopropylic alcohol. *T. E. Thorpe. Jour. Chem. Soc.* 71, *920* (*1897*). Pure isopropyl alcohol boils at about 82°. On adding water the boiling-point falls. No other evidence can be found indicating the existence of hydrates. The author shows by means of density determinations and fractional distillation that there is no undissociated compound of isopropyl alcohol and water. *W. D. B.*

On the cryoscopic behavior of orthonitrophenol. *G. Ampola and C. Rimatori. Rend. Acad. Lincei,* (*5*) 6, *II*, *31* (*1897*). The changes of the apparent reacting weight with the concentration are of the same general nature as with phenol. As constant for orthonitrophenol we may take 74.37, this being the mean obtained from experiments with eight different solutes. The values from which this mean is calculated are arbitrary ones, since the authors do not take the data for infinite dilution nor do they give any reason for the particular selections made. Orthonitrophenol shows marked superfusion phenomena. *W. D. B.*

Cryoscopic investigation of the acid amids. *K. Auwers. Zeit. phys. Chem.* 23, *449* (*1897*). Freezing-point determinations for forty-eight acid amids in naphthalene as solvent. In all cases the apparent reacting weight increases with the concentration. The same general result is obtained as with the phenols, that the ortho compounds show the lowest percentage variation and the para compounds the highest. The author is not inclined to attribute the abnormal behavior to the presence of a hydroxyl group, though regarding the experiments as by no means conclusive. *W. D. B.*

Contributions to the study of hyponitrous acid. *A. Hantzsch and A. L. Kaufmann. Chem. News,* 75, *232, 244, 255, 268* (*1897*). From freezing-point determinations in acetic acid it appears that the formula for benzylhyponitrite is $(C_7H_7ON)_2$. Attempts to formulate the rate of decomposition of hyponitrous acid failed, owing to a secondary formation of nitrous acid. *W. D. B.*

Migrant matter. *S. H. Emmens and N. W. Emmens. Chem. News,* 76, *37* (*1897*). A disk of silver and a disk of lead were connected by a copper spiral. It is stated that, inside of three months, the lead showed traces of silver. *W. D. B.*

Poly-Component Systems

On some equilibria in three-component systems with two liquid phases. *F. A. H. Schreinemakers. Zeit. phys. Chem.* 23, *649* (*1897*). In this paper there is a discussion of the general form of the isotherm for two liquid phases and vapor. Chloroform, water, and alcohol is the instance cited, though the general relations can be shown much better experimentally with ether, water, and alcohol. The author shows the effect produced by continuous adding of any one of the components to any solutions, without however touching upon the physical signification of the different parts of the isotherm. Experiments of Traube and Neuberg with ammonium sulfate, alcohol, and water are then referred to as showing the form of the isotherm when the curve for two liquids and vapor is cut off by the curve for solid, liquid, and vapor and the results thus obtained are confirmed by the author's own measurements with ethylene cyanid, sodium chlorid, and water. It seems to the reviewer that the subject would be far more intelligible if the author had begun with the boundary curves and had then considered the isotherms with reference to these, instead of proceeding in the reverse order. It is certainly rational to begin with the simplest case. *W. D. B.*

Rise of freezing-point in benzene solutions. *R. Mihály. Zeit. phys. Chem.* **24**, *13* (*1897*). Addition of water to a mixture of benzene with alcohol, phenol, or acetic acid, raises the temperature at which benzene separates, even when there is but one liquid phase. It is noted that the condition for this phenomenon is that the water shall be insoluble in benzene and soluble in the other component—Cf. McIntosh, this Journal, 1, 474 (1897)—but this is then ignored and the results attributed to polymerization. *W. D. B.*

Absorption of nitrous oxid by aqueous solutions. *W. Roth. Zeit. phys. Chem.* **24**, *114* (*1897*). Determination of the densities and absorption coefficients of nitrous oxid at five temperatures (5° C. to 25° C.) of aqueous solutions of urea, glycerol, oxalic acid, phosphoric acid, and sodium chlorid. In every case the absorption coefficient decreases with increase in the concentration of the solution: with urea solutions, however, the change is hardly noticeable; with sodium chlorid it is very great. The results may be expressed with sufficient accuracy by an empirical formula due to Jahn. The author considers this difference between the absorption in pure water and in solutions, to be in contradiction of thermodynamic theory. "Theoretically the molecular concentration of the gas in pure water ought to be the same as that in dilute aqueous solutions: this is true only for the solutions of a non-electrolyte—urea; sodium chlorid does not obey this law, even in 1/60-normal solution." If, however, the solubility, or the degree of dissociation of the sodium chlorid, be affected by addition of nitrous oxid, which seems very probable, the solubility (absorption coefficient) of the nitrous oxid in sodium chlorid solution must necessarily differ from that in pure water (1, 633). *W. L. M.*

Generation of "active oxygen" by the slow oxidation of sodium sulfite. *W. P. Jorissen. Zeit. phys. Chem.* **23**, *667* (*1897*). Solutions of sodium sulfite are quickly oxidized in the air to sulfate; while solutions of sodium arsenite in the presence of excess of sodium bicarbonate remain unchanged. If, however, the two be mixed, a quantity of arsenite is converted to arsenate, equivalent to the amount of sulfite oxidized; in other words, when sodium sulfite is oxidized, an amount of oxygen is rendered 'active,' equal to that absorbed by the sulfite. The paper contains references to numerous other cases of 'induced oxidation.' Compare also the author's experiments with benzaldehyde, phosphine, etc. (1, 513, 514). *W. L. M.*

Heats of neutralization of acids and bases in dilute aqueous solutions. *H. Crompton. Jour. Chem. Soc.* **71**, *951* (*1897*). The author assumes that the replacement of one element or group by another always gives the same heat effect provided there is no change of state. This is not true experimentally. He deduces from this assumption that the real effect due to the neutralization of a base by an acid must be equal to the heat evolved when one reacting weight of water passes from vapor to liquid. The experimental data differ by about thirty per cent. in the case cited. *W. D. B.*

Reduction of molybdic anhydrid by hydrogen. *M. Guichard. Comptes rendus*, 125, *26*, *105* (*1897*). Below 470° hydrogen reduces MoO_3 to MoO_2; above 470° this latter oxid is reduced to the metal. The author believes that these two are the only oxids of molybdenum. *W. D. B.*

Action of telluric chlorid and fluorid on the corresponding acids. *R. Metzner. Comptes rendus*, 125, *23* (*1897*). Incomplete data with regard to some ternary compounds of tellurium. *W. D. B.*

Velocities

The equilibrium between ethyl alcohol and sulfuric acid. *A. Zaitschek. Zeit. phys. Chem.* 24, *1* (*1897*). The author begins with an enumeration of the various 'hydrates' discovered in solutions of sulfuric acid by Mendelejeff, Pickering, and others; and "as essential discrepancies exist in the literature, with regard to the higher hydrates," proposes to solve the problem by an appeal to chemical mechanics. After preliminary experiments, which show that the reaction in question is reversible, he mixes sulfuric acid, water and alcohol in varying (known) quantities, heated to 45° C. until equilibrium was reached, and determined the amount of ethyl-sulfuric acid formed, by titration with normal soda.

"For a bimolecular reversible reaction, Guldberg and Waage's law takes the following form:—

$$\frac{\textit{conc. Alcohol} \times \textit{conc. Acid}}{\textit{conc. Water} \times \textit{conc. Ether}} = \mathrm{K} \quad \text{(a constant).}$$

From my experiments, it appears that K remains constant [within 20 percent.] only under the assumption that sulfuric acid exists in solution as ortho-sulfuric acid, H_6SO_6...two mols of water present are subtracted (being united with the H_2SO_4) and the quantity of 'free' water remaining is employed in calculating K.... Even in 98 per cent. H_2SO_4 and in $H_2SO_4 + H_2O$ the sulfuric acid *is in the form of ortho-acid*.... Even when a large excess of water is present the ortho-acid remains undecomposed, which proves that no higher hydrates are formed...calculations of K assuming the existence of various hydrates of C_2H_6O (and of $C_2H_5—SO_4H$) gave very variable values, hence my investigations exclude the existence of hydrates of alcohol (and of $C_2H_5—SO_4H$)...

"According to the equation

$$C_2H_5OH + H_6SO_6 \rightleftarrows C_2H_5—SO_4H + 3H_2O$$

it would seem that...the concentration of the water should be raised to the third power (in calculating K).... As, however, constant values for K can be obtained only when the first power is employed, the reaction must take place according to the equation

$$C_2H_5SO_4H + H_2O = C_2H_5OH + H_2SO_4$$

and the H_2SO_4 so formed reacts with water *to form the ortho-acid* with such great velocity that it has no effect on the equilibrium." The theory here detailed holds only for mixtures in which the alcohol is in excess; when the concentration of the sulfuric acid is greater than that of the alcohol, no assumption of hydrates enables the author to obtain constant values for K,—"the reaction no longer obeys the law of mass action." *W. L. M.*

On the etherification of monosubstituted benzoic acids. *V. Meyer. Zeit. phys. Chem.* 24, *219* (*1897*) ; *and*, **On the rates of etherification of monosubstituted benzoic acids and of the saponification of their ethers.** *A. M. Kellas. Zeit. phys. Chem.* 24, *221* (*1897*). His extended experiments with di-ortho-substituted benzoic acids led V. Meyer to anticipate that, among the monosubstituted benzoic acids, the ortho compounds would prove much more slowly etherified and their ethers more slowly saponified than the corresponding meta and para isomers. With a view of testing this generalization by experiment, Kellas has compared the amounts of ether produced in a given time, when fixed quantities of the isomeric acids are heated with excess of methyl or ethyl alcohol and hydrochloric acid. In every case (*o*-, *m*- and *p*-, methyl-, chlor-, brom-, iodo-, oxy-, and nitrobenzoic acid) the ortho isomer was the most slowly etherified, and (excepting the nitro acids) the meta the most rapidly. Similarly with the saponification of the ethers by caustic potash. *W. L. M.*

The formation of anilids. *H. Goldschmidt and C. Wachs. Zeit. phys. Chem.* 24, *353* (*1897*). In connection with experiments on diazoamido bodies (1, 612), Goldschmidt was led to the hypothesis that the solution of an anilin salt in anilin contains free acid, and, although in very small quantity, the ions corresponding to the latter. From this point of view a solution of acetic acid in anilin is analogous to one of acetic acid in alcohol, and the formation of acetanilid to that of ethyl acetate; the reaction should consequently be 'bimolecular' and be accelerated by addition of strong acids. These predictions were confirmed by measurements of the rates of formation of acetanilid, propionanilid and acet-*o*-toluid; and of the acceleration in the formation of acetanilid produced by adding anilin picrate, hydrobromid or hydrochlorid.

W. L. M.

On the rate of solution of solids in their own solutions. *A. A. Noyes and W. R. Whitney. Zeit. phys. Chem.* 23, *689* (*1897*). If a sparingly soluble substance be cast in a cylindrical form and placed in a small amount of solvent, the surface may be considered as approximately constant. One would then naturally expect that the rate of solution at any moment might be proportional to the difference between the actual concentration and the concentration of the saturated solution. This was found to be the case with lead chlorid and benzoic acid in water. *W. D. B.*

On the rate of crystallization. *J. Friedländer and G. Tammann. Zeit. phys. Chem.* 24, *152* (*1897*). Measurements on the rate of crystallization of supercooled benzophenone, azobenzene, hydrocinnammic acid, benzoic anhydrid, diphenylamin and guaiacol. Down to 15° supercooling, the reaction velocity increases. With more supercooling there comes a period of constant rate followed by a decrease. During the temperature interval with constant reaction velocity, the size of the tube has no effect, except that the period of decreasing rate begins at a higher temperature in narrow tubes, owing to the increased radiation.

W. D. B.

On the thermal conductivity of nitrogen peroxid. *G. Magnanini and G. Malagnini. Rend. Accad. Lincei*, (*5*) 6, *II*, *22* (*1897*). The authors determined the rates of cooling for equal volumes of different gases under the same conditions, and expressed their results by means of a reaction velocity equation. For hydrogen, oxygen, carbonic acid and air, concordant results were obtained, but this was not the case with nitrogen peroxid where the heat of dissociation came in as a disturbing factor. *W. D. B.*

Electromotive Forces.

Theory of the capillary electrometer. *U. Behn. Wied. Ann.* 61, *748* (*1897*). Warburg applies his theory of electric polarization to the phenomena of the capillary electrometer as follows: In the unpolarized electrometer:—

Hg (large meniscus) | H_2SO_4 dil. | Hg (small meniscus)

the electrolyte at both Hg-surfaces contains a small quantity of Hg-salt dissolved. By cathodic polarization the concentration of the Hg-salt at the small meniscus is electrolytically diminished; this brings about an increase in the surface tension of the Hg which reaches a maximum when all Hg-salt is precipitated. In support of this view, Warburg advances the following facts:—

1. Mercury is soluble in electrolytic solutions containing air;
2. Addition of Hg-salt to the electrolyte diminishes the surface tension of the mercury;

which are supplemented in the present paper by the following experiments of Behn:

3. H_2S added to the electrolyte (H_2SO_4) gradually blackens both Hg-surfaces; if, however, the small meniscus be kept at its maximum surface tension (by a suitable E. M. F.) it remains quite bright.
4. If the larger meniscus with dilute H_2SO_4 containing Hg-salt dissolved be placed in one vessel, and the small meniscus with pure dilute H_2SO_4 in a second (both vessels provided with stirring apparatus and communicating by means of a suitable siphon), and an E. M. F. of 0.5 to 0.6 volt be introduced (maximum surface tension corresponds to 0.8 V); Hg is precipitated at the cathode (large meniscus), and dissolved at the anode, in quantities equal to each other and equivalent to 94 per cent. of the silver precipitated in a silver voltameter in the circuit.
5. Experiments with Paschen's dropping mercury electrodes (D), and with quiet mercury (Q), resulted as follows:

D in H_2SO_4 dil. + Hg_2SO_4 | either D or Q in H_2SO_4 dil. 0.77 V
Q in H_2SO_4 dil. + Hg_2SO_4 | either D or Q in H_2SO_4 dil. 0.05 V.

"Whether the electrode in the Hg_2SO_4 solution be a dropping electrode or quiet mercury, is without influence on the E. M. F.; in the pure dilute H_2SO_4 on the other hand, only the quiet mercury can become covered with a layer containing Hg_2SO_4; consequently the dropping electrode gives the E. M. F. corresponding to the maximum surface tension, while with quiet mercury only a very small E. M. F. is observed." *W. L. M.*

Theory of the residual current. *E. Salomon. Zeit. phys. Chem.* 24, *55* (*1897*). "What causes the apparently unlimited persistence of the polarizing current in the case of electrolysis between polarized electrodes with E. M. F. less than that necessary for decomposition?" To this question of v. Helmholtz the author answers:—

If a galvanic current be passed between electrodes of the metal *M* through a solution containing one of its salts *Mx*, *M* will go into solution at the anode and will be deposited in equal quantity at the cathode. This causes an increase in the concentration c_1 of the *M*-ions at the anode, and a corresponding decrease (of c_2) at the cathode, and the concentration cell thus set up causes the 'E. M. F. of polarization E′.' A second consequence of this difference in concentration is the initiation of a process of diffusion of *M*-ions from the anode to the cathode. In order that a stationary state may be reached, the quantity *s* of *M* that passes from anode to cathode by diffusion, must be replaced by an equal quantity transported in the opposite direction; this is effected by the 'residual current' I.

Ohm's law furnishes a relation between E′, I, *w* (the resistance of the solution), and E, the external E. M. F., while Nernst's theories of the E. M. F. of concentration cells and of diffusion in electrolytic solutions connect E′ and *s* respectively with c_1 and c_2, and thus render the theory of the residual current accessible to quantitative control.

Measurements with slightly acid solutions of mercurous nitrate between mercury electrodes gave results in very good agreement with the theory; with silver, copper, and lead greater difficulties were encountered. From the formulas deduced, if I be known, the concentration of the *M*-ions in the electrolyte may be calculated; the author takes advantage of this to determine the solubility of silver chlorid, and to elaborate a 'residual current method' for use in volumetric analysis. *W. L. M.*

The depolarization of mercury and platinum electrodes. *R. Klein. Wied. Ann.* 62, *259* (*1897*). Measurements, with a capillary electrometer of the rates of depolarization of open cells. By making one of the electrodes much larger (300 times) than the other, anodic and cathodic polarization could be studied separately.

The longer the charging current has passed, *i. e.*, the greater the alteration of concentration at the small electrode (which causes polarization, see previous review), the longer should be the time required for depolarization; on the other hand, the time required should be decreased by raising the temperature (which assists diffusion), or by adding a salt of the electrode metal (metal salt). Anodic depolarization should be slower than cathodic, for in the latter case the return to the initial state is achieved not only by diffusion, but also by formation of salt. The results of the author's experiments are in agreement with these predictions of the theory.

On combining Fick's law of diffusion with an expression for the E. M. F. of polarization as function of the concentrations of the 'metal-salt' at the two electrodes, a formula was obtained which expresses the rate of depolarization in satisfactory agreement with the author's measurements. (See 1, 268).

W. L. M.

On the temperature coefficients of the potential of the calomel electrode with different dissolved electrolytes. *T. W. Richards. Zeit. phys. Chem.* 24, *39* (*1897*). The author has determined the difference of potential when two calomel electrodes, connected by a solution of chlorid, are heated to different temperatures. The temperature coefficient changes with the concentration. Allowing for the dissociation, it is not a function of the solute, hydrochloric acid and ammonium chlorid being exceptions. The potential difference seems to be approximately a logarithmic function of the temperature. The slight inconstancy of the calomel electrode when the solution is stirred is shown to be due to the formation of mercuric chlorid. The author speaks of the Gibbs-Helmholtz formula when he means the Helmholtz formula. This is a common, but deplorable error. *W. D. B.*

A gas cell. *W. Borchers. Zeit. Elektrochemie*, 4, *42* (*1897*). In the improved form of the cell the anode is carbon surrounded by cuprous chlorid solution and coal gas as before. The cathode is now iron or lead and is covered with manganese peroxid in basic calcium chlorid solution through which air is blown. The solutions are separated by a porous cell. It is stated that either or both electrodes may be carbon, platinum, lead or iron without affecting the electromotive force. The most favorable results obtained from the cell are 0.6 volt and 0.01 ampere. Less satisfactory results are obtained on substituting $SnCl_4$, $MnCl_2$, $MnSO_4$ or $FeSO_4$ for the cuprous chlorid. Measurements are promised but not given to show that the oxidation of the illuminating gas really is the source of the current. Complete oxidation is no longer claimed since the formation of oxalic acid has been recognized. *W. D. B.*

The electrometer as indicator in the titration of acids and bases. *W. Böttger. Zeit. phys. Chem.* 24, *253* (*1897*). Gold electrodes, covered with palladium black and saturated with hydrogen, were used as reversible electrodes. The advantage in this arrangement is that there is practically no tendency for the hydrogen to diffuse into the gold substratum, so the concentration of the hydrogen in the surface layer remains very constant. With strong acids and bases there is a change of about 0.4 volt at the neutralization point; with weaker acids and bases the effect is not so pronounced, but it is still very noticeable until we come to such bases as anilin. With phosphoric acid we get two sudden changes in the electromotive force; the first being the one shown by methyl orange for the monobasic acid; the second being the one obtained with phenolphthalein for the dibasic acid. *W. D. B.*

On titration with the galvanometer as indicator. *E. Salomon. Zeit. Elektrochemie*, 4, *71* (*1897*). Silver electrodes, dipping into a known quantity of standard potassium chlorid solution, are connected with a galvanometer and a cell. Silver nitrate solution is then run in from a burette. Very little current passes until there is an excess of silver nitrate, the change then being very sudden. The method is said to be better than that of Volhard. *W. D. B.*

On a standard thermal mercury volt-meter. *C. Camichel. Comptes rendus*, 125, *90* (*1897*). The expansion of a column of mercury under the action of the current is used as a means of measuring potential differences. A constant current is presupposed. *W. D. B.*

Magnetism and electromotive force: a correction. *A. H. Bucherer. Wied. Ann.* 61, *807* (*1897*). A correction, which leaves the final result unaffected (1, 448). *W. L. M.*

Electrolysis and Electrolytic Dissociation

Displacement of concentrations by the current in solutions of electrolytes. *F. Kohlrausch. Wied. Ann.* 62, *209* (*1897*). Mathematical treatment of the changes in concentration, produced by a current in a solution of one or more electrolytes, neglecting changes taking place at or near the electrodes, and changes in concentration produced by ordinary diffusion.

If α represent the concentration (in electrochemical equivalents) of one of the ions A at a point, x, y, z in the solution, a its electrical motivity, V the electrical potential at the given point, and t the time; the rate of change of the concentration of A may be represented by the equation

$$\frac{\partial \alpha}{\partial t} = \frac{\partial}{\partial x}\left(a\alpha\frac{\partial V}{\partial x}\right) + \frac{\partial}{\partial y}\left(a\alpha\frac{\partial V}{\partial y}\right) + \frac{\partial}{\partial z}\left(a\alpha\frac{\partial V}{\partial z}\right).$$

As very little is known of the dependence of a on the concentrations of the various electrolytes which may be present in the solutions, an exhaustive treatment of the subject is, for the present, impossible; except in the case of very dilute solutions (where the various motivities may be set constant) and in some few special cases studied by Hittorf. The following are a few of the author's results:

1. Free ions can in no case be generated in the interior of a solution, whatever be the motivity and concentrations of the ions dissolved;

2. The current produces *no alterations* in the concentrations of, (*a*) homogeneous solutions, (*b*) solutions where the rates of the various ions, or the ratios of their rates, are independent of the concentration;

3. Expressions are obtained for the rates of displacement of concentrations in cylindrical solutions with a linear current;

4. The case of discontinuity in the composition of the electrolytic solution is considered, and the theory of Lodge's experiment for 'rendering the motion of the ions visible' is deduced. *W. L. M.*

Electrical transference of colloids. *A. Coehn. Zeit. Elektrochemie*, 4, *63* (*1897*). Most colloids behave like particles in suspension and move towards the anode under the influence of the electric current. Colloids which are also salts move in the opposite direction. In dialyzed iron there are no ferric ions. No reference is made to the work of Picton and Linder, this Journal, 1, 622 (1897). *W. D. B.*

Determination of the affinity constants and heats of dissociation for some nitrogen acids. *E. Baur. Zeit. phys. Chem.* 23, *409* (*1897*). The Ostwald dissociation formula describes the change of conductivity for amidotetrazol and nitrourethane between 0° and 40° and for nitrourea between 0° and 20°. At 30°, and still more markedly at higher temperatures, nitrourea is decomposed by water. The dissociation constants increase to two and three fold in passing from 0° to 40°. The author integrates the van't Hoff formula on the assumption that the heat of dissociation is independent of the temperature and then calculates this value from his experimental data. *W. D. B.*

Partition of the current among the various ions of a solution. *E. v. Stackelberg. Zeit. phys. Chem.* 23, *493* (*1897*). The relations between the current E, concentrations (in electrochemical equivalents) α, β, ..., and motivities a, b, ... of the ions A, B, ..., on the one hand, and the quantities of these ions dA, dB, ..., transported to the electrodes in unit time, on the other, may be expressed by the equations :—

$$dA = \frac{dV}{dx} a\alpha. \text{ etc.}$$

But, if λ be the conductivity of the solution and dV/dx the fall of potential along the line of current,—

$$\frac{dV}{dx} = \frac{E}{\lambda}$$

which is Ohm's law ; and

$$\lambda = \sum(a\alpha + b\beta + \dots),$$

the law of Kohlrausch. Hence

$$dA = \frac{E a\alpha}{\sum(a\alpha + b\beta + \dots)}.$$

W. L. M.

On the relation between the temperature and the transference number of cadmium in aqueous solutions. *V. Gordon. Zeit. phys. Chem.* 23, *469* (*1897*). Since the electromotive force of the cell Cd | $CdSO_4$ | $CuSO_4$ | Cu increases with rising temperature, it was thought possible that this might be due in part to increased formation of complex cadmium salts, and that this would show itself in a decrease of the transference number with rising temperature. Experiment showed that the transference numbers for cadmium in cadmium salts vary greatly with the concentration, but not perceptibly with the temperature.

W. D. B.

On the electrolytic precipitation of nickel from an aqueous solution of sulfate or chlorid, I. *F. Foerster. Zeit. Elektrochemie*, 4, *160* (*1897*). If the solution to the neutral sulfate be heated to 50°–90° there is no difficulty in precipitating nickel in a coherent form provided the current density is *1* amp/qdm or higher and a nickel anode is used. With nickel chlorid the results are almost as satisfactory, provided the solution be kept acid. When the nickel anode contains C, Si, Cu, Mn, Fe, and Co, there are no traces of the first four to be found in the metal at the cathode. On the other hand the iron and cobalt are not removed. With a solution containing nickel, iron, and cobalt in known quantities it was found that the first precipitate of nickel contained relatively more of the iron and cobalt than the solution. There is here an apparent contradiction with the results of Neumann ; but it is by no means certain that the two sets of experiments are comparable. The electrolysis of a nickel chlorid solution with a carbon anode did not give satisfactory results. *W. D. B.*

An attempt to measure with a voltameter the metal precipitated in electrolytic separations. *H. Danneel. Zeit. Elektrochemie,* 4, *153* (*1897*). Freudenberg, Zeit. phys. Chem., 12, 97 (1893), found a very noticeable discrepancy between the amount of silver precipitated from a mixture of silver and copper salts and the amount of silver precipitated in the voltameter by the same current. In this paper there are measurements bearing on this point. Separating silver and copper in acid solutions the author found discrepancies varying from ten to ninety per cent., due to the residual current. This is not caused by the precipitation and redissolving of copper as assumed by Freudenberg, because experiments without any copper salt showed practically the same residual current. It seems rather to be due to oxygen dissolved in the solution and acting as a hydrogen depolarizer.

Contrary to expectation, excellent results were obtained with zinc salts and the author recommends the use of a zinc voltameter for high current densities. With cadmium salts the results are less good than with zinc; but far more satisfactory than with copper or silver. The author describes an ingenious modification of the mercury voltameter. Using a Mohr's balance he determines the change in weight of one electrode while the current is passing. *W. D. B.*

On the temperature coefficient of solutions of salts in mixtures of alcohol and ether. *C. Cattaneo. Rend. Accad. Lincei,* (*5*) 6, *II, 89* (*1897*). Solutions of ferric chlorid in ether show decreasing conductivity with rising temperature. Addition of sufficient alcohol changes the sign of the temperature coefficient. This change takes place when there are from 65 to 75 parts of alcohol to 100 parts of ether. The exact concentration is a function of the amount of ferric chlorid present, the highest concentrations of alcohol corresponding to the lowest of ferric chlorid. *W. D. B.*

On the relation of electrochemistry to organic chemistry. *K. Elbs. Zeit. Elektrochemie,* 4, *81* (*1897*). A brief summary of the applications of electrochemistry to organic chemistry. *W. D. B.*

On the reactions among ions and their importance for electrochemistry. *F. W. Küster. Zeit. Elektrochemie,* 4, *105* (*1897*). A popular experimental lecture which may be read with profit by anyone who is seeking simple but striking lecture experiments. *W. D. B.*

The electrolytic preparation of iodoform. *K. Elbs and A. Herz. Zeit. Elektrochemie,* 4, *113* (*1897*). The best temperature is 60° and the current density should be one ampere per square decimeter. Increase in the concentration of potassium iodid or of alcohol increases the percentage yield of iodoform as does a decrease in the amount of sodium carbonate. Over 97 per cent. of the theoretical amount of iodoform can be separated pure. With acetone instead of alcohol, practically no iodoform is obtained. The attempt to make bromoform electrolytically was not a success. *W. D. B.*

On the electrolysis of alkaline salts of the fatty acids. *P. Rohland. Zeit. Elektrochemie,* 4, *120* (*1897*). On electrolysis of the potassium salts of capronic, caprylic and heptylic acids, there is formed in each case one saturated hydrocarbon. From the potassium salts of unsaturated acids there are formed mixtures of unsaturated hydrocarbons. *W. D. B.*

On the synthesis of organic acids. *W. V. Miller. Zeit. Elektrochemie*, 4, *55* (*1897*). On electrolyzing a mixture containing the potassium salt of a monobasic acid and the ethyl potassium salt of a dibasic acid, the anions unite forming a mixed diester of the dibasic acid. The best result is obtained when the ratio of the two salts is three to one, the salt of the monobasic acid being in excess. No ester is formed during the electrolysis of ethylbenzyl malonate, but if potassium acetate be added there is formed *a*-methyl hydrocinnammic ester and also dibenzylsuccinic ester. *W. D. B.*

Electrochemical introduction of hydroxyl into azobenzene. *J. Heilpern. Zeit. Elektrochemie*, 4, *89* (*1897*). The solution at the anode was azobenzene dissolved in concentrated sulfuric acid; at the cathode it was caustic potash or potassium chromate. Starting with five grams of azobenzene and electrolyzing for five hours with a current of 3–4 amperes, the author succeeded in preparing five grams of tetraoxyazobenzene. *W. D. B.*

On nitrogurets. *H. Pauli. Zeit. Elektrochemie*, 4, *137* (*1897*). Grove electrolyzed ammonium chlorid solutions with a zinc anode and platinum cathode obtaining, eventually, at the cathode a substance consisting chiefly of zinc and nitrogen and having a specific gravity of 4.6, Phil. Mag., [3], **18**, 548 (1841). This substance he called a nitroguret. Analogous compounds were obtained with cadmium and copper. The author has repeated these experiments and finds that the precipitate is zinc and contains no nitrogen. With increasing current density the specific gravity of the precipitate decreases from 6.5 to about 4.0 and then increases rapidly to the first value. This change of density is due to occluded gases and, curiously enough, it is not stated what these gases are. It is not clear how the precipitate can be pure zinc and yet contain "occluded gas, only part of which passes off in a vacuum."

W. D. B.

The calculation of the capacity of a lead accumulator with varying currents. *C. Liebenow. Zeit. Elektrochemie*, 4, *58* (*1897*). The author deduces the approximate formula

$$E_t = E_{max} - \int_0^t \left(1 + \frac{a}{2\sqrt{\mathfrak{T}}}\right) i\,dt$$

where E_t is the number of ampere hours which can be obtained from the accumulator after it has been discharging for a time t; E_{max} is the largest number of ampere hours that the accumulator can possibly give; $\mathfrak{T}$ is the time elapsed since the discharge; a is a constant to be determined and i is the current. The paper also contains some excellent comments on the practical behavior of the accumulator. *W. D. B.*

An electrochemical process for changing alternating into direct currents. *L. Graetz. Zeit. Elektrochemie*, 4, *61*; *Wied. Ann.* **62**, *323* (*1897*). The author has taken advantage of the phenomenon of unipolar conductivity first studied by Erman. In a cell in which oxygen is given off at an aluminum anode it requires a potential difference of more than twenty-two volts before any current passes. On attempting to pass an alternating current through a series of these cells there will be obtained an intermittent direct current provided the electromotive force of the alternating current divided by the number of aluminum cells is not greater than twenty-two volts. *W. D. B.*

On a thermal mercury ammeter. *C. Camichel. Comptes rendus*, 125, *20* (*1897*). Known currents are passed for definite periods round a thermometer and the rise of temperature noted. After the instrument has been thus calibrated, it can be used as an ammeter. In the measurements cited one ampere corresponded to a rise of about 1.3°. *W. D. B.*

A differential telephone for determining the resistance of electrolytes. *R. Federico. Nuovo Cimento*, (*4*), 6, *161* (*1897*). The most essential of the many ingenious modifications introduced by the author is the differential telephone, a double instrument through which the current runs in opposite directions. It is stated that a difference of one-twentieth of an ohm can readily be detected in a total resistance of ten thousand ohms. *W. D. B.*

Conduction of heat and of electricity, II. *G. Bredig. Zeit. phys. Chem.* 23, *545* (*1897*). The author shows from Jäger's figures that the equivalent conductivity of salt solutions for heat, like that for electricity, is an additive property; and points out the analogy between ion transport along the line of fall of electrical potential, and Soret's experiments on the alteration of concentration along a line of fall in temperature; which suggests the conception of a *thermal* transport-rate analogous to Hittorf's electrical transport rates. Zinc sulfate and cupric sulfate, which are almost identical in equivalent weight, ion velocities and inner friction, have, also, equal conductivities for heat. *W. L. M.*

The conductivity of electrolytes for very rapid electric oscillations. *J. A. Erskine. Wied. Ann.* 62, *454* (*1897*). Between a generator of Hertz's waves and a receiver, is brought a layer of the electrolyte whose resistance is to be measured; and the depth of the layer which just prevents sparking in the receiver is determined: if various electrolytes be employed, the depths vary directly as the specific resistances. Instead of observing the spark in the receiver, the author introduced a test-needle into the windings of the latter, and observed the effect on a magnetometer. The resistances of solutions of eleven salts and acids, as measured in this manner, came very close to those determined with direct currents by Kohlrausch. *W. L. M.*

On Hall's phenomenon in liquids. *F. Florio. Nuovo Cimento*, (*4*), 6, *108* (*1897*). A continuation of the discussion with Bagard (1, 268, 386, 532). The author maintains the non-existence of the phenomenon and attributes Bagard's results to his having produced concentration differences by electrolysis before making his measurements. *W. D. B.*

Influence of magnetism on the conductivity of ferric chlorid solutions. *G. Milani. Nuovo Cimento*, (*4*) 6, *191* (*1897*). Neesen found, in 1884, that a magnetic field exercises a slight influence on the conductivity of a ferric chlorid solution when the current runs parallel to the lines of force. These experiments seem to have been faulty and the author claims, on the strength of his own observations, that no such effect occurs. *W. D. B.*

Dielectricity and Optics

The dielectric properties of liquid mixtures, particularly of dilute solutions. *J. C. Philip. Zeit. phys. Chem.* 24, *18* (*1897*). In order to calculate the dielectric constant of a mixture from those of its components, formulas are set up analogous to the n- and the n^2-formulas for the refractive index—n being replaced by $\sqrt{K}$ (K being the dielectric constant). Both formulas agree very well for mixtures with $K < 5$, the former is the better for mixtures whose one component has a large K; in many cases, however, neither suffices. The dielectric constants of solutions of alcohols in benzene and in toluene were determined by a method based on that of Nernst, and the 'constants' for the alcohols were calculated by the $\sqrt{K}$ formula. The values obtained increased with rising concentration of the solution; this the author attributes to polymerization of the alcohols. *W. L. M.*

On the rate of depolarization and on dielectric constants. *R. Abegg. Wied. Ann.* 62, *249* (*1897*). It was suggested that the measurements of Dewar and Fleming (1, 706) do not give dielectric capacities only, but these values plus the polarization capacities. It is then shown that the rate of depolarization decreases rapidly with falling temperature. Since the rate of depolarization is a function of the rate of diffusion and this latter decreases with falling temperature, it follows that the polarization capacity also decreases with falling temperature. The article closes with a few words on the author's formula for the change of the dielectric constant with the temperature. *W. D. B.*

On a method for determining the dielectric constants of solids. *H. Starke. Wied. Ann.* 61, *804* (*1897*). With the method previously described (1, 706), the liquids had to have very low conductivities. Ethylene chlorid was found to be useful as one liquid, but required frequently to be redistilled over sodium. By employing Nernst's new method of rapid oscillations, (1, 630) many more pairs of liquids can be used and the amount of solid taken may be decreased. *W. D. B.*

Molecular refraction and dispersion of extremely dilute aqueous salt solutions. *D. Dijken. Zeit. phys. Chem.* 24, *81* (*1897*). Optical measurements at 16° C., with a slightly modified form of Borghesius's refractometer,—using sodium and hydrogen light. Densities, to six decimal places, by weighing a glass balloon suspended in the solutions. Twelve salts were studied, in concentrations from one equivalent in 1, to one in 128 liters. The author combines his results with those of others, and finds that the molecular refraction of the dissolved salts (as calculated by the n-formula) is an additive property, and is nearly independent of the concentration. *W. L. M.*

Molecular rotations of optically active salts. *H. Crompton. Jour. Chem. Soc.* 71, *946* (*1897*). In order to show the superfluousness of the dissociation theory, the author advances the hypothesis that the molecular rotation of an optically active acid is unaffected by the nature of the alcohol with which it unites to form an ester. Leaving out of account as abnormal amyl formate and acetate, the supposed constant varies from 4.0 to 5.3. *W. D. B.*

On the retardation of electric vibrations. *D. A. Goldhammer. Zeit. phys. Chem.* 23, *686* (*1897*). See review in this Journal, 1, 628. "Wedell-Wedellsborg is right in saying that the energy of a vibrating body first passes out and then returns; but as the return takes place only after an infinite time when the vibrating system is completely isolated in space, it follows, independently of all special theories of electricity, that all free vibration, even if accompanied by no generation of heat, etc., must eventually become retarded."
W. L. M.

Experiments on the chemical action of electrical oscillations, II. *A. de Hemptinne. Zeit. phys. Chem.*, 23, *483* (*1897*). The first paper (1, 630) was devoted to a study of the rate of decomposition of gases. In this paper there are experiments on the relation between the wave length and the pressure at which luminescence appears. With allyl alcohol the pressure varies very little with the wave length, while with acetone, propyl aldehyde, methyl alcohol and ethyl alcohol there is evidently a relation between the two, though apparently not the same relation in the four cases. For a given wave length there is a marked change of pressure with change of the reacting substance. The author was not able to confirm Ebert's results on the spectra of vapors, Wied. Ann. 53, 144 (1894). *W. D. B.*

Convenient arrangement for making Lenard rays, and some experiments with these rays. *T. Des Coudres. Wied. Ann.* 62, *134* (*1897*). When exposed to the Lenard rays potassium chlorid becomes violet, sodium chlorid yellowish-brown, potassium bromid blue, calcium platinocyanid reddish-brown and barium platinocyanid orange-red. *W. D. B.*

Experiments with Röntgen rays. *A. Voller and B. Walter. Wied. Ann.* 61, *806* (*1897*). Winkelmann and Straubel find that the refractive index of iron for Röntgen rays is extremely close to unity. This agrees well with the authors' measurements on copper, aluminum and the diamond (1, 791).
W. L. M.

Zeeman's Phenomenon. *W. König. Wied. Ann.* 62, *240*, (*1897*). Description of an improved apparatus for observing the state of polarization of the lines of the spectrum, when broadened by the influence of a magnetic field (1, 703). The improvements consist: 1, In dividing the field of view into two parts, which can be brought into opposite states of polarization, and directly compared one with another; 2, In using as source of light, not the magnetized flame itself, but the dark absorption lines produced by passing the light from an arc lamp through it. With this arrangement the spectra can be photographed. *W. L. M.*

Crystallography, Capillarity and Viscosity

The crystalline structure of gold and platinum nuggets and gold ingots. *A. Liversidge. Jour. Chem. Soc.* 71, *1125* (*1897*). The object of the paper is to show that gold nuggets are not formed of superimposed coatings due to successive deposits of gold from solution. The polished and etched surfaces of gold nuggets were found to be markedly crystalline and the same is true for gold ingots. Twenty photographs are given so that the reader can judge for himself as to the facts. *W. D. B.*

The surface tension of water. *P. Volkmann. Wied. Ann.* 62, *507* (*1897*). Reply to Quincke (1, 751). The author defends his measurements of 1894 and 1895: the results there given for carefully determined temperatures were, in each case, the mean of from twenty-seven to fifty-four observations, "the overwhelming majority of which agreed within one one-thousandth of their value."
W. L. M.

The heat effect on moistening powders. *T. Martini. Nuovo Cimento,* (*4*), 6, *58* (*1897*). On moistening animal charcoal with different liquids a rise of temperature is noted varying from 8° to 20° depending on the nature of the liquid and the state of the charcoal. Curiously enough the order of the liquids is not the same with powdered and with granular charcoal, ether causing a greater rise of temperature with the former than does benzene or carbon bisulfid, while the reverse is the case with the granular charcoal. *W. D. B.*

The viscosity of non-conducting liquids in a constant electrical field. *G. Quincke. Wied. Ann.* 62, *1* (*1897*). Spheres of glass, quartz and other materials were suspended between condenser plates, the space filled with the liquids to be examined and the condenser plates connected with a Leyden battery. Using a Mohr's balance and having the spheres swing perpendicularly to the lines of force, the logarithmic decrement of the amplitude, $\lambda—\lambda^{\circ}$ may be taken as a measure of the increase in the viscosity of the liquid. This was found to be directly proportional to the dielectric constant of the liquid and to the potential difference, inversely proportional to the distance between the plates. The increase in the viscosity parallel to the lines of force is two-thirds to one-sixth of that perpendicular to the lines of force. *W. D. B.*

SOLUTIONS OF SILICATES OF THE ALKALIES

BY LOUIS KAHLENBERG AND AZARIAH T. LINCOLN

INTRODUCTION

The electrical conductivity of solutions of sodium silicates has been investigated by F. Kohlrausch,[1] who worked mainly with the compounds corresponding to the formulæ Na_2SiO_3 and $Na_2O.3.4SiO_2$, although he also tested the conductivity of solutions containing sodium hydroxide and silicic acid in other proportions varying from pure NaOH to the acid silicate just mentioned. Kohlrausch obtained the solution of the normal silicate by dissolving the crystallized salt ($Na_2SiO_3 + 9H_2O$) in water while that of the acid silicate was prepared by boiling the solution of the normal salt with excess of silicic acid. By mixing sodium hydroxide with various quantities of the acid silicate, the other solutions mentioned were obtained. Kohlrausch found that a dilute solution of sodium silicate conducts electricity better than that of any other salt of equivalent concentration and concludes that this is due to the fact that in solution this salt suffers hydrolytic decomposition into sodium hydroxide and silicic acid. In concentrated solutions Na_2SiO_3 was found to be a rather poor conductor. Dilute solutions of the acid silicate were also found to conduct well, while strong solutions showed an abnormally low conductivity. This behavior is also explained by the hydrolytic decomposition of the salt. Kohlrausch[2] appears to give this explanation in rather a tentative way, for, besides the fact that silicate solutions have an alkaline reaction and that the alkali they contain can be estimated by titrating with a normal acid, he had simply the results of conductivity determinations upon which to base his argument. No

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[1] Zeit. phys. Chem., 12, 773 (1893).

[2] See paragraph 2, p. 773; also p. 778, loc. cit.

doubt the high conductivity of a solution of Na_2SiO_3, which, if the salt were supposed to dissociate into the ions $2Na$ and SiO_3, would necessitate the assumption that the latter ion has a mobility exceeding that of the chlorine ion by about 70 percent, is an excellent reason for believing that the silicate is decomposed into NaOH and silicic acid and that the great conductivity of the solution is due to the presence of the mobile ion OH; nevertheless a determination of the freezing-points of solutions of silicates together with conductivity investigations, would more definitely answer the question as to whether these compounds are hydrolytically decomposed, and would furthermore enable one to make a quantitative estimate of the extent of such decomposition. To determine the extent of the hydrolytic decomposition of the silicate from the electrical conductivity of its solution, is not possible, for the silicic acid split off exercises an unknown retarding influence on the movements of the ions. It is possible only to state as Kohlrausch does that in very dilute solutions the decomposition is very great and that probably even in strong solutions it is still appreciable. Colloidal silicic acid has but very little effect on the freezing-point, as is well known; indeed, in the case of a solution of sodium silicate the lowering of the freezing-point caused by the colloidal silicic acid present, is generally so small that for most purposes it may be left out of consideration. From this it is evident that from the lowering of the freezing-point of a silicate solution the extent of the hydrolytic decomposition of the salt may be calculated very approximately. The present investigation was undertaken in order to throw more light on the nature of silicates in solution; for this purpose the freezing-points and the electrical conductivity of solutions of various silicates were determined.

EXPERIMENTAL PART

The solutions that were investigated are those of the silicates of sodium, potassium, lithium, rubidium, and caesium. These solutions were in all cases prepared by adding to a solution of silicic acid, obtained by dialysis according to the well-known method of Graham,[1] the required amount of a standard solu-

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[1] Phil. Trans. Roy. Soc. London, 1861.

tion of the pure hydroxide of the alkali metal. That a solution of sodium silicate thus prepared is the same as that obtained by dissolving the salt, will be shown below. It is a well established fact that a solution of NaCl is the same as that obtained by mixing equivalent quantities of NaOH and HCl[1] and consequently it seemed at first unnecessary to prove that a solution of Na_2SiO_3 is the same as a solution of equivalent amounts of silicic acid and caustic soda; but because in the case of silicate solutions equilibrium is established only after a measurable period of time[2] and because objections might possibly arise to using a colloidal solution of silicic acid in the preparation of silicate solutions and then finding that the latter contain colloidal silicic acid, it was thought best not to omit the experimental proof.

Dialyzed solutions of silicic acid were prepared using crystallized $Na_2SiO_3 + 9H_2O$ and also commercial solutions of water-glass from different manufacturers. In each case the dialysis was carried on until no more chlorides were present in the solutions. No difference was found in the behavior of the solutions of the silicates prepared from the various colloidal silicic acid solutions thus obtained. The strength of the silicic acid solutions was determined by evaporating a measured quantity to dryness, igniting and weighing the SiO_2; the purity of the latter was always established by finally volatilizing the same with hydrofluoric acid—no residue remained.

The solutions of the hydroxides of sodium and potassium were obtained by allowing the metals to act upon water freed from carbon dioxide. The hydroxides of lithium, rubidium and caesium were prepared by treating the sulphates of these metals with equivalent amounts of barium hydroxide. The strength of the solutions of these alkaline hydroxides was determined by comparison with a carefully standardized solution of hydrochloric acid.

The freezing-point determinations were made with the apparatus of Beckmann. The thermometer was graduated to hundredths of a degree and admitted of judging the thousandths

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[1] Ostwald. Zeit. phys. Chem., 2, 80 (1888).

[2] Kohlrausch. loc. cit., p. 783.

by use of a lens. The usual precautions[1] in making the freezing-point determinations were carefully observed.

The electrical conductivity was measured according to the method of Kohlrausch. In preparing the various solutions, water carefully freed from carbon dioxide and ammonium salts, was used. The water was first distilled from potassium bichromate plus sulphuric acid and then redistilled from barium hydroxide. A condenser of block tin was used; this was found to yield satisfactory results. The water thus obtained was carefully protected from the carbon dioxide of the air, and special precautions were taken in carrying out all the experiments to exclude the influence of carbon dioxide.

In preparing the silicate solutions the aim was to get fairly strong solutions with which to begin. In attempting this by the method of mixing caustic alkali with colloidal silicic acid some difficulty was encountered. The advantage of using this method of getting the solutions of the various silicates, is clearly that, by means of it, it is possible to more conveniently get the alkali and the silicic acid into solution in any desired proportions. The disadvantage is that very strong solutions cannot be thus prepared for the reason, that, when strong solutions of caustic alkali and silicic acid are mixed, the latter gelatinizes. Various attempts to get a solution of the normal silicates of sodium or potassium stronger than one-eighth of a gram-molecule per liter failed because the solutions gelatinized before the proper amount of alkali had been added. Still more difficulty was encountered in preparing the solution of the normal silicate of lithium. In this case a solution containing one thirty-second of a gram-molecule per liter was the strongest that could readily be obtained. In mixing the alkali with the silicic acid solution, it was found best to add the former to the latter gradually, always shaking the mixture and waiting until the precipitate that forms temporarily is completely dissolved before adding more alkali. It is best also to heat the silicic acid solution while the alkali is being added. The colloidal solution of silicic

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[1] See Ostwald's Hand. u. Hilfsbuch.

acid was slightly opalescent in appearance; the solutions of the silicates, however, were invariably perfectly clear.

Tables 1 to 9 give the results of the cryoscopic determinations. In the first column under *v* is given the volume in liters in which one gram-molecule of the salt expressed by the formula is contained. The second column gives the observed lowering of the freezing-point. In the third column are the molecular weights calculated on the supposition that the salt when in solution has the composition indicated by the formula. The fourth column gives the molecular weights calculated on the supposition that there is in the solution only the alkaline hydroxide; that is to say, in this calculation no account was taken of the silicic acid present. The solution of silicic acid that was used in preparing the silicate solutions according to the method above described contained 12.2180 grams SiO_2 per liter and had a freezing-point of −0.018°, which corresponds to the molecular weight 1019.

Table 1

Na_2SiO_3 Mol. Wt. = 121.58

v	Freezing-point	Mol.Wt.	Mol.Wt. (NaOH)
8	0.695	41.3	27.0
12	0.498	38.4	25.2
16	0.385	37.3	24.4
24	0.280	34.2	23.9
32	0.210	34.9	22.4
48	0.150	31.9	20.9
64	0.110	32.6	21.4

($\frac{1}{4}$ of 121.58 = 30.39)

($\frac{1}{2}$ Mol. Wt. NaOH = 19.88)

Na_2SiO_3 (Obtained by fusion)

v	Freezing-point	Mol.Wt.
32	0.200	36.5
48	0.140	34.8
64	0.108	33.8
96	0.077	31.6

Table 2

$NaHSiO_3$ Mol. Wt. = 99.7

v	Freezing-point	Mol.Wt.	Mol.Wt. (NaOH)
8	0.332	70.9	31.0
12	0.263	59.7	26.1
16	0.202	58.3	25.5
24	0.146	53.7	23.5
32	0.110	53.5	23.4

($\frac{1}{2}$ of 99.7 = 49.85)

Table 3

$Na_2Si_6O_{11}$ Mol. Wt. = 361.34

v	Freezing-point	Mol.Wt.	Mol.Wt. (NaOH)
32	0.178	119.9	27.0
48	0.139	102.4	23.1
64	0.104	100.3	22.6
96	0.089	79.9	18.0
128	0.059	90.4	20.4

($\frac{1}{4}$ of 361.34 = 90.33)

Table 4

K_2SiO_3 Mol. Wt. = 153.46

v	Freezing-point	Mol. Wt.	Mol. Wt. (KOH)
8	0.710	51.1	37.1
12	0.503	48.1	34.9
16	0.394	45.4	32.9
24	0.279	43.5	31.4
32	0.215	42.2	30.6
48	0.146	41.4	30.0
64	0.110	41.2	29.9
96	0.082	36.8	26.7

(¼ of 153.46 = 38.36)

(½ Mol. Wt. KOH = 27.85)

Table 5

$KHSiO_3$ Mol. Wt. = 115.64

v	Freezing-point	Mol. Wt.	Mol. Wt. (KOH)
8	0.326	83.8	40.4
12	0.248	73.4	35.4
16	0.196	69.7	33.6
24	0.153	59.5	28.7
32	0.110	62.1	29.9
48	0.078	58.4	28.1

(½ of 115.64 = 57.82)

Table 6

Li_2SiO_3 Mol. Wt. = 89.76

v	Freezing-point	Mol. Wt.	Mol. Wt. (LiOH)
32	0.228	23.3	12.4
48	0.166	21.2	11.3
64	0.120	22.1	10.4
96	0.090	19.6	10.4
128	0.071	18.5	9.9

(¼ of 89.76 = 22.88)

(½ Mol. Wt. LiOH = 11.92)

Table 7

$Li_2Si_5O_{11}$ Mol. Wt. = 329.52

v	Freezing-point	Mol. Wt.	Mol. Wt. (LiOH)
32	0.172	113.2	16.4
48	0.139	93.3	13.5
64	0.112	86.9	12.6
96	0.077	84.3	12.2
128	0.062	78.5	11.4

(¼ of 329.52 = 82.38)

Table 8

Rb_2SiO_3 Mol. Wt. = 245.38

v	Freezing-point	Mol. Wt.	Mol. Wt. (RbOH)
64	0.139	52.1	43.2
96	0.098	49.3	40.9

(¼ of 245.38 = 61.34)

(½ Mol. Wt. RbOH = 50.83)

Table 9

Cs_2SiO_3 Mol. Wt. = 339.60

v	Freezing-point	Mol. Wt.	Mol. Wt. (CsOH)
64	0.102	98.3	86.1
96	0.068	98.3	86.0

(¼ of 339.60 = 84.9)

(½ Mol. Wt. CsOH = 74.38)

The first part of table 1 gives the results obtained from freezing solutions of Na_2SiO_3 prepared by mixing solutions of silicic acid with caustic soda as above described; the second part gives the results obtained from freezing solutions of Na_2SiO_3

prepared by dissolving the salt obtained by fusing the alkali and the acid together. It will be observed that the freezing-points of the corresponding dilutions agree fairly well and justify the conclusion that the solutions are identical. The fact that the depressions in the second series are not quite as large as those in the first, is very likely due to the slight formation of carbonates in case of the salt obtained by fusion, for in the process of fusing it is especially difficult to exclude the influence of carbon dioxide. Tests of the electrical conductivity of the solutions obtained in these two different ways also pointed to the fact that they are identical. The salt obtained by fusion of course had a slightly lower conductivity for the same reason that its solution possessed a slightly higher freezing-point.

Table 1 shows that the molecular weights calculated on the assumption that the substance in solution has the formula Na_2SiO_3 approach as their limit the value of one-fourth the calculated molecular weight of Na_2SiO_3. There are then in the dilute solutions four part-molecules active in lowering the freezing-point. The action of water on the silicate may be expressed by the equation

$$Na_2SiO_3 + \text{water} = 2\overset{+}{Na},\ \overset{-}{OH} + \text{colloidal silicic acid.}$$

The four part-molecules that are active in lowering the freezing-points are thus two sodium ions and two hydroxyl ions. As stated above the effect of the colloidal silicic acid on the freezing-point can, at least for the more dilute solutions investigated, be considered too small to take into account. The results show that this hydrolytic decomposition is nearly complete for the concentration $v = 48$, and that it has progressed to the extent of 64.8 percent[1] even when $v = 8$. The last column of the table giving the molecular weights calculated on the assumption that there is only NaOH in the solution, confirms in a striking manner what has just been said. These results approach as their limiting value one-half the molecular weight of NaOH. This

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[1] This calculation as well as the similar ones that follow has been made on the supposition that the caustic alkali present in the solution has suffered practically complete electrolytic dissociation.

is what would be expected since this compound dissociates into the ions Na and OH.

The investigations of solutions containing $NaHSiO_3$ yielded the results in table 2. Here the molecular weights calculated from the observed lowerings on the assumption that the dissolved substance is $NaHSiO_3$ give values that approach as their limit one-half of the molecular weight of $NaHSiO_3$. This shows that in the dilute solutions there are two part-molecules active in lowering the freezing-point; these are sodium and hydroxyl ions as before. The equation expressing the action of water on $NaHSiO_3$ may be written

$$NaHSiO_3 + \text{water} = \overset{+}{Na},\ \overset{-}{OH} + \text{colloidal silicic acid}.$$

This decomposition is nearly complete at the same concentration as that of Na_2SiO_3, and even when $v = 8$ it has progressed to the extent of 40.7 percent. As in the case of table 1, the values in the last column (obtained on the supposition that the solution is simply one of NaOH) approach the limit of one-half the molecular weight of NaOH.

Table 3 gives the results obtained by freezing solutions of the more acid silicate $Na_2Si_5O_{11}$. This salt was selected because a lithium silicate of analogous formula occurs in nature. The molecular weights in the third column approach as a limit the value of one-fourth the molecular weight of $Na_2Si_5O_{11}$.[1] Here again then there are four part-molecules active in lowering the freezing-point. The equation

$$Na_2Si_5O_{11} + \text{water} = 2\overset{+}{Na},\ \overset{-}{OH} + \text{colloidal silicic acid}$$

expresses the hydrolytic decomposition that takes place. This decomposition is practically complete at $v = 128$ and has gone on to the extent of 67.3 percent even when $v = 32$. In the fourth column the molecular weights calculated on the basis that there is only NaOH in solution again approach as a limit the value of one-half of the molecular weight of NaOH. This salt then behaves very much like those of tables 1 and 2 except that the

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[1] The small molecular weight found corresponding to the concentration $v = 96$ is no doubt due to experimental error.

hydrolytic decomposition is not as far advanced at the same stage of dilution. This is to be expected from the law of mass action. For a like reason $NaHSiO_3$ is not quite as far dissociated hydrolytically at the same degree of dilution as Na_2SiO_3, though here the difference is less since the amount of silicic acid present has only been doubled, while in the salt $Na_2Si_5O_{11}$ there is five times as much acid (to the same amount of sodium) as is contained in the normal salt.

Tables 4 and 5 show the behavior of solutions of K_2SiO_3 and $KHSiO_3$ respectively. What has been said of the sodium compounds applies also to these salts. The action of water on these silicates may be expressed by analogous equations. At $v = 8$ the normal salt is dissociated 66.9 percent and the acid salt 39 percent. In both cases the dissociation is practically complete at $v = 48$.

The lithium silicates investigated yielded the figures in tables 6 and 7. The normal salt is decomposed to the extent of 95.5 percent at $v = 32$, while at $v = 48$ the decomposition is practically complete as in the case of the analogous sodium and potassium salts. The salt $Li_2Si_5O_{11}$ is hydrolytically dissociated 67.7 percent and this decomposition is practically complete at $v = 128$. The behavior of the lithium salts then is perfectly analogous to that of the potassium and sodium salts.

The determinations made with rubidium and caesium silicates are given in tables 8 and 9. The quantities of these alkalies that were available were small and hence but few determinations were made. A glance at the results shows that these silicates behave like those of the other alkalies. The solutions investigated were quite dilute and in them, as the results show, the hydrolytic decomposition had gone on very far. The lowerings obtained with the rubidium salt are greater than they ought to be theoretically. This is probably due to the fact that the rubidium salt, from which the hydroxide of rubidium that was used was prepared, contained some sodium. As the quantity of rubidium salt available was small a special analysis to ascertain the amount of sodium present was not made.

The results of the determinations of the electrical conductivity of the solutions are contained in tables 10 and 11. The former table contains the conductivity of solutions of the free alkalies at 25° C. It was necessary to make these determinations, for the conductivity of solutions of the alkaline hydroxides at 25° C. could not be found in the literature, and only by comparing the conductivity of solutions of the alkaline silicates with that of solutions of the free alkalies, can an idea of the extent of the retarding influence that the colloidal silicic acid has on the movements of the ions, be gained.

Kohlrausch[1] noticed that on diluting silicate solutions the conductivity changed for a time and finally became constant. The time of this variation and the degree of the latter depended of course on the conditions of experiment. Kohlrausch investigated this time factor as well as the variation of the conductivity of sodium silicate solutions with the temperature. He found that in some cases equilibrium was established in the solution in a few minutes, in others it took five hours or more. The time effects studied by Kohlrausch were also observed by us and on the whole we were able to confirm his experiments as far as we went. It was not the purpose of this investigation, however, to study this time effect further, and for this reason the conductivity of the solutions was determined only after equilibrium had become established in them. The strongest silicate solution was prepared as already described, then the various dilutions ($v = 16$ to 1024) were prepared in thoroughly cleaned and steamed flasks, which were kept tightly corked. The dilutions were made by means of carefully calibrated pipettes. At the end of five to six hours (when equilibrium had practically become established) the contents of the various flasks were quickly transferred to the resistance cell and the conductivity determined.

In tables 10 and 11 v denotes the volume in liters in which one gram-equivalent of the compound indicated by the formula is contained, and λ denotes the equivalent conductivity expressed as usual in mercury units.

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[1] Loc. cit.

Table 10

v	NaOH λ	KOH λ	LiOH λ	v	NaOH λ	KOH λ	LiOH λ
1	157.5	....	....	64	199.1	220.4	189.2
2	181.2	196.7	157.6	128	199.0	218.4	189.2
4	188.1	207.2	171.0	256	196.3	215.0	184.0
8	194.7	213.1	179.2	512	188.9	208.0	174.9
16	197.4	216.7	185.9	1024	181.8	201.4	170.0
32	199.0	219.1	189.3				

(The water used had a specific conductivity of 1.7 × 10^{-6}. This has not been deducted in the above table.)

Table 11

v	Na_2SiO_3 λ	$NaHSiO_3$ λ	$Na_2Si_5O_{11}$ λ	K_2SiO_3 λ	$KHSiO_3$ λ	Li_2SiO_3 λ	$Li_2Si_5O_{11}$ λ
8	105.3	72.4	....	....	87.3	....	....
16	112.0	78.8	....	130.9	110.3	....	....
32	117.8	84.9	73.0	176.4	117.6	125.0	55.4
64	115.0	90.1	79.9	182.6	126.2	126.0	61.6
128	119.5	103.7	87.3	185.5	133.4	129.2	67.5
256	95.7	114.2	93.1	187.1	141.7	130.2	72.6
512	91.8	133.1	101.1	191.8	155.9	138.5	78.9
1024	104.8	148.5	113.3	182.5	175.6	145.2	90.6

(The conductivity of the water which was 1 × 10^{-6} has been deducted in each case.)

It will be observed that in table 10 the values for λ increase as v increases until they reach a maximum after which they decrease. This behavior of the alkaline hydroxide is well known and is to be ascribed to impurities in the water. Table 11 shows that in case of the normal silicates of sodium and potassium the values for λ also pass through a maximum. In case of the acid silicates of sodium and potassium and those of lithium the values for λ do not pass through a maximum. It will be noted that the conductivity of the normal salts is uniformly greater than that of the acid salts of the same metal. The values of λ for $v = 256$ to 1024 in the case of Na_2SiO_3 are less than those for the acid silicates at the same concentrations; this, however, is undoubtedly due to experimental error. A redetermination of λ

for these concentrations was contemplated, but was not carried out, as it is especially difficult to get a mixture of the silicic acid solution and caustic soda in the proportions required by the formula Na_2SiO_3, owing to the fact that the mixture gelatinizes just before the entire quantity of alkali has been added.

By comparing the values for λ in table 10 with those of the salt of the corresponding metal in table 11, the effect of the presence of the silicic acid on the conductivity may be seen. It will be observed that even in the most dilute solutions of the normal salts the values for λ still fall considerably short of equalling those of the hydroxides. The values of λ in table 10 pass through their maximum at about $v = 32$ to 64; at this concentration then the hydroxides are practically completely dissociated. It will be recalled that from the cryoscopic determinations on the normal silicate solutions it was inferred that in the latter hydrolytic decomposition is practically complete at $v = 48$. Although the errors of measurement in the freezing-point determinations are greater than in the measurement of the electrical conductivity, yet it would appear safe to say that the increase in the value of λ for the silicate solutions beyond $v = 64$, is mainly due to a decrease of the retarding influence of the silicic acid on the movements of the ions.

The conductivity of solutions of caesium and rubidium silicates was also determined. Unfortunately the water used in making the dilutions had become contaminated, a fact which was later discovered, and hence the figures obtained are not given here. It may be stated, however, that the figures obtained showed beyond any reasonable doubt that the silicates of these alkalies behave in a manner entirely analogous to that of the silicates of the other alkalies.

SUMMARY OF RESULTS AND GENERAL REMARKS

The results of the foregoing investigation may be briefly summarized as follows:—

1. The conclusion of F. Kohlrausch that in solutions of sodium silicates these salts are hydrolytically decomposed into

sodium hydroxide and colloidal silicic acid, has been confirmed by investigating the freezing-points of such solutions.

2. The freezing-points and the electrical conductivity of solutions of the silicates of potassium, lithium, rubidium, and caesium, show that these salts are also decomposed by water into the colloidal silicic acid and the hydroxide of the alkali metal. The silicates of the alkalies all show an analogous behavior when dissolved in water.

3. The same solution results whether a silicate is dissolved in water or whether solutions of caustic alkali and colloidal silicic acid in proper proportions are mixed.

4. Since colloidal silicic acid has but little effect on the freezing-point the degree of hydrolytic decomposition of the silicates can be calculated from the lowering of the freezing-point of their solutions.

5. Silicates of the general formulæ M_2SiO_3 and $MHSiO_3$ are practically completely hydrolytically dissociated when one gram-molecule is contained in 48 liters. Silicates of the general formula $M_2Si_5O_{11}$ are practically completely decomposed by water when one gram-molecule is present in 128 liters.

6. A comparison of the electrical conductivity of silicate solutions with that of solutions of the alkaline hydroxides, shows that the values of the former approach the latter as the solutions become more dilute, the retarding influence that the silicic acid has on the mobility of the ions gradually becoming less.

The conclusions here arrived at are of general interest inasmuch as silicates occur in greater or less quantities in almost all natural waters. If the silicates of the alkalies are so easily de composed by water, how much more readily would silicates of the alkaline earths and the heavier metals be hydrolytically decomposed, especially since solutions of these salts are always exceedingly dilute because the compounds are so difficultly soluble.

Of the waters of 859 springs in various parts of the United States[1] the one that contains the most silica is that of the Deep Rock Mineral Spring at Oswego, N. Y. According to an analy-

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[1] See Bull. U. S. Geol. Survey, 32, 35 (1886).

sis made in 1871 by S. H. Douglas it contains the molecular weight of SiO_2 in grams in 48.84 liters.[1] Next to this is Opal Spring in Yellowstone National Park in the Gibson Geyser Basin, for according to an analysis made by Henry Leffmann in 1882, its water contains one gram-molecule SiO_2 in 65.15 liters. The analyses of the other 857 springs show that the waters of but three of them contain over one gram-molecule SiO_2 in 140 liters and only fourteen others contain more than a gram-molecule in 350 liters. The waters of the remaining 840 springs contain much smaller amounts of silica, usually less than one gram-molecule in 3500 liters.

Justus Roth's[2] compilation of the analyses of river waters from different parts of the globe (chiefly European, however) shows that the largest amount of silica was found in the water of the Rhine. A sample taken near Strassburg contained one gram-molecule SiO_2 in 1250 liters. According to the same authority the Atlantic Ocean contains one gram-molecule SiO_2 in 531 liters. Of the many analyses of the waters of springs of various kinds located in different parts of the globe that have been collected by Roth, none show a greater content of silica than one gram-molecule in 80 liters and of course most of them very much less.

In the face of these facts and the results of the above investigations it appears safe to say that in natural waters silicic acid always occurs in the colloidal state; only in very rare instances are the solutions of the silicates so concentrated that they are not practically completely hydrolytically decomposed. This conclusion will no doubt be of value to the mineralogist and geologist in explaining the formation of various siliceous deposits and the alterations produced in rocks by the action of water. It might also prove to be of value to the plant physiologist in explaining how plants take up various constituents from the soil.

Laboratory for Physical Chemistry,
University of Wisconsin, Madison, Nov. 18, 1897.

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[1] It seems almost that the figures in the report must be a misprint.

[2] Allgemeine u. chemische Geologie, Vol. I.

ON THE GENERAL PROBLEM OF CHEMICAL STATICS

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(Concluded)

4. *The Composition of a System in Equilibrium is uniquely Determined.*—The theorems just demonstrated all relate to the *determinate composition* of the different phases of the system: the assertion that the phase a has a determinate composition is intended to mean that the system of positive ratios

$$Y_{a_a}, Y_{b_a}, \ldots, Y_{k_a},$$

subject to the relation

$$Y_{a_a} + Y_{b_a} + \cdots + Y_{k_a} = 1,$$

has a limited or unlimited number of determinations *not forming a continuous series*; but it is not intended to mean that this number of determinations reduces to *unity*, whereby the composition of the phase a would become *uniquely determinate.* In this latter sense of the word 'determinate', the foregoing theorems are, in general, false. It appears, therefore, that the following rigorously true theorem adds something to the insight into the laws of chemical mechanics just reached:—

If, with determinate values of the temperature T, *the pressure* Π, *and the masses* $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$ *of the independently variable components, any chemical system can assume two different states of equilibrium, whereby in each case the system is made up of the same number of phases of the same nature, then each of these phases will have the same composition in both states.*

Let $\alpha, \beta, \ldots, \phi$ denote the ϕ phases occurring in the two states, and let

$$m_{a_\alpha},\ m_{b_\alpha},\ \ldots,\ m_{k_\alpha}, \tag{30}$$

and

$$m'_{a_\alpha},\ m'_{b_\alpha},\ \ldots,\ m'_{k_\alpha} \tag{30a}$$

denote respectively the independent masses found in the phase α in the two cases. When these masses have the values (30), the function F_{a_α} shall be denoted by F_{a_α}; when they have the values (30*a*), this function shall be denoted by F'_{a_α}; and when they have arbitrary values

$$\mu_{a_\alpha},\ \mu_{b_\alpha},\ \ldots,\ \mu_{k_\alpha}$$

it shall be denoted by Φ_{a_α}. Now we know that, for the masses (30) to correspond to a state of equilibrium of the system, it is necessary and sufficient that

$$\begin{aligned}
&F_{a_\alpha}\delta m_{a_\alpha} + F_{b_\alpha}\ m_{b_\alpha} + \cdots + F_{k_\alpha}\delta m_{k_\alpha}\\
&+F_{a_\beta}\delta m_{a_\beta} + F_{b_\beta}\delta m_{b_\beta} + \cdots + F_{k_\beta}\delta m_{k_\beta}\\
&+\cdots\\
&+F_{a_\phi}\delta m_{a_\phi} + F_{b_\phi}\delta m_{b_\phi} + \cdots + F_{k_\phi}\delta m_{k_\phi} = 0
\end{aligned} \tag{13}$$

for every set of values of

$$\delta m_{a_\alpha},\ \delta m_{a_\beta},\ \ldots,\ \delta m_{k_\alpha},\ \ldots,\ \delta m_{k_\phi}$$

that satisfies (1*a*) and (3*a*). Likewise, for the masses (30*a*) to correspond to equilibrium, it is necessary and sufficient that, for the same sets of values of

$$\delta m_{a_\alpha},\ \delta m_{a_\beta},\ \ldots,\ \delta m_{k_\alpha},\ \ldots,\ \delta m_{k_\phi},$$

we have

$$\begin{aligned}
&F'_{a_\alpha}\delta m_{a_\alpha} + F'_{b_\alpha}\delta m_{b_\alpha} + \cdots + F'_{k_\alpha}\delta m_{k_\alpha}\\
&+F'_{a_\beta}\delta m_{a_\beta} + F'_{b_\beta}\delta m_{b_\beta} + \cdots + F'_{k_\beta}\delta m_{k_\beta}\\
&+\cdots\\
&+F'_{a_\phi}\delta m_{a_\phi} + F'_{b_\phi}\delta m_{b_\phi} + \cdots + F'_{k_\phi}\delta m_{k_\phi} = 0.
\end{aligned} \tag{13a}$$

The masses (30) and (30*a*) both being such that the equations (3) and (1) are satisfied, *the values of* $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_r$ *being the same in both cases*, it is clear that the quantities

$$\left.\begin{aligned} \delta m_{a_\alpha} &= \epsilon(m'_{a_\alpha} - m_{a_\alpha}), \\ \delta m_{b_\alpha} &= \epsilon(m'_{b_\alpha} - m_{b_\alpha}), \\ &\ldots \\ \delta m_{k_\alpha} &= \epsilon(m'_{k_\alpha} - m_{k_\alpha}), \\ &\ldots \\ \delta m_{k_\phi} &= \epsilon(m'_{k_\phi} - m_{k_\phi}), \end{aligned}\right\} \tag{31}$$

where ϵ denotes any infinitesimal, are such that the equations (1*a*) and (13*a*) are satisfied; whence follows, because of (13) and (31),—

$$\begin{aligned} &F_{a_\alpha}(m'_{a_\alpha} - m_{a_\alpha}) + F_{b_\alpha}(m'_{b_\alpha} - m_{b_\alpha}) + \cdots + F'_{k_\alpha}(m'_{k_\alpha} - m_{k_\alpha}) \\ &+ \cdots \\ &+ F_{a_\phi}(m'_{a_\phi} - m_{a_\phi}) + F_{b_\phi}(m'_{b_\phi} - m_{b_\phi}) + \cdots \\ &+ F'_{k_\phi}(m'_{k_\phi} - m_{k_\phi}) = 0, \end{aligned} \tag{32}$$

and also

$$\begin{aligned} &F'_{a_\alpha}(m'_{a_\alpha} - m_{a_\alpha}) + F'_{b_\alpha}(m'_{b_\alpha} - m_{b_\alpha}) + \cdots + F'_{k_\alpha}(m'_{k_\alpha} - m_{k_\alpha}) \\ &+ \cdots \\ &+ F'_{a_\phi}(m'_{a_\phi} - m_{a_\phi}) + F'_{b_\phi}(m'_{b_\phi} - m_{b_\phi}) + \cdots \\ &+ F'_{k_\phi}(m'_{k_\phi} - m_{k_\phi}) = 0. \end{aligned} \tag{32a}$$

Let x be a quantity continuously variable from 0 to 1, and put

$$\left.\begin{aligned} \mu_{a_\alpha}(x) &= m_{a_\alpha} + (m'_{a_\alpha} - m_{a_\alpha})x, \\ \mu_{b_\alpha}(x) &= m_{b_\alpha} + (m'_{b_\alpha} - m_{b_\alpha})x, \\ &\ldots \\ \mu_{k_\alpha}(x) &= m_{k_\alpha} + (m'_{k_\alpha} - m_{k_\alpha})x, \\ &\ldots \\ \mu_{k_\phi}(x) &= m_{k_\phi} + (m'_{k_\phi} - m_{k_\phi})x. \end{aligned}\right\} \tag{33}$$

When x varies from 0 to 1, $\mu_{a_\alpha}(x)$ varies continuously and in a unique sense from m_{a_α} to m'_{a_α}, thus representing for each value of x an acceptable value of the mass m_{a_α}. Consider the function

$$\begin{aligned}\Psi(x) = {} & (m'_{a_\alpha} - m_{a_\alpha})\, \Phi_{a_\alpha}(x) + (m'_{b_\alpha} - m_{b_\alpha})\, \Phi_{b_\alpha}(x) + \cdots \\ & + (m'_{k_\alpha} - m_{k_\alpha})\, \Phi_{k_\alpha}(x) \\ & + \cdots \\ & + (m'_{a_\phi} - m_{a_\phi})\, \Phi_{a_\phi}(x) + (m'_{b_\phi} - m_{b_\phi})\, \Phi_{b_\phi}(x) + \cdots \\ & + (m'_{k_\phi} - m_{k_\phi})\, \Phi_{k_\phi}(x),\end{aligned} \tag{34}$$

where $\Phi_{a_\alpha}(x)$ denotes Φ_{a_α} when

$$\mu_{a_\alpha},\ \mu_{b_\alpha},\ \ldots,\ \mu_{k_\alpha}$$

are replaced in the latter by the functions

$$\mu_{a_\alpha}(x),\ \mu_{b_\alpha}(x),\ \ldots,\ \mu_{k_\alpha}(x)$$

defined by equations (33). For $x=0$, the function $\Psi(x)$ reduces to the first member of (32); for $x=1$, it reduces to the first member of (32*a*); hence

$$\Psi(0)=0, \quad \Psi(1)=0.$$

It follows therefore, because of the theorem of Rolle, that there exists at least one value θ, lying between 0 and 1, such that

$$\frac{d\Psi(\theta)}{d\theta}=0. \tag{35}$$

Forming $d\Psi(x)/dx$, from (33) and (34), we find

$$\begin{aligned}\frac{d\Psi(x)}{dx} = {} & \frac{\partial\Phi_{a_\alpha}}{\partial\mu_{a_\alpha}}(m'_{a_\alpha} - m_{a_\alpha})^2 + \frac{\partial\Phi_{b_\alpha}}{\partial\mu_{b_\alpha}}(m'_{b_\alpha} - m_{b_\alpha})^2 + \cdots \\ & + \frac{\partial\Phi_{k_\alpha}}{\partial\mu_{k_\alpha}}(m'_{k_\alpha} - m_{k_\alpha})^2 \\ & + \sum_{ij}\left(\frac{\partial\Phi_{i_\alpha}}{\partial\mu_{j_\alpha}} + \frac{\partial\Phi_{j_\alpha}}{\partial\mu_{i_\alpha}}\right)(m'_{i_\alpha} - m_{i_\alpha})\,(m'_{j_\alpha} - m_{j_\alpha}) \\ & + \text{etc.},\end{aligned}$$

in which μ_{a_α} and Φ_{a_α} are written for $\mu_{a_\alpha}(x)$ and $\Phi_{a_\alpha}(x)$; and $\sum_{ij}$ denotes a summation over all the combinations, taken without repetition, of the indices, a_α, b_α, ..., k_α taken two at a time; and '+ etc.' denotes a sum of terms, similar to the first and relating to the phase β, ..., ϕ. From (35) it follows that

$$\begin{aligned}&\frac{\partial\Phi_{a_\alpha}(\theta)}{\partial\mu_{a_\alpha}(\theta)}(m'_{a_\alpha}-m_{a_\alpha})^2+\frac{\partial\Phi_{b_\alpha}(\theta)}{\partial\mu_{b_\alpha}(\theta)}(m'_{b_\alpha}-m_{b_\alpha})^2+\dots\\&\quad+\frac{\partial\Phi_{k_\alpha}(\theta)}{\partial\mu_{k_\alpha}(\theta)}(m'_{k_\alpha}-m_{k_\alpha})^2\\&\quad+\sum_{ij}\left[\frac{\partial\Phi_{i_\alpha}(\theta)}{\partial\mu_{j_\alpha}(\theta)}+\frac{\partial\Phi_{j_\alpha}(\theta)}{\partial\mu_{i_\alpha}(\theta)}\right](m'_{i_\alpha}-m_{i_\alpha})(m'_{j_\alpha}-m_{j_\alpha})\\&\quad+\text{etc.}\qquad\qquad=0.\end{aligned}\tag{36}$$

From (7) and (8) of the Preliminary Chapter it appears that the sum of terms that, in the first member of equation (36), relates to any one of the phases can only be zero or positive; consequently, for equation (36) to hold, it is necessary and sufficient that each one of these sums of terms be equal to zero. From equation (6) of the Preliminary Chapter the equations so reached are seen to be equivalent to

$$\left.\begin{aligned}&\frac{m'_{a_\alpha}-m_{a_\alpha}}{\mu_{a_\alpha}(\theta)}=\frac{m'_{b_\alpha}-m_{b_\alpha}}{\mu_{b_\alpha}(\theta)}=\dots=\frac{m'_{k_\alpha}-m_{k_\alpha}}{\mu_{k_\alpha}(\theta)},\\&\dots\\&\frac{m'_{a_\phi}-m_{a_\phi}}{\mu_{a_\phi}(\theta)}=\frac{m'_{b_\phi}-m_{b_\phi}}{\mu_{b_\phi}(\theta)}=\dots=\frac{m'_{k_\phi}-m_{k_\phi}}{\mu_{k_\phi}(\theta)}.\end{aligned}\right\}\tag{37}$$

From equations (33) and (37) follow

$$\begin{aligned}&\frac{m'_{a_\alpha}}{m_{a_\alpha}}=\frac{m'_{b_\alpha}}{m_{b_\alpha}}=\dots=\frac{m'_{k_\alpha}}{m_{k_\alpha}},\\&\dots\\&\frac{m'_{a_\phi}}{m_{a_\phi}}=\frac{m'_{b_\phi}}{m_{b_\phi}}=\dots=\frac{m'_{k_\phi}}{m_{k_\phi}},\end{aligned}$$

whereby the theorem in question is proved.

This theorem leads directly to another—

In order that a system, whose temperature, pressure, the masses of its independently variable components, and the number and nature of its phases are known, can assume two different states of equilibrium, it is necessary and sufficient that each of these states be indifferent.

5. *Stability of the Equilibrium of a System under Constant Pressure.* — After having examined the determination of the state of equilibrium of a system at a constant temperature and under a constant pressure, we will now turn to the study of the conditions under which this equilibrium is stable. It will be stable if it corresponds to a minimum of the function H, in which Π and T are regarded as constants; and as the equation (13), the condition of equilibrium of the system, is found by putting

$$\delta H = 0$$

for all virtual variations that leave Π and T unchanged, we shall be assured that the equilibrium is stable if we have

$$\delta^2 H > 0$$

for these same variations.

The variables

$$m_{a_\alpha},\ m_{b_\alpha},\ \ldots,\ m_{k_\alpha},\ \ldots,\ m_{k_\phi}$$

are not independent; they are subject to the conditions (1), in which $M_{1\alpha}$, $M_{2\alpha}$, …, $M_{c\alpha}$, …, $M_{c\phi}$, are regarded as replaced by their values (3); but because the relations so obtained are linear in

$$m_{a_\alpha},\ m_{b_\alpha},\ \ldots,\ m_{k_\alpha},\ \ldots,\ m_{k_\phi}$$

we can put

$$\delta^2 m_{a_\alpha} = 0,\ \delta^2 m_{b_\alpha} = 0,\ \ldots,\ \delta^2 m_{k_\alpha} = 0,$$

$$\ldots$$

$$\delta^2 m_{a_\phi} = 0,\ \delta^2 m_{b_\phi} = 0,\ \ldots,\ \delta^2 m_{k_\phi} = 0.$$

From this follows, because of equations (10) and (12),

$$2\delta^2 H = \frac{\partial F_{a_\alpha}}{\partial m_{a_\alpha}}(\delta m_{a_\alpha})^2 + \frac{\partial F_{b_\alpha}}{\partial m_{b_\alpha}}(\delta m_{b_\alpha})^2 + \cdots + \frac{\partial F_{k_\alpha}}{\partial m_{k_\alpha}}(\delta m_{k_\alpha})^2$$

$$+ \sum_{ij}\left(\frac{\partial F_{i_\alpha}}{\partial m_{j_\alpha}} + \frac{\partial F_{j_\alpha}}{\partial m_{i_\alpha}}\right)\delta m_{i_\alpha}\delta m_{j_\alpha}$$

$$+ \text{etc.,} \tag{38}$$

the symbols $\sum\limits_{ij}$ and '+ etc.' retaining their signification in equation (36). But we know [Preliminary Chapter, (6), (7), and (8)] that

$$\frac{\partial F_{a_\alpha}}{\partial m_{a_\alpha}}(\delta m_{a_\alpha})^2 + \frac{\partial F_{b_\alpha}}{\partial m_{b_\alpha}}(\delta m_{b_\alpha})^2 + \cdots + \frac{\partial F_{k_\alpha}}{\partial m_{k_\alpha}}(\delta m_{k_\alpha})^2$$

$$+ \sum_{ij}\left(\frac{\partial F_{i_\alpha}}{\partial m_{j_\alpha}} + \frac{\partial F_{j_\alpha}}{\partial m_{i_\alpha}}\right)\delta m_{j_\alpha}\delta m_{i_\alpha} > 0, \tag{39}$$

at least when

$$\frac{\delta m_{a_\alpha}}{m_{a_\alpha}} = \frac{\delta m_{b_\alpha}}{m_{b_\alpha}} = \cdots = \frac{\delta m_{k_\alpha}}{m_{k_\alpha}},$$

a case in which the sign of inequality in (39) must be replaced by the sign of equality. Equation (38) shows us then that

$$\delta^2 H > 0, \tag{40}$$

at least when

$$\left.\begin{array}{l} \dfrac{\delta m_{a_\alpha}}{m_{a_\alpha}} = \dfrac{\delta m_{b_\alpha}}{m_{b_\alpha}} = \cdots = \dfrac{\delta m_{k_\alpha}}{m_{k_\alpha}}, \\ \cdots \\ \dfrac{\delta m_{a_\phi}}{m_{a_\phi}} = \dfrac{\delta m_{b_\phi}}{m_{b_\phi}} = \cdots = \dfrac{\delta m_{k_\phi}}{m_{k_\phi}}, \end{array}\right\} \tag{41}$$

a case in which the inequality (40) must be replaced by the equation

$$\delta^2 H = 0. \tag{42}$$

Now, for a set of values of

$$\delta m_{a_\alpha}, \delta m_{b_\alpha}, \ldots, \delta m_{k_\alpha}, \ldots, \delta m_{k_\phi}$$

to exist, satisfying equations (41), which are equivalent to equations (8), it is necessary and sufficient that the system be in an indifferent state; whence the theorem:—

The state of equilibrium of a heterogeneous system, at constant temperature and under a constant pressure, is always a stable state; at least when it is not at the same time an indifferent state.

Even when the state is indifferent, the inequality (40) still holds for all virtual changes other than those that satisfy the equations (40), that is to say, for all virtual changes other than those that leave unchanged the composition of each phase. So:

Even when the state of equilibrium of a system is indifferent, it is surely stable; provided that those changes that do not affect the composition of the several phases are excluded.

These considerations fail to apply when the state of equilibrium is indifferent, an infinitesimal change then leaving unaltered the composition of each phase; but we have seen, at the close of section 2, that a system in an indifferent state is subject to a *finite* change that leaves unaltered the composition of each phase, and that, consequently, cannot disturb an initial state of equilibrium. So we may say:

When the state of equilibrium of a system, at constant temperature and under constant pressure, is indifferent, it is stable for changes that vary the composition of certain phases, and it is indifferent for those that vary the composition of no phase.

CHAPTER III

GENERAL PRINCIPLES OF THE CHEMICAL STATICS OF HETEROGENEOUS SYSTEMS AT CONSTANT VOLUME

1. *Conditions of Equilibrium of a Heterogeneous System at Constant Volume: the Phase Rule.*—We shall preserve here the definitions and notation of the preceding chapter. Let V denote

the total volume of the system, and $V_\alpha, V_\beta, \ldots, V_\phi$ the volumes of its ϕ phases. We have

$$V_\alpha + V_\beta + \cdots + V_\phi = V. \qquad (1)$$

A virtual change leaving invariable the total volume must be subject to the condition

$$\delta V_\alpha + \delta V_\beta + \cdots + \delta V_\phi = 0. \qquad (2)$$

The inner thermodynamic potential $\mathfrak{F}$ of the system will have the form

$$\mathfrak{F} = \mathfrak{F}_\alpha + \mathfrak{F}_\beta + \cdots + \mathfrak{F}_\phi, \qquad (3)$$

where $\mathfrak{F}_\alpha, \mathfrak{F}_\beta, \ldots, \mathfrak{F}_\phi$ are the corresponding potentials of the individual phases $\alpha, \beta, \ldots, \phi$.

The conditions of equilibrium of the system, at constant volume, are expressed by writing

$$\delta\mathfrak{F} = 0 \qquad (4)$$

for all virtual changes at constant temperature and volume, or, indeed, because of (3), by

$$\begin{aligned}&\frac{\partial\mathfrak{F}_\alpha}{\partial V_\alpha}\delta V_\alpha + \frac{\partial\mathfrak{F}_\alpha}{\partial m_{a_\alpha}}\delta m_{a_\alpha} + \frac{\partial\mathfrak{F}_\alpha}{\partial m_{b_\alpha}}\delta m_{b_\alpha} + \cdots + \frac{\partial\mathfrak{F}_\alpha}{\partial m_{k_\alpha}}\delta m_{k_\alpha}\\ &+ \cdots\\ &+ \frac{\partial\mathfrak{F}_\phi}{\partial V_\phi}\delta V_\phi + \frac{\partial\mathfrak{F}_\phi}{\partial m_{a_\phi}}\delta m_{a_\phi} + \frac{\partial\mathfrak{F}_\phi}{\partial m_{b_\phi}}\delta m_{b_\phi} + \cdots + \frac{\partial\mathfrak{F}_\phi}{\partial m_{k_\phi}}\delta m_{k_\phi} = 0 \qquad (5)\end{aligned}$$

for every set of values of

$$\delta m_{a_\alpha},\ \delta m_{b_\alpha},\ \ldots,\ \delta m_{k_\alpha},\ \ldots,\ \delta m_{k_\phi},$$
$$\delta V_\alpha, \delta V_\beta,\ \ldots,\ \delta V_\phi$$

that satisfies equations (1*a*) and (3*a*) of the preceding chapter, and equations (2) of the present chapter. This condition separates at once into several others: in the first place we have the $\phi - 1$ equations

$$\frac{\partial\mathfrak{F}_\alpha}{\partial V_\alpha} = \frac{\partial\mathfrak{F}_\beta}{\partial V_\beta} = \cdots = \frac{\partial\mathfrak{F}_\phi}{\partial V_\phi}; \qquad (6)$$

and thereupon the equation

$$\begin{aligned}
&\frac{\partial \mathfrak{F}_\alpha}{\partial m_{a_\alpha}}\delta m_{a_\alpha}+\frac{\partial \mathfrak{F}_\alpha}{\partial m_{b_\alpha}}\delta m_{b_\alpha}+\cdots+\frac{\partial \mathfrak{F}_\alpha}{\partial m_{k_\alpha}}\delta m_{k_\alpha}\\
&+\cdots\\
&+\frac{\partial \mathfrak{F}_\phi}{\partial m_{a_\phi}}\delta m_{a_\phi}+\frac{\partial \mathfrak{F}_\phi}{\partial m_{b_\phi}}\delta m_{b_\phi}+\cdots+\frac{\partial \mathfrak{F}_\phi}{\partial m_{k_\phi}}\delta m_{k_\phi}=0 \qquad (7)
\end{aligned}$$

for every set of values of

$$\delta m_{a_\alpha},\ \delta m_{\ \alpha},\ \ldots,\ \delta m_{k_\alpha},\ \ldots,\ \delta m_{k_\phi}$$

that satisfies equations (1*a*) and (3*a*) of the preceding chapter. By a reasoning analogous to that yielding the equations (15) of the preceding chapter, it can be proved that the condition (7) is equivalent to

$$\theta = k_\alpha + k_\beta + \cdots + k_\phi - c \qquad (8)$$

linear and homogeneous relations, with purely numerical constant coefficients, among the functions

$$\frac{\partial \mathfrak{F}_\alpha}{\partial m_{a_\alpha}},\ \frac{\partial \mathfrak{F}_\alpha}{\partial m_{b_\alpha}},\ \ldots,\ \frac{\partial \mathfrak{F}_\alpha}{\partial m_{k_\alpha}},\ \ldots,\ \frac{\partial \mathfrak{F}_\phi}{\partial m_{k_\phi}};$$

let these relations be denoted by

$$\left.\begin{aligned}
&g_1\left(\frac{\partial \mathfrak{F}_\alpha}{\partial m_{a_\alpha}},\ \frac{\partial \mathfrak{F}_\alpha}{\partial m_{b_\alpha}},\ \ldots,\ \frac{\partial \mathfrak{F}_\alpha}{\partial m_{k_\alpha}},\ \ldots,\ \frac{\partial \mathfrak{F}_\phi}{\partial m_{k_\phi}}\right)=0,\\
&g_2\left(\frac{\partial \mathfrak{F}_\alpha}{\partial m_{a_\alpha}},\ \frac{\partial \mathfrak{F}_\alpha}{\partial m_{b_\alpha}},\ \ldots,\ \frac{\partial \mathfrak{F}_\alpha}{\partial m_{k_\alpha}},\ \ldots,\ \frac{\partial \mathfrak{F}_\phi}{\partial m_{k_\phi}}\right)=0,\\
&\cdots\\
&g_\theta\left(\frac{\partial \mathfrak{F}_\alpha}{\partial m_{a_\alpha}},\ \frac{\partial \mathfrak{F}_\alpha}{\partial m_{b_\alpha}},\ \ldots,\ \frac{\partial \mathfrak{F}_\alpha}{\partial m_{k_\alpha}},\ \ldots,\ \frac{\partial \mathfrak{F}_\phi}{\partial m_{k_\phi}}\right)=0.
\end{aligned}\right\} \qquad (9)$$

The $\phi - 1$ equations (6), and the θ equations (9) are *the conditions of equilibrium of the system.*

To discuss the determination of this equilibrium, we choose as auxiliary variables the quantities

$$\Upsilon_{a_\alpha},\ \Upsilon_{b_\alpha},\ \ldots,\ \Upsilon_{k_\alpha},\ \ldots,\ \Upsilon_{k_\phi},$$

defined by equations (16) of the preceding chapter, and also the specific volumes

$$u_\alpha,\ u_\beta,\ \ldots,\ u_\phi$$

of the different phases, specific volumes that are defined by the equations

$$\left.\begin{aligned} \mathfrak{M}_\alpha u_\alpha &= V_\alpha, \\ \mathfrak{M}_\beta u_\beta &= V_\beta, \\ &\dots \\ \mathfrak{M}_\phi u_\phi &= V_\phi. \end{aligned}\right\} \tag{10}$$

The function $\mathfrak{F}_\alpha$ is obviously a homogeneous function of the first degree of the variables V_α, m_{a_α}, m_{b_α}, ..., m_{k_α}. Its partial derivatives

$$\frac{\partial \mathfrak{F}_\alpha}{\partial V_\alpha}, \frac{\partial \mathfrak{F}_\alpha}{\partial m_{a_\alpha}}, \frac{\partial \mathfrak{F}_\alpha}{\partial m_{b_\alpha}}, \dots, \frac{\partial \mathfrak{F}_\alpha}{\partial m_{k_\alpha}}$$

are therefore homogeneous functions of the zero degree of the variables

$$V_\alpha, m_{a_\alpha}, m_{b_\alpha}, \dots, m_{k_\alpha};$$

in other words, they are functions of the temperature T, and the variables

$$u_\alpha, Y_{a_\alpha}, Y_{b_\alpha}, \dots, Y_{k_\alpha}.$$

Let

$$\frac{\partial \mathfrak{F}_\alpha}{\partial V_\alpha} = \Phi_\alpha(u_\alpha, Y_{a_\alpha}, Y_{b_\alpha}, \dots, Y_{k_\alpha}, T), \tag{11}$$

$$\left.\begin{aligned} \frac{\partial \mathfrak{F}_\alpha}{\partial m_{a_\alpha}} &= \phi_{a_\alpha}(u_\alpha, Y_{a_\alpha}, Y_{b_\alpha}, \dots, Y_{k_\alpha}, T), \\ \frac{\partial \mathfrak{F}_\alpha}{\partial m_{b_\alpha}} &= \phi_{b_\alpha}(u_\alpha, Y_{a_\alpha}, Y_{b_\alpha}, \dots, Y_{k_\alpha}, T), \\ &\dots \\ \frac{\partial \mathfrak{F}_\alpha}{\partial m_{k_\alpha}} &= \phi_{k_\alpha}(u_\alpha, Y_{a_\alpha}, Y_{b_\alpha}, \dots, Y_{k_\alpha}, T), \end{aligned}\right\} \tag{12}$$

analogous notation being adopted for the remaining phases β, ..., ϕ.

Because of equations (11), the $\phi - 1$ equations (6) become

$$\left.\begin{aligned}&\Phi_\alpha(u_\alpha,\ \Upsilon_{a_\alpha},\ \Upsilon_{b_\alpha},\ \ldots,\ \Upsilon_{k_\alpha},\ \mathrm{T})\\ =\ &\Phi_\beta(u_\beta,\ \Upsilon_{b_\alpha},\ \Upsilon_{b_\beta},\ \ldots,\ \Upsilon_{k_\beta},\ \mathrm{T})\\ =\ &\ldots\\ =\ &\Phi_\phi(u_\phi,\ \Upsilon_{a_\phi},\ \Upsilon_{b_\phi},\ \ldots,\ \Upsilon_{k_\phi},\ \mathrm{T});\end{aligned}\right\}\tag{13}$$

and the equations (12) transform the θ equations (9) to expressions of the form

$$\left.\begin{aligned}&\Psi_1(u_\alpha,\ u_\beta,\ \ldots,\ u_\phi,\ \Upsilon_{a_\alpha},\ \Upsilon_{b_\alpha},\ \ldots,\ \Upsilon_{k_\alpha},\ \ldots,\ \Upsilon_{k_\phi},\ \mathrm{T})=0,\\ &\Psi_2(u_\alpha,\ u_\beta,\ \ldots,\ u_\phi,\ \Upsilon_{a_\alpha},\ \Upsilon_{b_\alpha},\ \ldots,\ \Upsilon_{k_\alpha},\ \ldots,\ \Upsilon_{k_\phi},\ \mathrm{T})=0,\\ &\ldots\\ &\Psi_\theta(u_\alpha,\ u_\beta,\ \ldots,\ u_\phi,\ \Upsilon_{a_\alpha},\ \Upsilon_{b_\alpha},\ \ldots,\ \Upsilon_{k_\alpha},\ \ldots,\ \Upsilon_{k_\phi},\ \mathrm{T})=0.\end{aligned}\right\}\tag{14}$$

Adding to these the ϕ equations

$$\left.\begin{aligned}&\Upsilon_{a_\alpha}+\Upsilon_{b_\alpha}+\cdots+\Upsilon_{k_\alpha}=1,\\ &\ldots\\ &\Upsilon_{a_\phi}+\Upsilon_{b_\phi}+\cdots+\Upsilon_{k_\phi}=1,\end{aligned}\right\}\tag{15}$$

which are the equations (17) of the preceding chapter, we find altogether $\phi-1+\theta+\phi$ or, because of equation (8),

$$2\phi+k_\alpha+k_\beta+\cdots+k_\phi-c-1\tag{16}$$

equations (13), (14), and (15) among the

$$\phi+k_\alpha+k_\beta+\cdots+k_\phi+1\tag{17}$$

variables

$$\left.\begin{gathered}u_\alpha,\ u_\beta,\ \ldots,\ u_\phi,\\ \Upsilon_{a_\alpha},\ \Upsilon_{a_\phi},\ \ldots,\ \Upsilon_{k_\alpha},\ \ldots,\ \Upsilon_{k_\phi},\\ \mathrm{T}.\end{gathered}\right\}\tag{18}$$

These equations are independent of the quantities

$$\left.\begin{aligned}&\mathfrak{M}_\alpha,\ \mathfrak{M}_\beta,\ \ldots,\ \mathfrak{M}_\phi,\\ &\mathrm{V}_\alpha,\ \mathrm{V}_\beta,\ \ldots,\ \mathrm{V}_\phi,\\ &\mathfrak{M}_1,\ \mathfrak{M}_2,\ \ldots,\ \mathfrak{M}_c,\\ &\mathrm{V}.\end{aligned}\right\}\tag{19}$$

Among these quantities obtain the c relations (25) of the preceding chapter (where the quantities R have the values defined by equations (23) of the same chapter), as also the $\phi + 1$ relations (1) and (10) of the present chapter, or, all told,

$$c + \phi + 1 \tag{20}$$

relations.

The procedure to be adopted in the solution of our problem depends upon the *variance* of the system, that is to say upon the excess of the number (17) over the number (16); the value of this excess is

$$v = c + 2 - \phi. \tag{21}$$

Comparing this equation (21) with equation (26) of the preceding chapter we find that *the variance of a system composed of a given number* c *of independently variable components, distributed in a given number ϕ of phases, is the same whether the system be maintained under constant pressure or at constant volume.*

But an essential difference between systems under constant pressure and those at constant volume appears on comparing the number of the quantities (19) with the number (20) of the relation holding among them. If the quantities

$$V,\ \mathfrak{M}_1,\ \mathfrak{M}_2,\ \ldots,\ \mathfrak{M}_c$$

are supposed given, the 2ϕ unknown quantities

$$\left.\begin{array}{l} \mathfrak{M}_\alpha,\ \mathfrak{M}_\beta,\ \ldots,\ \mathfrak{M}_\phi, \\ V_\alpha,\ V_\beta,\ \ldots,\ V_\phi \end{array}\right\} \tag{22}$$

are involved in

$$c + \phi + 1 \tag{20}$$

equations. The number of these equations is then greater than the number of the unknown quantities (22) when c is greater than $\phi - 1$, that is to say when the system is divariant or polyvariant; in the case of a system under constant pressure an analogous excess appears only when c is greater than ϕ, that is to say when the system is polyvariant. For *systems of negative variance*, the number (17) of the variables (18) is less than the number (16) of the equations in which they occur; so these equations cannot in general be satisfied: *a system with negative variance cannot, in general, subsist in equilibrium.* For *invariant systems*, those characterized by the equation $v = 0$, the number (17) is equal to the number (16); the variables (18) are then in general determinate, even though the quantities

$$V, \mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$$

be not known.—

An invariant system at constant volume can be in equilibrium only at a definite temperature, which depends neither upon the volume of the system nor the masses of the independently variable components; the composition and density of each phase are likewise fixed independently of the volume and of these independent masses.

The unknown quantities (18) once determined, and the quantities $V, \mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$, having assigned values, to determine the 2ϕ unknown quantities (22) we shall have a number (20) of equations which, in the present case, becomes $2\phi - 1$. The unknown quantities (22) will, therefore, not be entirely determinate; one of them can be chosen arbitrarily.—

When the volume of a system and the masses of its independently variable components are given, the volume and the mass of each phase are not wholly determinate; one of these latter quantities can be chosen arbitrarily.

We will now consider *univariant systems*, for which $v = 1$. The number (17) exceeds (16) by unity, so one of the variables (18), as for example the temperature, can be chosen arbitrarily; the others will then be determined by the equations in which appear the quantities

$$V, \mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c.$$

A univariant system at constant volume can be, in general, in equilibrium at any temperature; at an assigned temperature the density and the composition of each phase are determinate independently of the volume of the system and the masses of its independently variable components.

The unknown quantities (18) once determined, and the values of V, $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$ being given, to determine the 2ϕ unknown quantities (22) we shall have a number (20) of equations that, in the present case, becomes 2ϕ. The unknown quantities (22) are, therefore, in general, determinate.—

The mass and the volume of each phase of a univariant system are, in general, determinate when the temperature, the masses of the independently variable components of the system, and the total volume are known.

Let us consider, finally, a *bivariant or polyvariant system*, and put

$$v = 1 + p, \tag{23}$$

where p denotes a positive integer. We shall then have, because of equation (21),

$$c = p + \phi - 1.$$

The 2ϕ unknown quantities (22) are related through

$$c + \phi + 1 \tag{20}$$

equations, that is to say, in the present case, by

$$2\phi + p$$

equations. The number of these equations is p greater than the number of the unknown quantities (22); and it must be expressed that p of these equations—which are equations (25) of the preceding chapter, and the equations (1) and (10) of the present chapter—are consequences of the 2ϕ others, when the former are considered as equations whose unknown quantities are the quantities (22).

If we observe that, because of equations (23) of the preceding chapter, the quantities $R_{1\alpha}, R_{2\alpha}, \ldots, R_{c\alpha}, \ldots, R_{c\phi}$ are functions of $\Upsilon_{a_\alpha}, \Upsilon_{b_\alpha}, \ldots, \Upsilon_{k_\alpha}, \ldots, \Upsilon_{k_\phi}$, we recognize easily that we obtain in this way, among the quantities

$$\left.\begin{array}{c} u_\alpha,\ u_\beta,\ \ldots,\ u_\phi, \\ \Upsilon_{a_\alpha},\ \Upsilon_{b_\alpha},\ \ldots,\ \Upsilon_{k_\alpha},\ \ldots,\ \Upsilon_{k_\phi}, \end{array}\right\} \tag{24}$$

and the assigned quantities

$$V,\ \mathfrak{M}_1,\ \mathfrak{M}_2,\ \ldots,\ \mathfrak{M}_c,$$

the p equations

$$\left.\begin{array}{l}\delta_1(u_\alpha, \ldots, u_\phi, Y_{a_\alpha}, \ldots, Y_{k_\phi}, V, \mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c) = 0,\\ \delta_2(u_\alpha, \ldots, u_\phi, Y_{a_\alpha}, \ldots, Y_{k_\phi}, V, \mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c) = 0,\\ \ldots\\ \delta_p(u_\alpha, \ldots, u_\phi, Y_{a_\alpha}, \ldots, Y_{k_\phi}, V, \mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c) = 0.\end{array}\right\} \qquad (25)$$

The

$$\phi + k_\alpha + k_\beta + \cdots + k_\phi$$

unknown quantities (24) are, therefore, related : *first*, in the

$$2\phi + k_\alpha + k_\beta + \cdots + k_\phi - c - 1 \qquad (16)$$

equations (13), (14), and (15), which depend further upon T; *second*, in the p equations (25), which depend further upon

$$V \ \mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c.$$

The number of these equations is

$$2\phi + k_\alpha + k_\beta + \cdots + k_\phi + p - c - 1,$$

or, because of equations (21) and (23),

$$\phi + k_\alpha + k_\beta + \cdots + k_\phi.$$

So this number is equal to the number of the unknown quantities (24), which are thus fixed by known values of the quantities

$$T, V, \mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c.$$

A bivariant or polyvariant system can be, in general, in equilibrium under arbitrarily assigned values of the temperature, the total volume, and the masses of the independently variable components; these values fix, in general, the density and the composition of each phase.

The equations (25) being satisfied, the $2\phi + p$ equations, obtained by combining the equations (1) and (10) of the present chapter with the equations (25) of the preceding chapter, reduce to 2ϕ equations, which determine the 2ϕ unknown quantities

$$\mathfrak{M}_\alpha, \mathfrak{M}_\beta, \ldots, \mathfrak{M}_\phi,$$

$$V_\alpha, V_\beta, \ldots, V_\phi.$$

The temperature, the volume, and the masses of the independently variable components of the system determine the mass and the volume of each phase.

2. *The Composition and Densities at Equilibrium are uniquely Determined.*—We can now demonstrate the following theorem, correlative to the theorem of Chapter II, Section 4.—

If any chemical system, with determinate values of the temperature T, *the volume* V, *and the masses* $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_r$ *of its initial components, can assume two different states of equilibrium, whereby in each case the system is made up of the same number of phases of the same nature, then each of these phases will have the same composition and the same specific volume in both states.*

Let

$$V_a,\ m_{a_a},\ m_{b_a},\ \ldots,\ m_{k_a} \tag{26}$$

be the volume and the independent masses of the phase a in the first state, and

$$V'_a,\ m'_{a_a},\ m'_{b_a},\ \ldots,\ m'_{k_a} \tag{26a}$$

the values of these quantities for the corresponding phase a' in the second state. When we assign to the variables $V_a, m_{a_a}, \ldots, m_{k_a}$ the values (26), the functions $\Phi_a, \phi_{a_a}, \ldots, \phi_{k_a}$, defined by the equations (11) and (12), shall be denoted by $\Phi_a, \phi_{a_a}, \ldots, \phi_{k_a}$; when the above values are replaced by the values (26*a*), these functions shall be denoted by $\Phi'_a, \phi'_{a_a}, \ldots, \phi'_{k_a}$; when, finally, the variables are assigned the arbitrary values

$$U_a,\ \mu_{a_a},\ \ldots,\ \mu_{k_a},$$

the functions shall be represented by $F_a, f_{a_a}, \ldots, f_{k_a}$. From equation (6) we now see that, for (26) to define a state of equilibrium of the system, it is necessary and sufficient that

$$\begin{aligned}&\Phi_a\delta V_a + \phi_{a_a}\delta m_{a_a} + \cdots + \phi_{k_a}\delta m_{k_a}\\ &+ \cdots\\ &+ \Phi_\phi\delta V_\phi + \phi_{a_\phi}\delta m_{a_\phi} + \cdots + \phi_{k_\phi}\delta m_{k_\phi} \doteq 0\end{aligned} \tag{27}$$

for every set of values of

$$\delta m_{a_a},\ \ldots,\ \delta m_{k_a},\ \ldots,\ \delta m_{k_\phi}$$
$$\delta V_a,\ \ldots,\ \delta V_\phi$$

that satisfies equations (1*a*) and (3*a*) of the preceding chapter and equation (2) of the present chapter, for the given set of values of $V, \mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_r$. For (26*a*) to define a state of equilibrium of the system, it is necessary and sufficient that

$$\begin{aligned}&\Phi'_\alpha \delta V_\alpha + \phi'_{a_\alpha} \delta m_{a_\alpha} + \cdots + \phi'_{k_\alpha} \delta m_{k_\alpha} \\ &+ \cdots \\ &+ \Phi'_\phi \delta V_\phi + \phi'_{a_\phi} \delta m_{a_\phi} + \cdots + \phi'_{k_\phi} \delta m_{k_\phi} = 0 \qquad (27a)\end{aligned}$$

for the same sets of values of the variations of the masses and the volumes. Taking account of equations (1) and (3) of the preceding chapter, and equation (1) of the present chapter, it is seen that we can put

$$\begin{aligned}\delta V_\alpha &= \epsilon(V'_\alpha - V_\alpha), \\ &\cdots \\ \delta V_\phi &= \epsilon(V'_\phi - V_\phi), \\ \delta m_{a_\alpha} &= \epsilon(m'_{a_\alpha} - m_{a_\alpha}), \\ &\cdots \\ \delta m_{k_\phi} &= \epsilon(m'_{k_\phi} - m_{k_\phi}),\end{aligned}$$

ϵ being any infinitesimal.

Equation (27) then requires

$$\begin{aligned}&\Phi_\alpha(V'_\alpha - V_\alpha) + \phi_{a_\alpha}(m'_{a_\alpha} - m_{a_\alpha}) + \cdots + \phi_{k_\alpha}(m'_{k_\alpha} - m_{k_\alpha}) \\ &+ \cdots \\ &+ \Phi_\phi(V'_\phi - V_\phi) + \phi_{a_\phi}(m'_{a_\phi} - m_{a_\phi}) + \cdots + \phi_{k_\phi}(m'_{k_\phi} - m_{k_\phi}) = 0, \qquad (28)\end{aligned}$$

while (27*a*) calls for

$$\begin{aligned}&\Phi'_\alpha(V'_\alpha - V_\alpha) + \phi'_{a_\alpha}(m'_{a_\alpha} - m_{a_\alpha}) + \cdots + \phi'_{k_\alpha}(m'_{k_\alpha} - m_{k_\alpha}) \\ &+ \cdots \qquad (28a) \\ &+ \Phi'_\phi(V'_\phi - V_\phi) + \phi'_{a_\phi}(m'_{a_\phi} - m_{a_\phi}) + \cdots + \phi'_{k_\phi}(m'_{k_\phi} - m_{k_\phi}) = 0.\end{aligned}$$

Let x be a quantity variable continuously from 0 to 1, put

$$\left.\begin{aligned}U_\alpha(x) &= V_\alpha + (V'_\alpha - V_\alpha)x, \\ &\cdots \\ U_\phi(x) &= V_\phi + (V'_\phi - V_\phi)x, \\ \mu_{a_\alpha}(x) &= m_{a_\alpha} + (m'_{a_\alpha} - m_{a_\alpha})x, \\ &\cdots \\ \mu_{k_\phi}(x) &= m_{k_\phi} + (m'_{k_\phi} - m_{k_\phi})x.\end{aligned}\right\} \qquad (29)$$

For all values of x, lying between 0 and 1, these equations define a system having the volume V, and formed from the independent masses $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$. We will now consider the function

$$\begin{aligned}\Psi(x) = {} & (V'_\alpha - V_\alpha)F_\alpha(x) + (m'_{a_\alpha} - m_{a_\alpha})f_{a_\alpha}(x) + \cdots \\ & + (m'_{k_\alpha} - m_{k_\alpha})f_{k_\alpha}(x) \\ & + \cdots \\ & + (V'_\phi - V_\phi)F_\phi(x) + (m'_{a_\phi} - m_{a_\phi})f_{a_\phi}(x) + \cdots \\ & + (m'_{k_\phi} - m_{k_\phi})f_{k_\phi}(x), \end{aligned} \tag{30}$$

where $F_\alpha(x), f_{a_\alpha}(x), \ldots, f_{k_\alpha}(x)$ denote the functions $F_\alpha, f_{a_\alpha}, \ldots, f_{k_\alpha}$ when $V_\alpha, m_{a_\alpha}, \ldots, m_{k_\alpha}$ are assigned the values (29).

For $x = 0$, the function $\Psi(x)$ reduces to the first member of (28); for $x = 1$, it reduces to the first member of (28*a*); hence

$$\Psi(0) = 0, \qquad \Psi(1) = 0.$$

It follows, therefore, because of the theorem of Rolle, that there exists at least one value θ, lying between 0 and 1, such that

$$\frac{d\Psi(\theta)}{d\theta} = 0. \tag{31}$$

Taking account of equations (11), (12), (29), and (30), it is easily seen that this equation (31) can be written

$$\begin{aligned} & \frac{\partial^2 \mathfrak{F}_\alpha(\theta)}{[\partial U_\alpha(\theta)]^2}(V'_\alpha - V_\alpha)^2 + 2\left[\frac{\partial^2 \mathfrak{F}_\alpha(\theta)}{\partial U_\alpha(\theta)\partial \mu_{a_\alpha}(\theta)}(m'_{a_\alpha} - m_{a_\alpha}) + \cdots \right. \\ & \left. + \frac{\partial^2 \mathfrak{F}_\alpha(\theta)}{\partial U_\alpha(\theta)\partial \mu_{k_\alpha}(\theta)}(m'_{k_\alpha} - m_{k_\alpha})\right](V'_\alpha - V_\alpha) \\ & + \frac{\partial^2 \mathfrak{F}_\alpha(\theta)}{[\partial \mu_{a_\alpha}(\theta)]^2}(m'_{a_\alpha} - m_{a_\alpha})^2 + \cdots + \frac{\partial^2 \mathfrak{F}_\alpha(\theta)}{[\partial \mu_{k_\alpha}(\theta)]^2}(m'_{k_\alpha} - m_{k_\alpha})^2 \\ & + 2\sum_{ij}\frac{\partial^2 \mathfrak{F}_\alpha(\theta)}{\partial \mu_{i_\alpha}(\theta)\partial \mu_{j_\alpha}(\theta)}(m'_{i_\alpha} - m_{i_\alpha})(m'_{j_\alpha} - m_{j_\alpha}) \\ & + \text{etc.} = 0. \end{aligned} \tag{32}$$

Herein $\mathfrak{F}_a(x)$ denotes the function $\mathfrak{F}_a$ when its variables V_a, m_{a_a}, …, m_{k_a} are replaced by the values $U_a(x)$, $\mu_{a_a}(x)$, …, $\mu_{k_a}(x)$ defined by equations (29). Suppose these new values to suffer the variations

$$\left.\begin{aligned} \delta V_a &= \epsilon(V'_a - V_a), \\ \delta m_{a_a} &= \epsilon(m'_{a_a} - m_{a_a}), \\ &\dots \\ \delta m_{k_a} &= \epsilon(m'_{k_a} - m_{k_a}); \end{aligned}\right\} \tag{33}$$

the pressure necessary to maintain the phase in equilibrium will suffer a variation

$$\delta \Pi_a = \epsilon \pi_a(x);$$

whence, and by reason of equation (18)of the Preliminary Chapter, the equation (32) can be written

$$\begin{aligned} &\frac{1}{\dfrac{\partial^2 \mathfrak{F}_a(\theta)}{[\partial U_a(\theta)]^2}} [\pi_a(\theta)]^2 \\ &+ \frac{\partial^2 H_a(\theta)}{[\partial \mu_{a_a}(\theta)]^2} (m'_{a_a} - m_{a_a})^2 + \dots + \frac{\partial^2 H_a(\theta)}{[\partial \mu_{k_a}(\theta)]^2} (m'_{k_a} - m_{k_a})^2 \\ &+ 2 \sum_{ij} \frac{\partial^2 H_a(\theta)}{\partial \mu_{i_a}(\theta) \partial \mu_{j_a}(\theta)} (m'_{i_a} - m_{i_a})(m'_{j_a} - m_{j_a}) \\ &+ \text{etc.} = 0. \end{aligned} \tag{34}$$

Because of (7), (8), and (16) of the Preliminary Chapter, this equation can hold only when : *first*, for each of the phases a, β, …, ϕ there obtains an equation of the form

$$\begin{aligned} &\frac{\partial^2 H_a(\theta)}{[\partial \mu_{a_a}(\theta)]^2} (m'_{a_a} - m_{a_a})^2 + \dots + \frac{\partial^2 H_a(\theta)}{[\partial \mu_{k_a}(\theta)]^2} (m'_{k_a} - m_{k_a})^2 \\ &+ 2 \sum_{ij} \frac{\partial^2 H_a(\theta)}{\partial \mu_{i_a}(\theta) \partial \mu_{j_a}(\theta)} (m'_{i_a} - m_{i_a})(m'_{j_a} - m_{j_a}) = 0; \end{aligned} \tag{35}$$

second, when

$$\pi_a(\theta) = 0, \quad \pi_\beta(\theta) = 0, \quad \dots, \quad \pi_\phi(\theta) = 0. \tag{36}$$

Because of equations (6) of the Preliminary Chapter, the equaitons (35) are equivalent to

$$\left.\begin{array}{l}
\dfrac{m'_{a_\alpha} - m_{a_\alpha}}{\mu_{a_\alpha}(\theta)} = \dfrac{m'_{b_\alpha} - m_{b_\alpha}}{\mu_{b_\alpha}(\theta)} = \dots = \dfrac{m'_{k_\alpha} - m_{k_\alpha}}{\mu_{a_\alpha}(\theta)}, \\
\dots \\
\dfrac{m'_{a_\phi} - m_{a_\phi}}{\mu_{a_\phi}(\theta)} = \dfrac{m'_{b_\phi} - m_{b_\phi}}{\mu_{b_\phi}(\theta)} = \dots = \dfrac{m'_{k_\phi} - m_{k_\phi}}{\mu_{k_\phi}(\theta)},
\end{array}\right\} \quad (37)$$

which are transformed by (29) into

$$\left.\begin{array}{l}
\dfrac{m'_{a_\alpha}}{m_{a_\alpha}} = \dfrac{m'_{b_\alpha}}{m_{b_\alpha}} = \dots = \dfrac{m'_{k_\alpha}}{m_{k_\alpha}}, \\
\dots \\
\dfrac{m'_{a_\phi}}{m_{a_\phi}} = \dfrac{m'_{b_\phi}}{m_{b_\phi}} = \dots = \dfrac{m'_{k_\phi}}{m_{k_\phi}}.
\end{array}\right\} \quad (38)$$

These equations express that each of the phases α, β, …, ϕ has the same composition in both states of equilibrium of the system.

According to equations (37), the variations (33) necessitate no variation of the composition of the phase α; that they produce no variation of the equilibrium-pressure (which is expressed by the first equation (36)), it is necessary and sufficient that they produce no variation of the specific volume of the phase α. Now this specific volume is subject to a variation

$$\delta u_\alpha = \frac{[\mu_{a_\alpha}(\theta) + \dots + \mu_{k_\alpha}(\theta)]\,\delta V^{\alpha} - U_\alpha(\theta)\,[\delta m_{a_\alpha} + \dots + \delta m_{k_\alpha}]}{[\mu_{a_\alpha}(\theta) + \dots + \mu_{k_\alpha}(\theta)]^2};$$

the first equation (36) is therefore equivalent to the equation

$$[\mu_{a_\alpha}(\theta) + \dots + \mu_{k_\alpha}(\theta)]\delta V_\alpha - U_\alpha(\theta)[\delta m_{a_\alpha} + \dots + \delta m_{k_\alpha}] = 0. \quad (39)$$

Putting

$$\mathfrak{M}_\alpha = m_{a_\alpha} + \dots + m_{k_\alpha},$$

$$\mathfrak{M}'_\alpha = m'_{a_\alpha} + \dots + m'_{k_\alpha}$$

we find easily, by means of equations (29) and (33), that equation (39) becomes

$$\frac{V_\alpha}{\mathfrak{M}_\alpha} = \frac{V'_\alpha}{\mathfrak{M}'_\alpha},$$

which equation expresses that the specific volume of the phase a is the same in both states of the system. This demonstrates the theorem in question.

3. *Different States at an Assigned Volume.*—A theorem, complementary to the above, answers the question whether the total masses $\mathfrak{M}_\alpha, \mathfrak{M}_\beta, \ldots, \mathfrak{M}_\phi$ and the total volumes $V_\alpha, V_\beta, \ldots, V_\phi$ of the different phases are determined by the temperature T, the volume V, and the independent masses $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$ of the whole system. This question leads immediately to the other,—if the independent masses $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$ of the system, and the composition and density of each of its phases are fixed, can it assume two different distributions *at the same volume* V? If it can, we shall say that the state of the system is 'indifferent at constant volume.'

Retaining the notation of Section 2 of the preceding chapter, which treats indifferent systems whose volumes remain arbitrary, we have to add to the conditions defining such a system the condition that the volume remains the same in both distributions. Denoting by $u_\alpha, u_\beta, \ldots, u_\phi$ the specific volumes of the different phases, which volumes remain the same in both distributions, the new condition is

$$u_\alpha(\mathfrak{M}'_\alpha - \mathfrak{M}_\alpha) + u_\beta(\mathfrak{M}'_\beta - \mathfrak{M}_\beta) + \cdots + u_\phi(\mathfrak{M}'_\phi - \mathfrak{M}_\phi) = 0,$$

which is transformed by equations (10) of the preceding chapter to

$$u_\alpha \mathfrak{M}_\alpha P_\alpha + u_\beta \mathfrak{M}_\beta P_\beta + \cdots + u_\phi \mathfrak{M}_\phi P_\phi = 0. \qquad (40)$$

So, for a state of the system to be indifferent at constant volume, it is necessary and sufficient that there exist ϕ quantities P_α, $P_\beta, \ldots, P_\phi$, which satisfy the c equations (9) of the present chapter, and the equation (40); or, in all, $c+1$ equations homogeneous in $P_\alpha, P_\beta, \ldots, P_\phi$. Whence:

When the number of phases of a system exceeds the number of the independently variable components by at least two, the system is, in general, in an indifferent state at constant volume; but it is not so if the number of phases be less than this.

Reasoning analogous to that of Section 2 of the preceding chapter leads at once to the following propositions:—

If the given masses $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_c$ of c independently variable components of a system can be distributed in ϕ phases in such wise that the state of the system will be indifferent at constant volume, it will be possible to distribute these phases in an infinity of other ways, whereby, at constant total volume of the system, the mass of each phase will indeed change, but its composition and specific volume will remain unchanged.

For it to be possible to subject a system to a virtual change that shall vary neither the total volume, nor the composition and density of such phase, it is necessary and sufficient that the state of the system be indifferent at constant volume.

4. *Stability of the Equilibrium of a System at Constant Volume.*—From considerations analogous to those developed in Section 5 of the preceding chapter we shall show that the stability of the equilibrium of a system maintained at constant temperature and volume is assured if

$$\delta^2\mathfrak{F} > 0 \tag{41}$$

for every virtual change of the system.

We note equation (3); we observe that the variables V_α, V_β, $\ldots$, V_ϕ are connected only by the linear and homogeneous relation (1), which allows us to take

$$\delta^2 V_\alpha = 0,\ \delta^2 V_\beta = 0,\ \ldots,\ \delta^2 V_\phi = 0;$$

and we note that, since the variables $m_{a_\alpha}, \ldots, m_{k_\alpha}, \ldots, m_{k_\phi}$ are also connected only by linear and homogeneous relations, we can take

$$\delta^2 m_{a_\alpha} = 0,\ \ldots,\ \delta^2 m_{k_\alpha} = 0,\ \ldots,\ \delta^2 m_{k_\phi} = 0;$$

whereby it appears that the equation (41) can be written

$$\begin{gathered}\frac{\partial^2\mathfrak{F}_\alpha}{\partial V^2_\alpha}(\delta V_\alpha)^2 + 2\left(\frac{\partial^2\mathfrak{F}_\alpha}{\partial V_\alpha \partial m_{a_\alpha}}\delta m_{a_\alpha} + \cdots + \frac{\partial^2\mathfrak{F}_\alpha}{\partial V_\alpha \partial m_{k_\alpha}}\delta m_{k_\alpha}\right)\delta V_\alpha \\ + \frac{\partial^2\mathfrak{F}_\alpha}{\partial m^2{a_\alpha}}(\delta m_{a_\alpha})^2 + \cdots + \frac{\partial^2\mathfrak{F}_\alpha}{\partial m^2{k_\alpha}}(\delta m_{k_\alpha})^2 + 2\sum_{ij}\frac{\partial^2\mathfrak{F}_\alpha}{\partial m_{i_\alpha}\partial m_{j_\alpha}}\delta m_{i_\alpha}\delta m_{j_\alpha} \\ + \text{etc.} > 0.\end{gathered} \tag{42}$$

Let $\delta\Pi_\alpha$ denote the increase of the exterior pressure, necessary to maintain the phase α, considered separately, in equilibrium after the virtual change considered. Comparing equations (15) and (17) of the Preliminary Chapter with the inequality (42), transforms this last into

$$\begin{aligned} &\frac{1}{\dfrac{\partial^2 \mathfrak{F}_\alpha}{\partial V^2_\alpha}} (\delta\Pi_\alpha)^2 + \frac{\partial^2 H_\alpha}{\partial m^2_{a_\alpha}} (\delta m_{a_\alpha})^2 + \dots + \frac{\partial^2 H_\alpha}{\partial m^2_{k_\alpha}} (\delta m_{k_\alpha})^2 \\ &+ 2 \sum_{ij} \frac{\partial^2 H_\alpha}{\partial m_{i_\alpha} \partial m_{j_\alpha}} \delta m_{i_\alpha} \delta m_{j_\alpha} \\ &+ \text{etc.} = 0. \end{aligned} \tag{43}$$

The expressions (6), (7), (8), and (18) of the Preliminary Chapter show that (43) is always satisfied when: *first*—

$$\left. \begin{aligned} &\frac{\delta m_{a_\alpha}}{m_{a_\alpha}} = \frac{\delta m_{b_\alpha}}{m_{b_\alpha}} = \dots = \frac{\delta m_{k_\alpha}}{m_{k_\alpha}}, \\ &\dots \\ &\frac{\delta m_{a_\phi}}{m_{a_\phi}} = \frac{\delta m_{b_\phi}}{m_{b_\phi}} = \dots = \frac{\delta m_{k_\phi}}{m_{k_\phi}}, \end{aligned} \right\} \tag{44}$$

and *second*—

$$\delta\Pi_\alpha = 0, \ \delta\Pi_\beta = 0, \ \dots, \ \delta\Pi_\phi = 0, \tag{45}$$

in which case the inequality (43) becomes an equation; the equations (44) signify that the virtual change in question does not affect the composition of any of the phases of the system.

This point reached, a reasoning analogous to that of Section 2 shows that the equations (45) are equivalent to the statement that the virtual change in question does not vary the specific volume of any of the phases of the system. We arrive thus at the theorem:—

If the state of equilibrium of a system at constant temperature and constant volume is not indifferent at constant volume, it is stable; if it is indifferent at constant volume, it remains stable, provided that the possibility of changes that do not affect the composition and the volume of each phase is excluded.

In this last case the foregoing analysis does not apply; but here the propositions of the preceding section show directly that the equilibrium is indifferent.

It follows, accordingly, from incontestable and purely physical postulates, that every true chemical equilibrium of a system maintained at constant temperature and pressure or at constant temperature and total volume is either stable or indifferent. Under these conditions no instable chemical equilibrium is possible.

Cabrespine, August 29, 1897.

ON INTEGRATING FACTORS[1]

BY PAUL SAUREL

The differential equation

$$X_1dx_1 + X_2dx_2 + \dots + X_ndx_n = 0, \quad n \geqq 3, \qquad (1)$$

in which X_1, X_2, … are functions of x_1, x_2, …, is said to be integrable when there exist functions u and M such that

$$du \equiv MX_1dx_1 + MX_2dx_2 + \dots + MX_ndx_n. \qquad (2)$$

M is called an integrating factor and

$$u = \text{constant}$$

is an integral of the differential equation.

In the case of two variables the differential equation is always integrable, that is to say there always exist functions u and M which satisfy equation (2).

In any case, since

$$du \equiv \frac{\partial u}{\partial x_1}dx_1 + \frac{\partial u}{\partial x_2}dx_2 + \dots + \frac{\partial u}{\partial x_n}dx_n,$$

it follows that

$$\frac{\partial u}{\partial x_1} \equiv MX_1, \quad \frac{\partial u}{\partial x_2} \equiv MX_2, \quad \dots, \quad \frac{\partial u}{\partial x_n} \equiv MX_n;$$

and the equations of the form

$$\frac{\partial^2 u}{\partial x_r \partial x_s} \equiv \frac{\partial^2 u}{\partial x_s \partial x_r}$$

may be written

$$\frac{\partial}{\partial x_r}(MX_s) = \frac{\partial}{\partial x_s}(MX_r), \quad r \neq s; \ r, s = 1, 2, \dots, n. \qquad (3)$$

These, as is well known, are the necessary and sufficient condi-

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[1] This mathematical paper is printed here because its results are necessary for the development of some theoretical studies that are to follow.—EDITORS.

tions that M should be an integrating factor of the differential equation.

Another well-known theorem is that the ratio of any two integrating factors gives an integral function of the differential equation. It may be proved as follows: If M_1 and M_2 be any two integrating factors, they must satisfy equations (3). These when expanded give

$$M_1 \frac{\partial X_s}{\partial x_r} + X_s \frac{\partial M_1}{\partial x_r} = M_1 \frac{\partial X_r}{\partial x_s} + X_r \frac{\partial M_1}{\partial x_s}$$

and

$$M_2 \frac{\partial X_s}{\partial x_r} + X_s \frac{\partial M_2}{\partial x_r} = M_2 \frac{\partial X_r}{\partial x_s} + X_r \frac{\partial M_2}{\partial x_s}.$$

Multiply the first of these equations by M_2, the second by $-M_1$, and add; the result is

$$X_s\left(M_2 \frac{\partial M_1}{\partial x_r} - M_1 \frac{\partial M_2}{\partial x_r}\right) = X_r\left(M_2 \frac{\partial M_1}{\partial x_s} - M_1 \frac{\partial M_2}{\partial x_s}\right),$$

or

$$\frac{X_s}{M_2 \frac{\partial M_1}{\partial x_s} - M_1 \frac{\partial M_2}{\partial x_s}} = \frac{X_r}{M_2 \frac{\partial M_1}{\partial x_r} - M_1 \frac{\partial M_2}{\partial x_r}},$$

which, after dividing each denominator by M_2^2, gives

$$\frac{X_s}{\frac{\partial}{\partial x_x}\left(\frac{M_1}{M_2}\right)} = \frac{X_r}{\frac{\partial}{\partial x_r}\left(\frac{M_1}{M_2}\right)}, \quad r \neq s; \; r, s = 1, 2, 3, \ldots n.$$

The differential equation may thus be written in the form

$$\frac{\partial}{\partial x_1}\left(\frac{M_1}{M_2}\right) dx_1 + \frac{\partial}{\partial x_2}\left(\frac{M_1}{M_2}\right) dx_2 + \cdots + \frac{\partial}{\partial x_n}\left(\frac{M_1}{M_2}\right) dx_n = 0,$$

and

$$\frac{M_1}{M_2} = \text{constant}$$

is therefore an integral.

As a corollary to this theorem it follows that if there be an integrating factor M_1 which contains only one of the variables, it is unique. For, since the ratio of any two integrating factors gives an integral function of the differential equation, this ratio must contain all the variables; if, therefore, M_1 contains only one of the variables, any other integrating factor M_2 must contain the remaining variables, and may contain all the variables.

It now remains to establish the necessary and sufficient conditions for the existence of an integrating factor which shall contain but one of the variables, x_1 for example. Equations (3) yield the $n - 1$ conditions

$$M \frac{\partial X_1}{\partial x_r} = M \frac{\partial X_r}{\partial x_1} + X_r \frac{dM}{dx_1}, \; r = 2, 3, \dots n,$$

or, in better form

$$\frac{\dfrac{\partial X_1}{\partial x_r} - \dfrac{\partial X_r}{\partial x_1}}{X_r} = \frac{\dfrac{dM}{dx_1}}{M}, \; r = 2, 3, \dots n; \qquad \text{(I)}$$

and the $\frac{(n-1)(n-2)}{1.2}$ conditions

$$M \frac{\partial X_s}{\partial x_r} = M \frac{\partial X_r}{\partial x_s}$$

or

$$\frac{\partial X_s}{\partial x_r} = \frac{\partial X_r}{\partial x_s}, \; r \neq s; \; r, s = 2, 3, \dots, n. \qquad \text{(II)}$$

The right-hand member of each of equations (I) is a function of x_1 alone, the same must therefore be true of the left-hand members. Thus the necessary conditions for the existence of an integrating factor which shall contain x_1 alone, are that the left-hand members of equations (I) shall be identically equal to one and the same function of x_1, and that equations (II) be satisfied identically—in all $\frac{n(n-1)}{1.2}$ conditions.

These are also the sufficient conditions. For if they be satisfied, put $\frac{\frac{dM}{dx_1}}{M}$ equal to one of the expressions

$$\frac{\dfrac{\partial X_1}{\partial x_r} - \dfrac{\partial X_r}{\partial x_1}}{X_r};$$

this, upon integrating, gives

$$Ce^{\int \frac{\frac{\partial X_1}{\partial x_r} - \frac{\partial X_r}{\partial x_1}}{X_r} dx_1}$$

in which C is an arbitrary constant. And, the function M thus determined is an integrating factor, for the conditions (3) are all satisfied in virtue of equations (I) and (II).

In the case of two variables, the necessary and sufficient condition for the existence of an integrating factor containing x_1 alone is that

$$\frac{\frac{\partial X_1}{\partial x_2} - \frac{\partial X_2}{\partial x_1}}{X_2} = f_1(x_1).$$

If, at the same time, the condition for a factor containing x_2 alone be satisfied, *viz:*

$$\frac{\frac{\partial X_2}{\partial x_1} - \frac{\partial X_1}{\partial x_2}}{X_1} = f_2(x_2),$$

upon dividing the first equation by the second, it appears that

$$\frac{X_1}{f_1(x_1)} = - \frac{X_2}{f_2(x_2)},$$

and that accordingly the differential equation may be put into the form

$$f_1(x_1)dx_1 - f_2(x_2)dx_2 = 0$$

in which the variables are separate. That is to say, if the differential equation in two variables have an integrating factor containing x_1 alone, and another factor containing x_2 alone, then the variables are separable. The converse is not true.

New York, January, 1898.

VAPOR-TENSION OF CONCENTRATED HYDROCHLORIC ACID SOLUTIONS

BY F. B. ALLAN

That hydrogen chloride gas in aqueous solution does not obey Henry's law has been known for a long time, and explained by the chemical action of water on the gas. If this chemical action resulted only in the electrolytic dissociation of the hydrogen chloride, the relation between the undissociated molecules in a given volume of the solution and the pressure of the gas should be a constant. These experiments were made to ascertain whether the dissociation of the acid would explain this exception to the law.

The measurements were made by passing air through a bottle of about 60 cc capacity closed by a rubber stopper with two perforations, through three parallel tubes each about 20 cm long and 2 cm in diameter and inclined at a slight angle to the horizontal, and through a set of Liebig bulbs. The bottle and tubes were almost full of the solution. The air passed into the bottle by means of a small glass tube drawn out to so fine a point that the spherical form of the air bubbles could not be detected and all that was visible was a line from the end of the tube to the surface of the liquid. The first tube was connected with the second by a smaller and longer glass tube bent back so that the current of air passed in the same direction in each. The second tube was connected in the same way with the third. Where these small tubes were sealed into the larger ones they were drawn out to a fine point so that the formation of large bubbles was avoided. The rate at which the bubbles passed through the columns of liquid was determined by the inclination of the tubes. A blank bulb was placed after the Liebig bulbs to prevent danger from spurting, and then followed two sets of Geissler bulbs containing water for the absorption of the hydrogen chloride.

A regular flow of gas was secured by forcing the air at increased pressure through the very small inlet in the bottle, while an aspirator connected with a manometer at the end of the apparatus decreased the pressure necessary to send the air through, and gave an easy means of determining the volume of air used. It was found that practically all the hydrogen chloride gas was absorbed by the water in the first Geissler bulbs.

Under a pressure represented by about 6 feet of water, air passed through the tubes at the rate of 200 cc per hour. The aspirator was a 2.5 liter-jar, and the air was measured by weighing the water which had been allowed to run out, making the required correction for difference of aqueous tension, pressure, etc. About 500 cc of air were used for each experiment, but this volume was increased for the more dilute solutions.

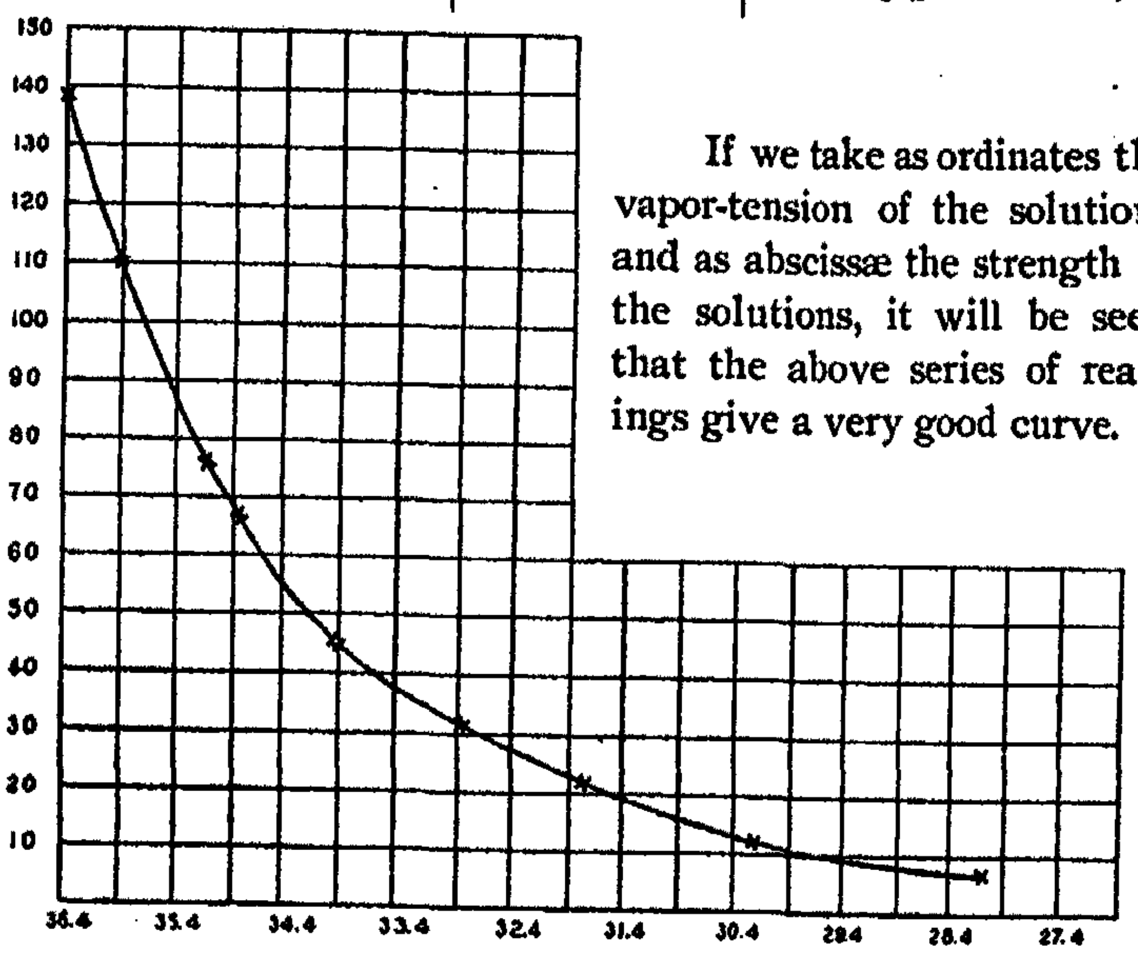
That the air was saturated in passing through the apparatus was shown by the fact that the weight of the Liebig bulbs was not altered by a ten hours' run. The experiments were conducted in a constant temperature room whose temperature did not vary more than one-tenth of a degree during the course of an experiment.

Column I of the following table shows strength of acid solutions used; column II the number of cc of $\frac{N}{20}$ potash solution required to titrate the contents of the Geissler bulbs and calculated to 500 cc of air; column III the vapor-pressure of hydrogen chloride over these solutions taken from the average of the duplicate experiments and expressed in millimeters of mercury.

TABLE I

Temp. 18.4° C

I	II	III
36.40 pct	46.20 46.40	138.1
35.90	35.25 35.15	109.8
35.10	23.00 23.20	75.8
34.85	20.00 20.00	66.6
33.90	13.50 13.35	46.0
32.85	9.45 9.40	32.7
31.75	6.25 6.15	21.9
30.20	3.35 3.20	11.8
28.10	1.55 1.50	5.5



If we take as ordinates the vapor-tension of the solutions and as abscissæ the strength of the solutions, it will be seen that the above series of readings give a very good curve.

Now if the vapor-tension be taken as proportional to the undissociated hydrogen chloride, column III in Table I will also represent the relative amounts of undissociated hydrogen chloride in a constant volume of the different solutions and we may calculate from these numbers the relative amounts of undissociated hydrogen chloride in solutions which contain a constant amount of the gas in solution.

Column I contains the same values as column I in Table I, but expressed as the liters containing a gram-molecule, column II the relative amounts of undissociated hydrogen chloride.

TABLE II

I	II	I	II
0.0840	100.0	0.0945	26.2
0.0854	80.6	0.0983	18.2
0.0876	56.9	0.1040	10.3
0.0883	50.4	0.1128	5.2
0.0912	35.8		

Thus, the highest possible value for undissociated hydrogen chloride in a 28.1 percent acid is 5.2 or the degree of dissociation is 94.8. But this value for dissociation can be shown to be much too low, as in that case the concentration of the ions in a 30 percent acid would be greater than in a 31 percent acid.

We may compare with the above, the dissociation as calculated from Kohlrausch's conductivity measurements at 18°C[1] and also Jones' measurements by the freezing-point method.[2]

TABLE III

v	μ_v	μ_v/μ_∞ $(\mu_\infty = 345.5)$	Normal	v	Dissociation
0.100	60.0	17.4	0.1228	8.1	88.8
0.200	142.0	41.1	0.08127	12.3	89.7
0.333	201.0	58.2	0.03619	27.6	94.4
1.	278.0	80.5			
2.	301.7	87.3			
10.	324.4	93.9			

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[1] Ostwald. Lehrbuch II. 1, 722.

[2] Jones. Zeit. phys. Chem. 12, 628 (1893).

It will be seen from this table that 94.8 is an impossible value for the dissociation of hydrochloric acid solutions so concentrated as one gram-molecule in 0.1128 liters.

It is concluded, therefore, that electrolytic dissociation is not an adequate explanation of the fact that hydrochloric acid solutions do not obey Henry's law.

The curve of vapor-tension will also represent the 'chemical potential' of the acid solutions.

The Chemical Laboratory of the University of Toronto,
December, 1897.

NEW BOOKS

Text-Book of Physical Chemistry.[1] *By Clarence L. Speyers. 14 × 20½ cm; pp. vii and 224. New York: D. Van Nostrand Company, 1897. Price: cloth $2.25.*—This book, which 'represents what the author has been in the habit of teaching his senior class in the chemical course', is divided into ten chapters under the following headings:—1. Some General Remarks on Energy (15 pp); 2. Gases (8 pp); 3. Heat (16 pp); 4. Physical Change (37 pp); 5. Equilibrium (38 pp); 6. Chemical Kinetics (7 pp); 7. Phases (16 pp); 8. When temperature is variable (6 pp); 9. Electrochemistry (54 pp); 10. Ions (3 pp). A collection of problems is appended to each section.

The subject is treated from 'the energy point of view'; the author regards, *defines* in fact, the different forms of matter as 'collections of forms of energy in space'; he is confident that 'the materialistic interpretation has passed its prime and has no promise for the future'; and, in his opinion (p. 20),

> the kinetic theory is a troublesome thing and is becoming an object of ridicule. It has never directed the chemist to any new discovery or idea, unless it may be van der Waals's theory, and that would probably have come any way.

The molecular interpretation of the laws of chemical combination is accordingly rejected in favor of the 'explanation of the energy theory' (p. 5),

> which says that a collection of energies can only be in equilibrium when there is a fixed relation between all the associated forms of energy. Consequently when two collections combine and form a third collection, they can only do so in the proportion that keeps the relation between all the forms existing in the third collection fixed.

A similar 'explanation' is provided for the variations from Boyle's law (p. 21):

> When we raise the pressure on a gas greatly, we find that Boyle's law no longer expresses the relation between pressure and volume even approximately .... The energy theory says that this is because the factors of the volume energy in imperfect gases are not inversely proportional. For moderate intensity they are inversely proportional, but when the intensity is high, the factors are no longer inversely proportional.

Like many adherents of the 'materialistic interpretation' that he condemns, the author evidently considers that a problem is solved when it is merely translated into the language of his own 'point of view'.

It will probably be generally agreed that the subjects to which particular attention should be given in a text-book of physical chemistry, in the present state of the science, are *first* the laws of energy, with special reference to the 'entropy principle', and *second* the facts and theories concerning osmotic pressure.

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[1] It has seemed best that this book should be reviewed by a member of the staff, because it is the first formal treatise on Physical Chemistry to appear in America.—*Editors.*

With regard to the first of these, the author's 'energy point of view' differs very widely from that of everyday thermodynamics: in no respect more remarkably, perhaps, than in the use he attempts to make of the principle of the conservation of energy. On page 12, this principle does duty as the condition of equilibrium:

> *Conditions of Equilibrium.*—. . . Two opposing energies of different kinds are in equilibrium when an infinitesimal increase of one energy necessitates an equivalent decrease of the other. That is, when $dE_1 = dE_2$.

Is the reader to infer that when two forms of energy are *not* in equilibrium (*e. g.*, when a heavy body is falling to the ground) that an increase of one energy (kinetic) does *not* necessitate a decrease of the other (energy of position)?

A little further on, the same principle is made to take the place of Clausius's second law, in 'determining how much of a given quantity of heat energy can be converted into work'. As this point is of fundamental importance, the words of the text are quoted at some length (p. 34):

> We make the gas pass through a *cycle* of changes. [1]*A cycle of changes is a series of changes such that the final and initial states are identical.* . . . In a *reversible cycle the energy obtained at the end of the cycle is just equal to the energy consumed.* There is neither a leakage nor a gain of energy. In a *non-reversible cycle* . . . *there is either a leakage or a gain of energy.* This [is] an ideal arrangement. There are no reversible cycles in nature, but the conclusions we reach through a reversible cycle are nevertheless of great importance. They are the results of perfect action, and on comparison with actions such as we find in nature, lead to the detection of the causes of imperfection.
>
> [Here follows a two-page argument leading to the equation $dW = Q(dT/T)$.] We have deduced the relation between W and Q in a particular way, but the result must be the same whatever way we follow, provided, of course, Q_1, Q_2, T_1, T_2 are the same. For if not, we take the cycle which yields the larger quantity of work, and with this work run the other cycle backward to the initial state. The result is that a reversible cycle which yields a certain quantity of work, on reversal, is able to assimilate a larger quantity of work than it yields and yet be in the same final state after each operation. This means a destruction of energy.

It is only too plain that the author has failed to grasp the distinction between reversible and non-reversible cycles, and (in consequence of this, no doubt) the import of the second law itself. Confusion of this sort is contagious; when it infects a text-book it is apt to become epidemic.

The treatment of the second subject, Osmotic Pressure, is no more satisfactory than that of the first. No mention is made of Pfeffer's experiments, no concrete example given of a 'diaphragm permeable to the solvent but impermeable to the solute'; on the contrary, we are informed that (p. 64):

> On the semipermeable diaphragm, the pressure is due solely to the dissolved substance, not to the solvent, for this can pass through the diaphragm. No direct experiment has ever shown the existence of this pressure on the semipermeable diaphragm, but nevertheless we cannot doubt its existence. In no way can we explain osmotic action nor a large number of other phenomena, nor account for the relations of some forms of energy. We shall call this pressure ... *osmotic pressure.*

Declining the author's invitation to 'run through a cycle [very much] like that used in getting the second law of thermodynamics' let us turn to the following remarkable paragraph (p. 76):

> *Liquid and Vapor.*— . . . We may look upon the vapor of a solvent as existing in the solvent in the same state that any other substance would be in when dissolved

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[1] The italics are the author's.

> in that solvent. Its concentration is, therefore, measured by its osmotic pressure. Let π_0, ϕ_0, denote respectively osmotic pressure and osmotic volume of the dissolved vapor in the pure solvent; ... p_0, v_0, the pressure and volume of the vapor in contact with the pure solvent .... .
>
> (1) By means of a semipermeable diaphragm let a gram-molecule of dissolved vapor pass from the pure solvent. The available work is $-\pi_0\phi_0 = -RT$.
>
> (2) Let the gram-molecule of dissolved vapor expand .... .
>
> (3) Let it then pass into the solution. ...
>
> (4) Let x gram-molecules pass out of the solution in the form of vapor. ... where x is the number of gram-molecules of gaseous vapor necessary to make one gram-molecule of dissolved vapor.
>
> (5) Let the x gram-molecules of vapor be compressed .... .
>
> (6) Let the x gram-molecules be driven into the pure solvent. ...
>
> The cycle is now complete [and two pages are devoted to discussing its results].

Have these sentences any meaning? If the 'pure solvent' is on *one* side of the semipermeable diaphragm in (1) what is on the other? The text-book furnishes no information on this head. If more of the same 'pure solvent', π_0 is obviously zero; if air, or a vacuum, the 'cycle' is reduced to an absurdity. What is the "dissolved vapor" dissolved in, in (2)? Finally to what is the diaphragm *semi*-permeable? Are we to imagine two quantities of the same 'pure solvent', one containing more of its own vapor dissolved than the other? It seems most probable that the whole paragraph has been written in pursuance of a formal analogy, with little thought of the meaning of the phrases employed.

One or two instances more will suffice to show that the qualities that characterize the passages quoted above are common to the whole book. On page 16 we read:

> The factors of volume energy are pressure and volume .... The volume energy in a perfect gas does not change with the volume; for the product of the two factors is constant; that is, $p_1v_1 = p_2v_2 = p_0v_0 =$ constant.

On page 18 however, in flat contradiction,

> So long as the gas remains a perfect gas and its mass does not change, so long the volume energy of the gas remains constant, *whether T changes or not.*

Whole pages are devoted to 'explanations' in the 'language of the energy theory' and to discussions of the 'state' of substances in solution, of the 'cause' of osmotic pressure, and of similar meta-physical questions; while other matters, including some of the first importance, are cut off with a word. Photochemistry has been entirely omitted, since 'as yet there are hardly any theories connecting light energy and so-called chemical energy'. A discussion of van der Waals's equation 'would lead us too far from our subject of physical chemistry'; and the theory of corresponding states is 'too physical'. The theory of individual E. M. F. is gone into at considerable length, but the fundamental hypotheses on which all is made to depend are passed over with the words (p. 183):

> It would seem that the mercury [of the ray electrode] takes the same potential as the solution,

and (p. 184):

> Careful experiment has shown that the p.d. between metals is very slight.

Similarly with the theory of chemical equilibrium. On page 87 we read:

> The condition of equilibrium for a system is $dU \geqq 0$, when the change of entropy is zero; ..... $dS \leqq 0$ when the change of internal energy is zero.

no reference is made to the condition of equilibrium on page 12 (see above), and no foundation is offered for this equation, which is to serve as basis for the argument of the whole chapter, save the remark that these equations

> are expressions of experience; they are altogether empiric.

In fine, the closing words of the preface of this remarkable text-book,

> whoever works through it conscientiously, paying particular attention to the problems, will get a very fair idea of Physical Chemistry,

like much else in the volume, can only be regarded as founded upon a misapprehension. *W. Lash Miller*

Krystallometrie. *By J. F. C. Hessel. Oswald's 'Klassiker der exakten Wissenschaften,' Nos. 88 and 89; 19½ × 12½ cm.; pp. 192 and 165. Leipzig: W. Engelmann, 1897. Price: marks, 3.00 and 2.80.* The greater part of the work (237 pages in the present edition) is devoted to a purely geometrical study of figures in space, ending with an enumeration of, and system of nomenclature for, all possible degrees of symmetry with reference to an axis. The problem is then specialized by introducing the law of rational indices; thus leading to a methodical deduction of the 32 possible classes of crystals, which forms the bases of all subsequent treatment of the subject.

Twenty-eight pages on the history of crystallography serve as an appendix to the book, which is provided with 131 clearly printed figures, a table of contents, and notes by E. Hess. *W. Lash Miller*

Traité élementaire de Mécanique chimique, fondée sur la Thermodynamique. *By P. Duhem. Vol. II; 18 × 25 cm; pp. 378. Paris: A. Hermann, 1898. Price: paper 12 francs.*—The first volume of this work has already been reviewed (1, 426); the second is now ready, treating of vaporization phenomena, continuity between the liquid and gaseous states, and dissociation of gases. It is therefore a treatise on one-component systems, with such incursions into the field of two-component systèms as are made necessary by the dissociation of compounds. While this is neither the simplest nor the most complete way of handling the subject, it is a very natural one. After starting with such a substance as ice and studying the effect of changes of pressure and temperature, it seems reasonable to take up next such compounds as calcium carbonate or ammonium sulfhydrid. The two cases differ fundamentally, as a matter of fact; but it is rather interesting to see dissociating compounds treated as an intermediate step between one-component and two-component systems, and not as more complex instances of binary systems. Though it is not so stated, this particular arrangement was doubtless chosen so that the author could pass directly from a consideration of nitrogen peroxid and of acetic acid to a study of substances like phosphorus pentachlorid and hydriodic acid. Purely as a matter of personal preference the reviewer would have welcomed a different classification, but the one adopted is logical and has been carried through consistently—which is all that anyone has a right to demand.

To the mathematician the present volume may not be as interesting as the preceding one; but, on the other hand, it will appeal very strongly to the experimental theorist, who will find in it many useful and unfamiliar facts, as well as suggestions for a vast amount of important research. It is impossible to read any six consecutive pages without coming across something which is both valuable and well put. The first chapter treats of saturated vapors, and the discussion is not confined to the exact formula of Clausius but is made to include the more or less empirical variations suggested by Dupré and by Bertrand. The second chapter is devoted to the phenomena of boiling, and it is a pleasure to note that the subject is developed in such a way as to conform to the experimental facts and not to a simplified statement of them. Ordinarily we do not distinguish between boiling and distilling, because the two phenomena are apt to occur together. Duhem makes a sharp distinction. By boiling he means the formation of bubbles in the mass of the liquid. As is well known, this is not a question of pressure only but involves the theory of capillarity. It is from this point of view that the author has treated the subject, and it is only when we look at it in this way that some of the peculiarities attending distillation under diminished pressure become intelligible. In the third chapter the pages on the change of melting point with pressure give the most complete statement of the facts to be found anywhere, even the latest work of Demerliac being included. Of more theoretical value is the part of this same chapter devoted to the existence of solid phases in metastable equilibrium. The theory of 'apparent false equilibrium' is brought in here to explain the phenomena, and it is shown from the experiments of Lussana that for each pressure there are two temperatures between which either of two modifications of ammonium nitrate can exist, provided the other form is not present. It is interesting to compare Duhem's results with those of Ostwald. The limits of the fields for metastable equilibrium, as defined by Ostwald, coincide with the limiting curves for 'apparent false equilibrium' as defined by Duhem; but Ostwald has considered only the special case of a supercooled liquid while Duhem's theory is general and applies to all boundary curves.

The third chapter closes with an account of the rate of change of one solid modification into the other. It should be noticed that Duhem predicts the existence of a maximum rate of solidification for supercooled liquids, a phenomenon which has since been observed experimentally by Tammann.

In the fourth chapter the author considers the dissociation curve for two solids and vapor, showing the accuracy with which one can calculate the heat of formation of the compound from the pitch of the curve. The clear way in which the assumptions involved are set forth, is very satisfactory. While most of us are perfectly cognizant of these assumptions if catechized, yet there is inevitably a tendency to overlook them when not on the witness stand,—a tendency which can best be counteracted by a detailed enumeration of these points in the standard treatises.

The fifth chapter deals with the triple point and with the curves radiating from it. The very striking experiment of Gernez illustrating the difference of vapor pressure between solid and supercooled acetic acid will probably be as new to most readers of the book as it was to the reviewer, while the frank statement that there are many forms of red phosphorus marks a distinct advance in the development of the science of things as they are.

As has already been stated, the second part of the volume is devoted to the discussion of the continuity between the liquid and gaseous states. Of special interest are the pages on the heat of vaporization, and the remarks on the effects due to gravity, viscosity and capillarity. The treatment of the pressure-volume, pressure-temperature and volume-temperature relations is complete and very satisfactory.

The last one hundred and fifty pages deal with dissociation in the vapor phase. It is assumed, of course, that the gas laws hold for the systems under consideration. The author then defines the molecular weight of an element as double its atomic weight, justifying this on the ground that any definition is permissible if adhered to and that this one possesses the merit of simplicity. This is true but not sufficient. A single negative advantage does not counterbalance a series of positive disadvantages. Aside from this blemish the remainder of the book is nearly as satisfactory as the earlier portions. There are some omissions. The dissociation of hydriodic acid is considered without reference to the work of Bodenstein, while the curious behavior of methyl ether hydrochlorid is not even hinted at. On the other hand we have a very satisfactory discussion of the dissociation of nitrogen peroxid, of ammonium carbamate and of ammonium cyanid. The last chapter deals with the complications introduced by false equilibrium, the experiments of Pélabon on selenium hydrid serving to illustrate the theory.

To those who are interested in the future development of chemistry this last chapter may well seem the most important in the book. During the last ten years physical chemistry has developed along lines laid down by van 't Hoff; during the next ten years the guiding impulse will be found in the theories of Duhem. The question of the carbon compounds has been one with which the physical chemist could not grapple. As long as 'passive resistance to change' was a formula for classifying our ignorance, no material progress was possible. Now that this phrase admits of mathematical definition, it becomes a watchword instead of a stumbling block. This change of position has come about within the last eighteen months and is due entirely to Duhem. To meet the theoretical difficulties presented by the behavior of selenium hydrid and of sulfur he has worked out the theory of false equilibrium and the theory of permanent changes. It will take years to develop these two principles and to apply them intelligently to the whole field of organic chemistry; but Duhem has shown us the way to go about the task and it is merely a question of time when organic chemistry will cease to be a brilliant monument of empiricism and will become an integral part of the science of chemistry.

There are some minor defects in this volume. The same amount of information could have been given in fewer words. The spelling of proper names is lax, Horstmann and Battelli being the worst sufferers. 'Apparent false equilibrium' is clumsy and should be replaced by some simpler phrase. The reader will hardly realize that it is possible to take anything except pressure, temperature, and masses as the independent variables. Apart from a few such points the reviewer has only words of praise for the book. It gives a masterly exposition of the subject and will exert an immense influence on scientific thought. It should be owned by everyone, read by everyone, and expounded to everyone.

Wilder D. Bancroft

The Capillary Electrometer in Theory and Practice. *Part I. By G. J. Burch. Small octavo; pp. 54. London: The 'Electrician' Printing and Publishing Co., 1896.*—This excellent little pamphlet is reprinted from the Electrician. In it the author describes in detail his method of making a capillary electrometer, and then shows the way to detect and record very rapid changes of electromotive force with this instrument by photographing the meniscus. The subject is a fascinating one and is treated admirably. The pamphlet should be in every laboratory. *Wilder D. Bancroft*

Electrochemistry, Inorganic. *By G. Gore. The Electrician Series. Third Edition; Small octavo; pp. 134. London: The 'Electrician' Printing and Publishing Co., 1897.*—This is a series of scrappy notes reprinted from the Electrician. The volume "is intended to contain, in systematic order, the chief principles and facts of electrochemistry, and to supply to the student of electroplating or electrometallurgy a scientific basis upon which to build the additional practical knowledge and experience of his trade." The promise of the introduction is not realized in the text. By no stretch of the imagination can the book be called scientific, systematic, or complete. One can only regret the state of things that makes a third edition possible. *Wilder D. Bancroft*

Tafeln und Tabellen zur Darstellung der Ergebnisse spektroskopischer und spektrophotometrischer Beobachtungen. *Arranged by Th. W. Engelmann. Leipzig: W. Engelmann, 1897. Price: 1.80 marks. Each spectrum plate is sold separately, at 1 mark per 10 copies.*—There are two plates. The first consists of six colored reproductions of the spectrum, with wave-lengths marked. The upper one contains the Fraunhofer lines and a couple of others. The five other spectra are intended to be shaded so as to represent the solutions which are being studied. The second plate has the colored solar spectrum at the top of the page and below this is coordinate paper on which to record the photometric data. Accompanying the plates are two tables, one giving extinction coefficients, the second the relative intensities for different thicknesses or for different concentrations. The publisher furnishes ten copies of each of the two plates, in a heavy brown paper envelope, together with the two tables and instructions for use. These will be of great service to all who are making photometric measurements. *Wilder D. Bancroft*

Die Mechanik in Ihrer Entwickelung, historish-kritsch dargestellt. *By Ernst Mach. Internationale wissenschaftliche Bibliothek, Band 59. Third, enlarged and revised, edition; 12½ × 19½ cm; pp. xii and 505. Leipzig: F. A. Brockhaus, 1891. Price: paper 8 marks, bound 9 marks.*—We have already had occasion three times to refer with enthusiasm in this Journal (1, 170, 430, 499) to the publication of Mach's magnificent researches in the philosophy of physical science; and it is with pleasure that we again recur to the subject, in connection with the issue of a new edition of Mach's *Mechanik*. The comparatively rapid sale of two large editions of this work is pleasingly indicative of the interest that it has aroused, and of the eminently wholesome influence that it is exerting upon the development of contemporary scientific thought and upon the spread of a due appreciation of historical research.

In arrangement the book falls into two distinct parts, of which the first considers primarily the growth of the ideas that are fundamental in mechanics proper; while the second is devoted to a discussion of what we know, and not of hypotheses that we make, in the physical sciences,—and to the relation in which mechanics stands to other departments of knowledge. Especially weighty, in connection with this last topic, is Mach's recommendation that systematic science be based on facts and not on hypotheses :—

"All hypotheses of fluids or media may be eliminated from the theory of electricity as superfluous, if we reflect that electrical conditions are all given by the values of the potential function V and the dielectric constants. If we assume the differences of the values of V to be measured (on the electrometer) by the forces, and regard V and not the quantity of electricity as the primary notion or measurable physical attribute, we shall find the quantity of electricity . . . and the energy . . . to be *derived* notions, in which no conception of fluid or medium is contained. If we purify the entire domain of physics in this way, we shall restrict ourselves wholly to the quantitative conceptual expression of actual facts. All superfluous and futile notions will thereby disappear, and the imaginary problems to which they give rise will be forestalled. . . .

"The removal of notions whose foundations are historical, conventional, or accidental, can best be effected by a comparison of the conceptions obtaining in the different departments, and by finding for the conceptions of each department the corresponding conceptions of others. We discover thus that temperatures and potentials correspond to the velocities of mass motions, . . . thermal capacities to masses, the energy of an electric charge to quantity of heat, quantity of electricity to entropy, and so on. The pursuit of such resemblances and differences lays the foundation of a *comparative physics*, which will ultimately render possible the concise expression of extensive groups of facts, without *arbitrary* additions. We shall then possess a homogeneous physics, unmingled with artificial atomic theories." (pp. 487-9.)

Obvious as is the necessity for carrying out such a programme, it is amazing that this has not yet been attempted seriously by anybody; if the people who write textbooks on the various branches of physics and chemistry would write what they know, instead of what they imagine, how sweet this world would be. But the simplest and most natural and straightforward way of doing a thing appears usually to be the last one to be adopted.

An important fact that is made very clear by Mach is that "the broad view expressed in the principle of the conservation of energy is not peculiar to mechanics, but is a condition of logical and sound scientific thought generally." The content of our conviction that 'effects' are uniquely determined by 'causes', that a given set of physical circumstances always induces the same physical consequences, lies in our recognition that all physical phenomena are interrelated, and, so, mutually dependent. Indeed, if this were not true we should be put to what Clifford called "permanent intellectual confusion." Now from this conviction, that given changes are determined uniquely by the attendant circumstances, it follows that purely periodical variations of these circumstances can only condition periodical recurrence of the resulting [the accompanying, or the related] changes; that is to say, no permanent physical change can occur without the simultaneous appearance of some other physical change as an outstanding compensation. But this statement is the essence of the energy law; and "with the perception of this truth is dissipated any metaphysical mysticism that might still adhere to the principle of the conservation of energy." Mach's luminous and deeply satisfying discussion of this matter is to be recommended earnestly to the attention of those especially who have been carried away by the eloquence of the protagonist of the new 'energetics.'

Many other points of general interest might be adduced from this remarkable work; and much emphasis might be laid upon the obvious truth that a comprehension of the fundamental principles of mechanics should be a part of the intellectual equipment of every devotee of physical science; but enough has been said already, and those who are interested in these matters will read the book. The present edition has been revised throughout, the appendices of the second edition have been incorporated into the text, and a certain amount of new matter—largely relating to the work of Hertz—has been added. The book is clearly printed and has a good index. *J. E. Trevor*

Modes of Motion. *By A. E. Dolbear. 13 × 19 cm; pp. iv and 119. Boston: Lee and Shepard, 1897. Price: cloth 75 cents.*—Of the three chapters of this book, the first presents the tenet that energy is always the energy of motion, the second that 'matter' is made up of vortex-ring atoms and that the 'ether' is continuous, and the third gives mechanical explanations of electric and magnetic phenomena. The whole treatment is chiefly dogmatic, and its keynote appears in the statement that: "by explanation is meant the presentation of the mechanical antecedents of a phenomenon" (p. 7); that "the mechanical antecedent of every kind of phenomenon is to be looked for in some adjacent body possessing ... the ability to push" (p. 12); and that "the transformation [of one kind of energy into another] is a mechanical process" (p. 47). The author pretends to know that 'matter' is made up of atoms of approximately known dimensions (pp. 19, 23, etc.); that at absolute zero an atom is an elastic, whirling body, (p. 43); that gravitation is ether pressure (p. 53); that no distinction is now made between cohesion and chemical affinity (p. 81); and so forth. His logic is illustrated by the conclusions: that water is composed of two kinds of atoms, because these atoms can be separated and recombined (p. 21); that atoms really vibrate at a definite rate, because these vibrations produce ether-waves of measurable length (p. 50); etc. And his ignorance of the fundamental principles of the energy theory is brought out in the misleading statement that, "energy is not a simple factor, but is a product of two factors" (p. 12); to which are added the illustrations, "the product of a mass with a velocity, a mass with a temperature, a quantity of electricity into a pressure"—all of which are perversely incorrect. He adds: that the idea of a substantiality of energy is evidently wrong, because energy is a product of two factors (p. 67); and that "action at a distance contradicts all experience, ... and is repudiated by every one who once perceives that energy has two factors, substance and motion" (p. 87). And after all this, to be told that "metaphysical reasoning may be very unsound"! (p. 63).

The publishers' announcement says that the book is intended for persons who have an interest in phenomena of all kinds; but it will really interest only those who care for pseudoscience and for the mechanistic view run mad. There is nothing scientific about it. It cannot possibly do any good, and it is too silly and incoherent to do much harm. *J. E. Trevor*

Lehrbuch der Experimentalphysik. *By Adolph Wüllner. Fifth, revised edition; Vol.* 3, *Magnetism and Electricity; 16 × 24 cm; pp. xv and 1414. Leipzig: B. G. Teubner, 1897. Price: paper 18 marks.*—It is with pleasure that we record the appearance of the third volume of the new edition of Wüllner's compendious treatise on general physics, a book which, as all know, has been of great service in aiding a whole generation of physicists, one might almost say two generations of them, to get their first broad idea of physics as a whole. And the book plays an important part in the literature of physical chemistry, since it presents extensively and in good arrangement those parts of physics that the physical chemist requires to know. Indeed, four hundred and fifty pages, or about one-third, of the present volume are devoted to electrochemistry pure and simple.

Like most treatises on electricity and magnetism, this volume sets out with a chapter on the potential function. The importance of this topic in physical chemistry is not always appreciated: one of the facts that the scientific chemist needs to comprehend and to bear in mind is that the thermodynamic theory of chemical processes and of their equilibria is founded on the potential theory, and that the idea of the potential is an essential element of any theory of electrochemistry. The next two sections of the book are devoted to magnetism and frictional electricity, topics which have of course little immediate bearing on chemical matters, and these sections are followed by a treatment of 'galvanism', or electrochemistry proper. Here appears a systematic review of work on the electrocapillary phenomena, the various forms of the voltaic cell, Ohm's law, the measurement of current, resistance, and differences of potential, the electromotive forces of important cells, thermocurrents and their theory, Joule's law, electrolysis and conductivity, polarization, accumulators, concentration currents, and the osmotic theory of Nernst. The concluding chapters consider electrodynamics, electromagnetism and diamagnetism, induction, and electric waves.

It is a matter for congratulation that so experienced a teacher and competent a man of science as Wüllner has devoted himself to the development of a treatise of this sort. The character and scope of the present volume, in particular, make it a reference book on electrochemistry, worthy to stand beside the comprehensive works of Ostwald and of Wiedemann; and four successive revisions of the original text have doubtless made it quite what the author desires it to be. The book will be of great use to the special student, and it should be in every university library. Proper name and subject indexes have been provided. *J. E. Trevor*

Physical Problems and Their Solutions. *By A. Bourgougnon. Van Nostrand Science Series, No. 113. 10 × 16 cm; pp. 228. New York: D. Van Nostrand Company, 1897. Price: boards 50 cents.*—This little book presents a series of over two hundred practical problems in mechanics, sound, light, heat and electricity, prefaced by introductory remarks on the necessity of adhering to the same system of units in working out a physical problem, and accompanied, in each case, by the solution itself. Something of this sort should be used in connection with every introductory course in general physics. We note, as having particularly physicochemical interest, the problems on calorimetry, and those involving the laws of Boyle and of Gay-Lussac,—which latter, curiously, appear in different parts of the book instead of being combined into a single expression. The book in its present form might well be made very serviceable for purposes of instruction, though, personally, we do not like the perverse metaphysics implied in the idea of "the properties of matter" (preface), and we object to the classification of 'heat' as one of the "natural forces."

J. E. Trevor

The Entropy-Temperature Analysis of Steam-Engine Efficiencies. *By Sidney A. Reeve. 15 × 24 cm; 20 pp. New York: Progressive Age Publishing Co., 1897.*—For the analysis of steam engine efficiencies the author of this brochure has arranged a diagram, whose field is divided by rectangular coordinate-axes into four quadrants with the respective axes: pressure and volume, pressure and temperature, entropy and volume, entropy and temperature. He proposes that ordinary indicator diagrams be plotted in the pressure-temperature quadrant, and that the corresponding entropy-temperature diagrams be constructed from them; the manner in which this is to be done is made clear in the text. The resulting entropy-temperature diagram shows directly the various heat-wastes in the engine whose cards are under examination; for the quantities of heat received and imparted are represented by areas on the diagram, and the ideal thermodynamic performance of the machine can be plotted at the same time from the fundamental data of boiler pressure, condenser temperature, etc. It thus becomes possible to read from the figure the losses of efficiency from wire-drawing, incomplete expansion, etc.,—that is to say, the economic character, in detail, of the working of the engine.

The description of the diagram is prefaced by a sensible account of the signification of the entropy idea; and it is accompanied by a big blank for practical use, in which are drawn, once for all, in the above-mentioned quadrants, the theoretical curves for water. Duplicate copies of the blank can be had from the publishers. The whole publication is an interesting practical application of the thermodynamics of one-component systems. We learn from the preface that, curiously enough, the author knows only by hearsay that the initial investigation of entropy-temperature diagrams is due to Gibbs. 'Entropy' on page 10, ten lines from below, should be 'temperature.'

J. E. Trevor

Elements of the Differential and Integral Calculus. *By William S. Hall. 16 × 23 cm; pp. xi and 249. New York: D. Van Nostrand Company, 1897. Price: cloth $2.25.*—We have here another of the introductory treatises on the calculus, which, in these days, American authors in particular are providing with profusion; and it, like all the others, is intended primarily to subserve the purposes of instruction 'in colleges and technical schools'. Commendable features of the book are its simultaneous development of both the differential and the integral calculus, its brevity, its supply of interesting and simple problems taken from geometry and mechanics, and its use of the symbol ∂ in partial differential coefficients—a proceeding which adds greatly to the clearness of the treatment of partial derivatives. In establishing the fundamental formulas for differentiation, the method of limits is used: this will meet universal approval, but when differentials are introduced we had rather see them defined as quantities whose ratios are the limiting ratios of simultaneous increments of function and variable, than to be told that a differential is "the difference between two consecutive values of the variable." When integration is taken up we find general integrals considered first, and definite integrals thereafter, as is usual. The reviewer can but think, however, that this hoary custom is ill advised; a straightforward treatment of definite integrals at the outset would be more rational and would certainly tend to render more intelligible the signification of the 'constant of integration.' The author's arrangement is good, and he has rounded his book off with a satisfactory short chapter on differential equations. Everything considered, the text appears to be well adapted to the use for which it is intended. *J. E. Trevor*

Annuaire du Bureau des Longitudes, *pour* 1898. *9½ × 15 cm; pp. vi and 806; with two magnetic maps. Paris: Gauthier-Villars et Fils. Price: paper 1.50 francs, or 1.85 francs postpaid.*—This compact little volume contains, as usual, a mass of scientific information not to be found assembled elsewhere. The following articles of especial interest appear in the issue for the present year: On the stability of the solar system, by H. Poincaré; On the scientific work of H. Fizeau, by A. Cornu; Some progress, made with the aid of photography, in the study of the surface of the moon, by M. Loewy and P. Puiseux; On the work done in 1897 at the observatory of Mont Blanc, by J. Janssen; Addresses delivered at the fiftieth academic anniversary of M. Faye,—January 25, 1897, by J. Janssen and M. Loewy. The book contains, also, extensive tables of densities, freezing and boiling temperatures, specific heats, critical data, coefficients of expansion, indices of refraction, and heats of formation,—the last compiled by Berthelot.

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of Journal articles that bear upon any phase of Physical Chemistry

General

On a possible change of weight in chemical reactions. *F. Sanford and Miss L. E. Ray. Phys. Rev.* 5, *247* (*1897*). Inspired by Landolt's work, Zeit. phys. Chem. 12, 1 (1893), the authors have studied the reduction of silver from an ammoniacal solution of the oxid by means of grape sugar. In two series there is an apparent loss of weight and in three there is an apparent increase. The largest variation is 0.08 mg in a total weight of one hundred and twenty-one grams. The probable error as given by the authors seems to be a mathematical fiction quite devoid of significance. *W. D. B.*

A new method of determining the specific heats of liquids. *R. L. Litch. Phys. Rev.* 5, *182* (*1897*). A current is passed through a coil placed in a vessel containing the liquid to be studied. The temperature is kept constant by running in more of the same liquid from a vessel in which it is kept at a constant lower temperature. When the mass of liquid dropped, the difference of temperature, the current, the resistance and the mechanical equivalent of heat are known, the specific heat of the liquid can be calculated. By passing the same current through two calorimeters containing different liquids, the mechanical equivalent of heat can be eliminated from the equation.

W. D. B.

The atomic mass of tungsten. *W. L. Hardin. Jour. Am. Chem. Soc.* 19, *657* (*1897*). The conclusion drawn from a careful study of the subject is that the reduction of tungsten trioxid to tungsten is a reaction which is valueless for the purpose of determining the combining weight of tungsten.

W. D. B.

On a constant temperature bath. *A. Gouy. Jour. de Phys.* (*3*) 6, *479* (*1897*). The bath is so surrounded by non-conducting material that the fall of temperature is 0.002° per minute for a temperature difference of 15° between the bath and the room. The bath is heated by an incandescent lamp placed in a brass tube. The current is regulated by an alcohol-mercury thermostat. To avoid errors due to changes in the form of the mercury meniscus, the wire which completes the contact is made to oscillate vertically. It is said to be easy to keep the temperature constant to within 0.0002° if the barometer remains constant. A change of one centimeter of mercury in the barometric pressure means a difference of 0.001° owing to the compressibility of the alcohol. The bath itself holds about one hundred liters and a current of three milliamperes is said to be sufficient. *W. D. B.*

Heat and cold regulator. *C. Richter. Elektrochem. Zeit.* 4, *155* (*1897*). The expansion of air forces up a mercury thread, closing an electric circuit and cutting off the supply of gas. The apparatus can be obtained from C. Richter of Berlin. *W. D. B.*

One-Component Systems

Stereochemistry of the phenylnitrocinnamic acids. *M. Bakunin. Gazz. chim. Ital.* 27, *II*, *34* (*1897*). There are three isomeric nitrophenylcinnamic acids, and each occurs in two crystalline modifications. The meta acid has been studied the most thoroughly because it is the easiest to make. Neither modification changes into the other in the dark. Exposed to direct sunlight each modification changes to a limited extent into the other when in solution. The rate of change is affected by the presence of iodin or of carbon, and it is proposed to study this action more in detail. *W. D. B.*

Relations between the chemical composition and some physical properties of liquids. *E. van Aubel. Jour. de Phys.* (*3*) 6, *531* (*1897*). Colson has stated that isomeric liquids have nearly identical coefficients of expansion. A reference to the tables of Landolt and Börnstein shows this not to be the case. The replacement of hydrogen or hydroxyl by chlorin, bromin or iodin diminishes the conductivity for heat, the specific heat and the heat of vaporization ; but increases the density. In all these cases the introduction of iodin causes the most change and that of chlorin the least. On passing from a fatty acid to the corresponding alcohol, the density and conductivity decrease while the specific heat and the heat of vaporization increase. *W. D. B.*

On the volume of vapor produced by evaporating one cubic centimeter of a liquid at its boiling-point. *J. A. Groshans. Wied. Ann.* 61, *780* (*1897*). A. Masson has shown that a volume of one gram of vapor at the boiling point is approximately the same for members of small groups of closely related bodies, *e. g.* the haloid mono-substitution products of benzene. The author combines this relation with his "theorem of corresponding temperatures" and obtains this formula for substances containing C, H and O :—

$$\frac{xd}{B} = const,$$

d denoting the density of the liquid at its boiling point, B the number of atoms in the molecule, and x a whole number or simple fraction (1, 741). In the examples quoted, the 'constant' varies from 21 to 24 for ethers, from 29 to 65 for alcohols, and from 36 to 47 for acids. *W. L. M.*

Further application of the method of approximations to Maxwell's theory of gases. *H. Benndorf. Sitzungsber. Akad. Wiss. Wien*, 105, (*IIA*) *646* (*1896*). "Among the greatest beauties of Maxwell's theory of gases is the method by which the hydrodynamic equations are deduced. Beginning with a general functional equation, Maxwell obtains the ordinary hydrodynamical equations by specializing the function and neglecting all terms but those of the highest order. If, however, terms of the next order be taken into consideration, the equations for friction and for conduction of heat appear of themselves. It is, consequently, of great interest to extend the same approximate calculation to include terms of still lower orders; the possibility that the results might lead to the discovery of new facts is alone sufficient inducement; although, considering the arbitrary nature of the fundamental hypotheses, an accurate agreement between theory and experiment can hardly be anticipated."

The 'arbitrary hypotheses' referred to are the kinetic theory, with the special assumptions that the 'gas is monatomic, the molecules are material points which repel one another with a force reciprocally proportional to the fifth power of the distance, and the external forces acting on this gas are not functions of the velocities of the molecules, nor, explicitly, of the time.'

The author brings his paper to a conclusion without instituting any comparison between the results of experiment and those of his lengthy and involved calculations. *W. L. M.*

On the calculation of the variations of the gases from the laws of Boyle and Charles and on their dissociation. *L. Boltzmann. Sitzungsber. Akad. Wiss. Wien*, 105, (*IIA*) *695* (*1896*). Formulas to replace that of van der Waals are deduced by combining various assumptions as to the forms and repulsing forces of molecules, with a theorem on their distribution in space; the results agree in part with those of Lorentz and of Jaeger.

The second part of the paper is devoted to a theory of dissociation, based on the following special assumptions. "The atoms are elastic spheres, ... immediately adjoining a small part of the surface of each atom is a small space, the 'sensitive space', ... it is only when the relative positions of two atoms is such that their sensitive spaces partially coincide, that the two atoms can exert attractive force on each other, ... these attractive forces may be called the 'chemical forces'." The consequences of this theory are developed, with the satisfactory result that "from very simple assumptions we have arrived at the well-known fundamental equations of the dissociation of gases. There is, naturally, not the slightest difficulty in treating the more complex cases of dissociation according to the same principle ... When the sensitive space is distributed uniformly over the whole surface of the atom, the laws of liquefaction of the gases may be obtained; since as soon as a noticeable number of double atoms exist, numerous aggregates of many more atoms will immediately be formed." *W. L. M.*

Contribution to the theory of gases. *G. Jaeger. Sitzungsber. Akad. Wiss. Wien*, 105, (*IIA*) *791* (*1896*). The paper contains:—

1. A deduction of van der Waals's equation, from the ordinary assumptions of the kinetic theory, but by an improved method.

2. Determination of a (in van der Waals's equation) as a function of T. "An exact representation of f(T) is probably impossible; we will, however, attempt to render plausible a temperature function which is in every respect in agreement with experiment." With help of the theory of probability, the author succeeds in rendering plausible an expression which "agrees in every respect with experiment—even in its application to the dissociation of gases."

3. As the relation between the average inner energy of each gas molecule and the average energy of progressive motion is independent of temperature, the quantity of heat that must be supplied to bring about the dissociation of a molecule is proportional to T. From this it follows, that, for adiabatic expansion without performance of work, the fall in temperature is proportional to the difference in pressure, and inversely to the square of the absolute temperature — in agreement with Joule's and Thompson's experiments on air and carbon dioxid.

"In the good agreement between experimental results and the formulas deduced from our theory" the author sees "a certain guarantee of the correctness of our views." He would be much more likely to secure the reader's adherence to the views in question, could he but account for the striking paucity of new results obtained by means of a theory so successful at "accounting for" and "rendering plausible" results arrived at independently of it. *W. L. M.*

The scientific papers bearing on the compression and liquefaction of gases. *C. G. von Wirkner. Zeit. comp. flüss Gase*, 1, *50, 71, 103*, (*1897*). A historical sketch of the subject, very useful for reference. *W. D. B.*

On the volatility of compounds containing fluorin. *L. Henry. Recueil Trav. Pays-Bas*, 16, *218* (*1897*). Reviewed (1, 632) from Bull. Acad. roy. Belg. (3) 33, 195 (1897).

On the chemical decomposition of sulfur. *T. Gross. Elektrochem. Zeit.* 4, *112* (*1897*). By fusing together ferrous sulfate and potassium chlorate the author claims to have obtained a substance δ which has many of the properties of silicon ; but which is said to be a new element. For some unexplained reason the author does not see fit to prepare this substance on a large scale. He has not yet decided whether this substance δ is the same as the "bythium" previously isolated by him (1, 620). *W. D. B.*

Two-Component Systems

On the solubility of ammonia in water at temperatures below 0° C. *J. W. Mallet. Am. Chem. Jour.* 19, *804* (*1897*). The solubility curve for ammonia in water at 74.4 mm pressure is curiously wavy, appearing to have a point of inflection at about —10° and another at about —25°. This latter may be due to experimental error since the partial pressure of the ammonia is high at that temperature. *W. D. B.*

The theory of osmotic pressure and the hypothesis of electrolytic dissociation. *H. Crompton. Jour. Chem. Soc.* 71, *925* (*1897*). It is assumed that van 't Hoff assumed, in working out the relation between concentration and change of freezing point, that the solvent had the same reacting weight as liquid and as vapor. From this it follows that we must always insert a correcting factor for the association of any liquid solvent. The value of this idea would be increased if there were any grounds for the assumptions. It is also assumed that solid acetic acid is supposed to be in equilibrium with a solution of benzene in acetic acid when the vapor pressure of the solid acetic acid at that temperature is equal to the total pressure of the vapor in equilibrium. As might be expected, interesting conclusions may be and are drawn from these premises. The author also states that pure ice does not separate from a mixture of alcohol and water. *W. D. B.*

The dissociation of electrolytes as measured by the boiling-point method. *H. C. Jones and S. H. King. Am. Chem. Jour.* 19, *753* (*1897*). Measurements of the boiling points of solutions of potassium iodid and of sodium acetate in alcohol with the modified Beckmann apparatus (1, 743). In a one percent potassium iodid solution the dissociation seems to be about twenty-six percent and the authors call attention to the fact that the ratio of this dissociation to the dissociation in a corresponding aqueous solution is about the same as the ratio of the dielectric constants of alcohol and water. In a one percent solution of sodium acetate there seems to be less than two percent dissociation; but the authors think that this is due to an impurity of potassium acetate.

W. D. B.

Racemism and pseudoracemism. *F. S. Kipping and W. J. Pope. Jour. Chem. Soc.* 71, *989* (*1897*). When a dextrorotatory and a laevorotatory compound combine to form an inactive compound the authors call the inactive substance a racemic compound if its "crystallographic properties differ in a marked manner from those of its active components" and a pseudoracemic compound if its "crystallographic properties resemble those of its active constituents so closely as to render distinction difficult." The racemates would then be compounds while the pseudoracemates would correspond to isomorphous solutions. The distinction seems to have merits, but the authors are not clear as to what they mean by their words and therefore leave the reader in a hopelessly confused state. If the distinction is sound, a mixture containing the dextrorotatory and laevorotatory modifications not in equivalent quantities should give two kinds of crystals if a racemate be formed and only one set if a pseudoracemate is possible. This simple experiment was not tried. This is but one of many cases where a knowledge of the general principles of chemical equilibrium would be of advantage to the organic chemist. *W. D. B.*

Solution of liquids and solids in gases. *P. Villard. Séances Soc. Phys. Paris*, 1896, *234*. Reviewed (1, 255) from Jour. de Phys. (3) 5, 453 (1896).

Electrolysis and Electrolytic Dissociation

The influence of temperature on the migration velocity of the ions. *A. Campetti. Atti. Accad. Sci. Torino*, 32, *735* (*1897*). With a copper sulfate solution containing 1.93 percent of the hydrated salt, the transference number for the anion is 0.636 at 15° and 0.612 at 47°. With a 4.73 percent solution the values are 0.658 at 7°, 0.651 at 18° and 0.628 at 48°. With a zinc sulfate solution containing 3.93 percent of the hydrated salt the corresponding values are 0.666 at 15° and 0.674 at 46°, while a 7.36 percent solution gave 0.678 both at 15° and at 45°. This last solution was peculiar in that the values calculated from the change of concentration at the anode were about eight percent smaller than those based on the change of concentration at the cathode. The author explains this by assuming that the water of crystallization does not form part of the solvent under these circumstances. With a 3.36 percent solution of lead nitrate the transference number for the anion was 0.495 at 8°, 0.509 at 15° and 0.493 at 45°. All these results are in flat contradiction with those of Lussana, Atti Istituto Veneto, 3, (1892). The author gives reasons for his belief that Lussana's measurements are inaccurate. *W. D. B.*

On the energy of some bases with mixed properties. *G. Carrara and U. Rossi. Rend. Accad. Lincei,* (5) 6, *152, 208* (*1897*). By bases with mixed properties the authors mean substances like glycocoll containing an acid and a basic group which may each neutralize the other. From determinations of the conductivity of the hydrochlorids the hydrolytic dissociation and therefore the strength of these bases can be calculated, as has been shown by Walker. The order as found is α-dimethylhydroxysulfidopropionic acid, dimethylhydroxysulfidoacetic acid, diethylhydroxysulfidoacetic acid, betain and β-dimethylhydroxysulfidoacetic acid, the first being a stronger base than urea and the last weaker than pyridin. Substituting selenium for sulfur increases the strength of the base. *W. D. B.*

The formation of mercury films by an electrical process. *R. Appleyard. Proc. Phys. Soc. Lond.* 15, *119* (*1897*). "If a sheet of gelatine, damp leather, or similar permeable substance is used as a separating diaphragm between two bodies of mercury, and a current is sent through it, a film of mercury is deposited upon the surface connected to the positive pole of the battery. The film remains on the diaphragm after the removal from the apparatus."

W. D. B.

On a peroxynitrate of silver. *E. Mulder and J. Heringa. Recueil Trav. Pays-Bas,* 15, *235* (*1896*); 16, *57* (*1897*). The black compound formed at the anode of a silver voltameter (*1*, 323) has the empirical formula $3Ag_2O.5O.AgNO_3$. It contains no water and loses five of oxygen slowly at ordinary temperatures, explosively at high temperatures. From a study of the substance while undergoing slow decomposition, the authors conclude that the formula $3Ag_2O_4.AgNO_3$ represents the facts better than any other. *W. D. B.*

The self-recording of electric currents by electrolytical methods. *P. Grützner. Elektrochem. Zeit.* 4, *97* (*1897*). A piece of paper which has been dipped in starch and potassium iodid solution is passed at a regular rate over two platinum electrodes. The author discusses at length the drawings obtained by using alternating or intermittent direct currents. The article contains many illustrations. *W. D. B.*

Gold, zinc and electrolysis. *E. Andreoli. Elektrochem. Zeit.* 4, *149* (*1897*). A description of the different methods of reducing gold from a cyanid solution and a discussion of the relative merits of the electrolytic process and the precipitation with zinc. *W. D. B.*

THE EQUILIBRIA OF STEREOISOMERS, I

BY WILDER D. BANCROFT

Duhem[1] has recently published a series of papers in which he has developed a theory of 'permanent changes' and has also shown the way in which this theory can be applied to explain the behavior of supercooled sulfur. There are many facts in organic chemistry which become more intelligible when considered from this same point of view. It will be better, for the purpose in hand, to substitute the graphical for the analytical method. Since the phenomena are all qualitative, no quantitative test of the theory is possible and the graphical method has the advantage of enabling one to take in the whole field at a glance. What we have then to consider is the form of the diagram for a system in which there are two modifications in equilibrium in the liquid phase. Suppose we have the two constituents α and β. If we introduce the limiting condition $\alpha \rightleftarrows \beta$, we are dealing with a one-component system. If we take into account the element of time there are then three possibilities. Equilibrium is reached practically instantaneously. No approach to equilibrium can be detected except under special conditions. Equilibrium is reached in a measurable length of time. In the first case the system will behave in all respects like any other one-component system. The second case presupposes a state of false equilibrium and will be discussed in a subsequent paper. In the third case the system will appear to contain two components provided we act rapidly enough and one component provided we act slowly. The concentration-temperature diagram

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[1] Zeit. phys. Chem. 22, 545; 23, 193, 497 (1897).

for such a system is given in Fig. 1. If the two constituents are the only solid phases which can occur and if two liquid phases are impossible, the diagram would consist solely of the boundary curves AD and BD provided neither constituent could change at all into the other. The curve AD shows the coexisting concentrations and temperatures for the α modification in equilibrium as solid phase with solution and vapor. The curve BD gives the corresponding values when the β modification is solid phase. Since the two constituents can change one into the other, these two curves can be realized experimentally only by working with a certain degree of speed. The line YX gives the relative concentrations of the two modifications at different temperatures after equilibrium is reached. This line cuts AD at X. At this temperature, therefore, the α modification can exist in stable equilibrium with liquid and vapor. This line represents, for liquid and vapor, what Duhem calls the "natural state."

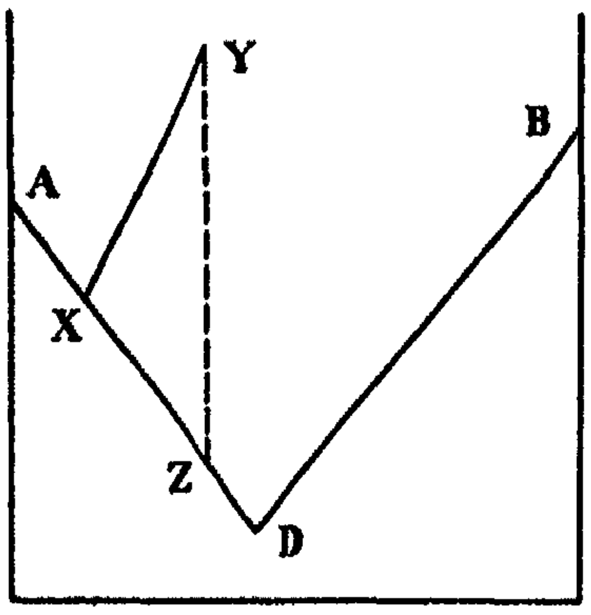

Fig. 1.

From the diagram we can make the following predictions. If we take the α modification and heat it quickly we shall find that it melts more or less sharply at the temperature denoted by A. On cooling the melt it will be found not to begin to solidify until a lower temperature is reached. What this temperature will be, depends in general on the temperature to which the liquid is raised and the length of time during which it is kept at that temperature. The cause for this change of freezing-point is the conversion of some of the α modification into the β modification, this latter lowering the freezing-point of the former just as any other substance would. If the α modification be just melted and cooled at once, the concentration will have changed but little, the freezing-point will have been lowered not more than a fraction of a degree in some cases and the system, solid, solution and vapor, will be represented by a point on AD lying very near A. By longer heating or by heating to a higher temperature and thus increasing the reaction velocity, the percentage of the β modification will be increased and the freezing-point lowered correspondingly. We will suppose next that we cool the system suddenly when the relative concentrations in the liquid phase are those represented by the point X. The α modification will separate at the temperature corresponding to X and the mass will solidify without change of temperature provided the further cooling be done with sufficient slowness. If the system be cooled rather rapidly and if the reaction velocity is low, the α modification will crystallize faster than the β modification can change back and the solution will become more concentrated with respect to the β modification. The freezing-point will fall and the system will pass along XD. One of two things is possible. Either the solution will solidify completely before the point D is reached, owing to the complete conversion of the β into the α modification or the β modification will appear as solid phase at the point D. If we do not cool the solution so much; but stop, for instance, at a temperature represented by the point Z, we shall find that the freezing-point of this solution rises with time owing to the β modification changing back into the α modification, diluting the solution. This rise of freezing-point will cease when the temperature of the point X is reached, the "natural" freezing-point of the system. If we fuse the α modification and keep the liquid at some temperature until equilibrium is reached, we shall then have the composition of the solution represented by the point at which that particular isotherm cuts the line YX. If we cool the system very slowly, there will be a gradual displacement of the equilibrium, the system will pass through the states represented by the line YX and the α modification will begin to crystallize at the temperature of the point X. If we have kept the system at the temperature of the point Y until equilibrium is reached and then cooled suddenly, the solid phase will not appear until the temperature of the point Z is reached. On standing, the freezing-point will rise more or less slowly to the temperature of the point X. If the line XY slant to the right, as in the diagram, raising the temperature to which the system is heated will lower the apparent freezing-point or temperature at which the solid phase first appears. If the line XY slants to the left, raising the temperature to which the system is heated raises the apparent freezing-point while this point will be independent of the temperature if the line XY is vertical.[1] It is assumed explicitly in each of these three cases that the system is kept heated at constant temperature until equilibrium is reached and that the cooling is sudden.

In order to obtain some of these changes it is not necessary to fuse the α modification. At any temperature above that of the point X the final state of stable equilibrium is represented by a point on the line XY. If the α modification be kept long enough at any temperature between that of the point X and that of the point Y, it will liquefy spontaneously. If we start with the pure β modification, melt it at the temperature of the point B and cool it suddenly, we shall find a lowering of the freezing-point due to the formation of some of the α modification. By prolonging the time during which the liquid is heated and then cooling suddenly, the system can be made to pass along the curve BD, the freezing-point falling continually. A little longer heating will cause the apparent freezing-point to rise, the system passing from D to X. At temperatures between those of the points D and B the β modification will liquefy spontaneously. If the temperature is below that of the point X, the liquid will solidify gradually to crystals of the α modification. If the tem-

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[1] If soluble sulfur be taken as the α modification and insoluble sulfur as the β modification, the line XY will slant first to the right and then to the left, the change of direction coming at about 170°.

perature is above that of the point X, liquid and vapor is stable state and no crystals will be formed. At temperatures below that of the point D the β modification will change into the α modification without liquefaction.

The α modification is therefore the stable one. The temperature of the point X would be the freezing-point and the melting-point of the crystals provided the equilibrium were reached instantaneously. In such a case it would be impossible to realize any of the curves ADB except the point X. In the case that we are actually considering, in which a measurable time is necessary before equilibrium is reached, the crystals which separate as the system passes along the curve AD will melt at the temperature of the point A if heated rapidly while the crystals which separate as the system along the curve BD will melt at the temperature of the point B if heated rapidly. If we define the triple point as the temperature at which solid, liquid and vapor are in stable equilibrium, we have in our hypothetical α modification a case in which a solid can be heated above the triple point. It is to be noticed that no assumption has been made as to the relative temperatures of the points A and B. If the temperature of the point B is higher than that of A we shall have a case in which the more stable modification is the one with the lower apparent melting-point. Ostwald[1] has recently called attention to the fact that, of two solid modifications, the higher melting one will be the more stable if only one liquid modification is formed. This conclusion ceases to hold if the assumption, made explicitly by Ostwald, is not applicable.

In the discussion, it has been shown what is to be expected when two liquid modifications are possible. It is possible, of course, to reverse the reasoning and specify what phenomena will suffice to enable us to predict the existence of two liquid modifications. If a solid substance melts at one temperature and freezes at another, this is proof positive of the existence of two liquid modifications provided no decomposition takes place. This test is applicable to all cases. There is another test which is

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[1] Zeit. phys. Chem. 22, 313 (1897).

absolute as far as it goes. If the more fusible of two solid modifications be the more stable, we are justified in deducing the existence of two liquid modifications. The difficulty with this is that the converse is not necessarily true. If the less fusible of two solid modifications be the more stable, it does not follow that only one liquid modification is possible.

In the preceding pages I have pointed out some of the conclusions which may be drawn when one applies to the general case the principles laid down by Duhem in his paper on the behavior of sulfur. It now remains to be seen how far these results can be verified experimentally. The first case that we will take up is that of stilbene dichlorid, $C_6H_5.CHCl.CHCl.C_6H_5$, studied by Zincke.[1] The *α* modification melts at 192–193° and can be sublimed between watch-glasses without decomposition. If heated above the melting-point, the freezing-point falls and can be dropped to 160–165°, but no lower. This is in exact accordance with the theory. The temperature of 192–193° is that of the point A, while the point X would then be denoted by 160–165°. From the experiments of Zincke, it is impossible to determine whether this range of five degrees at the point X is due to differences in the temperature of heating and a large displacement of the equilibrium with the temperature or whether Zincke was actually realizing part of the curve XD owing to the slow rate of change of one modification into the other. This however is immaterial as far as the general theory is concerned and is of interest merely when considering this particular case. The *β* modification melts at about 93°. When heated for a short time above its melting-point, there seems to be no change until the initial temperature of heating is about 160°. Then the freezing-point rises rapidly and soon reaches 160–165°, beyond which it cannot be forced. Here we have only partial confirmation of the theory. Our hypothesis requires that the freezing-point should first fall and then rise, remaining constant at the temperature 160–165°. Only the latter requirement, of the rise of freezing-point, was realized by Zincke. Fortunately this gap has been

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[1] Liebig's Annalen, 198, 115 (1879).

filled in by Lehmann.[1] He found that if the α modification were just melted and cooled at once, the freezing-point was lowered some five degrees. On heating for a longer time, the freezing-point rose again. Lehmann assumes the existence of a third modification in this case; but, under the circumstances, this is not probable. The explanation of Zincke's experiments would seem to be not that the substance remained unchanged on heating above the melting-point, but that he failed to cool the melt until after the freezing-point had begun to rise again and that the crystals which first separated in the neighborhood of 94° were really the other modification. It was only when he heated the substance to a higher temperature that the reaction velocity increased sufficiently to enable him to detect a noticeable rise of temperature. This explanation is made reasonably certain by the experiments of Lehmann, just referred to; but it is, of course, desirable that the experiments should be repeated by somebody. The fact that the α modification can be sublimed between watch-glasses seems to be a proof that two modifications exist in the vapor as well as in the liquid phase. This has been shown to be true in other cases.

Each of the two stilbene dichlorids has been isolated as solid phase and the one with the higher melting-point has been found to be the more stable. With acetaldoxime, $CH_3CH:NOH$, the higher melting modification is the more stable; but the other or β modification has not yet been obtained as a solid. Acetaldoxime has been studied rather carefully by Dunstan and Dymond.[2] I quote from their second paper, p. 209: "The pure acetaldoxime boils at 114.5° (corr). and, when supercooled in ice after having been recently distilled, it almost entirely solidifies to a mass of long, stout, acicular crystals, which, if pressed quite free from adhering liquid, melt at 46.5° (corr.); the entire mass melts several degrees lower. ... When these crystals are melted, and the liquid is kept at the melting-point for a short time, it does not solidify until it has been cooled several degrees below the temperature at which the crystals melted, even if a

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[1] Molekularphysik, I, 206.

[2] Jour. Chem. Soc. 61, 470 (1892); 65, 206 (1894).

crystal of the original substance is introduced into it. The longer the liquid is heated in this way, the greater is the reduction of the freezing-point, but the maximum reduction it has been found possible to effect is to 13°, that is, 33.5° below the melting-point of the original substance. The fall to this point occurs slowly when the temperature is near that of melting, but if the original liquid is heated at 100°, the change is rapidly brought about and freezing cannot be effected above 13°, by "touching off" with a crystal. No chemical decomposition accompanies the change; the liquid freezing at 13° distils constantly at 114.5°, and furnishes, on combustion, the same data as the original crystals. The liquid thus produced does not, however, consist entirely of a new modification of acetaldoxime; it behaves as a solution of the solid oxime in a liquid modification. The liquid does not completely solidify, and the crystals which separate from it at 13° consist of the original modification; when pressed quite free from adhering liquid, they melt at 46.5°. The residual liquid, when further cooled, yields more of these crystals, and by repeating the process, the whole of the liquid may be obtained as the crystalline modification. At all temperatures an equilibrium seems to be established between the two modifications; the lower the temperature, the more of the crystalline form is produced and vice-versa.[1] Although it is possible to separate the solid modification in a pure state, no method we have tried has been successful in leading to the isolation of the pure liquid."

This quotation shows that the theory is applicable to this particular instance. Referring back to the diagram Fig. 1, the point A denotes the melting-point of the crystals 46.5°; the melt is found to begin to solidify at temperatures varying between 46.5° and 13°, the point X of the diagram, depending on the length of heating and the highest temperature reached. The liquid does not solidify entirely at the temperature of X and the

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[1] This conclusion, though a very natural one, is not really justified by any of the facts discovered by Dunstan and Dymond. Subsequent work in my laboratory by Mr. Carveth has shown that the equilibrium is practically independent of the temperature.

authors have realized a small portion of the curve XD. They have not noticed that solutions which had been cooled, say to 0°, would freeze some days later at a higher temperature; but they do record that the whole of the liquid mass can be converted into crystal in time. Here the lowering of the freezing-point of the crystals takes place so slowly at 46.5° that no precautions are necessary to determine the melting-point of the crystals. We shall see later that this is not always the case. Freezing-point determinations in benzene and in acetic acid showed that the crystals and the liquid had the same molecular weight. It was also noticed that the solid acetaldoxime will liquefy spontaneously on standing at ordinary temperatures. Propionaldoxime behaves like acetaldoxime.[1] The α modification melts at 21.5°; the temperature at which solid, liquid and vapor are in equilibrium is $-11.5°$; the crystals liquefy spontaneously at 0°; the β modification has never been obtained in the pure state.

With benzaldoxime, $C_6H_5CH:NOH$, we have the higher melting form the less stable. Our knowledge of this substance is due in large part to Beckmann[2] and to Luxmoore.[3] The α modification melts at 34° and the β modification at 130°. The stable triple point has not been determined; but the crystals obtained are the α modification. Since the temperature of the stable triple point is lower than room temperature, both of the modifications should liquefy spontaneously. This is the case experimentally, though Beckmann states that if the β modification be obtained absolutely pure, it may be kept for a very long time at ordinary temperatures without liquefying.

The peculiarity of forming two mutually convertible isomers is characteristic of most of the oximes, and it is very often the lower melting form which is the more stable. As yet another example, we may take the *p*-anisaldoxime.[4] The α modification

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[1] Dunstan and Dymond. Jour. Chem. Soc. 65, 221 (1894).

[2] Ber. chem. Ges. Berlin, 20, 2766 (1887); 22, 429 (1889); 23, 1680 (1890).

[3] Jour. Chem. Soc. 69, 177 (1896).

[4] Beckmann. Ber. chem. Ges. Berlin, 25, 1680 (1890); Goldschmidt. Ibid. 23, 2163 (1890).

melts at 61–62° and is the more stable. The β modification melts at 133° and changes over slowly if kept at its melting-point. It would be easy to fill pages with accounts of other oximes each furnishing further proof of the applicability of Duhem's theory; but it will be more profitable not to confine ourselves to one class of compounds.

Phenylisonitromethane, $C_6H_5CH_2NO_2$, melts at 84° if heated rapidly.[1] On standing it changes spontaneously into an oil. In a benzene solution it was found that the iso-compound at first gave values for the reacting weight much higher than the normal. On standing, the freezing-point fell slowly till the normal depression was reached. From this the authors conclude that the reacting weight of the iso-compound is double that of the other compound. This is rather unusual. In the vast majority of cases the reacting weights of the two modifications have proved identical. In this particular case the result is still more surprising because the normal compound does not conduct while the iso-modification is an acid about as strong as acetic acid. Of course, it is possible that the explanation of the anomaly is due to this very fact since organic acids give abnormally high values in benzene solution. Bromphenylnitromethane melts at 60° and is stable. The iso-compound melts at 89–90° and changes spontaneously into the lower melting form.

The so-called α dimethyl ketol or ketoxybutane,[2]

$$CH_3CO.CHOH.CH_3,$$

is an oil which crystallizes after long standing. The crystals are known as the β modification and melt at 127–128°. If the β modification be kept heated for a while and then cooled, the original oil is obtained which, in the course of time, solidifies as before. If the freshly cooled oil be stirred vigorously with something rough, such as a piece of zinc, crystals are formed which melt at 96–98° and are known as the γ modification. These γ crystals liquefy spontaneously to an oil which finally solidifies to the β crystals. All three forms give a liquid

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[1] Hantzsch and Schultze. Ber. chem. Ges. Berlin, 29, 699, 2251 (1897).

[2] v. Pechmann and Dahl. Ber. chem. Ges. Berlin, 23, 2425 (1890).

boiling at about 140–142°. It is obvious that the α modification is merely a mixture of the β and γ modifications. The β modification is the stable one and the stable triple point (X in Fig. 1) lies between the ordinary temperature and 127°. With the γ modification we have a striking instance of the case which was illustrated rather unsatisfactorily by the β modification of stilbene chlorid, namely of a spontaneous lowering of the freezing-point followed by a spontaneous rise. With the β stilbene chlorid, the lowering was only some four or five degrees. With the γ dimethyl ketol it is at least a hundred degrees. The crystals liquefy spontaneously and then the liquid solidifies to the other kind of crystals. We must also have a marked change of the equilibrium with the temperature. If this were not the case, the freezing-point of the β modification could be lowered by heating only to about the neighborhood of the stable triple point while, as a matter of fact, the equilibrium is displaced to such an extent that the γ crystals are the first to appear. If, in Fig. 1, the line XY had been slanted still more so that the projection of Y, the point Z, had fallen on the curve BD we should have the state of things which has been found by v. Pechmann and Dahl. We may draw yet another interesting conclusion from these experiments. It is no uncommon thing to read that 'an oil was obtained which gradually crystallized after standing three or four weeks in a vacuum desiccator'. It would advance the science very much if, under these circumstances, people would distinguish between the two sets of conditions which may have existed. It is possible that, in any given case, the oil did not crystallize because no crystals were present to start the reaction. Under these circumstances one must wait until what seems like chance starts the crystallization. This is the state of the freshly cooled dimethyl ketol and the γ crystals. The solution is supercooled with respect to them and yet the crystals do not form readily. This is the state of things which is tacitly assumed to exist in almost all cases where one obtains oils which crystallize later. The second possibility is that two liquid modifications occur and that the oil cannot crystallize at once. Since the reaction velocity may be very low, it might well be weeks before the oil was in a state of superfusion. This can be realized also with the freshly cooled dimethyl ketol. In the course of time crystals of the β modification do separate; but it would be no use to add one of these crystals at the beginning because it would dissolve, the relative concentration, at that time, being such that the solution is supercooled with respect to the γ crystals and not with respect to those of the β modification. It would be a very simple matter for an organic chemist to decide between these two alternatives. All he has to do, after his oil has solidified, is to take out three or four crystals, heat the rest of the mass, cool it quickly and, as soon as it is cold, throw in one of the crystals. If the crystal dissolves he has two liquid modifications. If the crystal grows he can draw no conclusion. If his crystal disappears, all he has to do is to wait a suitable length of time and then add another crystal.

Returning from this digression we will next consider the experiments of Grünhagen[1] on the behavior of diorthotoluidin methylene, $(CH_3C_6H_4.NH_2)_2CH_2$. An oil is obtained that, on standing, changes slowly into the β modification which melts at 135°. The reverse change was not noticed, presumably because it was not looked for. Diparatoluidin methylene separates also as an oil which solidifies slowly to the β modification melting at 156°. In all probability these two instances differ from that of the dimethyl ketol chiefly in that the α compounds have not yet been obtained as solids. It should be noticed, however, that the evidence is indirect and not conclusive.

A more interesting case is that of formylphenylacetic ester,[2] $HCO.CH.C_6H_5.CO_2C_2H_5$. The solid modification melts at 69–70°. At ordinary temperatures the solid liquefies spontaneously, while at lower temperatures (no figures given) the liquid changes back into crystals. This is precisely analogous to the behavior of acetaldoxime.

Krückeberg[3] has found that α benzazocyanacetic ester,

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[1] Liebig's Annalen, **256**, 285 (1890).

[2] W. Wislicenus. Ber. chem. Ges. Berlin, **20**, 2930 (1887); **28**, 767 (1895).

[3] Jour. prakt. Chem. (2) **46**, 579 (1892); **47**, 591 (1793); **49**, 321 (1894). Cf. Haller. Comptes rendus, **106**, 1171 (1884).

$C_6H_5N_2HC.CN.CO_2C_2H_5$, melting at 125°, changes into the β modification, melting at 82°, by continued heating to 130°. The two modifications have practically the same solubility in alcohol, while in benzene the β modification is about twelve times as soluble as the other. A third isomer melting at 106–108° is merely a mixture of the other two. Two modifications of *o*-tolueneazocyanacetic ester are known. The α crystals melt at 85° and change readily into the β crystals melting at 133°. Here the form with the higher melting-point is the more stable. On the other hand the α crystals of *p*-tolueneazocyanacetic ester melt at 116–118°, while the more stable β crystals melt at 74–75°. With *m*-xyleneazocyanacetic ester and pseudocymeneazocyanacetic ester the α modifications melt at 74–75° and 100° respectively, while the more stable β modifications melt, one at 166°, and the other at 136°.

It has been shown by v. Baeyer and Villiger[1] that the *cis*-lactonic acid of the oxydimethyltricarballylic acid,

$$(CH_3)_2C.CO_2H.CH.CO_2H.CHOH.CO_2H,$$

melts at 207°, and that after fifteen hours heating at 150° nine-tenths of it is converted into the *trans*-modification melting at 211–212°. On heating, the latter goes back to a certain extent into the former. Kjellin[2] found that diazoniumacetacetic ester, $C_6H_5N_2.HC.COCH_3.CO_2C_2H_5$, melts at 80–84° if heated rapidly and that the freezing-point drops to below 50°. He did not succeed in obtaining the second isomer as a solid phase. The less stable form of *o*-chlordiazoniumacetacetic ester melts at 83°, the more stable form at 62–63°, while the temperature of the stable triple point seems to be about 59°. It is of interest to note that the more stable modification is about four times as soluble in ligroïn as the other. Only one solid isomer of *s*-tribromdiazoniumacetacetic ester has been isolated, but its melting-point is 121–123°, while the freezing-point may drop as low as 95–107°.

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[1] Ber. chem. Ges. Berlin, 30, 1958 (1897).

[2] Ber. chem. Ges. Berlin, 30, 1965 (1897).

Raikow[1] describes two forms of α-methyl cinnamic acid, $C_6H_5.CH:CCH_3.COOH$, the more stable melting at 82°, the other at 74°. Claisen[2] reports that dibenzoyl acetone,

$$(C_6H_5CO)_2HC.CO.CH_3,$$

80–81°, crystallizes from hot alcohol as the isomer which melts at 109–112° on rapid heating and at 107–110° when heated more slowly. The reverse change can be brought about by heating with carbon tetrachlorid. Here we are dealing with the effect of the solvent and we are handicapped by having very little information in regard to the behavior of the pure substances. For this reason it is possible merely to call attention to this as a case well worthy of careful study.

According to Walther[3] β-diazoamidobenzene, $C_6H_5N_2NHC_6H_5$, melts at 81° and, on heating, changes into the α modification which melts at 98–100°. Kipping[4] says of benzylidenehydrindone, $C_6H_4:(CH_2)(CO)C:CHC_6H_5$: "The crystals obtained from a solution of benzylidenehydrindone in a mixture of chloroform and light petroleum melt sharply at 109–110°; if, however, after the substance has solidified, it is reheated, it melts at about 90°, but not always completely, the remainder melting at 109–110°. In some cases the portions which have been melted once, begin to liquefy at 90° and then, although the temperature is rising, gradually become completely solid, melting for the second time at 109–110°; it is also a curious fact that the presence of the liquid formed by the crystals melting at 90° does not lower the melting-point of the modification which liquefies at 109–110°; on keeping the crystals of lower melting-point at ordinary temperatures, they are transformed into the more stable modification." This is not entirely clear, but the case would seem to be analogous to that of dimethyl ketol. On heating the stable or 110° modification above its melting-point the equilibrium is displaced so much that, on cooling, some of the other modification

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[1] Ber. chem. Ges. Berlin, 20, 3396 (1887).
[2] Liebig's Annalen, 277, 184 (1893).
[3] Jour. prakt. Chem. (2) 55, 548 (1897).
[4] Jour. Chem. Soc. 65, 499 (1894).

separates. I am inclined to consider 90° as the eutectic point of the two modifications, corresponding to the point D in Fig. 1. The temperature of the stable triple point evidently is about 109–110° and coincides very closely with the melting-point of the stable compound, unless, as is possible, the stable modification could be made to melt higher by more rapid heating. The less stable modification, according to this hypothesis, would melt at some temperature above 90°, and it is a pity that it was not obtained pure. Kipping recognized that a second modification was formed. This is not always the case. I find a statement[1] that the methyl ester of mucophenoxybromoxime,

$$C_4H_2(OC_6H_5)BrNO_3CH_3,$$

melts at 168–170° when heated very rapidly and at 150–165° when heated slowly. Mucophenoxybromoxime anhydrid melts at 124–126° or 121°, depending on the rate of heating. The corresponding figures for phenoxybrommaleinimid are 148–150° and 144–145°; for the methyl ester of mucophenoxychloroxime they are 162–166° and 156–160°. Since no mention is made of any decomposition, it seems certain that each of these substances exists in at least two modifications. Unfortunately this was not perceived by the authors and they did not investigate the phenomena.

Sudborough[2] has noticed some very curious facts which he has not studied with care. Chlorstilbene, $C_6H_5.CCl:CCl.C_6H_5$, occurs usually as an oil. On heating, this oil solidifies, forming crystals which melt at 54°. A similar change occurs with methyl chlorstilbene, $C_6H_5.CCH_3:CCl.C_6H_5$, the crystals melting at 117–118°. Since no mention is made of a reverse reaction, these experiments will have to be repeated.

The most valuable single experimental paper on two liquid modifications with which I am familiar is one by J. Wislicenus.[3] He is the only man who seems to have any real appreciation of the importance of determining experimentally the conditions necessary for the change of one isomer into another. In the

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[1] Hill and Widtsoe. Am. Chem. Jour. 19, 631 (1897).

[2] Ber. chem. Ges. Berlin, 25, 2237 (1892).

[3] Dekanatsschrift, Leipzig, (1890).

paper just referred to, there is much material to which Duhem's theory applies. When maleic acid, $CO_2H.CH:CH.CO_2H$, is heated just above its melting-point, it changes slowly into fumaric acid, the more stable modification. The reverse change is not realizable experimentally because the temperature of the stable triple point lies above 200° (apparently about 225°) and, at this temperature, maleic acid cannot exist. Fumaric acid changes therefore into the decomposition products of maleic acid, namely maleic anhydrid and water.[1] Not having the theory to guide him, Wislicenus did not notice that the freezing-point of the fused maleic acid dropped at first and began to rise only when the fumaric acid begun to crystallize. There can be no doubt that this takes place. The tolanedibromid, $C_6H_5.CBr:CBr.C_6H_5$, melting at 205°, is the more stable form, the one melting at 68.5° the less stable. A liquid mass is obtained if either modification be kept long enough at 180°; a solid mass is obtained if either modification be kept long enough at 160°. The temperature of the stable triple point cannot be far from 170°. At each temperature at which liquid is possible, a definite equilibrium is reached.[2] This was easily shown experimentally, because the lower melting form is about one hundred and twelve times as soluble in alcohol as the other. Tolanedichlorid occurs in two forms, one melting at 143°, the other at 63°. On heating, each changes partly into the other. Experiments are also given to show the rate at which each of the α-chlorcrotonic acids, $CH_3.CH:CCl.COOH$, changes into the other, also for the two β-chlorcrotonic acids, $CH_3.CCl:CH.COOH$.

These instances are sufficient to show the varied nature of substances to which Duhem's theory is applicable and the way in which it is to be applied when we are considering the pure substances only. In the second paper I shall take up the question of stability when another component is added, which may or may not form compounds with the two modifications.

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[1] If fumaric acid is sublimed at temperatures below that of the stable triple point, it passes over unchanged. Cf. Tanatar. Liebig's Annalen, 273, 32 (1892).

[2] This must be the case because we have one component and two phases.

ACETALDOXIME

BY HECTOR R. CARVETH

The experiments of Dunstan and Dymond[1] upon the freezing-point of acetaldoxime brought out so many unexpected phenomena that it seemed worth while to repeat their observations, supplementing them wherever necessary. The writer's results corroborate those of Dunstan and Dymond in every detail. The oxime was prepared by mixing equivalent quantities of aldehyde ammonia and hydroxylamine hydrochloride, extracting with ether, drying with calcium chloride, distilling off the ether and purifying the residue by fractional distillation. The fraction boiling at 114.5° is a liquid which remains unchanged at ordinary temperatures but solidifies partially when cooled in ice. When the crystals are dried thoroughly, preferably on a filter plate which is kept cold, they show a melting-point of 47° if heated fairly rapidly. If one keep the tube containing the liquid at this temperature for a short time, say a minute, and then take it out into the air it will be noticed that, although the contents solidify, they do not present the same crystalline appearance as before. Some liquid is present with the crystals, although it may be only to a very slight extent. When the melting-point is taken again, it is found to be lower than the original one and by no means so sharply defined. On repeating the operations of melting and freezing, one arrives finally at a point where the liquid in the capillary melting tube does not solidify at ordinary temperatures but does when cooled to 13°. A set of measurements taken from my note book will illustrate this; the acetaldoxime was in a sealed capillary tube to prevent possible absorption of moisture.

'Crystals thoroughly dried in capillary tube showed M. Pt.

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[1] Jour. Chem. Soc. 61, 471 (1892); 65, 206 (1894).

47°. Crystallized on being taken out into air, immediately after melting. Heated for five minutes at 55°. Solidified in the air (19°). Remelted at 42°. Again solidified in the air. Melting-point now becomes uncertain, starting at 36° and melting completely at 41.5°. Resolidified in air. Upper part begins to fuse at 31°, all melted at 40°. Other consecutive fusion points are 28°, 26°, 22°, 18.7° and finally, on allowing to stand several days in the sealed capillary, it remains liquid at ordinary temperature.'

Such peculiar behavior suggests the idea that probably the acetaldoxime was contaminated by some other substance or that a depolymerization had taken place. This question has, however, been settled by Dunstan and Dymond. They studied the crystals and the liquid with care and found that the two had the same boiling-points and gave practically the same depressions of the freezing-point in benzene and in acetic acid. No difference could be detected analytically. Moreover, by freezing the oil, draining off the liquid and freezing again, it was found possible to convert practically all the liquid into the solid modification. These results alone would show the insufficiency of Franchimont's[1] objection that the non-crystallization of the oxime is due to impurities. The work of Bourgeois and Dambmann[2] is also important in its bearing on this point. By changing the oxime into an imidosulfonic acid, they obtained it ultimately in a state of undoubted purity. They then state that their observations on acetaldoxime and on propionaldoxime are in accord with those obtained by Dunstan and Dymond.

From the experiments of the writer it was apparent that the duration in time of heating and the temperature at which this was done exercised an influence on the freezing-point. Accordingly the crystals were melted and distilled quickly at the normal boiling-point (114.5°); the liquid froze at 13° instead of at 47°. With many—probably most—other oximes a similar result is obtained, the distillate beginning to freeze at one temper-

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[1] Recueil Trav. Pays-Bas, 10, 236 (1892).

[2] Ber. chem. Ges. Berlin, 26, 2856 (1893).

ature while the crystals melt at a much higher temperature—the melting-point of the original crystals.

It was noticed that when the acetaldoxime froze at 13°, it did not act like a pure substance. It did not solidify at constant temperature. There was always considerable liquid left which, when drained off rapidly, began to freeze only at temperatures below 13° provided the measurements were made the same day. Repeating the process of freezing and draining off the mother-liquor four times gave a liquid which began to solidify at 8°. When the crystals obtained from this liquid had been thoroughly and carefully dried, they showed a melting-point of 47°. If, however, the liquid is distilled after each draining, it is found to boil at 114.5° and to crystallize, on cooling, at 13°. If the liquid with a freezing-point of 8° be allowed to remain for several weeks at ordinary temperatures, the freezing-point will rise to the original value of 13°. No theoretical significance attaches to the lowest freezing-point obtained since it was only the smallness of the amount of material at command which prevented lower values from being obtained.[1] It is evident that it is not impurities which cause such variations of the freezing-point. The material is always pure acetaldoxime and the freezing-point depends on the previous history of the compound.

In this displacement of the freezing-point, acetaldoxime does not stand alone. Dunstan and Dymond observed similar phenomena with propionaldoxime. This substance melts at +21.5° After distillation, the liquid begins to freeze at −11.5° while, by further cooling, it is possible to obtain a liquid which does not begin to solidify at −21°. They make no mention of a gradual rise of freezing-point and assume that they had a solution of the solid in the liquid oxime at this lowest temperature.

Although the rate of change of the freezing-point of acetaldoxime is a function of the temperature to which the substance is heated, the final equilibrium is independent of the temperature. It has already been noticed that heating to 114.5° causes the freezing-point to drop from 47° to 13°. If the crystals are kept

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[1] In other experiments the freezing-point has been forced below 0°.

long enough at 20° they will liquefy and if the liquid is allowed to stand for ten days or so and then cooled, the freezing-point will be found to be 13°. In other words, the equilibrium is not displaced by the temperature. Dunstan and Dymond assumed that it was; but that was because they paid little or no attention to states of stable equilibrium.

The explanation of these apparently abnormal results is a very simple one. We have merely to assume an equilibrium in solution between two modifications of acetaldoxime with the further proviso that equilibrium is reached fairly slowly at ordinary temperatures. We can then predict all the phenomena that have been observed. The general theory of such cases has been outlined by Professor Bancroft[1] so that it will only be necessary to make a very brief reference to it here. If we designate the crystals melting at 47° as the α modification and the unknown form as the β modification, the experimental data will be represented by the diagram, Fig. 1. The line AXH represents the compositions of the solutions which can coexist temporarily, with the α crystals. The line YX represents the relative concentrations of the two modifications in the solution phase when the system is in equilibrium. This line runs parallel to the axis of ordinates because it has been shown that the equilibrium

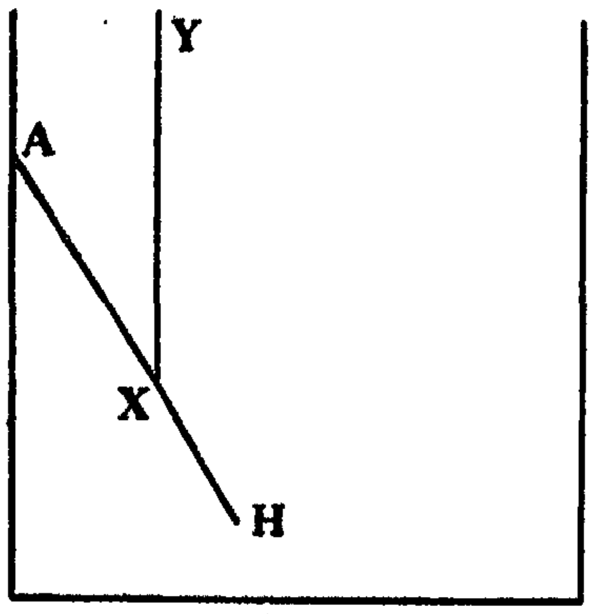

Fig. 1.

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[1] Jour. Phys. Chem. 2, 143, (1898).

is not displaced by change of temperature. This involves the additional conclusion that the heat of transformation of one modification into the other is zero. The absolute position of the line YX cannot be given because there is, as yet, no analytical method for determining quantitatively the relative amounts of the two modifications. The constant boiling-point shown by all solutions quite independently of the initial temperature of freezing, is to be interpreted as due to the fact that equilibrium is reached with great rapidity at 114.5°. This conclusion is confirmed by the fact that all solutions that have been heated above 100° begin to freeze at 13° regardless of the length of heating at the higher temperature.

In the diagram, the point A denotes the melting-point, 47°, of the crystals while X is the stable triple point with a temperature of 13°. It was not possible to pass down the curve AXH to the point at which the β modification separates as solid phase because the solution at 13° contains so little of the second form that there is practically no liquid left after the system has been cooled a little below zero degrees. Some semi-quantitative measurements on the relative masses of solid and liquid after different rates of cooling will illustrate this. The ordinary method of drawing off liquid from crystals is not really of sufficient accuracy for such an experiment; but some results have been obtained which will give a general idea of the phenomena. In the first three experiments a weighed amount of the oxime was put into a Brühl filtering apparatus, partially frozen, and kept at a stated temperature for some time ; then drained and the liquid and solid weighed separately.

1. Liquid frozen and kept at 9° for 24 hours.
   Solid 3.8 g; liquid 6.0 g.
2. Liquid frozen and kept at 0° for 1 hour: then kept at 9° for 24 hours.
   Solid 4.5 g; liquid 3.3 g.
3. Liquid frozen and kept at 0° for 2.5 hours.
   Solid 8.3 g; liquid 2.6 g.
4. Kept liquid in ice-box six weeks; no liquid could be drained off by means of an ordinary pressure pump.

All the experiments which have been made by Dunstan and Dymond or by the writer show that above 13° the solution is the stable form and below it the crystals which melt at 47°. Franchimont[1] reports that he obtained the α modification by crystallizing from ether at ordinary temperature. This seemed sufficiently surprising to warrant repeating the measurements. The results are exactly as he says and yet his statement is misleading, not to say inaccurate. If acetaldoxime be dissolved in ether and the solution allowed to evaporate spontaneously in a watch-glass, a crystalline residue is obtained. If one places a thermometer in the solution, one finds that the spontaneous evaporation has cooled the liquid below 13° and it is therefore not surprising that crystals are formed. If the solution evaporates at the constant temperature of 18° the acetaldoxime remains as a liquid and no crystals are formed.

Measurements were made to ascertain whether any change of vapor pressure could be detected as the solid liquefied. Two methods were used, the direct measurement by the Ramsay and Young method,[2] and the differential method of Andreae.[3] By direct measurement no difference could be detected. The corresponding temperatures and pressures are given in Table I, the pressures being in millimeters of mercury.

TABLE I

Temp.	Press.	Temp.	Press.
20°	8	30.2°	14
23	9	32.7	16
25.4	10.3	35	18
27	11.5	38	21.2
28	12.2	41	25

The differential method gave more positive results. When one arm of the apparatus held the solid and the other liquid, it was observed that after 24 hours at 18–20° the solid had become liquid and had lost one milligram in weight which corresponded

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[1] Recueil Trav. Pays-Bas, 10, 236 (1892).
[2] Phil. Trans. 175, 37 (1884).
[3] Zeit. phys. Chem. 7, 241 (1891).

exactly to the gain in weight of the other arm. In a second experiment the differential apparatus was kept in the ice-box for some time. Being undisturbed, the liquid remained supersaturated for some days. After ten days the weighings were taken and it was found that the solid had increased in weight very slightly, about 0.7 milligram, while the liquid had lost in weight. From this one may conclude that the vapor pressure of the liquid is lower than that of the solid above 13° and higher than it below this temperature. Since the difference between the vapor pressures is very small at any temperature, it is to be expected that the rate of change will be very slow. The writer has observed, after keeping a test-tube containing acetaldoxime at 0° for six weeks, that there were still traces of liquid upon the crystals.

It must be kept in mind that the theory requires that the total vapor pressure of the solution be less than that of the solid above 13° and greater than it below that temperature only in case there is but one modification in the vapor. It has already been shown that two modifications of acetaldoxime are present in the liquid phase and there is evidence in favor of the view that two modifications exist in the vapor phase as well.

When distilling under diminished pressure, the products of the distillation depend on the nature of the substance in the distilling flask. When starting with a liquid freezing at 13°, the distillate freezes at 13°. On subliming the solid under diminished pressure, it was noticed that in the arm of the condenser, which was at 20°, there was formed a solid. This became liquid in the course of time, as did also the solid in the distilling flask. It seems probable that the distillate has the same composition as the substance in the distilling flask. In other words, the same change takes place in the vapor as in the liquid and the same equilibrium is reached in the two cases. The difference between the vapor in equilibrium with the solid at say 20° and that in equilibrium with the liquid at the same temperature, may be one of partial pressures and not one of total pressures. On the other hand, it must be remembered that the argument from the nature of the distillate is not conclusive with regard to the vapor. The distillation of arsenic and of benzophenone are cases in point. The formation of an instable form by distillation is not accepted as a proof of the existence of two kinds of vapors any more than the precipitation of yellow mercuric iodide by water proves the existence of two modifications of mercuric iodide in a methyl alcohol solution. While admitting the force of this argument, there are reasons for believing that it does not apply in the case of acetaldoxime. The fact that the nature of the distillate varies continuously with the nature of the distilling substance, would seem to exclude the possibility of serious disturbing effects due to a spontaneous appearance of a metastable phase. It must also be admitted that the existence of two liquid modifications in equilibrium makes the existence of two modifications in the vapor very probable.

Some experiments were made to determine whether the equilibrium between the two modifications in the solutions was displaced by acetone. Acetaldoxime is an especially good case for such an experiment because the line YX is parallel to the axis of coordinates. If acetone be added to the liquid freezing at 13° and the freezing-point be determined at once and again after some time has elapsed, the second freezing-point will coincide with the first or it will not. If the two readings are the same, no displacement has occurred. If the second reading is higher than the first, the acetone has caused the formation of more of the α modification at the expense of the β form. If the second reading is lower than the first, the reverse reaction has taken place. Unfortunately the amount of pure acetaldoxime available for this experiment was only about ten grams, and it was not found possible to determine the freezing-points with sufficient accuracy to warrant any conclusion being drawn. An excess of acetone was then added and the solution cooled in a mixture of solid carbonic acid and ether. Even at the lowest temperature, about −80°, the crystals which separated were the α modification. From this the conclusion may be drawn that acetone does not displace the equilibrium markedly to the side of the β modification.

It is well known that sunlight changes soluble into insoluble sulfur under certain conditions, and a flask containing acetaldoxime was placed in the sunlight every day for some time in hopes that the contents of the flask might solidify. No effect could be detected.

The results of this paper may be summarized as follows:

1. All the freezing-point phenomena can be accounted for on the assumption of an equilibrium between two modifications in the liquid phase.
2. The relative amounts of these two modifications is *not* a function of the temperature.
3. It is probable that two modifications exist in the vapor.
4. The liquefaction of the crystals is not accompanied by a measurable change of vapor pressure.
5. The temperature of the stable triple point is 13°.
6. Sunlight does not produce any visible effect.
7. The β modification does not crystallize from acetone solution even at about $-80°$.

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NAPHTHALENE AND AQUEOUS ACETONE

BY HAMILTON P. CADY

At the suggestion of Prof. Bancroft I have made a partial investigation of the system naphthalene, acetone, and water. The acetone used was purified by drying with calcium chlorid and fractionating. The naphthalene was recrystallized from alcohol. The mixtures of acetone and water were made up so as to contain approximately 10, 20, 30, 40, 50, 60 and 70 percent of acetone by weight. Naphthalene in excess was added to each solution and the temperatures determined at which a second liquid phase first appeared. In order to determine the composition of the liquid phase at this point, the following method was adopted: A weighed quantity of naphthalene was added to a known weight of the mixed liquids, the amount being just sufficient to cause the formation of two liquid phases. The consolute temperature of the system was then determined, and the experiment repeated several times with different amounts of naphthalene. If the results are plotted using the weights of naphthalene in a constant quantity of the mixed liquids as abscissas and the temperatures as ordinates, we shall get a series of curves. The composition of the liquid phase at the moment when the system passes from solid, solution and vapor to solid, two solutions and vapor is given by the point at which the prolongation of the curve for that particular mixture of acetone and water cuts the ordinate for the temperature at which the change takes place. This method requires no analyses and is of advantage in this case where ordinary quantitative analysis would be very difficult. The method involves but one assumption, that the field for two liquid phases and vapor lies within the boundary curve. Preliminary experiments showed that this was the case for no unsaturated solution of naphthalene, acetone and water could be found which formed two liquid layers upon heating.

Considerable difficulty was experienced in determining the consolute temperatures. Owing to the volatility of the acetone the solutions could not be heated in corked test-tubes. Pressure flasks were tried but proved unsatisfactory for, sooner or later, they would leak and perhaps spoil a series of determinations. It was finally found necessary to seal each mixture of aqueous acetone and naphthalene in a glass tube. This was, of course, a laborious process since separate tubes had to be made for each determination.

The experimental data are given in Tables I-III. In Table I are given the percentage acetone in the aqueous acetone, the amounts of naphthalene added to one hundred grams of the aqueous acetone and the corresponding consolute temperatures for the resulting solutions. In Table II are the temperatures at which different solutions begin to separate into two layers in presence of solid naphthalene and the compositions of these solutions. In Table III are the data for portions of various isotherms, obtained by interpolation from the figures in Table I.

Table I

Percentage acetone.	Naphthalene in 100 grams solvent. Consolute temperatures.					
10.01	0.109	78°	0.125	85°	0.127	90°
19.94	0.368	83	0.433	92	0.447	94
30.04	0.585	61.1	0.674	68	0.801	74
41.20	1.038	41	1.587	67.4	3.745	100.5
49.99	2.790	39.2	4.019	58	4.960	74
60.33	7.082	39.3	7.383	43.2	7.901	49.8
70.12	16.067	28.2	17.978	49	....	....

Table II

Acetone	Water	Naphthalene	Temperature
10.00	89.92	0.08	65.5°
19 91	80.00	0.09	55.3
29.92	69.67	0.41	45.0
40.81	58.22	0.97	38.0
48.67	48.68	2.65	32.2
57.43	36.64	5.93	28.5
60.43	25.75	13.82	28.2

Table III

$(CH_3)_2CO$	70°	10.01	19.88	29.84	40.53	47.73
H_2O		89.90	79.89	69.46	57.82	47.76
$C_{10}H_8$		0.09	0.23	0.70	1.65	4.51
$(CH_3)_2CO$	60°	19.93	29.87	40.62	47.97	56.04
H_2O		79.95	69.56	57.96	48.02	35.75
$C_{10}H_8$		0.12	0.57	1.42	4.01	8.21
$(CH_3)_2CO$	50°	29.91	40.72	48.23	56.55	
H_2O		69.63	58.08	48.28	36.08	
$C_{10}H_8$		0.46	1.20	3.49	7.37	
$(CH_3)_2CO$	40°	40.79	48.43	56.99	59 65	
H_2O		58.20	48.49	36.34	25.31	
$C_{10}H_8$		1.01	3.18	6.67	15.04	
$(CH_3)_2CO$	30°	57.36	60.35			
H_2O		36.58	25.70			
$C_{10}H_8$		6.06	13.95			

The addition of a very small quantity of naphthalene raises the consolute temperature so much that, if isotherms 10° apart be plotted on triangular coordinate paper, the curves lie so close together as to be indistinguishable for the greater part of their course. For this reason it was not deemed advisable to represent the results graphically. In the solid diagram with the temperature measured along the vertical axis, the surface for two solutions and vapor would rise almost perpendicularly from the boundary curve.

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INDICATORS

BY JOHN WADDELL

According to the dissociation theory an indicator must be a weak base or a weak acid in which one of the ions has a different color from that of the undissociated substance.[1] Under these circumstances, the presence in the solution of a liquid in which the indicator dissociates to a less extent than in water should cause the color due to the ion to disappear more or less. This is a familiar phenomenon with salts. A solution of cobaltous chloride in alcohol is blue;[2] addition of a few drops of water turns it pink, while the blue color can be brought back again by adding ether. With some indicators addition of alcohol does not cause the disappearance of the color due to the ion. Since substances do dissociate electrolytically in alcohol, it does not follow that the theory is defective. No such explanation would apply in the case of benzene or chloroform and, at the suggestion of Professor Bancroft, I have undertaken some experiments to determine the effect of various organic solvents. Nine indicators were taken and tested in presence of alcohol, acetone, ether, benzene and chloroform.

Fluorescein.—Fluorescein was the first indicator tested. Its formula is $O{:}(C_6H_3OH)_2{:}C\overline{O.C_6H_4C}OOH$. In aqueous acid solution this color is yellowish-green, changing to green fluorescence when alkali is added. When fluorescein is dissolved in a little alcoholic potash,[3] the green fluorescence is very marked. Addition of alcohol increases the fluorescence; acetone does not cause the fluorescence to disappear though changing it from green

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[1] Ostwald. Lehrbuch, I, 799.

[2] Cf. Bödtker. Zeit. phys. Chem. 22, 508 (1897).

[3] The alcoholic potash referred to in this article was decinormal.

to amber. Ether, benzene and chloroform discharge[1] the fluorescence which can be brought back by addition of alcohol. The following data will illustrate this.

Some fluorescein was dissolved in 0.5 cc decinormal alcoholic potash. The fluorescence was discharged by adding 3.5 cc ether, brought back by the addition of 0.27 cc alcohol, discharged again by 2.1 cc ether, brought back by 0.25 cc alcohol and again discharged by 2.1 cc ether. There is no reason to suppose that this alternation could not be repeated almost indefinitely. In a similar experiment with benzene instead of ether, the fluorescence was discharged by 7 cc benzene, restored by 0.2 cc alcohol and again discharged by 3.5 cc benzene. In a third experiment the fluorescence was discharged by 7 cc chloroform, brought back by 0.9 cc alcohol and again discharged by 10 cc chloroform. When the fluorescence was discharged, the solutions were pink by transmitted light instead of almost colorless. This is due to the precipitation of fine particles of the salt of fluorescein. Adding a large excess of ether precipitates a red substance which dissolves in alcohol, giving a strong green fluorescence. An excess of benzene produces the same effect, while with chloroform much less precipitate is formed. It was thought that the discharging of the fluorescence by the addition of ether, benzene and chloroform might have been due to the precipitation of the fluorescein; but the following experiment shows that the phenomenon is not due to this alone. Several test-tubes were allowed to stand for a couple of weeks until the precipitate had settled to the bottom. The nearly colorless supernatant liquid was poured off and found to give the green fluorescence on addition of alcohol.

When a good deal of fluorescein is dissolved in a little aqueous ammonia no fluorescence is observed; but this appears at once on diluting with water or alcohol, less readily with acetone. If ether, chloroform or benzene be added to the acetone solution, the fluorescence can be made to disappear.

A solution of fluorescein in acetic acid has a color between

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[1] I use "discharge" when the color disappears but can be brought back again; "destroy" when the change is irreversible.

green and yellow. Addition of alcohol made the color very much fainter, almost discharging it. Water made this solution change to a yellowish-green;[1] but this color could be forced back by more alcohol. It is to be noticed that the alcohol has a marked effect in acid solutions, though little or none in presence of alkalies. Acetone, ether, benzene and chloroform behave like alcohol. The green obtained in the acid solution is quite different from that in alkaline solution and does not fluoresce. The color obtained by adding the organic solvents is the same whether the solution be acid or alkaline.

These phenomena accord well with the theory provided we assume that fluorescein is both a base and an acid. The fluorescence is then due to the dissociated acid ion and is made to disappear by ether, benzene and chloroform. In alcohol and acetone the dissociation is sufficient to make the fluorescence visible. If the basic ion is yellowish-green we should expect to have this color disappear on adding the organic solvents, which is the case experimentally.

To many it may seem surprising to treat fluorescein as a base; but there is a fair amount of experimental evidence in favor of this view. Baeyer[2] notes that the solubility of fluorescein in water is increased by addition of acid. Nencki and Sieber[3] have made salts of acetfluorescein while Dale and Schorlemmer[4] have obtained crystalline compounds of hydrochloric acid with aurin. The chemical phenomena are thus in accord with the conclusions made necessary by the color changes. We may say therefore that undissociated fluorescein gives a colorless solution, the acid ion a green fluorescence, while the basic ion is yellowish-green. The only unsatisfactory point is one cited by R. Meyer[5] that, for the same concentration, the fluorescence is greater in alcohol than in water. No satisfactory explanation of this phe-

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[1] Solutions containing alcohol or acetone show less yellow color than aqueous acetic acid alone.

[2] Liebig's Annalen, 183, 6 (1876).

[3] Jour. prakt. Chem. (2) 23, 544 (1881).

[4] Liebig's Annalen, 196, 88 (1879).

[5] Zeit. phys. Chem. 24, 489 (1897).

nomenon can be given at present. It is to be noted that a similar phenomenon occurs with aqueous ammonia. If a large amount of fluorescein be added to a small amount of aqueous ammonia, there is no fluorescence even when the ammonia is dilute. When a little fluorescein is added to a large amount of aqueous ammonia, there is fluorescence even when the ammonia is very concentrated. The important point seems to be the volume concentration of the fluorescein.

Cyanine.—Cyanine has the empirical formula[1] $C_{29}H_{35}N_2I$. Aqueous alkaline solutions are blue, acid solutions colorless. A solution of cyanine in alcoholic potash is also blue. Addition of ether destroys the color. This is not a case of forcing back dissociation, because the blue color could not be brought back by water, alcohol or potash. With benzene, chloroform or acetone similar results are obtained, the only difference being that the change is not so rapid. Addition of chloroform gives a green color; if the solution be diluted at once with alcohol, the blue color is brought back. If the solution be allowed to stand or if it be heated, nothing will bring back the blue.

Addition of hydrochloric acid to the alcoholic solution of cyanine discharges the color which can be brought back by alcohol or acetone, less readily by ether, benzene or chloroform. The experiment is not a very satisfactory one because care must be taken to prevent adding an excess of hydrochloric acid. With a weaker acid, such as acetic acid, the effect is much more marked.

If aqueous acetic acid be taken, two liquid layers are formed on addition of chloroform or benzene, the aqueous one being colorless, the other deep blue. Addition of alcohol causes both solutions to become blue.

It is clear that these phenomena are in accord with the theory on the assumption that the undissociated base is blue and the ion colorless. Addition of alcohol, acetone, ether, benzene, or chloroform to the acid solution forces back the dissociation.

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[1] Cf. Hoogewerff and van Dorp. Recueil Trav. Pays-Bas, 3, 337 (1884).

Paranitrophenol.—Paranitrophenol has the formula

$$HO.C_6H_4.NO_2.$$

In aqueous alkaline solution the color is greenish; in acid solution pale yellow. The solution in acetone has a pale straw color; all the aqueous solutions, even the most concentrated, are yellowish-green. The reason for this is that paranitrophenol is not a very weak acid and the color due to the ion is therefore perceptible in aqueous solution. If one adds paranitrophenol continuously to a constant quantity of alcohol, the concentration of the ions increases, of course, with the total concentration. The green color does not increase continually, as one might have expected; it passes through a maximum. Here we probably have to deal with the sum of two effects, the color due to the undissociated substance and that due to the ion. While we are not surprised at seeing a solution of cupric bromide change from blue to brownish-black with increasing concentration, it is a little startling to note a change when the color of the undissociated substance is so weak as in the case of paranitrophenol.

When more than a drop of caustic potash solution is added to alcoholic paranitrophenol, it is practically impossible to force back the dissociation completely. With ammonia instead of caustic potash, ether, benzene, chloroform and acetone discharge the green color, acetone being the least effective. With aqueous ammonia, benzene, and chloroform form two liquid phases, the aqueous solution being colored and the other nearly colorless.[1] Addition of the organic solvents to an acetic acid solution of paranitrophenol causes no visible change.

These phenomena are perfectly intelligible on the assumption that the ion is colored. Acetone, ether, benzene and chloroform force back the dissociation markedly in presence of the weak base ammonia, not so effectively in the presence of caustic potash. A very pretty experiment is to add ammonia to a solution of paranitrophenol in acetone, discharge the color with ether and then bring back an intense green color by adding alcohol or

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[1] Orthonitrophenol behaves like paranitrophenol.

water. This reaction can be obtained even when so much ammonia is present that it can be easily detected by the smell.

Phenolphthalein.—Solid phenolphthalein is an anhydride and its formula may be written $(C_6H_4OH)_2 : C\overline{O.C_6H_4C}O$. Alkalies turn the solution red, while acid solutions are colorless. Alcohol, acetone, ether, benzene and chloroform discharge the red color even in presence of caustic potash; the experiment is more effective if a good deal of phenolphthalein be taken.[1] With ammonia instead of potash, the change of dissociation is more marked.[2] These experiments confirm the accepted doctrine that the red color is due to the ion. It was noticed that heating a decolorized solution sometimes caused the red color to reappear. On cooling the reverse change took place. This is probably connected in some way with the other curious fact that concentrated aqueous potassium hydroxide decolorizes a phenolphthalein solution. As the significance of this reaction is being studied by Professor Orndorff, this point was not worked out carefully.

Methyl Orange.—Methyl orange has the formula

$$(CH_3)_2N.C_6H_4.N_2.C_6H_4SO_3H.$$

What I used was apparently the sodium salt because, when incinerated, it left a residue of sodium sulfate. The solution in acetone or alcohol has a pure yellow color, while the aqueous solution is reddish orange. This would tend to show that the undissociated substance is yellow and the dissociated red. The color of the aqueous alkaline solution is yellow, that of the aqueous acid solution red. When methyl orange is dissolved in alcoholic potash addition of ether, benzene or chloroform leaves the yellow color unchanged. Addition of acetone causes a change to green or orange, depending upon the amount of caustic potash present; but this is due to suspended particles of the precipitated salt.

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[1] Jones failed to obtain a change of color with KOH and alcohol. Am. Chem. Jour. 18, 377 (1896).

[2] The action of the ammonia on the phenolphthalein may be neglected. Long. Am. Chem. Jour. 11, 84 (1889).

Addition of alcohol, acetone, ether, benzene or chloroform to an acidified solution changes the color from red to yellow. It is very difficult to realize this when hydrochloric or sulfuric acid is taken. With monochloracetic acid or still better with acetic acid, it is very easy to obtain the change of color. Adding water to the yellow solution brings back the red color. These results all show that the undissociated substance is yellow and that the ion, whatever it may be, is red. This is in flat contradiction to Ostwald's view[1] that the substance is an acid, the ion being yellow and the undissociated compound red. Küster[2] maintains that methyl orange is a strong base whose properties are unaffected by the presence of the sulfonic acid group. He explains the phenomena as follows: "In aqueous solutions the hydrogen ions formed by the primary ionization of the sulfonic acid group mainly attach themselves to the nitrogen atom and carry over their positive charge so that the remarkable group $\overset{+}{N}H(CH_3)_2.C_6H_4.N_2.C_6H_4.S\overset{-}{O}_3$ is formed, which is at once positively and negatively charged, and can therefore contribute nothing to the conductivity. This hybrid ion is colored a relatively feeble red, while the anion $N(CH_3)_2.C_6H_4.N_2.C_6H_4S\overset{-}{O}_3$ is an intense yellow. This last, therefore, although present in relatively small amount in the aqueous solution, will, notwithstanding, determine the color. By the addition of hydrogen ions this is carried over practically entirely into the hybrid ion so that the color of the latter appears. Since this dissociates to a very small extent according to the equation

$$\overset{+}{N}H(CH_3)_2.C_6H_4.N_2.C_6H_4S\overset{-}{O}_3 = N(CH_3)_2C_6H_4.N_2.C_6H_4S\overset{-}{O}_3 + \overset{+}{H},$$

it therefore behaves as a very weak acid. Like other weak acids its dissociation must be forced back practically to zero by a very small addition of hydrogen ions. The change of color must therefore be sharp as it really is." This is very ingenious; but is open to the criticism of playing fast and loose with the conception of a strong base. The possibility of forming a dis-

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[1] Anal. Chemie, 105.

[2] Zeit. anorg. Chem. 13, 136 (1897).

sociated hydrochloride on the addition of hydrochloric acid is ignored entirely. It is clear also that another assumption must be made, namely that the undissociated sodium salt has the same color as the undissociated sulfonic acid. If this were not the case, solutions of the sodium salt in chloroform, etc., would not be yellow. I shall make this assumption also[1] and the dissociation of the sulfonic acid groups then ceases to be of importance colorimetrically. It seems to me more reasonable to consider methyl orange as a weak base, much weaker than dimethylamidoazobenzene, owing to the entrance of the sulfonic acid group. Like ammonia, it would be dissociated but slightly in water, while the hydrochloride would be highly dissociated. The free base being yellow and the ion red, all the phenomena become intelligible. In aqueous solutions what I have called the free base would correspond to Küster's anion, while the dissociation product would be Küster's hybrid ion. The difference between the two views is that I consider the yellow substance to be present in large amounts when the sodium salt of methyl orange is dissolved in pure water, while Küster assumes the contrary, and is thus forced to make an extra assumption of intensity of color. So far as I can see, my way of looking at the matter represents the chemical and physical phenomena rather better than Küster's does.

Corallin.—Corallin is a mixture of aurin and methyl aurin. The aqueous alkaline solution is red, the acid solution yellow. Addition of ether, benzene, chloroform or acetone to the alkaline solution destroyed the color. As was the case with cyanine, the color could be restored by adding water at once. Better results were obtained by using less potash, and the best results of all by acidifying the solution with chloracetic acid and then neutralizing with alcoholic potash. It was then possible to change the color from red to yellow and to bring it back. As with many of the other indicators the phenomena are obtained more satisfactorily when ammonia is substituted for potash. From the experiments of Dale and Schorlemmer[2] already cited, it was to be

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[1] It is made tacitly in the case of all indicators.

[2] Liebig's Annalen, 196, 88 (1879).

expected that corallin would behave like a base and like an acid. This is true, though not in a very satisfactory manner. A solution of corallin in acetic acid is golden yellow; addition of acetone makes the color much paler, but adding water does not bring back the original tint. The color remains pale, but the yellow becomes a little browner. On the other hand, evaporating the solution made the yellow color more intense so that it is possible that we are dealing with a substance resembling paranitrophenol in that the absolute concentration of the indicator has a marked effect on the tint. Better results were obtained with phenacetolin. It was hardly to be expected that such a mixture as corallin would be very satisfactory. The phenomena suggest the view that the acid ion is red, the basic ion yellow and the undissociated substance pale yellow.

Phenacetolin.—Phenacetolin or phenacetein is said to have the formula $C_{16}H_{12}O_2$. The aqueous alkaline solution is bright pink, the acid solution yellow. When the alcoholic solution is acidified with acetic acid, addition of acetone, ether, benzene or chloroform changes the color from yellow to a faint pink. The solution in concentrated ammonia is brownish-red. Addition of alcohol, acetone, ether, benzene or chloroform changes the color to a pale yellowish pink. Water changes this at once to a bright pink. The change from bright to faint pink and back again can be made as often as desired, alcohol being less effective than acetone in forcing back the dissociation.[1] Phenacetolin is therefore both a base and an acid, the bright pink being due to the acid ion, the yellow to the basic ion, while the undissociated substance is pale pink in solution.

Lacmoid.—The aqueous alkaline solution is blue, the acid solution red. When acidified with acetic acid, addition of alcohol or acetone changed the color to blue, water bringing it back to red. Addition of ether, benzene or chloroform made the solution colorless at first; on standing a faint blue appeared, which could be changed to a faint red by adding water. On adding

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[1] The change of color in the alkaline solution is more easily obtained, the purer the phenacetolin. Some that I prepared myself gave the best results.

ammonium acetate, acetic acid and much ether, a very little alcohol brought the blue color at once.

From the experiments with alcohol and acetone we are justified in concluding that lacmoid is a base, the ion being red and the undissociated substance blue. This evidence is of some value since its constitution is unknown and the question as to the acid or basic character has been an open one.[1]

Turmeric.—Turmeric or curcumin may be represented by the formula $C_6H_3(OH)(OCH_3).CH(C_5H_5)COOH$. The aqueous alkaline solution is red, the acid solution yellow. Addition of alcohol, acetone, ether, benzene, or chloroform to a solution made red by ammonia changed the color to yellow. Turmeric is therefore an acid,[2] the ion being red and the undissociated substance yellow. One curious phenomenon was noted. An alcoholic ammonia was added to a solution of turmeric in aqueous alcohol and a bright red color obtained. This solution was divided into two equal parts. To one of these alcohol was added, discharging the color which was then brought back on addition of water, though the tint was a little paler. Addition of water to the other portion also discharged the red color which could be restored partially by addition of alcohol. It usually took more water than alcohol to discharge the color, and addition of alcohol to the aqueous solution did not bring it back so intensely as did addition of water to the solution which was mainly alcohol. It would seem that there is a certain concentration for which the red color is most pronounced. This idea is confirmed by the fact that when too much water has been added and the maximum intensity has been passed, addition of more turmeric made the red color more pronounced. The most probable explanation is that excess of alcohol forces back the electrolytic dissociation, while excess of water brings about sufficient hydrolytic dissociation to cause the red color to disappear. This hypothesis is to be considered merely as a provisional one and in no sense final.

The general results have been grouped in two tables, so

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[1] Cf. Mohr's Titrirbuch, 6th edition, 79.

[2] Cf. Jackson and Menke. Am. Chem. Jour. 4, 77 (1882).

that they can be seen at a glance. In order to economize space, the order in the tables is not that of the text.

There is but one point that needs further discussion. It has been shown that forcing back the dissociation gives practically the same color in acid and in alkaline solutions. Whether the colors, resulting in the two cases, are absolutely identical could only be answered after a spectroscopic investigation. For the present purpose it is sufficient that the difference, if any, is not noticeable to the eye. As has already been pointed out, this would seem to necessitate the assumption that the color, in solution, of the undissociated salt is the same or nearly the same as the color of the undissociated acid or base. This cannot be a general truth because cupric chloride and cupric bromide solutions are striking instances to the contrary. It is, therefore, very desirable not to be forced to make this assumption, even though it may be correct in many cases. In connection with this it will be well to consider that the change of color is more easily obtained with ammonia or acetic acid than with caustic potash or hydrochloric acid. This was a little surprising because the salts of weak acids and weak bases are dissociated to a very considerable extent[1] and the difference between a potassium and an ammonium salt should not be enormous.[2] On the other hand, we know that the salts of weak acids and weak bases are hydrolyzed by water, breaking up to a certain extent into undissociated acid and undissociated base. If we could assume that an analogous change took place in other solvents, all the difficulties would disappear at once. If ammonium acetate, for instance, is changed by acetone, let us say, into anhydrous ammonia and acetic acid, that would explain everything. We should get a change of color readily in an ammoniacal solution, because the ammonia could be set free, whereas the potassium

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[1] Nernst. Theor. Chemie, 402.

[2] Potassium acetate and ammonium acetate in aqueous solutions have about the same conductivity. This is not the case in aqueous alcohol. Whatever the explanation of this may be, it is important to note that the conductivity determinations confirm the color experiments, that the concentration of the ions is more readily affected by alcohol when an ammonium salt is taken instead of a potassium salt.

Table I

Fluorescein,

acid and base

Alkaline solution

Water	green fluorescence
Alcohol	green fluorescence
Acetone	amber fluorescence
Ether	nearly colorless
Benzene	nearly colorless
Chloroform	nearly colorless

Acid solution

Water	greenish yellow
Alcohol	nearly colorless
Acetone	nearly colorless
Ether	nearly colorless
Benzene	nearly colorless
Chloroform	nearly colorless

Phenacetolin,

acid and base

Alkaline solution

Water	red
Alcohol	pale pink
Acetone	pale pink
Ether	pale pink
Benzene	pale pink
Chloroform	pale pink

Acid solution

Water	yellow
Alcohol	pale pink
Acetone	pale pink
Ether	pale pink
Benzene	pale pink
Chloroform	pale pink

Phenolphthalein,

acid

Alkaline solution

Water	red
Alcohol	colorless
Acetone	colorless
Ether	colorless
Benzene	colorless
Chloroform	colorless

Acid solution

Water	colorless

Paranitrophenol,

acid

Alkaline solution

Water	yellowish green
Alcohol	yellowish green
Acetone	pale yellow
Ether	pale yellow
Benzene	pale yellow
Chloroform	pale yellow

Acid solution

Water	pale yellow

Cyanine,

base

Acid solution

Water	colorless
Alcohol	blue
Acetone	blue
Ether	blue
Benzene	blue
Chloroform	blue

Alkaline solution

Water	blue

Table II

Methyl orange,
base

Acid solution

Water	red
Alcohol	yellow
Acetone	yellow
Ether	yellow
Benzene	yellow
Chloroform	yellow

Alkaline solution

Water	yellow

Turmeric,
acid

Alkaline solution

Water	red
Alcohol	yellow
Acetone	yellow
Ether	yellow
Benzene	yellow
Chloroform	yellow.

Acid solution

Water	yellow

Lacmoid,
base

Acid solution

Water	red
Alcohol	blue
Acetone	blue
Ether	faint blue
Benzene	faint blue
Chloroform	faint blue

Alkaline solution

Water	blue

Corallin,
acid and base

Alkaline solution

Water	red
Alcohol	red
Acetone	pale yellow
Ether	pale yellow
Benzene	pale yellow
Chloroform	pale yellow

Acid solution

Water	yellow
Other solvents	unsatisfactory

salt could not undergo the same change. With the strong acid, hydrochloric acid, the decomposition would be much less easily effected than with acetic acid. We should then expect to get the same color whether we added acetone to the acid or the alkaline solution because there is the same substance in the solution in the two cases. There is some evidence in favor of this view. Goldschmidt[1] has found it advisable to assume that aniline salts, when dissolved in aniline, are changed to a certain extent into aniline and the free acid. It seems reasonable to sup-

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[1] Zeit. phys. Chem. 24, 353 (1897).

pose that this would take place to a greater extent in other solvents where the concentration of the free aniline would be less. On the other hand, it must be recognized that there are, as yet, no data which can be taken as in any sense conclusive. While this question is a very interesting one, it does not lie within the immediate scope of this investigation and, for this reason, I have not taken it up experimentally.

The general conclusions to be drawn from this investigation may be stated as follows:

1. The dissociation theory enables us to predict the facts.
2. In alcohol and acetone the color of the ion is often perceptible.
3. Methyl orange as indicator is a weak base.
4. Lacmoid is a basic indicator.
5. Fluorescein and phenacetolin are both basic and acid indicators.
6. Corallin is probably both a basic and an acid indicator.
7. It is often possible to predict the acid or basic properties of an unknown compound from the color changes.
8. More satisfactory results are obtained with ammonia and acetic acid than with caustic potash and hydrochloric acid.
9. There is some evidence in support of the view that salts of weak acids and weak bases dissociate to a certain extent into free acid and free base in organic solvents.
10. With fluorescein, paranitrophenol, turmeric and corallin some interesting phenomena were observed, connected with the absolute concentration of the indicator.

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NORMAL ELEMENTS

BY D. MCINTOSH

Since the publication of the description of the Clark cell in 1873, many researches have been undertaken on standard cells, with the object of finding others more convenient or better in some respects than the Clark. Amongst these might be mentioned the Helmholtz, Gouy and Weston cells, each having some advantage and all a much lower temperature coefficient than the Clark. All these are, however, of comparatively high electromotive force, and are unsuitable for use with working batteries of single cells of low electromotive force,—such as the Edison Lalande. Since this battery is a very constant one, and is in every way suitable for many researches, where Daniell or Leclanché cells are usually employed—such as the measurement of the electromotive forces of gas cells—I have, under Professor Bancroft's direction, examined a number of cells, with the object of finding a convenient standard having an electromotive force in the neighborhood of 0.5 volt.

Method of measuring, apparatus, etc.—The measurements were made by the well-known Poggendorff Compensation method, using a Leclanché cell as a working element. During three months the working element varied but 0.1 volt. Instead of a galvanometer a Lippmann capillary electrometer was used, with a microscope magnifying about thirty diameters. With this a difference in electromotive force of 0.0005 V could be measured—an accuracy sufficient for the purpose. The Leclanché was switched into the circuit only for a moment at a time and was compared every little while with a Clark element made from the purest materials. This Clark element was compared with one made by the Imperial German Institute and its value was taken as $1.4336 + (15 - t)0.001$ volts.

For the purpose of comparison, a few Gouy, Helmholtz and lead chloride cells were made up and their electromotive forces measured.

Gouy Cell.—The Gouy cell[1] differs from the Clark in having mercuric oxide as a depolarizer instead of mercurous sulphate. In place of the saturated solution of $ZnSO_4$ a ten percent solution is used.

The zinc used was bought as chemically pure, rubbed smooth and amalgamated. The zinc sulphate was purified by heating a solution for several days with strips of zinc in order to precipitate foreign metals. This solution was filtered and sodium carbonate added to a portion. The precipitate after being carefully washed was added to the zinc sulphate; the solution was boiled for several hours, filtered and then evaporated to crystallization. After drying the crystals between filter-paper a ten percent solution was made up and its specific gravity determined.

The mercury was purified by shaking a number of times with dilute sulphuric acid, to which a few drops of a solution of chromic acid were added and then running it through a long column of ten percent nitric acid, according to the directions given by Ostwald.[2]

The mercuric oxide was of three kinds:

1. According to Gouy—by the addition of sodium carbonate at 40° C.
2. From $HgCl_2$.
3. The ordinary mercuric oxide of the laboratory.

The cells made from these materials gave practically the same electromotive force. Those made from the laboratory mercuric oxide were apparently a little lower than the others. Two prepared from the oxide which had been washed with water and zinc sulphate solution gave 1.3841 and 1.3848 volts at 12° C, Gouy's temperature coefficient being taken in making the reduction from 18°. To compare these values with those of Gouy who used the legal ohm, we must multiply by 1063/1060.

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[1] Jour. de Phys. (2) 7, 532 (1888).

[2] Hand und Hilfsbuch.

These then equal 1.3880 and 1.3887 at 12° C as compared with Gouy's 1.390. This difference, which is due probably to experimental errors, confirms Ostwald's conclusion[1] regarding the similarity of red and yellow mercuric oxide.

Calomel Cells.—The mercurous chloride used was prepared from a solution of mercurous nitrate by precipitation with hydrochloric acid. It was washed free from acid by decanting with cold water and dried in an air-bath at 60° C. It did not turn dark after three months' exposure to light and probably does not decompose when perfectly dry, as has been pointed out by Mr. Carveth. The zinc chloride was purified in much the same way as the sulphate and four differently concentrated solutions made up, and their specific gravities at 15° carefully determined. The above materials were used in making up the cells and their electromotive force determined from time to time.

ZnCl	Specific gravity	E. M. F. at 15°
1	1.747	0.9143
2	1.580	0.9560
3	1.469	0.9827
4	1.333	1.0284

On plotting these values on coordinate paper and drawing a smooth curve through them, one finds that a potential difference of one volt corresponds in this cell to a zinc chloride solution of specific gravity 1.410. Ostwald[2] found 1.409 and Carhart[3] found 1.391.

A cell consisting of zinc, zinc chloride, lead chloride and lead is described by Baille and Féry[4]. A few cells of this kind were made. The lead chloride used, was the laboratory reagent, purified by crystallization from hot water. The lead was puri-

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[1] Zeit. phys. Chem. 18, 159 (1894).
[2] Zeit. phys. Chem. 1, 403 (1887).
[3] Primärelemente, Halle p. 153.
[4] Jour. de Phys. (2) 9, 234 (1890).

fied according to the method of Stas[1] by heating to 40° C a solution of lead acetate with thin sheets of lead for some time, so as to precipitate copper and silver. This solution is filtered into dilute sulphuric acid and carefully washed with a solution of ammonium carbonate—so forming lead carbonate. A portion of this is changed to the oxide by heat and to the remainder dilute nitric acid is added, so that but a small part of the carbonate is left. The oxide of lead is added to the boiling solution of the nitrate in order to precipitate iron, and this is then filtered into a solution of carbonate of ammonium. The precipitated lead carbonate is reduced and purified by fusing twice with potassium cyanide.

The lead was employed in the form of an amalgam consisting of six parts of mercury to one part of lead by weight. The lead oxidizes and a film soon appears on the surface of the amalgam. By melting this one can pipette off the amalgam from below the surface and so obtain it pure.

A number of lead chloride cells were made up and an attempt was made to find the most constant. All were very satisfactory and had extremely low temperature coefficients.

The electromotive forces of three made with different concentrations of zinc chloride are given below:

	Sp. gr. $ZnCl_2$	E. M. F. at 20°
1	1.747	0.3913
2	1.469	0.4544
3	1.198	0.5060

At 0° C No. 2 gave an electromotive force of 0.4566; a difference of 0.002 volt for 20°. Baille and Féry found a change of 0.005 V for 46°.

By interpolation one sees that zinc chloride having a specific gravity of 1.23 corresponds to a cell of 0.5 volt. Baille and

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[1] Bull. Acad. roy. Belg. (2) 10, 294 (1860).

Féry report 1.157. Free acid in the zinc chloride solution raises the electromotive force markedly; but it seems impossible that this discrepancy is due to this cause.

A great many cells in which HgO was used as a depolarizer were made up and their electromotive forces determined. Among those tried were Pb, $PbSO_4$, HgO, Hg, about 0.9 V; Pb, $PbCl_2$, HgO, Hg, about 0.7 V; Cd, $CdCl_2$, HgO, Hg, about 0.85 V; Cd, $CdSO_4$ HgO, Hg, about 0.85 V. None of these were satisfactory, and indeed, two made up at the same time, and in exactly the same way, often showed a difference of 0.1 volt. There seemed to be some chemical action, which destroyed the mercuric oxide in a few days. The use of other oxides as depolarizers gave negative results.

Cells such as Cd, $CdSO_4$, $PbSO_4$, Pb (about 0.05 V); Cd, $CdCl_2$, $PbCl_2$, Pb (about 0.18 V), although constant enough had too low an electromotive force for the purpose required.

Pb, $CuSO_4$, $PbSO_4$, Pb gave an E. M. F. of about 0.4V. This cell was not very constant, due probably to difficulty in getting lead sulphate free from acid.

Cells of copper, copper sulphate, mercurous sulphate, mercury.—The Hg_2SO_4 was made from $HgNO_3$ by precipitation with H_2SO_4, although perhaps it would have been better to use $CuSO_4$ and to avoid free acid. The precipitate was washed with ice-water and dried in an air-bath at 60°. The sulphate showed no tendency to decompose although kept in the light for some months.

The copper sulphate was purified by heating with copper and then crystallizing. It was neutral to litmus paper. The copper electrodes were of pure copper bought for the purpose. Some were coated by copper deposited electrolytically from a $CuSO_4$ solution, but showed no difference from the others.

The cells were small test-tubes with platinum wire sealed in. The bottoms were covered with layers of mercury and mercurous sulphate; a paste of $CuSO_4$ and Hg_2SO_4 respectively. A hot saturated solution of $CuSO_4$ was introduced and the copper electrode enclosed (to prevent accidental internal short circuit.

ing) in a tube with a small hole and made air-tight with melted paraffin. The internal resistance was thus made very high but this is, in general, of little consequence.

A number of these cells were made up and their electromotive forces measured from day to day. The values increased but became constant at the end of a week. The results are given below.

After being made up

	One day at 17°	Three days at 17°	One week at 17.5°	Ten days at 17°
1	0.3563 V	0.3592 V	0.3608 V	0.3606 V
2	0.3563	0.3590	0.3608	0.3606
3	0.3560	0.3585	0.3605	0.3608
4	0.3563	0.3592	0.3588	0.3615

Temperature coefficient.—The cells were immersed in a water-bath, the temperature of which was regulated by an Ostwald thermostat, or in dishes and covered with melting snow. After three or four hours the E. M. F.'s were measured and measurements continued each hour until each cell showed the same electromotive force for two successive hours. They were then assumed to be in equilibrium and the last reading was taken as the correct one at this temperature.

	At 0°	16.5°	22°	30° C	41°
1	0.3663 V	0.3615 V	0.3576 V	0.3525 V	0.3509 V
2	0.3650	0.3615	0.3576	0.3525	0.3509
3	0.3645	0.3615	0.3584	0.3529	0.3505
4	0.3663	0.3606	0.3585	0.3533	0.3503
Mean	0.3655	0.3613	0.3580	0.3528	0.3506

The coefficient varies throughout, a result due probably to errors of experiment. Between 16.5° and 22° it is 0.0006 V and between 22° and 30° it is 0.00065 V per degree. The electromotive force decreases with rising temperature and, in the neighborhood of 16.5°, may be calculated by the formula $E = 0.3613 + (16.5 - t)0.0006$ volts.

The chemical reaction in the cell may be represented as follows: $Cu + Hg_2SO_4 = CuSO_4 + Hg_2$. Helmholtz has deduced mathematically and Jahn has shown experimentally that $\pi = \frac{Q}{\epsilon_0} + \frac{Td\pi}{dT}$, where π is E. M. F.; Q, sum of heats of reaction; T, absolute temperature, ϵ_0, quantity of electricity, and $\frac{d\pi}{dT}$, change of E. M. F. for 1° C.

Taking $\pi = 0.3613$ at 290°, $\epsilon_0 = 96540$ coulombs and $d\pi/dT = -0.0006$; we have $Q = 12000$ calories. Since the heat of formation of $CuSO_4 5H_2O$ is 201000 cal (Ostwald's *Lehrbuch*) the heat of formation of Hg_2SO_4 must equal 175000 cal. I am unable to find the value of this heat of formation so a comparison is impossible. If one used this number to calculate the electromotive force of a Clark, 1.427 volts is obtained instead of 1.434, taking the heat of formation of $ZnSO_4 7H_2O$ as 253000 cal.

Mechanical disturbances raise the electromotive force of the above cell, but after a short time it returns to its normal condition. On short circuiting through a resistance of one-half an ohm; it fell in three hours to 0.3536, but in a day had reached its original value. Here then we have a cell, which can be made in the ordinary way from common laboratory reagents, is quite constant and has a temperature coefficient lower than the Clark.

In order to try whether the temperature coefficient could be made smaller by using copper sulphate solutions of different concentrations, cells were made which contained $CuSO_4$ saturated at 0°C. These had an electromotive force of 0.363 at 20° C and showed no advantage in temperature coefficient and as, on account of leakage, the concentration slowly changed, this cell was not studied further.

To avoid effects due to mechanical disturbances, some cells were filled with solutions of $CuSO_4$ in agar-agar jelly. The jelly did not solidify properly with the concentration of copper sulphate employed, so that the addition of jelly proved of no advantage.

Lead chloride—calomel cells.—A number of cells containing Pb, $PbCl_2$, $HgCl_2$, Hg were made up and examined in the same ways as the others. They were made up either in test-tubes or in the H-shaped vessels first employed by Rayleigh. The lead used was the amalgam described above.

After making up

	One day at 21°	Two days at 21°	One week at 20°	Two weeks at 21°	Three weeks at 18°
1	0.5458	0.5389	0.5390	0.5384	0.5367
2	0.5397	0.5364	0.5365	0.5390	0.5345
3	0.5520	0.5426	0.5440	0.5346	0.5404
4	0.5458	0.5402	0.5390	0.5390	0.5367
5	0.5447	0.5402	0.5390	0.5371	0.5367
6	0.5483	0.5413	0.5385	0.5377	0.5367
			0.5384	0.5382	0.5363

A cell was made containing a saturated solution of $PbCl_2$ in agar-agar jelly. It gave an electromotive force of 0.5365 and was little affected by violent shaking.

Temperature coefficient.—The change of E. M. F. with temperature was measured in the way described above with the following results:

	E. M. F.	Mean
0°	0.5314 0.5323	0.5319
15°	0.5346 0.5346	0.5346
18°	0.5363	0.5363
21°	0.5382	0.5382
30°	0.5392 0.5398	0.5395

The electromotive force increases with the temperature and may be calculated approximately between 15° and 21° by the formula $= 5382 + (T - 21)\,0.0006$.

This cell, although not as satisfactory as the other, might by certain improvement and further study, be made a useful standard where cells of low electromotive force are employed. Some cells of this kind were made, having the lead chloride solution saturated at 0°. They had an electromotive force of 0.552 V at 18° C, but had no smaller temperature coefficient.

The chemical reaction in the cell may be represented as follows:

$$Pb + Hg_2Cl_2 = PbCl_2 + Hg_2.$$

Substituting the heats of formation in the Helmholtz equation, we have = 0.6120 V at 17° C. Experiment gives 0.5358 V.

The cells described above, although having too low an electromotive force for many purposes, are convenient to use in many ways and particularly with a low voltage battery—such as the Edison Lalande; doubtless others could be found, and a careful investigation may reveal a cell combining the advantages of the Clark and Weston and none of their disadvantages.

Cornell University

NEW BOOKS

Arbeiten des physikalisch-chemischen Instituts der Universität Leipzig. *Gesammelt und herausgegeben von W. Ostwald. Four volumes. Large octavo; pp. 555, 492, 656, 550. Leipzig: W. Engelmann, 1897. Price: paper 36 marks, bound 48 marks.*—The first number of the *Zeitschrift für physikalische Chemie* appeared in February, 1887. In the autumn of that year Ostwald moved from Riga to Leipzig. The laboratory that was assigned to him was small and inconvenient. Ten years later a handsome new building was erected by the Saxon government to accommodate the students of physical chemistry. In honor of the event Ostwald has collected in these four volumes most of the papers published by himself and his students during the first seven years of his stay in Leipzig. While the articles have already appeared in the *Zeitschrift für physikalische Chemie*, this is a stately collection which many people will be glad to own. In the first volume are papers on general theory, conductivity, dissociation of acids and of bases. In the second volume the subheads are molecular weight determinations, homogenous equilibrium, heterogeneous equilibrium and reaction velocity. The subjects treated in the third volume are potential differences, theory of the voltaic cell, application of the theory, and polarization. The papers in the fourth volume are classified under internal friction and diffusion, optical relations, thermal and volume phenomena, and miscellanea. The work is dedicated to the Saxon minister of education. *Wilder D. Bancroft*

Die wissenschaftlichen Grundlagen der analytischen Chemie, elementar dargestellt. *By W. Ostwald. Second, enlarged, edition; 13 × 21 cm; pp. x and 200. Leipzig: W. Engelmann, 1897. Price: paper 5 marks, bound 5.80 marks.*—"In remarkable contrast" says the author in his preface "to the perfection attained by the practical side of analytical chemistry, stands its scientific treatment. This is confined, even in the better class of books, almost exclusively to a statement of the chemical equations according to which the reactions involved should take place *under ideal conditions*. That, in practice, these fictitious complete reactions are invariably replaced by incomplete reactions leading to chemical equilibrium,—that there is no such thing as an absolutely insoluble substance, and no absolutely accurate method of separation or estimation—are facts which are not only hidden for the most part from the student, but, I fear, are not always so actively present to the consciousness of even the trained analyst as in the interests of a sound judgment of analytical methods and results would be desirable. ...

"Such a remarkable state of affairs always has its good reason; and it is necessary to state, without circumlocution, that analytical chemistry has had so long to wait for a scientific basis *because scientific chemistry itself has not had at its disposal the necessary general laws and points of view.* It is only in the last few years that, thanks to the rapid evolution of physical chemistry, it has become possible to set to work at a theory of the analytical reactions, after the general theory of chemical reactions and chemical equilibrium had been developed. In the following pages an attempt is made to show how much more light is thrown, from this side, upon familiar phenomena of everyday experience."

To the student whose equipment of chemical theory consists of certain vague but strongly held views on the subject of 'atoms', joined to a moderate proficiency in the art of 'balancing equations', strict attention to the numerous details prescribed in the handbook of analysis must necessarily appear of but secondary importance; hence a relatively large part of his time in the laboratory is spent in learning from sad experience the necessity of 'sticking closely to the book.' It is consequently of no slight importance that a work has appeared containing detailed discussions, from the theoretical side, of such subjects as for example the proper concentration of hydrochloric acid to employ when precipitating lead or antimony by hydrogen sulfid, as the perplexing behavior of solutions of ferric sulfocyanid, and as the 'abnormal' reactions of the chromic salt after heating, of mercuric chlorid and cadmium iodid solutions and of solutions containing ammonia or cyanogen.

All this and much more—the theory of 'indicators', of the use of sodium acetate, of 'excess of the reagent', of 'weak' and 'strong' acids, etc., etc.—is furnished by Ostwald's "*Wissenschaftlichen Grundlagen*", but until the course of lectures on elementary chemistry at present in fashion in most English and American colleges undergoes a radical change, terms such as 'chemical equilibrium', 'mass action', 'dissociation', 'ions' (the A, B, C of the 'scientific basis' offered) can convey but little meaning to beginners; and the very men to whom the work might be of the greatest advantage are debarred from benefiting by it. To the more advanced student however, to the practical analyst who works to become more than a mere handicraftsman, and above all to the instructor in chemical analysis, the work cannot be too highly recommended.

New in the second edition is a paragraph on 'complex compounds' and a long section on 'electrochemical analysis'. *W. Lash Miller*

Les Théories physico-chimiques. *By A. Reychler. 15 × 23 cm; 281 pp. Brussels: Lamertin, 1897.*—This book can best be described as a French version of Ostwald's smaller textbook. The point of view is atomistic and the author's position in regard to the electrolytic dissociation theory is that it describes the facts well, but is essentially artificial in nature. The difference between this point of view and that which is held in England (1, 449) is that the author recognizes that the essential feature of a hypothesis is that it shall express the facts while that is considered to be of secondary importance in England. Cf. Sutherland, Phil. Mag. [5] 44, 493 (1897).

The headings in the book are: fundamental theories; gaseous state; specific heats; structure formulas; periodic law; critical point; liquid state;

solutions; solid state; thermochemistry; electrochemistry; dissociation theory; mass law; reaction velocity and dissociation theory.

Wilder D. Bancroft

Das optische Drehungsvermögen. *By H. Landolt. Second edition; 14 × 22 cm; pp. xxiv and 655. Braunschweig: F. Vieweg & Sohn, 1898. Price: bound 18 marks.*—The first edition appeared in 1879 and our knowledge of optically active substances has increased so much since that time that this volume is an entirely new book in everything except name. Three classes of optically active substances are distinguished; substances which are optically active only in the crystalline state; substances which are optically active when melted, dissolved or crystalline; substances which are optically active only when melted or dissolved and not when crystalline. After the classification there comes a short chapter on optical theories and then the author takes up the relation between the amount of rotation and the chemical composition, discussing the theory of van 't Hoff and Le Bel as to asymmetric carbon and also the more recent developments in regard to asymmetric nitrogen.

Under the general title of optical modifications are grouped the subdivisions: calculation of the number of active modifications from the number of asymmetric carbon atoms; physical and chemical properties of the active modifications; formation of racemic compounds; decomposition of racemic compounds including some remarks on bacteria; formation of active isomers; conversion of active isomers; structurally neutralized modifications.

The second part of the book, some twenty pages, is devoted to the physical laws of circular polarization. Part III deals with the numerical values of the specific rotation and the change with the temperature, nature of solvent and concentration. The effect of adding other active or inactive substances to the solution is discussed at length; the phenomena of multirotation receive a chapter to themselves and six pages are devoted to a consideration of Guye's hypothesis.

Part IV, one hundred and forty pages, is given up to a most useful discussion of apparatus and methods. Part V treats of the technical analyses based on the rotation of the plane of polarized light, while Part VI deals with the rotation constants of optically active substances.

The author has been ably assisted in his work by others. The pages on the culture of bacteria are due to Lindner. Part IV was compiled by Schönrock; Part V by Schütt, while Part VI is largely the work of Berndt, Posner, Rimbach and Thierfelder. The work has been well done and there is much in the volume to interest everybody. The work of van 't Hoff and his pupils on inversion temperatures is described in detail; sixty pages are given to the application of the dissociation theory to the phenomena in aqueous solutions; the experiments of Levy and Trey on reaction velocity are cited, including the last paper of Trey's. The book needs no recommendation. No laboratory can dispense with it.

Wilder D. Bancroft

The Freezing-point, Boiling-point, and Conductivity Methods. *By H. C. Jones. 13 × 19 cm; 64 pp. Easton, Pa.: The Chemical Publishing Co., 1898. Price: 75 cents.*—It strikes the author as deplorable that the theory and practice of methods should sometimes be treated separately. He has tried to combine the two; but has left out most of the theory and a large part of the practice. No attempt is made to give complete references to the literature. The methods of Jones are described in detail, with many illustrations; but one searches in vain for any discussion of the methods of Nernst and Abegg, of Loomis, of Wildermann or of Ponsot. An unsophisticated reader might gather the erroneous impression that the methods of the author are generally accepted as the best. The reviewer notes with sorrow the assumption that N in the freezing-point and boiling-point formulas refers to the molecular weight of the liquid solvent.

Wilder D. Bancroft

Traité théorique et pratique d'Électrochimie. *By D. Tommasi. 18 × 28 cm; pp. 1142 and cxx. Paris: E. Bernard & Cie, 1890. Price: 40 francs.* —This enormous volume is a treasure-house of facts. The author has made no attempt to discuss the electrochemical theories; his object has been to bring together the data, bearing on electrolysis, that are scattered throughout the literature. In the main, the work has been well done and even the most casual reader will find many things to interest him as he skims the pages, while the careful student will learn much that he would have great difficulty in picking up elsewhere. It is a little curious that the book should have attracted so little attention in its way. Even now, eight years after publication, there is nothing to take its place. Of course, the chapter on syntheses in organic chemistry is out of date; but the rest of the book is as valuable as ever. It is much to be hoped that the author and publisher will see the way clear to getting out a new and revised edition before the close of the century. If that should be the case, the reviewer would suggest that two volumes are better than one when it comes to a question of over a thousand pages. *Wilder D. Bancroft*

Angewandte Elektrochemie. *By F. Peters. Second volume, Parts I and II. 13 × 18½ cm; Part I, pp. xii and 248; Part II, pp. xii and 215. (Elektrotechnische Bibliothek) Wien: A. Hartleben, 1898. Price: each part 3 marks.*—The first volume on primary cells and storage batteries has already been reviewed (1, 501). This second volume takes up the application of electrochemistry to inorganic substances, the metalloids and the alkali metals being treated in Part I and the other elements in Part II. The object of this volume is to present as complete a statement as possible of what has been done in electrochemistry, with references for each statement. To accomplish this in 450 small pages requires a great deal of condensation and the book becomes, of necessity, a compromise between a treatise on the subject and a bibliography. It is exactly this fact of a compromise which makes these volumes published by Hartleben so much better than the corresponding works of the *Aide-Mémoire* series. In the latter the bibliography disappears almost completely, a loss for which the improved literary style does not compensate.

This book of Dr. Peters is very complete. The references are brought down to the summer of 1897; the author's index is good and one certainly obtains a vast amount of information for the money. *Wilder D. Bancroft*

Électrochimie: Production électrolytique des Composés chimiques. *By A. Minet. 12 × 19 cm; 167 pp. Paris: Gauthier-Villars et Fils, 1897. Price: 2.50 francs.*—This new volume of the *Encyclopédie des Aide-Mémoire* is divided into two parts, one dealing with the synthesis of inorganic compounds, the other with the processes used in organic chemistry. Sixteen pages are devoted to solutions of acids and bases; forty-seven to sodium and potassium chlorids, and forty pages to other inorganic substances. In the second part are interesting remarks on the preparation and purification of alcohol; on dyestuffs; on iodoform, bromoform and chloroform; on tanning and on the application of electrolytic methods to the sugar industry. *Wilder D. Bancroft*

Neuere Kühlmaschinen. *By H. Lorenz. 13 × 21 cm; pp. viii and 219. München: R. Oldenbourg, 1896. Price: 5 marks.*—A detailed discussion of the different types of freezing machines in use in Europe. The treatment of the theoretical side of the problem is strictly non-mathematical. Although the book is intended almost exclusively for technical readers, there is an interesting chapter on the methods of Olszewski and of Pictet for reaching very low temperatures. There is one point that might well have been discussed a little more fully. It appears that the American freezing machines differ radically from those in use in Germany, and it is stated in several places throughout the book that not a single one of the American machines has proved a success in Germany. One would like very much to know whether this is due to a real inferiority in the American machines or to the conditions of use being radically different. Unfortunately the author does not go into this question at all, although it is obviously an important one to someone.

Wilder D. Bancroft

Ueber den natürlichen Zusammenhang der organischen mit den unorganischen Verbindungen. *By H. Kolbe. Ostwald's Klassiker der exakten Wissenschaften, No. 92. 12½ × 19½ cm; 42 pp. Leipzig: W. Engelmann, 1897. Price: 0.70 mark.*—This little paper of Kolbe's is certainly to be ranked as a classic. At a time when organic chemistry is struggling with the more or less vague conceptions of stereo-isomerism, tautomerism and 'physical' isomerism, it is highly profitable to place oneself back amidst the difficulties of a preceding generation. It is the failure to do this more often which handicaps our chemists and blinds them to the differences between facts and hypothesis. The number is edited by E. v. Meyer. *Wilder D. Bancroft*

Laboratory Experiments on the Class Reactions and Identification of Organic Substances. *By A. A. Noyes and S. P. Mulliken. Second revised edition. 14 × 20½ cm; 28 pp. Easton: The Chemical Publishing Co., 1897. Price: 50 cents.*—Used in the manner indicated by the authors, this little book will certainly be helpful in teaching. Variations or additions, etc., will occur to most instructors as more or less desirable, but unanimity in this regard would be as difficult to obtain as for any ideal elementary textbook. These premises granted, the authors seem to have selected and arranged their material very well. To those not specially interested, a "qualitative analysis" for organic chemistry may come somewhat as a surprise, but must nevertheless often prove of great assistance. To this end, the comprehensive tables to be published at an early date, as promised in a footnote, should prove a very desirable addition. *Frank K. Cameron*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry

One-Component Systems

Comments and experiments on the anomalies near the critical point. *J. P. Kuenen. Arch. néerl.* (*2*) 1, *274*, *277* (*1897*). Using the electromagnetic stirrer it was possible to confirm the observation of Gouy that the differences between the volumes at which the meniscus appears and disappears can be reduced to a very small value. The view of de Heen, that the density of the vapor depends on the amount of liquid, is rejected and the cause of the anomalies is sought in the presence of traces of impurity. After a brief exposition of the hypotheses of de Heen and of Battelli, the author considers the experiments of Galitzine in which ether vapor was separated from liquid ether and ether vapor by mercury. The experimental error is shown to be nearly two percent and the variations from the theory are less than this value in all cases where Galitzine used carefully purified ether. It was also shown that the mere act of sealing the capillary end of a tube containing ether made a difference in the properties of the ether so that it seems reasonable to attribute Galitzine's very surprising results to impurities in the ether used by him. *W. D. B.*

An attempt to determine the adiabatic relations of ethyl oxid. *E. P. Perman, W. Ramsay and J. Rose-Innes. Zeit. phys. Chem.* 23, *385* (*1897*). A suitable quantity of carefully purified ether was introduced into a horizontal calibrated tube, surrounded by a vapor jacket and provided with a manometer and a glass rod sealed in to communicate sound vibrations to the ether. After all air had been removed from the apparatus, the velocity of sound, V, in the ether vapor was determined by Kundt's method for various pressures and for temperatures at intervals of 10° C. from 100° C. to 200° C. The weight of ether employed in each case was calculated from observations of the volume, pressure p and temperature T by means of Ramsay and Young's tables; the temperatures were maintained by boiling brombenzene, anilin, etc., under constant pressure; and the wave lengths of the tone given out by the rod were determined in air, in hydrogen and in argon and controlled by experiments with a phonograph.

The results were plotted, the values of V^2 for equal volumes v (at intervals of 5 cc from 70 cc to 20 cc per gram of ether) obtained by graphic interpolation, and a diagram constructed with V^2/v as ordinates and T as abscissas in which the isochores proved to be straight lines.

This result was of considerable service in simplifying the mathematical discussion, which under the further assumption that for constant v, p is a linear function of T (Ramsay and Young) leads to formulas for V and E (the adiabatic elasticity), as functions of p and v and for p as a function of v in adiabatic expansion. The authors regard these expressions however as mere interpolation formulas, which are not to be employed beyond the limits of their experiments.

In a short appendix are given the results of experiments with liquid ether in the same apparatus, the first experimental determination of the adiabatic relations of a body other than a gas. "In the liquid it was easier to obtain well defined sound figures than in the gas .... If the numerical results be treated as before, the isochores [V^2/v and T diagram] are again found to be straight lines: the investigation was not carried further, as the necessary formulas seemed still more complicated than in the case of the greater volumes." A preliminary notice of this paper has already appeared, 1, 378. *W. L. M.*

Experiments with the micromanometer. *A. Smits. Arch. néerl.* (*2*) 1, *97* (*1897*). Reviewed (1, 596) from Kon. Akad. Wetensch. Verslag. Amsterdam, *1896-97*, *292*.

On a differential method for measuring differences of vapor pressures of liquids at one temperature and at different temperatures. *Lord Kelvin. Proc. Roy. Soc. Edinb.* 21, *429* (*1897*). Reviewed (1, 441) from Nature 55, 273, 295 (1897).

Two-Component Systems

On the dissociation of minium. *H. Le Chatelier. Bull. Soc. Chim. Paris* (*3*) 17, *791* (*1897*). The dissociation pressure of minium is 183 mm at 550° and 753 mm at 636°. The allotropic change of lead oxid takes place at 580°, while the fusion temperature is about 830°. Since the ordinary partial pressure of oxygen in air is about 150 mm, minium cannot form above 550°. *W. D. B.*

Comments on the vapor pressures of mutually soluble liquids. *W. Ostwald. Wied. Ann.* 63, *336* (*1897*). It is assumed, without making reference to Le Chatelier, that the partial pressures for two partially miscible liquids form wavy curves when plotted in the pressure-concentration diagram. The change with rising temperature is then considered. There is little that is new in the discussion except the assumption that the composition ot the vapor must always lie between the values for the two liquid phases. This assumption is not justified, toluene and sulfur being a typical instance of a series of cases in which this is not true. Occasional perusal of the current literature would make such mistakes impossible. *W. D. B.*

Experiments on the condensation and the critical phenomena of mixtures of two substances. *J. P. Kuenen. Zeit. phys. Chem.* 24, *667* (*1897*). This is a revised and enlarged edition of a paper published some years ago, Phil. Mag. [5] 40, 173 (1895). Mixtures of methyl chlorid and carbonic acid, and of nitrous oxid and ethane were studied. The two systems supplement each other. With the first the plait curve has a maximum pressure value higher than the critical pressure of either of the pure components; with the second the plait curve has a minimum temperature value lower than the critical temperature of

either of the pure components. This latter system is also interesting in that the pressure-concentration curve passes through a maximum value. The reviewer would suggest that a reference to the phase rule would make matters clearer. It is certainly unsatisfactory to take as the critical temperature and pressure of a given mixture the maximum temperature and maximum pressure under which liquid and vapor can coexist, because then the critical temperature is reached under a pressure that is not the critical pressure and conversely the temperature corresponding to the critical pressure is not the critical temperature. It is much better to consider the plait curve as the locus of the critical temperatures and critical pressures. It is at the plaitpoints that liquid and vapor become identical.
W. D. B.

Experiments bearing on the two folds in van der Waals's surface for mixtures. *J. P. Kuenen. Arch. nèerl.* (*2*) *1*, *270* (*1897*). Under some circumstances a second liquid phase has been observed on compressing certain mixtures of methyl chlorid and carbonic acid. A careful revision of the work shows that the second solution is not stable under any conditions. Dewar has stated that carbon bisulfid and carbonic acid are partially miscible liquids, while Thilorier claims that the second liquid phase is instable. Experiments by Kuenen show that the latter view is correct.
W. D. B.

On the expansion of solutions of ammonia salts, II. *H. Schiff and U. Monsacchi. Zeit. phys. Chem.* 24, *513* (*1897*). There have been studied aqueous solutions of ethyl, diethyl, triethyl and tetrethyl ammonium chlorids and alcoholic solutions of ethyl ammonium chlorid. All solutions occupy a larger volume than the salt plus the water. With tetrethyl ammonium chlorid the percentage expansion increases up to a certain concentration and then decreases. No such phenomenon occurs with the other salts. It is not possible to make any generalization as to the effect of substituting alkyl groups for hydrogen.
W. D. B.

The thermodynamics of gelatinization with special reference to starch. *H. Rodewald. Zeit. phys. Chem.* 24, *193* (*1897*). The author first shows how Clausius's equations (*Mech. Wärmetheorie*, I, Chap. 6, Equations 11, 12 and 13) may be applied to the case of gelatinization of starch by water at low temperatures, and then proceeds to an experimental determination of the heat of gelatinization (ice calorimeter), the contraction (pyknometer with petroleum spirit), and the coefficient of expansion, as functions of the amount of water in the starch. From the results he calculates the maximum pressure to be attained by mixing water with dry starch and also the vapor-tensions of the various mixtures (Kirchhoff's equation).

The author quotes van 't Hoff–Raoult's formula for obtaining the molecular weight of a substance in solution from the depression of the vapor-tension of the solvent; and as he "finds from a study of Planck's article that the application of this formula depends solely on the condition that $f-f'$ is independent of the temperature" proceeds to calculate the molecular weight of the starch from the vapor-tension of a jelly containing thirty-two per cent of water! The number obtained is 4370, corresponding to the formula $C_{162}H_{270}H_{135}$.
W. L. M.

Poly-Component Systems

On equilibria in solutions containing three components. Application of the phase rule to the system: β-naphthol, picric acid and benzene. *B. Kuriloff. Zeit. phys. Chem.* 24, *441* (*1897*). The author has determined the isotherms for *135°*, *120°*, *100°* and 29.5°; also the boundary curves with naphthol picrate and picric acid, naphthol picrate and benzene picrate, naphthol picrate and naphthol as solid phases. The temperatures of the quintuple points are 78.5° for picric acid, naphthol picrate, benzene picrate, solution and vapor; about + 4° for naphthol picrate, benzene picrate, benzene, solution and vapor; and practically the same temperature when naphthol replaces the benzene picrate as solid phase. It was not shown experimentally that there is a maximum temperature on the boundary curve for the monovariant system with naphthol picrate and benzene as solid phases. *W. D. B.*

The solubility of stannous iodide in water and in solutions of hydriodic acid. *S. W. Young. Jour. Am. Chem. Soc.* 19, *845*, *851* (*1897*). The author has made an extended series of solubility determinations at different temperatures. Stannous iodid and hydriodic acid form a solid compound having the formula $SnI_2 2HI$. The author finds experimentally that SnI_2 and $SnI_2 2HI$ can coexist as solid phases in equilibrium with solution and vapor at more than one temperature. This must necessarily be the case, since the system contains three components and four phases. A recognition of all that this connotes would have increased the value of the work immensely. *W. D. B.*

Observations on the hydrolysis of ferric chlorid. *W. Spring. Recueil Trav. Pays-Bas*, 16, *237* (*1897*). Concentrated solutions of ferric chlorid do not give a blue precipitate with potassium ferricyanid, while dilute solutions do. From this the author concludes that the first change in ferric chlorid may be represented by the equation: $Fe_2Cl_6 \rightleftarrows Fe_2Cl_4 + Cl_2$. To test this he adds chlorin to the solutions and finds that a greater dilution is necessary before the blue precipitate is formed. Similar facts are noticed with ferric bromid. Adding barium carbonate to ferric nitrate solutions increases the dissociation because the nitric acid is neutralized by the carbonate. *W. D. B.*

A study of zinc hydroxide in precipitation. *V. J. Hall. Am. Chem. Jour.* 19, *901* (*1897*). On adding caustic potash to a zinc chlorid solution it was found that zinc chlorid was occluded, the amount increasing until the ratio of caustic potash to zinc was *1.5* : 1; with two of caustic potash no chlorin was found in the precipitate. Increasing the total concentration increases the amount occluded while raising the temperature decreases it. When zinc sulfate and chlorid are present in solution, the sulfate is occlued and not the chlorid. No potassium salts are carried down under any circumstances. *W. D. B.*

The formation of benzoyl-, propionyl-, and acetyl-peroxids by 'active' oxygen. *W. P. Jorissen. Arch. néerl.* (*2*) 1, *261* (*1897*). Reviewed (1, 514) from Zeit. phys. Chem. 22, 54 (1897).

Osmotic Pressure and Diffusion

Osmotic measurements. *A. Ponsot. Bull. Soc. Chim. Paris*, (3) 19, *9* (*1898*). The mean of ten measurements of the osmotic pressure at 11.8° of a solution containing 1.235 cane sugar per liter is 870.4 mm of solution. Rejecting the two most extreme measurements the mean of the remaining eight is 869.1 mm of solution. The theoretical value is 870 mm of solution. There is nothing given to show the relative sizes of the vessel containing the solution and of the tube in which the solution mounts, so that one cannot tell whether the change of concentration is negligible or whether it has been taken into account. On the data as they stand there is no reason to assume any dissociation of sugar in dilute solutions. The author thinks that we can accept 18.7 as the cryoscopic constant for water with an error not exceeding one two-hundredth. *W. D. B.*

On the relation between the osmotic pressure and the vapor pressure of solutions. *A. A. Noyes and C. G. Abbott. Phys. Rev.* 5, *113* (*1897*). This is the theoretical introduction from an article published Zeit. phys. Chem. 23, 56 (1897) and reviewed (1, 745). *W. D. B.*

On osmotic pressure against an ideal semi-permeable membrane. *Lord Kelvin. Proc. Roy. Soc. Edinb.* 21, *323* (*1897*). Reviewed (1, 607) from Nature 55, 272 (1897).

Velocities

The velocity of the hydrolytic decomposition of carbonylsulfid. *G. Buchböck. Zeit. phys. Chem.* 23, *123* (*1897*). At ordinary temperatures water dissolves approximately its own volume of carbonylsulfid, which soon decomposes according to the equation:

$$COS + H_2O = CO_2 + H_2S.$$

The H_2S formed was determined volumetrically with iodin, special precaution being taken to avoid loss by oxidation or evaporation.

As expected, the reaction proved to be of the first order, the variation of k with T (15° C to 40° C) was in good agreement with van 't Hoff's logarithmic formula, and a rise of 10 degrees increased the velocity in the proportion of 1 to 3.6 or 4.0. Addition of acids or salts *diminished* the velocity of the decomposition, carbamid and glycerol increased it.

"When we compare the values of k for solutions containing acids and salts, we see at once that there is no essential difference between the catalytic influence of the acids and that of the salts. The smaller values for acid solutions may be accounted for in full accord with the regularities observed, by the small atomic weight of hydrogen. ... There is thus no necessity of ascribing to the acids any specific influence on the rate of the reaction."

The 'mechanism of the reaction' is discussed under the assumption of intermediate formation of thiocarbonic acid and its subsequent decomposition into H_2S and CO_2. *W. L. M.*

On the speed of reduction of ferric alum by sugar. *J. H. Long. Jour. Am. Chem. Soc.* 19, *683* (*1897*). Ferric alum in solution is reduced by sugar, with

formation of ferrous salt and sulfuric acid, carbonic acid being evolved. The rate of change was determined by measuring the conductivity of the solution at stated intervals and interpreting these results by means of a previously prepared table. The rate is proportional to the concentration of sugar (which is assumed to remain constant) and to the concentration of the ferric salt. The free acid accelerates the reaction. The results are calculated according to the formula $dx/dt = K(B + x)(A - x)$ where B is the sugar concentration and A the initial concentration of ferric alum. The term $B + x$ is supposed to represent the effect due to the sugar and to the free acid. This not being a proper formulation it is not surprising that no satisfactory constant is obtained.
W. D. B.

On the effect of light on the combination of hydrogen and bromine at high temperatures. *J. H. Kastle and W. A. Beatty. Am. Chem. Jour.* **20**, *159* (*1898*).—Experiments made at 196° show that bromin scarcely combines with hydrogen at all in the dark. In direct sunlight the change takes place rapidly while the rate is much less in diffused light. It seems probable even from the qualitative measurements that the reaction velocity is proportional to the intensity of the light. *W. D. B.*

On the influence of ferric oxid on the formation of sodium sulfate from sulfur dioxid, air and sodium chlorid. *J. Krutwig. Recueil Trav. Pays-Bas*, **16**, *173* (*1897*). Ferric oxid acts as a catalytic agent. Experiments made without it showed that about twenty-eight percent of the sulfur in iron pyrites was converted into sulfate after four hours at a red heat. With ferric oxid a seventy percent yield was obtained at high temperatures and ninety percent at lower temperatures. *W. D. B.*

Electromotive Forces

Remarks on a paper of Callendar and Barnes on the Clark cell. *K. Kahle. Wied. Ann.* **64**, *92* (*1898*). Callendar and Barnes, Proc. Roy. Soc. **62**, 117 (1897), claim to have obtained different and more accurate results than the author. It is asserted in this note that the discrepancies are imaginary.
W. D. B.

On the thermochemical theory of the cell with carbon electrodes. *D. Tommasi. Bull. Soc. Chim. Paris*, (*3*) **17**, *963* (*1897*). A reply to Reed showing the inaccuracy of the latter's assumption that, in the cell, carbon, sodium chlorid, lead peroxid, carbon, the electromotive force is due to the direct action of the sodium chlorid on the lead peroxid. *W. D. B.*

Remarks on a paper by T. W. Richards: On the temperature coefficients of the potential of the calomel electrode with different dissolved electrolytes. *A. Gockel. Zeit. phys. Chem.* **24**, *703* (*1897*). The author complains that Richards has overlooked much of the modern work on the subject. He admits that the discrepancy between his earlier measurements and those of Richards is due to his not having noticed the temporary formation of mercuric chlorid.
W. D. B.

The thermoelectric properties of some liquid metals. *W. B. Burnie. Proc Phys. Soc. Lond.* 15, *76* (*1897*). The author has studied copper-lead, copper-tin, copper-bismuth, copper-mercury thermoelements in the neighborhood of the melting-points of the second metal. The curve representing electromotive force and temperature shows only a slight change of direction at the melting-point with lead and with tin; but a very decided change with bismuth and with mercury. With solid bismuth marked differences were noted, depending on the rate at which the metal had been cooled from the molten state.

W. D. B.

Experimental investigation of electrochemical actinometers. *H. Rigollot. Jour. de Phys.* (*3*) 6, *520* (*1897*). When one of two otherwise identical electrodes is illuminated and the other is kept dark there is always found to be a difference of electrical potential. The amount of this difference varies with the strength of the light, the nature of the light and of the electrodes. In the author's experiments the maximum difference of potential was never more than three millivolts. In studying the effect of light from different parts of the spectrum it was found that with each electrode there was a maximum effect produced by light of some definite wave-length. The position in the spectrum of this maximum effect varies with the nature of the electrode. It can also be varied by coloring the electrode with eosin, erythrosin and other substances which change the sensitiveness of photographic plates for certain rays.

W. D. B.

Electrochemical notes. *H. Jahn. Wied. Ann.* 63, *44* (*1897*). When the current necessary to decompose eighteen milligrams of water is passed through a sulfuric acid solution, 68.25 cal are absorbed if the anode is platinum and the cathode mercury. The theoretical value is 68.4 cal. The absorption of 68.47 cal was noticed when the same current passed through a sodium hydroxid solution, both electrodes being platinum. With a sodium hydroxid solution and a mercury cathode the heat effect was 105.81 cal, very near the theoretical value for the formation of sodium amalgam. From this the author concludes that primary decomposition of water does not take place when a sodium hydroxid solution is electrolyzed between platinum electrodes. The flaw in the reasoning lies in the explicit assumption that a mercury cathode does not differ fundamentally from a platinum cathode.

The author has improved the Warren de la Rue cell, Zn | $ZnCl_2Aq$ | AgCl | Ag by using the double chlorid of zinc and potassium as electrolyte. The electromotive force of this cell can be represented by the equation $E = (1.0136 - 0.000194t)$ volt.

W. D. B.

On polarization at thin metallic membranes. *W. Nernst and A. M. Scott. Wied. Ann.* 63, *386* (*1897*). To settle the question whether the behavior of thin gold membranes is due to depolarization through the membrane or to conductivity through the pores, the authors have placed in one branch of a Kohlrausch bridge a solution divided into two parts by a gold diaphragm. In this way it was possible to distinguish between the resistance of the pores and the polarization capacity of the diaphragm. For medium thicknesses of gold leaf both effects come in, while for very thin membranes the depolarization effect becomes nearly zero.

W. D. B.

Electrolysis and Electrolytic Dissociation

Conductivity of solutions of some salts in pyridin. *S. v. Lasczynski and S. v. Gorski. Zeit. Elektrochemie,* 4, *290* (*1897*). The salts taken were KI, NaI, NH_4I, LiCl, KCNS, NaCNS and NH_4CNS. Potassium, sodium and ammonium iodids are more than fifty percent dissociated at two hundred liters dilution; potassium and ammonium sulfocyanates are dissociated to nearly the same extent while lithium chlorid shows almost no dissociation. The authors connect the behavior of lithium chlorid with its forming a crystalline compound, $LiCl2C_5H_5N$, although there is no corresponding effect in the case of salts in aqueous solution. Attention is called to the fact that the increase of the conductivity with the dilution passes through a maximum with some of the salts.

Electrolysis of a pyridin solution of lithium chlorid gave metallic lithium at the cathode. With potassium sulfocyanate a little metallic potassium was obtained; but for the most part it seemed to react with the solute forming potassium sulfid. With ammonium sulfocyanate the results were unsatisfactory, partly because the temperature was not kept constant. Magnesium, cerium, calcium and cobalt chlorids did not conduct nor did sodium precipitate the metals. Silver iodid, dissolved in pyridin, did not conduct; but metallic silver was precipitated by sodium. *W. D. B.*

The relation of the taste of acids to their degree of dissociation. *T. W. Richards. Am. Chem. Jour.* 20, *121* (*1898*). An attempt to distinguish between relative strengths of acid solutions showed that the untrained tongue of the experimenter could not distinguish with accuracy between two solutions differing only twenty percent in concentration. It is stated that one-thousandth normal hydrochloric acid is about as dilute a solution as can be recognized as tasting sour. [This seems improbable because the reviewer has known of its being suggested to substitute this strength of acid for ordinary vinegar, which latter is certainly sour to the taste. Perhaps the personal equation will account for some of the discrepancies observed.] A qualitative agreement was found between different acids; but the quantitative agreement with the dissociation theory was not good. Addition of potassium acetate to acetic acid solutions decreases the sourness very perceptibly. Neutralizing an acid by a base gives a practically tasteless solution. The author has made use of this fact in titrating solutions. In one series of six determinations the maximum variation from the true value was less than one percent, while the mean of the six measurements was accurate to within one-tenth of one percent, a very surprising result. The reviewer believes that the sense of taste has been used in distinguishing saccharin derivatives. *W. D. B.*

Comment on the note of R. Franchot entitled: "On nascent hydrogen." *D. Tommasi. Bull. Soc. Chim. Paris,* (*3*) 17, *961* (*1897*). Reprinted, with additions, from this Journal (1, 555).

Dielectricity and Optics

The refractive equivalents of the elements. *A. Hauke. Sitzungsber. Akad. Wiss. Wien,* 105, (*IIA*) *749* (*1896*). After a condensed, but thorough, historical account of the origin and application of the various formulas serving as definitions of the 'refractive equivalents', the author communicates the results of his measurements on aqueous solutions of salts of thirty metals; and, assuming that the molecular refraction is the sum of the atomic refractions, calculates the refractive equivalents of the elements (Lorentz formula). After correcting and adding to the results of his own measurements by those of other authors, he arranges the whole in tables and diagrams, to show the connection between refraction and atomic weight. *W. L. M.*

Refractive indices for very short electric waves. *A. Lampa. Sitzungsber. Akad. Wiss. Wien*, 105, (*IIA*) *1049* (*1896*); *Wied. Ann.* 61, *79* (*1897*). Continuation of the author's experiments (1, 630) with paraffin, ebonite, sulfur, benzene, glycerol, turpentine, alcohol, and water. *W. L. M.*

Arc spectra. *A. L. Foley. Phys. Rev.* 5, *129* (*1897*). With a vertical arc and vertical slit the lines decrease rapidly in numbers and in intensity as the slit is moved from the center to the outer edge of the arc. With a vertical arc blown sidewise by a horse-shoe magnet all the lines are found to have a maximum of intensity in the central violet region. With a horizontal arc and vertical slit the carbon lines are stronger near the positive carbon and the metallic lines near the negative carbon. It seems probable that the differences observed in the spectra are due chiefly, if not entirely, to temperature differences. Some remarkable results were obtained by using cored carbons containing metallic salts. The metallic lines are strongest near the negative carbon and "the order of the elements, as regards the tendency of their special lines to cling to the negative carbon, is the same as their order in the electropositive-negative series." Calcium passes, apparently electrolytically, from the positive to the negative carbon. The electrolytic nature of the arc was further confirmed by a series of measurements with unlike electrodes, the details of which are to be published later. From experiments on the spectrum of carbon the author inclines to the view that "the so-called cyanogen bands are due to carbon in the presence of nitrogen, but not combined with it. *W. D. B.*

Ultraviolet spark spectra of the elements. *F. Exner and E. Haschek. Sitzungsber. Akad. Wiss. Wien*, 105, (*IIA*) *989* (*1896*). Photographic reproductions of the spectra of cobalt and nickel, and twenty-four pages of data in tabular form. Compare (1, 624). *W. L. M.*

Spectroscopic studies of argon. *G. B. Rizzo. Atti. Accad. Sci. Torino*, 32, *570* (*1897*). Passing a continuous current of electricity for twenty-four hours through a tube containing argon causes no appreciable difference between the spectrum at the anode and that at the cathode. *W. D. B.*

Dissociation spectra of some melted salts. *A. de Gramont. Chem. News*, 76, *201* (*1897*). Reviewed (1, 529) from the complete paper, Ann. Chim. Phys. (7) 10, 214 (1897).

The spark spectra of compounds. *A. de Gramont. Bull. Soc. Chim. Paris*, (*3*) 17, *774, 778, 780, 897, 899, 900* (*1897*); 18, *54, 57, 58* (*1898*). Fused salts containing lithium, sodium, potassium, chlorin, bromin, iodin, sulfur or phosphorus give spark spectra showing the lines of these elements. The solid phosphorus compounds also give the lines for phosphorus. Cf. also, this Journal 1, 529. *W. D. B.*

The permeability of elements of low atomic weights to the Röntgen rays. *J. Waddell. Chem. News,* 76, *161* (*1897*). A criticism of the results of Gladstone and Hibbert on the relative permeability of lithium, sodium and potassium. One difficulty urged is that Gladstone and Hibbert do not define clearly what they mean by relative permeability. One that might have been advanced is that they do not state how they managed to study metallic calcium. The author notes the curious phenomenon that X-rays photographs of powders often show a peculiar granulation, which seems to stand in some relation to the coarseness of the powder. *W. D. B.*

The permeability of elements of low atomic weights to the Röntgen rays. *J. H. Gladstone and W. Hibbert. Chem. News,* 76, *197* (*1897*). A reply to Waddell, see previous review. The authors state that when they give the order of comparative permeability they mean "the permeability of an equal number of atoms, that is, equal atomic weights,—seven parts of lithium compared with twenty-three of sodium and thirty-nine of potassium." *W. D. B.*

Action of X-rays on electrified bodies. *L. Benoist and D. Hurmuzescu. Séances Soc. Phys. Paris,* 1896, *261*. Elaboration of a note, published in the *Comptes rendus,* 123, 1265 (1896) and reviewed (1, 456). *W. D. B.*

On the actino-electric phenomena of the Röntgen rays. *S. Puggenheimer. Comptes rendus,* 125, *19* (*1897*). When one of two similar electrodes dipped into a solution is exposed to the X-rays, the illuminated one becomes the cathode. *W. D. B.*

Fluorescence and chemical constitution. *R. Meyer. Zeit. phys. Chem.* 24, *468* (*1897*). An enumeration and comparison of substances which exhibit distinct fluorescence to the naked eye. The investigation is restricted to the fact of fluorescence without reference to the nature of the light emitted; and "as it is impossible to bring all fluorescent bodies under a common point of view—fluorspar, uranium glass, double cyanid of the platinum metals, quinine salts and fluorescein are too heterogeneous to be directly compared—the discussion is limited to a few [8] selected groups of organic compounds." Liquid solutions only are studied, as the fluorescence of crystals is of a different nature, the light emitted being, in most cases at all events, polarized.

The author finds that, with the restrictions mentioned above, fluorescence is accompanied by the presence of certain groups of atoms in the structural formula 'fluorophoric groups,' between benzene nuclei. Substitution of hydrogen by other groups or atoms weakens or completely destroys the fluorescence; the position of the substituting group is also of importance. The solvent employed influences the result: a given substance may fluoresce in some solvents and not at all in others; in certain cases this difference may be accounted for by electrolytic dissociation, in others this explanation is definitely excluded. *W. L. M.*

STUDY OF A THREE-COMPONENT SYSTEM

BY HECTOR R. CARVETH

Although it is several years since the triangular diagram in improved form was proposed by Roozeboom,[1] and although its advantages have been more recently illustrated by Bancroft,[2] there has been published, so far as the writer is aware, only one study of a three-component system with complete experimental details in respect to temperature-concentration changes.[3] The object of the present paper is to present the examination of such a system.

In order to deal with the simplest case possible, the components have been so chosen that

(1) they dissolve without decomposition to a homogeneous solution;

(2) they form neither solid solutions, mixed crystals, nor double salts;

(3) their respective melting-points do not lie too far apart. It was moreover thought desirable to work if possible with inorganic substances since these do not appear to have been studied to any extent in respect to their possibilities as solvents. If one will deal with a true three-component system of inorganic salts, it will be found necessary that the substances shall all have the same acid or basic radical. Other conditions which the ideal materials for such an examination must fulfil are those of purity of material and ease of handling. The choice of the nitrates of

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[1] Zeit. phys. Chem. 15, 143 (1894).

[2] Jour. Phys. Chem. 1, 403 (1897).

[3] Kuriloff. Zeit. phys. Chem. 24, 441 (1897). This appeared after the experimental work of this paper was finished.

lithium, sodium, and potassium has been found to suit the numerous requirements[1] enumerated above.

It had been hoped that in place of lithium nitrate, silver nitrate might be used, but it was found to decompose too readily at temperatures at which it was necessary to work. Theoretically this would have presented an important type since, according to Retgers,[2] the nitrates of silver and potassium form a double salt, while neither the nitrates of sodium and silver,[3] nor sodium and potassium form a double salt. The interest attached to this type theoretically would have been increased by the fact that the melting-point of silver nitrate lies below the eutectic temperature of the sodium potassium nitrate mixture.

As it appeared advisable to obtain a great number of measurements rather than exceptional accuracy in determining the freezing-points of the series of mixtures of the three components chosen, the following method was adopted. An iron cylinder 5 cm in diameter and 20 cm in length was closed at one end. It was then filled with a mixture of potassium and sodium nitrates that melted at 225°, or, in case the temperature of the bath needed to be lower than this, a Wood's fusible metal was used as the bath. Into this fusion bath was plunged a test-tube which held the mixture whose freezing-point was to be determined. The mixture was thus fused, and by use of a thermometer as stirring rod, solution was effected at as low a temperature as possible. The test-tube was then taken out into the air and stirred constantly until the first crystals appeared. It was then replaced in the fusion bath for a moment, taken out again, and the temperature at which the crystals first appeared was noted. The observation was repeated several times for each mixture, the mean being taken as the correct reading.

For measurements above 280°, a nitrogen mercury thermometer which had been carefully compared with the Reich-

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[1] The work of Krickmeyer (Zeit. phys. Chem. 21, 89 (1897)) shows that lithium, sodium and potassium salts form neither isomorphous mixtures nor double salts.

[2] Zeit. phys. Chem. 5, 451 (1890).

[3] Krickmeyer (loc. cit.) regards silver and sodium salts as capable of forming isomorphous mixtures. This accords with the work of Retgers.

sanstalts of the chemical and physical departments was used. The measurements below 280° were made by means of an ordinary mercury thermometer which also had been compared with the Reichsanstalts.

When lithium nitrate is fused in ordinary glass tubes, the sodium of the glass is replaced, the glass becomes opaque as if etched by hydrofluoric acid, and is then readily broken. The thermometers had therefore to be protected by a casing of very thin glass. It is apparent that with the use of such small amounts of material and this method of measurement, there is possibly an error of ± 2° as the maximum. As no conclusions will be drawn which such an error would invalidate, it has not seemed advisable to spend more time in avoiding this source of inaccuracy.

The sodium and potassium nitrates were found quite pure after being crystallized several times. The lithium nitrate was prepared from well washed lithium carbonate. It showed spectroscopic traces of other elements (sodium and calcium) but no impurity was detected by ordinary analytical tests. The sodium and potassium nitrates fused without noticeable decomposition; with the lithium salt however, there is a very slight decomposition,[1] which however is not very apparent until the temperature reaches 290°. Since only one measurement was made above this temperature when it was present in the mixture, it will be seen that no error is introduced in regarding it as stable.

In order to cover all combinations which may be represented in the triangle and to do so in such a way as to economize time and material the writer has chosen the amounts of each substance in the mixtures and examined the freezing-points after the following scheme:

First of all the freezing-point of pure sodium nitrate was taken. Then sufficient potassium nitrate was taken to make its weight 10 percent of the total weight of the mixture. The freezing-point was then taken, and then more potassium nitrate was added, sufficient to make its weight 20 percent of the total weight. The freezing-point of this mixture was then taken, etc.

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[1] Detected by evolution of gas, not by weighing.

When this plan is followed, first for the mixture of the potassium and sodium nitrates, then for the potassium and lithium, lithium and sodium salts, one may readily see that when the results are plotted on coordinate paper, the freezing-point of any combination of these three components taken two at a time is readily determined.

From the properties of the triangle it is apparent that when one selects any point on a side, as for example that representing 90 percent sodium nitrate with 10 percent lithium nitrate, (always by weight) and joins that point to the corner representing pure potassium nitrate, every point lying on this connecting line will represent a mixture in which the proportion of sodium nitrate is to the lithium salt as 9: 1.

The varying factor in passing along this line is the amount of potassium nitrate in the solution. Similarly other lines drawn from any point representing x percent of sodium nitrate and $(100-x)$ percent of the potassium salt to the point representing pure lithium nitrate will indicate mixtures in which the ratio of sodium to potassium nitrates is as x to $100-x$, while the amount of lithium nitrate may vary along this line from 0 percent to 100 percent. Accordingly lines have been drawn from points on the sodium lithium nitrate line representing 100 percent of either component, 90 percent of one and 10 percent of the other, 80 percent of first and 20 percent of second, etc., to the corner representing pure potassium nitrate, and other lines intersecting these have been drawn in a similar fashion from the side representing sodium potassium nitrates to the corner for pure lithium nitrate. Mixtures have then been made up corresponding to the points of intersections of these two series of lines. The advantages of this method of procedure are that one actual determination is used for two curves, as is later shown, and that the number of measurements is diminished. The disadvantage is that the corners of the diagram are not thoroughly examined which however, in cases like the present, is not a very serious matter.

In the tables which follow, there is given under the formula of each of the components the *percentage by weight* of that component in the mixture. In the column headed F. P. are given the freezing-points as observed.

Table I

(a)

No.	KNO_3	$NaNO_3$	$LiNO_3$	F.P.
1	....	100.00	....	308°
2	10.00	90.00	....	293
3	20.00	80.00	....	276
4	30.00	70.00	....	259
5	40.00	60.00	....	240
6	50.00	50.00	....	224
7	55.00	45.00	....	221
8	60.00	40.00	....	228
9	70.00	30.00	....	248
10	80.00	20.00	....	277
11	90.00	10.00	....	308
	100.00	....	....	337

(b)

	....	100.00	....	308°
1	....	90.00	10.00	283
2	9.09	81.82	9.09	271
3	18.37	73.47	8.16	260
4	27.84	64.96	7.22	243
5	37.50	56.25	6.25	228
6	47.34	47.34	5.26	215
7	52.00	43.00	5.00	209
	62.2	34.00	3.80	217

(c)

1	....	80.00	20.00	259°
2	8.16	73.47	18.37	251
3	16.66	66.67	16.66	244
4	25.95	59.56	14.89	233
5	34.78	52.18	13.04	221
	39.56	48.35	12.09	213
6	44.44	44.44	11.12	206
8	54.54	36.37	9.09	196
	59.77	32.27	8.06	201
9	65.11	27.91	6.98	215
	70.59	23.53	5.88	236
10	76.17	19.07	4.76	253
	81.33	14.94	3.73	273
	87.77	9.79	2.44	288

(d)

No.	KNO_3	$NaNO_3$	$LiNO_3$	F.P.
1	....	70.00	30.00	236°
2	7.21	64.95	27.84	231
3	14.90	59.58	25.52	226
4	23.08	53.84	23.08	218
5	31.82	47.73	20.45	209
6	41.17	41.17	17.66	196
7	46.11	37.72	16.17	188
8	51.23	34.14	14.63	180
9	62.02	26.58	11.40	195
	67.74	22.58	9.68	215
10	73.68	18.42	7.90	232

(e)

1	....	60.00	40.00	217°
2	6.25	56.25	37.50	214
3	13.04	52.17	34.79	210
4	20.45	47.73	31.82	206
5	28.57	42.86	28.57	198
6	37.50	37.50	25.00	185
7	42.31	34.61	23.08	179
8	47.37	31.57	21.06	173
9	58.33	25.00	16.67	172
	64.29	21.43	14.28	186
10	70.58	17.65	11.77	214
	77.27	13.64	9.07	243

(f)

1	....	50.00	50.00	206°
2	5.26	47.34	47.34	204
3	11.11	44.44	44.44	199
4	17.64	41.18	41.18	193
5	25.00	37.50	37.50	186
6	33.33	33.33	33.33	176
7	37.94	31.03	31.03	171
8	42.85	28.57	28.57	164
9	53.85	23.07	23.07	145
	60.00	20.00	20.00	158
10	66.66	16.67	16.67	184

(g)

No.	KNO_3	$NaNO_3$	$LiNO_3$	F.P.
1	....	40.00	60.00	214°
2	4.25	38.30	57.45	212
3	9.09	36.36	54.55	207
4	14.63	34.15	51.22	200
5	21.05	31.60	47.35	191
6	28.57	28.57	42.86	180
7	32.83	26.87	40.30	172
8	37.50	25.00	37.50	162
9	48.28	20.69	31.03	132
	54.54	18.18	27.27	120
10	61.54	15.39	23.07	154
	69.38	12.24	18.36	202

(h)

1	....	30.00	70.00	223°
2	3.22	29.03	67.74	221
3	6.97	27.92	65.11	218
4	11.39	26.59	62.02	213
5	16.66	25.00	58.33	207
6	23.08	23.08	53.84	199
7	26.83	21.95	51.22	195
8	31.03	20.69	48.28	188
	35.78	19.27	44.95	180
9	41.18	17.64	41.18	165
	47.37	15.79	36.84	148
10	54.54	13.63	31.89	130
	62.96	11.11	25.92	144
	70.59	8.82	20.59	192

(i)

1	....	20.00	80.00	234°
2	2.17	19.56	78.26	232
3	4.76	19.04	76.20	229
4	7.89	18.42	73.69	226
5	11.77	17.65	70.59	222
6	16.66	16.67	66.67	217
7	19.64	16.07	64.29	213
8	23.07	15.38	61.55	209
	27.09	14.58	58.33	204
9	31.81	13.64	54.55	195
	37.50	12.50	50.00	185
10	44.44	11.11	44.44	168
	53.12	9.37	37.50	144
	60.00	8.00	32.00	128
	70.00	6.00	24.00	172
	75.00	5.00	20.00	206
	80.00	4.00	16.00	237

(j)

No.	KNO_3	$NaNO_3$	$LiNO_3$	F.P.
1	....	10.00	90.00	244°
3	2.44	9.76	87.80	241
4	4.11	9.59	86.30	239
5	6.25	9.37	84.38	237
6	9.09	9.09	81.82	234
7	13.05	8.70	78.25	230
9	18.91	8.11	72.98	223
10	28.57	7.14	64.29	209
	36.17	6.38	57.45	195
	47.37	5.26	47.37	170
	60.00	4.00	36.00	138
	70.00	3.00	27.00	161
	75.00	2.50	22.50	197
	77.80	2.22	19.98	215

(k)

1	....	....	100.00	253°
	11.11	....	88.89	242
	25.00	....	75.00	224
	33.33	....	66.66	212
	40.00	....	60.00	200
	45.00	....	55.00	188
	50.00	....	50.00	174
	55.00	....	45.00	161
	60.00	....	40.00	143
	65.00	....	35.00	132
	70.00	....	30.00	139
	75.00	....	25.00	186
	80.00	....	20.00	223
	85.00	....	15.00	255
	90.00	....	10.00	290
	100.00	....	....	337

(l)

	....	100.00	....	308°
	....	90.00	10.00	283
	....	80.00	20.00	259
	....	70.00	30.00	236
	....	60.00	40.00	217
	....	50.00	50.00	206
	....	40.00	60.00	214
	....	30.00	70.00	223
	....	20.00	80.00	234
	....	10.00	90.00	244
	....	....	100.00	253

With the data here given it is possible to construct a fairly complete surface which will show the freezing-point of any mixture of the three components. In order to do this, it will be necessary to regard the temperatures as represented in a plane perpendicular to that in which the triangle lies. By marking off on these perpendiculars the temperatures of the freezing-points observed for the mixtures designated by the points from which the perpendiculars are erected, and by then connecting the series of points so obtained, one is able to make a surface; but as sections of the surface, represented by curves, may be made to indicate the salient points of the diagram, these alone will be considered.

In the present case, it has been found that two series of such curves give all the requirements. Of these, one series indicates the change of the freezing-point as one passes from pure KNO_3 to the various mixtures of ($NaNO_3 + LiNO_3$); the other series has as one component pure $LiNO_3$, and as the other ($NaNO_3 + KNO_3$) in fixed proportions. The first series is obtained directly from the measurements just given, then in the order in which they are grouped, each group thus giving a curve. Thus the series of measurements (*a*) when plotted on ordinary coordinate paper give the curve a_1Aa_2 (Fig. 1), series (*c*) gives curve c_1Cc_2 (Fig. 1) etc.

From the curves given in Figs. 1 and 2 one may see that the points of union of the two fusion curves occur at points which represent the temperatures and composition given below.

Table II

Point	Fig.	% KNO_3	% $NaNO_3$	% $LiNO_3$	F.P.
A	1	54.5	45.5	....	218°
B		55	40.5	4.5	206
C	1	55	36	9	194
D		55	31.5	13.5	174
E	1	55.5	26.7	17.8	162
F	2	56	22	22	142
G	2	54.5	18.2	27.3	120
H	2	56.5	13	30.5	126
I	2	60	8	32	128
J		63	3.7	33.3	128
K	2	66	....	34	129

In Figs. 1 and 2, the curves for series (b), (d) and (j) have been omitted, the latter two to avoid crowding the diagram, the former owing to having insufficient data to construct the curve. In order therefore to determine the point B, it was necessary to assume that the curve b_1Bb_2 pursues an intermediate course between a_1Aa_2 and c_1Cc_2, which assumption seems correct for at least one-half its course. From the method of determining these points where the change in curvature occurs, it is apparent that too great accuracy is not to be ascribed to any of the figures obtained in the preceding table. All that can be said is that the values are very probable. Several check measurements made after the curves had been determined bear out this view.

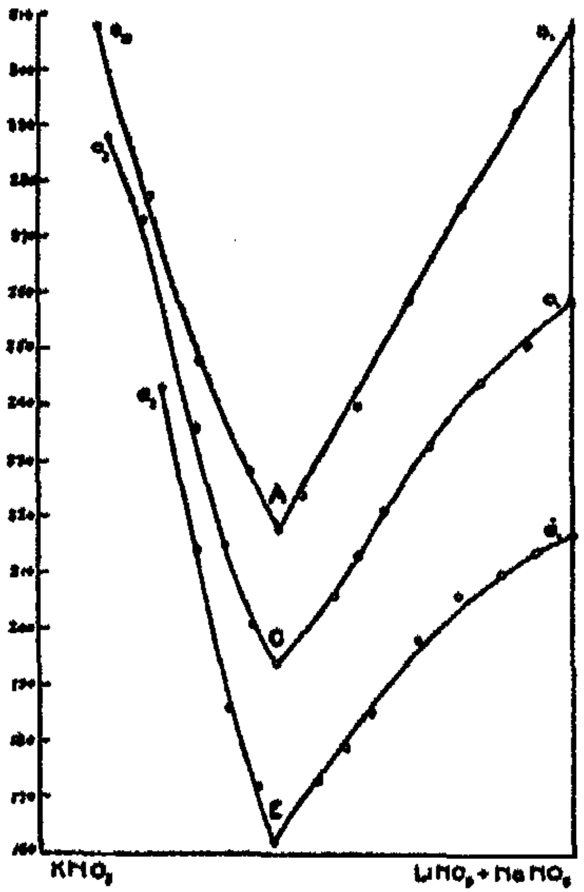

FIG. 1

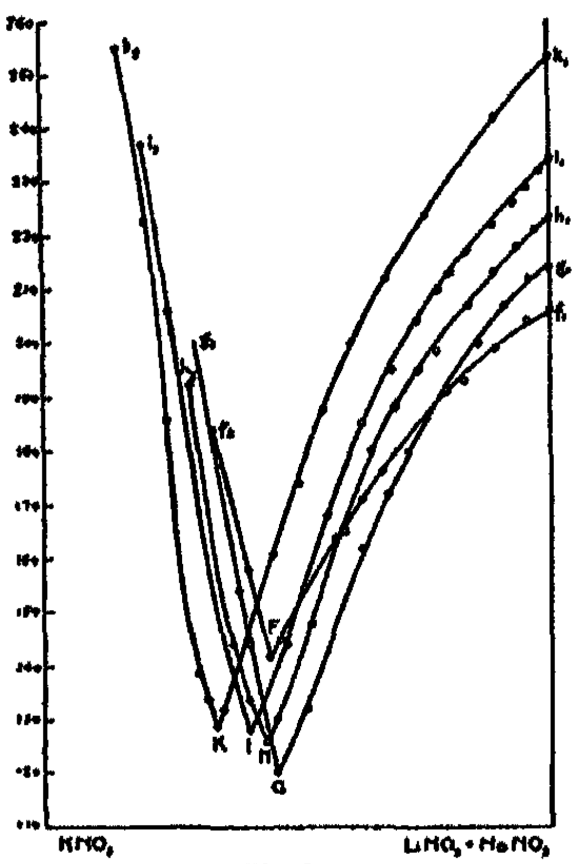

FIG. 2

When one is dealing with a two-component system which has at a certain temperature the two solids, solution and vapor in equilibrium, the mixture is called "eutectic". The points A and K represent binary eutectics—hence at the temperatures of 218° and 129° respectively the mixtures will solidify without change of temperature. At the points B–J, the mixtures will not solidify without change of temperature. These are hence not eutectic points, but merely mark the division line where one passes from one field to another. Refer for a moment to Fig. 1, curve e_2Ee_1. An examination of the crystals separating along the fusion curve e_2E would show that they were pure KNO_3. Along e_1E pure $NaNO_3$ separates. At E, temperature 162°, there is the monovariant system two solids, solution and vapor, differing from systems at A or K in having three components. Being monovariant, its diagrammatic position must be on a boundary curve.

In the case of Fig. 2, it will be found that in all the curves pure KNO_3 will separate along one branch of the curve while, along the other branch, pure $LiNO_3$ will separate, except in the case of the curve f_1Ff_2. Attention is directed to the fact that the curves of Fig. 1 seem to belong to one family, as also do those of Fig. 2, f_1Ff_2 being excepted. It is inserted in Fig. 2 to show the change from one family to the other. The difference in the curvature is due to the changes in the solid phase, KNO_3 and $NaNO_3$ being solid phases along the curves (*a*) (*b*) (*c*) (*d*) and (*e*), and KNO_3 and $LiNO_3$ along (*g*) (*h*) (*i*) (*j*) (*k*). Along f_1Ff_2 all three components appear as solid phases in different parts of the curve, but this cannot be shown with the results as developed up to the present.

If now one marks in on a triangular diagram the points which as just shown lie on the boundary lines, it will appear that the use of a similar series of curves with $LiNO_3$ as the pure component and ($NaNO_3$ + KNO_3) as mixture will give more boundary points, thus allowing of a complete demarcation of the fields. Referring back to the manner in which the composition of the various mixtures was determined before any measurements were taken, one may see that to construct such series of curves the data are all given in the preceding table. In the construction of the previous set of curves (Figs. 1 and 2) the data were used just as they are given—viz., in series, each series giving a curve. To save re-arrangement of the same table to determine the present set of curves, the measurements needed have been numbered. By taking all measurements numbered 1 and plotting them on coordinate paper, considering $LiNO_3$ as one component and $(NaNO_3)$[1] as the other, a curve is determined. With the measurements numbered 2, a curve somewhat similar in form is obtained, with $LiNO_3$ as one component and (90 percent $NaNO_3$ + 10 percent KNO_3) as the other. Similarly, curves may be obtained for the other measurements.

The compositions and melting-points of the mixtures denoted by the points where the several branches of these curves meet, are shown in the following table:

Table III

Curve No.	% KNO_3	% $NaNO_3$	% $LiNO_3$	F.P.
1	....	53	47	204°
2	5.5	49.5	45	202
3	11.2	44.8	44	198
4	17.0	39.5	43.5	189.5
5	23.8	35.7	40.5	183
6	31.2	31.2	37.5	173
7	34.6	28.4	37	166
8	39	26	35	155
9	49	21	30	127
10	56	14	30	120

These are determined as in the previous instance, not by direct measurement, but by continuation of the branches to their cutting point. The curves themselves are not presented in this paper.

By now plotting the results as obtained in the last two tables in the triangular diagrams and connecting the single points, thus forming the boundary curves, one may realize the different fields. These constitute the divariant systems where there are present, solid, solution and vapor. The boundary curves represent monovariant systems where two solids, solution and vapor may coexist. There are seven points in the triangular diagram

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[1] It has been thought advisable to collect the data for mixtures of $LiNO_3$ and $NaNO_3$ in (*l*) Table 1. The series comprises the first measurement taken in each one of the preceding series.

where nonvariant systems are possible—viz., the ternary eutectic point where the three solids can be in equilibrium with solution and vapor, three binary eutectics where the two solids composing the mixture coexist with solution and vapor, and the points representing each pure component. At each one of these seven points the solution may solidify without change of temperature, a confirmation of the rule that when *n* is the number of compounds with stable melting-points, the number of mixtures for which the solution solidifies without change of temperature is $2n + 1$.[1]

The theorem of van Rijn van Alkemade[2] which requires that, in passing along the boundary curves from the binary to the ternary eutectics, the temperature must fall is confirmed in this case. The binary eutectic mixtures A and K of Table 2 show melting-points of 218° and 129° respectively. The binary eutectic 1 of Table 3 has a melting-point of 204°. The ternary eutectic has a freezing temperature of 119° (approximately). The points on the boundary curves which are given in Tables 2 and 3 show clearly that the theorem of van Alkemade holds in this case.

The course of the isotherms for a system of this kind has been discussed fully by Bancroft.[3] The isotherm for 337° will consist of a point. All isotherms below 337° and above 308° will consist of a branch in the potassium nitrate corner (320°, Fig. 3). The isotherm for 308° will consist of a branch in the same corner and the point representing pure sodium nitrate. The isotherms between 308° and 253° will consist of two branches, one each in the fields where KNO_3 and $NaNO_3$ can exist as solids (290°, Fig. 3). For the 253° isotherm there are curves in the same two fields, and also the point representing pure lithium nitrate. The isotherms from 253° to 218° exist as three disconnected curves (230°, Fig. 3). The isotherm at 218° consists of three branches, of which two meet on the potassium sodium nitrate side; similarly all isotherms from 218° to 204°

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[1] Phase Rule, 132.

[2] Zeit. phys. Chem. 11, 289 (1893).

[3] Phase Rule, 156.

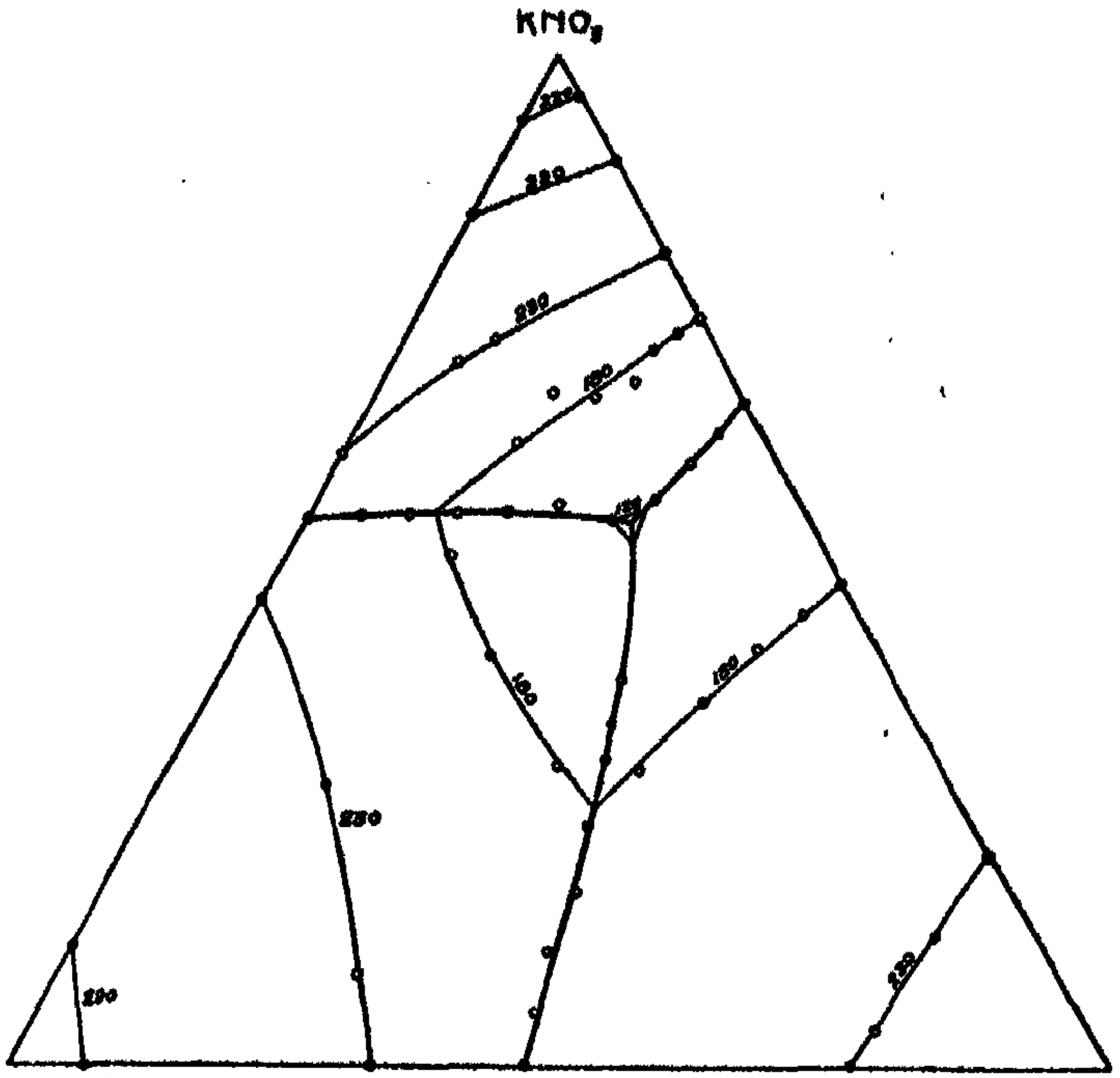

FIG. 3

consist of two connected branches and one not connected with the others. The isotherms for 204° and all down to 129° consist of three branches connected, but not forming a closed ring (180°, Fig. 3). All isotherms from 129° to 119°, the melting-point of the ternary eutectic, consist of closed curves of three branches (120°, Fig. 3). The isotherm for 119° consists of one point.

It will be noted by examining the isotherms which possess three distinct branches, that the points of change of direction of the curves indicate a change in the nature of the solid separating. The boundary curves could accordingly have been determined from a series of isotherms. In this particular system such a plan of procedure would have presented more experimental difficulties, but in cases such as were examined by

Bathrick[1] and Taylor[2] such a method has very decided advantages over the present.

Reference has been previously made to the course of the curve f_1Ff_2 (Fig. 2). The peculiarity is that along this curve it is possible to have each of the three components separating as solid phase. There should therefore be three distinct branches to the curve, and while it is possible to observe this from the data for series (f), the change of direction is very slight at the first break, where the percentage of potassium nitrate in the mixture is about thirteen. The occurrence of the breaks in the curve is shown better in Fig. 3, where the line drawn from the point representing equal amounts of lithium and sodium nitrates to that denoting pure potassium nitrate will pass first through the field where the lithium salt occurs as solid, then through the sodium and into the potassium nitrate field. As may be seen from the direction of the boundary curves in Fig. 3 this class of curves is by no means of infrequent occurrence. Had one no other guide, the difference between the curve f_1Ff_2 and the other curves in Fig. 2 would have led one to suspect a change in the nature of the solid separating.

It is not uninteresting to note the measurements which have been made by other observers on the freezing-points of the three salts in question. These are summarized in Landolt and Börnstein's *Tabellen.*

For the melting-point of potassium nitrate, Person (1849) observed 339°, Schaffgotsch (1857) 338.3°, Braun (1875) 342°, Carnelley (1876) 353 ± 1° by the calorimetric method, (1876) 332 ± 5° and (1878) 339 ± 2°, Guthrie 320°, while Maumené (1883) found 327°. The value obtained by the writer was 327° uncorrected, and 337° corrected.

For sodium nitrate the following values had been obtained: Person 310.5°, Braun 314°, Carnelley 319°, 316° and 330 ± 2°, Guthrie 305°, Maumené 298°. The writer found 308°.

The only previous measurements on lithium nitrate appear

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[1] Jour. Phys. Chem. 1, 165 (1896).

[2] Ibid. 1, 718 (1897).

to have been made by Carnelley who obtained 267 ± 8° by his calorimetric method, while direct observation gave 264°. In the present instance, the melting-point was found to be 253°.

The only systematic measurements which have been made on mixtures of two of these substances appears to have been taken by Schaffgotsch.[1] A comparison between his results and those of the writer are given in the following table. The numbers refer to the mixtures given in series (*a*); in the series S are given the melting-points observed by Schaffgotsch, in C those of the writer.

	1	2	3	4	5	6	7	8	9	10	11	12
S	313	298	287	262	244	229	225	230	250	280	311	338
C	308	293	276	259	240	224	221	228	248	277	308	337

As will be observed Schaffgotsch's values always lie higher than those observed by the present writer.

To those interested in the melting-points of inorganic materials, the great discrepancies which occur in the measurements made by different observers may occasion some surprise. It is not to be forgotten that accurate measurements at high temperatures are difficult to make by means of a mercury thermometer, while the thermoelectric method in its present form may not be suited to every laboratory. A thorough revision of the melting-points of many of the important inorganic compounds would be of considerable service for work at high temperatures in many of the fields of chemistry.

Had the method of thermometry been sufficiently accurate it would have proved extremely interesting to have noted whether these salts depress the freezing-points of each other according to the general laws. As is known these laws do not hold in concentrated solutions and since one has here to do with solutions of great concentration there is not to be expected a rigid agreement in this case. Making use of the data given by Person[2] for the heats of fusion and the melting-points of sodium and potassium nitrates, one finds it possible to calculate the

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[1] Pogg. Ann. 102, 293 (1857).

[2] Comptes rendus, 29, 300 (1849).

molecular lowering for each solvent by making use of the formula

$$E = \frac{0.02T^2}{W}$$

where E represents the molecular lowering of the freezing-point, T is the freezing temperature expressed in absolute degrees, and W is the latent heat of fusion. Person gives for KNO_3 $T = 333.5 + 273$, for W 48.9. Hence $E_{KNO_3} = 150.4$. For $NaNO_3$ he gives $T = 305.8 + 273$, $W = 64.87$, hence $E_{NaNO_3} = 103.2$.

Despite the fact that the solutions are all very concentrated, we shall apply to series (*a*) the formula

$$M = E\frac{g}{t}$$

where:

M is the molecular weight of the solute,
E is the molecular lowering of the freezing-point,
g is the relation (percent) of the solute to solvent,
t is the lowering of the freezing-point observed.

Calculation shows that for a ten percent solution of KNO_3 in $NaNO_3$, the molecular weight of the former is found to be 76.7 instead of 101. Measurements (3), (4), (5) and (6) of series (*a*) give 80.6, 90.3, 101.1 and 122.8 respectively.

When the KNO_3 acts as solvent for the $NaNO_3$, a similar rise in the molecular weight is observed on passing to the more concentrated solutions. Measurements (11), (10), (9) and (8) of series (*a*) give as the molecular weight of $NaNO_3$, 57, 62.6, 72.4 and 91.9 instead of the actual value 85. These measurements would indicate that the salts used above will probably at infinite dilution show, when dissolved in each other, a molecular weight considerably lower than the actual value.

The measurements given above may be used to ascertain if it is possible to employ the freezing-point method in analysis of salts. If one assumes that when $NaNO_3$ is added to KNO_3 it gives at ordinary dilutions a depression corresponding to half its molecular weight, it appears that for this method to be of service in analysis, the freezing-point must be determined to the tenth part of a degree if one would determine 0.028 percent of $NaNO_3$. With ordinary methods, such accuracy of measurement is at present impossible; but it appears not unreasonable to suppose that such a method could be made to apply as a very great help to the analyst when dealing with compounds such as the alkalies. The two requirements would be a considerable amount of material for the test, and a delicate method of thermometry.

At a time when great interest is taken as to whether the presence of two solutes gives a depression of the freezing-point equal to greater or less than their sum when taken separately, it would have been interesting to have subjected this case with its inorganic solvents to the test. As a general statement it may be remarked that here the depression is as a rule greater than the sum of the depressions when the substances are added singly. This would seem to conform to the rule given by Abegg[1] and supported by his measurements. Later work by McIntosh[2] showed that the Abegg rule is by no means general—that in fact "when the three components are miscible the sum of the single depressions is usually greater than the depression for the mixture; but this is not always true owing to disturbing conditions which are not yet defined." During these experiments no evidence has been found which points to the existence of two liquid layers or would indicate that the three components are not infinitely miscible one with the other. This case therefore is one where disturbing influences come into play.

It had been hoped that sufficient measurements might be found in the literature to illustrate the use of the triangular method of representation in a three-component system of metals. Despite the great number of measurements which have been made with various mixtures of three metals, the data are insufficient for the construction of a complete diagram. The very numerous and accurate experimental results of Heycock and Neville were the subject of considerable manipulation, but when they were represented in the diagram it was invariably found

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[1] Zeit. phys. Chem. 11, 259 (1893).

[2] Jour. Phys. Chem. 1, 474 (1897).

that these scientists had worked over a very small portion of the triangle (usually one corner) and that the same measurement was sometimes repeated apparently without being noticed. A plotting of their results for gold, cadmium and lead[1] would show a typical case of this.

Of course it is permissible and will often prove very useful to use the triangular diagram in such a fashion that any or all of its corners may represent a mixture of the three components taken two at a time provided always that the ratio of the two remains constant. Thus in studying the results of Heycock and Neville on gold, cadmium and lead, the writer found it convenient to use as corners, 100 percent lead, 80 percent lead and 20 percent cadmium, 80 percent lead and 20 percent gold.

An attempt was made to use the data given by Carnelley to construct a diagram for the three metals, bismuth, tin and lead. Here again the data are insufficient—a fact which is not surprising when it is considered that all the measurements taken during the present work are not sufficient to stamp the deductions as to changes of direction of the boundary curves as absolutely accurate. The study of such a system of metals—whether of three or more components—offers a most interesting field to the chemist or metallurgist; the isotherms and the boundaries of the fields can give much useful information in such technical work as the desilvering of lead, etc. The study of the crystalline structure of alloys, which is at present attracting so much attention, can undoubtedly be greatly facilitated by the use of such a diagram. When it is distinctly understood that as a rule, only within a certain field, one metal can crystallize out first, that in other portions it is possible to have two metals crystallizing out side by side, and at one point three metals, the importance of a uniform rate of cooling becomes apparent when rigorous comparisons are to be made. The use of the diagram is not however to be confined to cases where the mixture is perfectly homogeneous; in cases where two liquid layers appear, it is at present the only method of graphic representation.

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[1] Jour. Chem. Soc. 65, 68 (1894).

In the use of the triangular diagram as represented in this paper, the axis perpendicular to the plane of the triangle has been chosen to represent the variable, temperature. It may however be chosen to represent other variables, *e. g.* conductivity, time, pressure, etc. The first two will be given but a brief consideration since experimental data seem to be lacking.

If conductivity measurements of a three-component system be plotted as shown in this paper, it will be found (the other variables such as temperature and pressure being here constant) that a surface or series of surfaces will result. The examination of the discontinuities in such surfaces might afford much assistance in establishing the definitions of solvent and solute, while the graphical method employed might be of service in studies of the theories of dissociation or association.

When the perpendicular axis is used to represent the variable time,[1] it is possible to represent in the triangular diagram curves representing speed of reaction. Taking for the moment a concrete case of a bimolecular reaction—

dichloracetic acid + amylene ⇄ amylenester

one may readily see that within the triangular diagram there will be for each temperature a line passing through the triangle from pure amylene to pure acid, along which are represented the quantities of each substance present at equilibrium at this temperature. If now the temperature be fixed, and time be represented on the perpendicular axis, the curves representing speed of reaction pass from the sides of the triangle to the composition-time line of equilibrium. Of this line, little is known. It will be generally concave to the plane of the triangle since it is evident that a pure component cannot of itself change into another in an infinity of time. The possibility is not precluded however, that this line may also have a wavy appearance. For each temperature there will be a different line; the investigation of the relations between the series of lines offers many interesting features.

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[1] This suggestion is due to Professor Bancroft.

The extension of the application of the triangular diagram to a four-component system offers another way of presenting the Law of Mass Action graphically. Suppose we choose as the four components the classical case—alcohol, acid, ester and water. This choice is so made because the final equilibrium is, within certain limits, independent of the temperature (van 't Hoff) and hence the representation of temperature is unnecessary. The four-component system may then be represented by a tetrahedron as has been shown previously by Roozeboom. Of this each point represents pure components, each edge two-component, each face three-component and every point within the tetrahedron a four-component system. An examination of all the four component systems which can be in equilibrium, shows that their compositions are represented by points lying on a certain surface within the tetrahedron. It is owing to the mathematical properties of this surface that the Mass Law may be applied rigorously to the system chosen above.

If in place of the system chosen above there had been chosen one where the final equilibrium depends on the temperature, a series of different surfaces of equilibrium would have been obtained of such properties that they are connected by the van 't Hoff equation

$$\frac{d \log \mathrm{K}}{d\mathrm{T}} = \frac{q}{\mathrm{RT}^2}$$

These surfaces would prove especially interesting in the cases where double decomposition is possible. If in these cases there occur any discontinuities in the surfaces of equilibrium finally obtained, it will be apparent that the Mass Law formula in its general form is not applicable and that the equation for each surface is determined by the introduction into the formula of constants—such as has been done recently in the work of Bancroft and his students on three-component systems. The data for the construction of such a diagram appear to be lacking.

In this paper has been given:

(*a*) The experimental data as to the freezing-points of a considerable number of mixtures of lithium, sodium and potassium nitrates.

(*b*) The classification and interpretation of these results according to the Phase Rule.

(*c*) The suggestion as to the possibility of applying the freezing-point method in the case of analysis of inorganic salts.

(*d*) Reference to the probability that some inorganic salts when dissolved in others show a molecular weight lower than that obtained by the use of other solvents.

(*e*) A suggestion as to the importance of locating the fields of each component in an examination of the crystalline structure of alloys, and in technical metallurgical work.

Finally, attention has been especially drawn to the relations subsisting between the Mass Law and the equations of surfaces of equilibrium.

Cornell University, January, 1898.

NOTE ON THERMAL EQUILIBRIUM IN ELECTROLYSIS[1]

BY D. TOMMASI

The problem which we propose to solve is the following: Given a chemical compound capable of being oxidized or reduced, to find how it behaves when exposed simultaneously to an oxidizing and a reducing agent, these latter being considered as two equal and contrary forces. Theoretically two cases alone are possible: first, the two forces neutralize each other completely and then it is clear that the system remains in equilibrium; second, one of these forces overcomes the other. From the thermal data we can distinguish between these cases. Take, for instance, the system AB; submit it to a chemical action ($H_2 + O$),[2] and three cases may arise:[3]

(*a*) The system AB will undergo no change if

$$c\mathrm{AH}_2 + c\mathrm{BO} = c\mathrm{AO} + c\mathrm{BH}_2;^{4}$$

that is to say if the compound AB evolves the same amount of heat in being oxidized as in being reduced.

(*b*) The system AB will be reduced if $c\mathrm{AH}_2 > c\mathrm{BO}$.

(*c*) The system AB will be neutralized if $c\mathrm{AH}_2 < c\mathrm{BO}$.

To illustrate the meaning better let us take a concrete case: Let us submit nitric acid to the action of ($H_2 + O$). In this case the reduction of the nitric acid will take place only if this change evolves more heat than the oxidation of the ammonia. Accord-

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[1] Translated, from the author's French manuscript, by W. D. Bancroft.

[2] Mixture of electrolytic hydrogen and oxygen.

[3] We assume in these three cases that the same quantity of heat energy is necessary to begin the chemical reaction.

[4] c = heat of formation.

ing to the thermal data the formation of ammonia by the reduction of nitric acid evolves

$$HNO_3 + 4H_2 = NH_3 + 3H_2O + 179.2 \text{ cal}$$

and the change of ammonia into nitric acid evolves

$$NH_3 + 4O = HNO_3 + H_2O + 96.8 \text{ cal}$$

From this it follows that nitric acid will be completely reduced by $(H_2 + O)$ without any reverse reaction taking place; which has been completely confirmed experimentally.

The mixture $(H_2 + O)$ is obtained by the electrolysis of water containing in solution the chemical compound which is to be submitted to the action of $(H_2 + O)$. The gases are thus evolved in the ratio of their molecular weights and under the same physical and chemical conditions. The electrodes are made of platinum and brought as close together as possible. The liquid on which we act is stirred frequently and the current reversed occasionally. In the following table are collected the results which we have reached in submitting different chemical compounds, capable of being reduced or oxidized, to the simultaneous action of electrolytic hydrogen and oxygen.

Action of $(H_2 + O)$ *on Different Chemical Compounds*

Initial compound	Final compound
Nitric acid	Ammonia and nitrite
Potassium nitrate	" " "
Sodium nitrate	" " "
Potassium nitrite	Ammonia
Potassium chlorate	Perchlorate
Arsenic acid	No change
Potassium arsenate	" "
Arsenious acid	Arsenic acid
Potassium arsenite	Arsenate
Ferrous sulfate	Partial oxidation
Ferric sulfate	Partial reduction

From these experiments we can deduce the following laws:

1. *When a substance is submitted to two equal and contrary chemical actions, the reaction which involves the most heat will take place in preference, provided always that it can begin.*

Illustrations: Oxidation of arsenic acid and of alkaline arsenates; reduction of nitric acid, of nitrates and of alkaline nitrites.

2. *Of two chemical reactions that one which requires less heat to start it will always take place in preference, even though it evolves less heat than the other reaction.* Illustrations: Oxidation of chlorate; partial reduction of ferric sulfate (60 percent) and partial oxidation of ferrous sulfate (40 percent).

In the case of the chlorate, for instance, the heat or energy necessary to bring about the combination of hydrogen with the oxygen of the chlorate must be much greater than that required to bring about the combination of the oxygen with the chlorate, and that is without question the reason why the chlorate is changed into perchlorate rather than into chlorid, although the oxidation of the chlorate evolves less heat than its reduction. Let us cite, in closing, the following fact which will show in a conclusive way that the principle of maximum work is true only on the express condition that the reaction among the substances in solution can begin. If we electrolyze a solution of hydrogen peroxid, H_2O_2, acidified with sulfuric acid, we obtain at the negative pole an evolution of hydrogen due to the decomposition of water, which hydrogen does not reduce the hydrogen peroxid. Now how can we explain the fact that the electrolytic hydrogen, which nevertheless reduces a number of substances, whose decomposition absorbs heat, has no action on hydrogen peroxid, whose decomposition on the other hand takes place with evolution of heat? In other words, why does the electric current decompose water whose heat of decomposition is -69 cal rather than act on hydrogen peroxid whose heat of decomposition is $+21.6$ cal? We have shown[1] a similar fact with the following couple: zinc, acidified water, porous cup, hydrogen peroxid to which a drop of copper sulfate has been added, platinum. With this couple the precipitation of copper on the platinum takes place as soon as the circuit is closed and long before the hydrogen peroxide has been decomposed. We observe then in this couple the singular fact that hydrogen coming from the decom-

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[1] D. Tommasi. Traité théorique et pratique d'électrochimie, 526.

position of water reduces copper sulfate (exothermal compound), whose decomposition absorbs heat in consequence, rather than the hydrogen peroxid (endothermal compound) whose decomposition on the other hand takes place with evolution of heat.

BENZENE, ACETIC ACID AND WATER

BY JOHN WADDELL

The object of this investigation was to determine, as far as possible, the way in which acetic acid changes the mutual solubilities of benzene and water; in other words, to study the distribution ratio of acetic acid in benzene and water as solvents. There were two reasons for taking acetic acid as the consolute liquid. It could be determined by titration and Wright, Leon and Thompson[1] had already studied a similar system in which chloroform replaced the benzene.

The acetic acid was purified by crystallization till a fraction melting at 16° was obtained. Titration with decinormal potash[2] showed this to contain only 0.3 percent of water, an amount which would correspond to 0.015 cc in 5 cc of acetic acid and which falls within the limit of experimental error. The burette in which the acid was measured was connected with a reservoir containing the acid, and all air that entered the burette or the reservoir passed through calcium chloride tubes. The benzene was first heated with concentrated sulphuric acid and then distilled. The distillate was treated with metallic sodium and redistilled, going over within half a degree. Some portions of the benzene used were freed almost entirely from thiophene and any other substances which blacken concentrated sulphuric acid. Other portions were not purified so carefully; but I could detect no difference in my experiments. The water was obtained by adding alkaline permanganate solution to the distilled water of the laboratory and redistilling, rejecting the first and last por-

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[1] Proc. Roy. Soc. 49, 178 (1891).

[2] Supplied by Mr. Cushman.

tions. The burettes were calibrated against a 2 cc pipette which had been standardized with mercury. The burettes could be read to 0.02 cc.

The measurements were made in the usual way by adding varying amounts of benzene or water to 5 cc acetic acid and then running in the water or benzene till saturation was reached. The experimental error seems to be about three percent.

It was hoped that the results could be represented by one or two exponential formulas of the general form $xy^n = \text{const}$, where x and y refer to the amounts of benzene and water in a constant quantity of acetic acid. In case two curves were necessary, it was expected that the point of intersection would correspond exactly with the point at which the two solution phases become identical. Nothing of the sort was found. There is no discontinuity when the saturated solution changes from being the denser to being the less dense phase. Also when the data are plotted on logarithmic coordinates, the resulting curve is a wavy one. With the isotherm for 25°, one might easily consider the curve as nearly straight if one omitted some of the middle portions. This will be seen more clearly if we examine the experimental data given in Table I. The results have been recalculated into grams and represent grams of benzene and of water in 5.25 g acetic acid. In the table are also given the calculated values, assuming that the amounts of benzene and water vary according to the formula $xy^4 = 2.54$, where x refers to the benzene and y to the water. Under "calc" are the values obtained when one substitutes in the formula the found values for one of the components and solves for the other. The absolute difference between the calculated and the found values will be less if one solves for the component present in lesser amounts, and for this reason the water values are taken for comparison in the first part of the table and the benzene values in the last part. The bracketed values are those of the consolute point or the point where the two liquid phases become identical.

Table I

Temp. 25°

Formula $xy^{\frac{3}{2}} = \text{const} = 2.54$

$x = g$ benzene; $y = g$ water per 5.25 g acetic acid

x	y found	y calc	const	x calc	x found	y	const
17.58	0.24	0.28	2.07	1.89	1.76	1.22	2.37
8.8	0.42	0.44	2 42	1.01	0.88	1.86	2.22
7.91	0.44	0.46	2.30	0.90	0.80	2.00	2.26
7.03	0.51	0.51	2.56	0.40	0.39	3.43	2.47
6.15	0.59	0.55	2.79	0.32	0.29	4.0	2.32
5.27	0.63	0.62	2.64	0.23	0.21	5.0	2.34
4.38	0.72	0.70	2.67	0.17	0.18	6.0	2.64
[3.96	0.76]	0.75	2.62	0.14	0.17	7.0	3.14
3.52	0.85	0.81	2.75	0.11	0.13	8.0	2.94
2.64	0.99	0.98	2.61	0.09	0.11	9.0	2.97

If one could eliminate the three solutions in which there are 1.76, 0.88 and 0.8 grams of benzene, the other figures might easily seem to come within the limits of experimental error. This is not a possibility because these determinations can be made with great accuracy and the inapplicability of the formula becomes more evident when we consider the isotherm for 35°. Plotted on logarithmic coordinate paper, the general form of the curve is approximately that of a straight line, one-half of which has been displaced to a certain extent though still keeping approximately parallel with the other half. Since neither line is really straight, the curve may be described more accurately as half way between the letter S and an integral sign.[1] Under these circumstances it is not possible to make even the approximate calculation in Table I and the data are therefore given in Table II without comment. The constant quantity of acetic acid in each case is 5.25 g and the data for the consolute point are marked by a square bracket.

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[1] Special experiments showed that the miscibility of benzene and water was not of importance.

Table II

Temp. 35°

$x = g$ benzene ; $y = g$ water per 5 25 g acetic acid

x	y	x	y	x	y
17.60	0.29	[3.96	0.85]	1.12	1.71
13.20	0.35	3.52	0.91	0.88	1.97
8.8	0.46	2.64	1.05	0.50	2.94
6.16	0.62	1.76	1.30	0.30	4.50
5.28	0.72	1.41	1.50	0.20	6.50
4.4	0.79				

In order to construct the isotherms, using a triangular diagram, it is necessary to make the sum of the three components constant. This calculation has been made and the figures are given in Table III, the values being grams per hundred grams of solution and the consolute point being marked by a square bracket.

Table III

Concentrations expressed in grams per hundred grams

Temp. 25°			Temp. 35°		
Acid	Benzene	Water	Acid	Benzene	Water
22.7	76.2	1.1	27.9	70.3	1.8
36.3	60.8	2.9	36.1	60.6	3.3
38.5	58.1	3.4	46.7	47.0	6.3
41.0	55.0	4.0	50.3	42.1	7.6
43.6	51.3	5.1	[52.2	39.4	8.4]
47.1	47.2	5.7	54.2	36.4	9.4
50.7	42.3	7.0	58.6	29.6	11.8
[52.8	39.6	7.6]	63.1	21.2	15.7
54.7	36.8	8.5	64.3	17.3	18.4
59.2	29.8	11.0	65.0	13.9	21.1
63.8	21.5	14.7	64.9	10.9	24.2
65.6	11.0	23.4	60.4	5.8	33.8
65.0	10.0	25.0	52.0	3.0	45.0
57.6	4.3	38.1	44.0	1.7	54.3
55.0	3.1	41.9			
50.2	2.0	47.8			
45.9	1.6	52.5			
42.1	1.4	56.5			
39.0	1.0	60.0			
36.6	0.7	62.7			

By interpolation and extrapolation along the isotherm it is possible, without difficulty, to determine the coordinates of a solution containing any particular percentage of acetic acid. The next point was to determine the tie-lines. Measured amounts of acetic acid, benzene and water were allowed to stand in the constant temperature bath at 25° until the two liquid layers were in equilibrium. Portions of each layer were pipetted off and the acetic acid determined by titration. In the four sets of figures enclosed in brackets in Table IV, the composition of each of the lower or aqueous layers was obtained by drawing the tie-line from the point in the diagram given by the composition of the upper layer through the point representing the composition of the original mixture and noting where it cut the curve. Under the circumstances, this is the most accurate method for a reference to Table IV will show that a very slight difference in the percentage of the acid corresponds to great variations in the relative amounts of benzene and water. This method of procedure is justified by the fact that, in each of the cases in which both layers were analyzed, the tie-line passed accurately through the point of total composition. The data for the isotherm at 25° are given in Table IV.

Table IV

Temp. 25°

Concentrations expressed in grams per hundred grams

Upper layer			Lower layer		
Acid	Benzene	Water	Acid	Benzene	Water
0.46	99.52	0.02	9.4	0.18	90.42
1.30	98.64	0.06	16.5	0.31	83.19
3.1	96.75	0.15	28.2	0.53	71.27
5.2	94.55	0.25	37.7	0.84	61.46
7.0	92.66	0.34	43.9	1.5	54.6
8.7	90.88	0.42	48.3	1.82	49.88
8.9	90.67	0.43	49.5	1.93	49.57
10.5	88.99	0.51	53.2	2.72	44.08
16.3	82.91	0.79	61.4	6.1	32.5
⌈21.5	77.46	1.04	64.5	9.2	26.3⌉
22.8	76.10	1.10	65.0	10.0	25.0
30.5	67.37	2.13	66.0	13.8	20.2
⌊32.8	64.76	2.44	65.0	17.8	17.2⌋
46.5	47.9	5.6	60.0	29.0	11.0
52.8	39.6	7.6	52.8	39.6	7.6

Two points are very noticeable in this table. The amount of acetic acid in the aqueous layer passes through a maximum. A similar phenomenon has already been noted by S. F. Taylor[1] with alcohol, benzene and water. The more striking feature is that, just before the consolute point is reached, there is not only more benzene than water in both layers; but there is a great deal more benzene than water. As there is no real justification for comparing grams of benzene with grams of water, the data have been recalculated and are given in Table V, the values being reacting weights per hundred reacting weights in the solution.

Table V

Temp. 25°

Concentrations expressed in reacting weights per hundred

Upper layer			Lower layer		
Acid	Benzene	Water	Acid	Benzene	Water
0.60	99.31	0.09	3.02	0.04	96.94
1.68	98.06	0.26	5.61	0.08	94.31
3.97	95.39	0.64	10.59	0.19	89.22
6.60	92.35	1.05	15.50	0.27	84.23
8.81	89.76	1.43	19.35	0.51	80.14
10.90	87.35	1.75	22.39	0.65	76.96
11.12	87.09	1.79	22.88	0.69	76.43
13.02	84.87	2.11	26.31	1.03	72.66
19.69	77.13	3.18	35.20	2.68	62.12
25.41	70.48	4.11	40.46	4.45	55.09
26.85	68.84	4.31	41.66	4.93	53.41
34.10	57.97	7.93	45.83	7.38	46.79
36.15	54.86	8 99	47.78	10.05	42.17
45.57	36.11	18.32	50.44	18.74	30.82
48 53	28.08	23.35	48.53	28.08	23.85

Both of the salient points of the preceding table remain though the excess of benzene in the aqueous layer is decreased enormously.

It has been shown by S. F. Taylor that a formula of the general form $z_2''/z_1 = \text{const}$, expressed the distribution of alcohol between benzene and water.[2] In this formula z_1 represented

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[1] Jour. Phys. Chem. 1, 468 (1897).

[2] Ibid. 1, 471 (1897).

the amount of alcohol in the benzene phase referred to a constant quantity of benzene, while z_2 represented the amount of alcohol in the aqueous phase referred to a constant quantity of water. This general formula could not be expected to apply absolutely to the distribution of acetic acid between benzene and water because it has been found, in this investigation, that the course of the isotherm cannot be represented by the theoretical formula. It was quite conceivable however that the distribution of acetic acid between benzene and water might be represented with the same degree of approximation as was possible with the isotherm itself. The calculation has been made and the results are given in Table VI. The formula used is $z_2^{\frac{1}{2}}/z_1 = 10$, where z_1 denotes grams of acetic acid per gram of benzene in the less dense phase, and z_2 grams of acetic acid per gram of water in the more dense phase. Under "calc" are given the values for acetic acid per hundred grams of solution, in the less dense phase, which correspond to the "found" percentages of acetic acid in the more dense phase.

Table VI

Temp. 25°

Formula $z_2^{\frac{1}{2}}/z_1$ = const = 10

z_1 = g acid in benzene layer per g benzene

z_2 = g acid in aqueous layer per g water

Concentration expressed in grams per hundred grams

Acid in upper layer calc	found	Acid in lower layer	const
0.49	0.46	9.4	10.6
1.14	1.30	16.5	8.8
2 81	3.1	28.2	9.1
4.92	5.2	37.7	9.5
6.94	7.0	43.9	9.9
8.71	8.7	48.3	10.0
9.06	8.9	49.5	10.2
11.4	10.5	53.2	10.9
19.4	16.3	61.4	11.9
25.6	21.5	64.5	11.9
27.2	22.8	65.0	11.9
32.7	30.5	66.0	10.7
38.1	32.8	65.0	11.6
46.0	46.5	60.0	9.9
52.4	52.8	52.8	9.9

It will be noticed that the agreement between theory and experiment is pretty fair except just at the maximum for acetic acid where a very slight error makes a very large difference. A variation of one percent in the composition of the aqueous layer would account for the variation of twenty percent in the constant.

In the most dilute solution given in Table VI there is about twenty times as much acetic acid in one hundred grams of the aqueous layer as in a corresponding weight of the benzene phase. Two other determinations were made with more dilute solutions. In the one case 0.5 cc of acid was added to 10 cc benzene and 10 cc water; in the second case 0.1 cc of acid was taken. The analyses of the upper and lower layers were approximate only, owing to the small quantity of acid. These measurements were made in order to see whether the ratio of the acid in benzene to the acid in water would reach any definite limit. In the first experiment the ratio was 1:40; in the second 1:56. While these two estimations were only approximate, as has been said, they were sufficiently accurate to show that there is no apparent limiting ratio. These results are in accordance qualitatively and quantitatively with the theory of Nernst,[1] according to which relatively more and more of the acetic acid should pass into the aqueous phase as the solution becomes more dilute.

Table VII

Temp. 35°

Concentrations expressed in grams per hundred grams

Upper layer			Lower layer		
Acid	Benzene	Water	Acid	Benzene	Water
1.24	98.68	0.08	16.4	0.62	82.98
5.7	93.97	0.33	36.8	1.42	62.78
9.0	90.42	0.58	49.0	2.1	48.9
45.0	49.0	6.0	61.3	25.5	13.2
52.2	39.4	8.4	52.2	39.4	8.4

A few tie-lines have been determined at 35° and these are given in Table VII. Since the isotherm could not be expressed at all by any simple equation, it is not to be expected that any

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[1] Zeit. phys. Chem. 8, 124 (1891).

very satisfactory results would be obtained from a calculation of the coexisting phases. In spite of this the calculation has been made, using the same general formula as for the isotherm at twenty-five degrees, $z_2^{[illegible]}/z_1$ = const. As before z_1 is the amount of acetic acid in one gram of benzene and z_2 the amount of acetic acid, also in grams, per gram of benzene. The value of the exponential factor is the same in the two cases; but the integration constant is a little smaller at 35° than at 25°. The data are given in Table VIII.

Table VIII

Temp. 35°

Formula $z_2^{[illegible]}/z_1$ = const = 8.9
z_1 = *g* acid per *g* in benzene layer per *g* benzene
z_2 = *g* acid in aqueous layer per *g* water
Concentrations expressed in grams per hundred grams

Acid in upper layer calc	Acid in upper layer found	Acid in lower layer	const
1.28	1.24	16.4	9.2
5.2	5.7	36.8	8.1
10.2	9.0	49.0	10.1
42.5	45.0	61.3	8.4
50.7	52.2	52.2	8.7

The general results of this investigation may be summed up:

1. There is no sudden change of direction at the consolute point.

2. The isotherms for 25° and 35° cannot be represented by a simple exponential formula.

3. The distribution of acetic acid can only be represented approximately by a simple exponential formula.

4. The ratio of acetic acid in water to acetic acid in benzene increases indefinitely with increasing dilution.

5. The percentage acetic acid in the aqueous phase passes through a maximum.

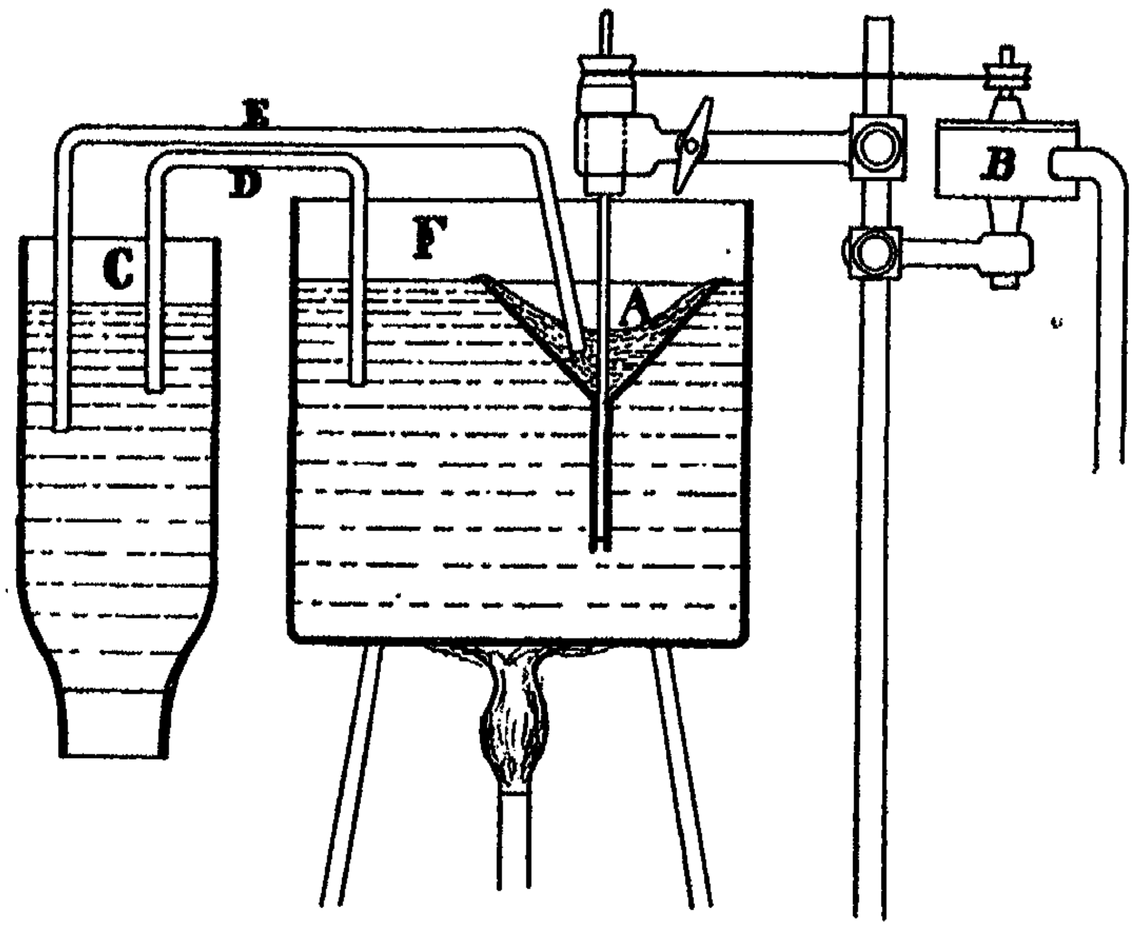
6. The ratio of benzene to water in the more dense phase is greater than unity over a portion of the isotherm, even when the concentrations are expressed in reacting weights.

Cornell University

A CONSTANT TEMPERATURE DEVICE

BY HAMILTON P. CADY

It is often necessary to keep a constant temperature in an apparatus which on account of its size or for some other reason cannot be immersed in a constant temperature bath. This may be done in various ways, one of which is to circulate water having a constant temperature around the apparatus. In order to keep the water circulating, the device illustrated in the cut has been found convenient.



A is an ordinary 75 mm glass funnel mounted on a glass rod and running in the bearings of an ordinary Witt stirrer. B is a Raabe turbine. F is a large water-bath kept at the desired temperature. C is the apparatus through which the water is to circulate. The siphon D connects C and F and consequently the water will come to the same level in both vessels. A is adjusted so that the top of the funnel comes just at the surface of the water in F. If the interior of the funnel be connected with C by the siphon E, the end of which is as near to the bottom of A as possible, water will flow from C into A until the level is the same in each. When equilibrium is reached the level of the liquid in A, F and C will be the same.

If now A be caused to rotate by the turbine, the water in A will be thrown out by the so-called centrifugal force and the level of the liquid in A will be lower than that in C. This will cause water to flow from C into A, thereby lowering the level of the water in C below that in F and causing water to flow from F into C. This will of course set up a circulation of water through C that will continue as long as A is rotated. If the siphons are made of moderately large tubing the amount of water that can be caused to circulate is surprising. The temperature in C can be maintained as constant as that in F, although of course slightly lower.

The rotating funnel has the advantage of not only keeping the water circulating through C but of thoroughly stirring that in F, for the water is drawn up from the bottom along the outside of the funnel and thrown off in a sort of a wave which is fully a centimeter in height when the apparatus is running at full speed. If the top of the funnel be placed at or near the surface of the water there will be no spattering. If however it be raised considerably higher, the water will be thrown off in small drops.

Water may be caused to circulate through a condenser by filling the condenser completely with water and placing one connecting tube in the funnel and the other in the bath. The condenser may of course be placed in any position either above or below the bath, provided it is not more than thirty feet above the latter.

It would seem that with this device a circulating liquid might be advantageously used instead of a vapor jacket in vapor density determinations when a series of measurements are to be made at different temperatures, for it would do away with the necessity of having a number of very pure substances, the temperature would be independent of barometric changes, and any desired change of temperature could be easily made without change in the apparatus. If temperatures above 100° are required, some other liquid such as high boiling paraffin or cottonseed oil may be substituted for water.

Cornell University

THE EQUILIBRIA OF STEREOISOMERS, II

BY WILDER D. BANCROFT

In the first paper[1] of the series, it was shown how Duhem's theory of permanent changes offered a satisfactory explanation of many phenomena connected with the change of one isomer into another. In this paper I shall discuss some of the changes due to the addition of one or more components. The cases to be treated may be classified as follows:

I. The new component forms no compound either with the α or the β modification.
  1. No reversal of stability.
    a. The β modification changes into the α modification without heat effect.
    b. The β modification changes into the α modification with evolution of heat.
    c. The β modification changes into the α modification with absorption of heat.
  2. Reversal of stability.
    a. Without displacement of equilibrium.
    b. With displacement of equilibrium.

It is obvious that a system coming under any of these heads will behave like a three-component system if we work rapidly and like a two-component system if we wait for the final equilibrium to be reached. We will begin with the case where the new component C forms no compound either with the α or the β modification, making the further proviso that the α modification

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[1] Jour. Phys. Chem. 2, 143 (1898).

shall be the stable form under all circumstances. The general diagrams for cases 1*a*, 1*b* and 1*c* are given in Fig. 1.

Working rapidly, we shall be able to realize the three boundary curves: DO with the α and the β modifications as solid phases; HO with the α modification and the component C as solid phases; EO with the β modification and the component C as solid phases. The α modification will be solid phase in the field ADOH; the β modification in the field BDOE; the component C in the field CEOH. At the point O we shall have the two modifications and the component C temporarily in equilibrium with solution and vapor. If, however, we wait until equilibrium is reached, the variance of the system drops from three to two; fields become lines; lines become points and points disappear. The point O ceases to be a possibility; the line ADB becomes the point X, while the surface of the triangle dwindles to a line

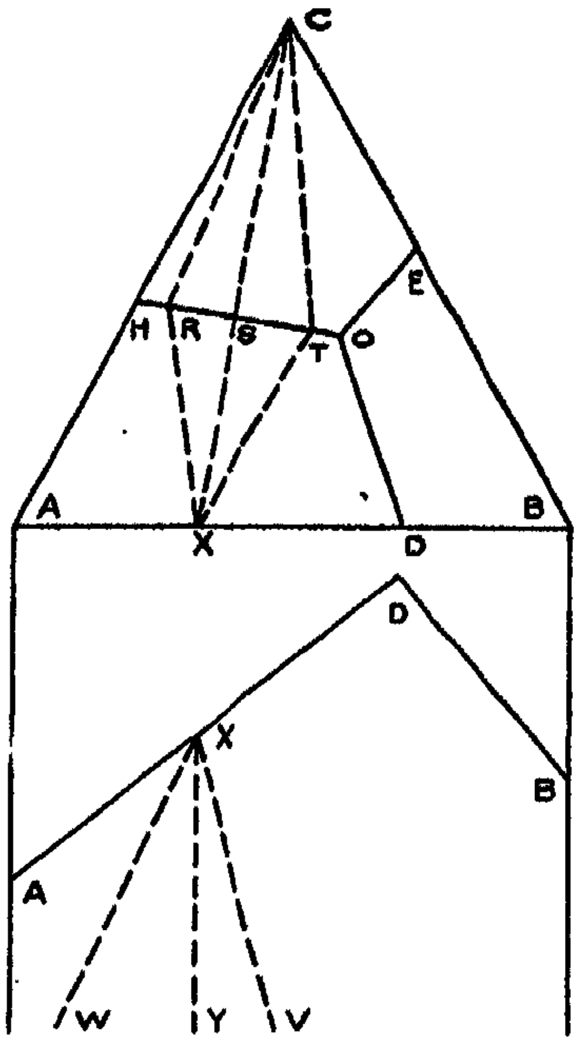

Fig. 1

connecting X and C. It is this line which interests us. If the equilibrium between the α and β modifications is independent of the temperature, as shown by the line YX, and if this equilibrium be affected but little or not at all by the component C, the boundary curves will form an approximately straight line from X to C, in other words XSC. If the component C displace the equilibrium to the side of the β modification the point S will move to the right along HO while it will move to the left along the same line in case the equilibrium be displaced to the side of the α modification.

The line XSC does not cut the field BDOE. Consequently, the β modification will not be stable under any circumstances, and the diagram conforms to the limiting condition imposed. Along the line XS the solid phase will be the α modification; along CS the component C will be solid phase; the point S will represent the stable quadruple point at which the α modification and the component C are in stable equilibrium, as solid phases, with solution and vapor. The temperature will rise in both directions from the stable quadruple point S along the boundary curves to X and C. In considering the effect of keeping a definite initial solution at a definite temperature, we must bear in mind that the temperature of the point S is necessarily higher than that of the point O and lower than that of H; but that it may be either higher or lower than that of D and of E. If, as is often the case, the temperature of the point X is higher than the melting-point of C, the temperature of S will usually be higher than that of E and lower than that of O.

If there is no solid phase, the change of concentration at constant temperature will be such that the system passes along a line parallel to the base of the triangle in the direction of the 'natural' surface. The lines YXSC all lie in this surface which is the locus of all states of stable equilibrium that include solution and vapor. Starting with a solution represented by some point on BEC the final result will be unsaturated solution and vapor if the temperature of E is higher than that of S. If the temperature of E be lower than that of S there will be some temperature for which an isothermal line parallel to the base of the triangle will cut both BE and XS. At this temperature, a solution saturated with respect to the β modification will change to a solution saturated with respect to the α modification. At constant temperature all solutions represented by points on BEC which contain more of the β modification than this one will form solutions unsaturated with respect to the α modification while all solutions represented by points on BEC, which contain less of the β modification than this one will change to solutions supersaturated with respect to the α modification, to the component C or to both these phases. In the first case the resulting system will be the solid α modification, solution and vapor, the composition of the solution being represented by the point on XS for the temperature in question. In the second case the final system will be solid C, solution and vapor, the composition of the solution being given by the point on CS corresponding to the temperature of the experiment. In case the resulting solution is supersaturated with respect to both solid phases, the phases finally in equilibrium will be the two solids and vapor.

Starting with a saturated solution represented by a point on AHC, the final equilibrium reached, at constant temperature, will always be unsaturated solution and vapor.

If the initial system be solid, solution and vapor instead of saturated solution and vapor, the change in the composition of the solution will no longer be represented by a line parallel to the base of the triangle. As long as the solid phase is present the system will pass along the isotherm for solid, solution and vapor; if the solid phase disappear at any point, the change from then on will be represented, as before, by a line parallel to the base of the triangle. Starting, with an excess of the β modification, from a point on BE having a temperature higher than that of the point D, there will be gradual decrease of the solid phase, the composition of the solution approximating more and more closely to that of the point on BD for the same temperature. Since the amount of the component C in the solution can never become zero, the solid β modification will disappear eventually and we shall have saturated solution and vapor, the changes of which have just been discussed at length. If we start, with an excess of the β modification from a point on BE, having a temperature lower than that of D, the system will pass along the isotherm, the concentration changing until, at the point where the isotherm cuts OD, the α modification appears as solid phase. The concentration will then remain constant until the whole of the β modification has changed into the α modification. The concentration will then vary until the solution has the composition of the point at which the isotherm cuts XS, the final system being the solid α modification, solution and vapor.

If we start, with an excess of the component C, from a point on CE or OH the final equilibrium will be, outwardly, the same as the initial one; namely, solid C, solution and vapor. The difference will be in the composition of the solution and, possibly, in the total amount of the solid phase. It is worth noting that if the lowering of the freezing-point of C due to a mixture of the α and the β modifications were the sum of the partial depressions of the modifications taken singly, the part of the isotherm in the field for C would be a straight line parallel to the base of the triangle. If this were true, the surface lying between HC and EC would be absolutely plane. It seems more probable, however, that the line CS lies below the plane passing through the lines HCE, in which case the isotherm will slant up towards C and the total amount of the solid C will decrease as the systems under consideration pass from their initial to their final states. Expressed in other words, the sum of the partial depressions of the freezing-point is less than the total depression due to the mixture.

If we start from the quadruple point E, with an excess of both solid phases, there will be, at first, no change in concentration. If the component C be present in excess, the β modification will disappear first and the system will behave in the same general way as any system represented by some point between C and E. If the modification be present in excess, the component C will be the first to disappear and the system will behave in the same general way as any system represented by some point between B and E.

If we start, with an excess of the α modification, from any point on AH, the final state will differ from the initial one in that some of the solid phase will have passed into solution. Starting from any point inside the triangle at a temperature below that of the point S and keeping the temperature constant, the phases, at equilibrium, will be the α modification, the component C and vapor.

The effect of changing the temperature is very simple. While the temperature rises or falls we shall get a combination of the phenomena always to be observed with three-component systems and the phenomena due to the changes at constant temperature. Which set of phenomena predominate will depend on the nature of the system studied and the rate of cooling.

So far we have only considered Case I *1a*, in which one of the assumptions was that the change of the β into the α modification took place without heat effect. Luckily, the other two cases *1b* and *1c* can be dismissed with a very few words. If the change of the β modification into the α modification be accompanied by evolution of heat, the curve for the equilibrium between the two modifications in the liquid phase before the addition of C may be represented by VX. If the addition of C displaces the equilibrium very little if at all, the stable boundary curves will have the form of XR and RC in Fig. 1. This substitution of VX, XR and RC for YX, XS and SC is the only difference between the two cases. In the same way the diagram, Fig. 1, will do duty for the case in which the β modification changes into the α modification with absorption of heat provided we replace YX, XS and SC by WX, XT and TC.

In the case last considered, it will be noticed that the stable quadruple point T lies very near the instable quintuple point O. This raises the question of the possibility of XT not cutting HO at all. If this were to happen, we should have a system classified under 2, with reversal of stability. The diagram for *2a* is given in Fig. 2. The stable boundary curves are XN, NS and SC. Along XN the α modification is solid phase; along NS the β modification and along SC the component C. The theorem of van Rijn van Alkemade enables us to predict that the temperature will rise along the boundary curve from S to N.

The α modification is now the stable form only between X and N; while, between N and S, the stable form is the β modification. At N we have a stable quadruple point with the two modifications as solid phases. It may be asked how this can come about in case, as is assumed here, there is no displacement of the equilibrium by the component C. So far as can be seen at present, this cannot occur under these conditions unless the two modifications can coexist as solid phases when the component C is not present. It should also be kept in mind that the line XNSC need not be so much curved as in the diagram. It has been found by Carveth,[1] while studying the system, potassium, lithium and sodium nitrates, that a straight line can be drawn from the potassium nitrate corner to the opposite side of the triangle, such that it cuts all three fields.

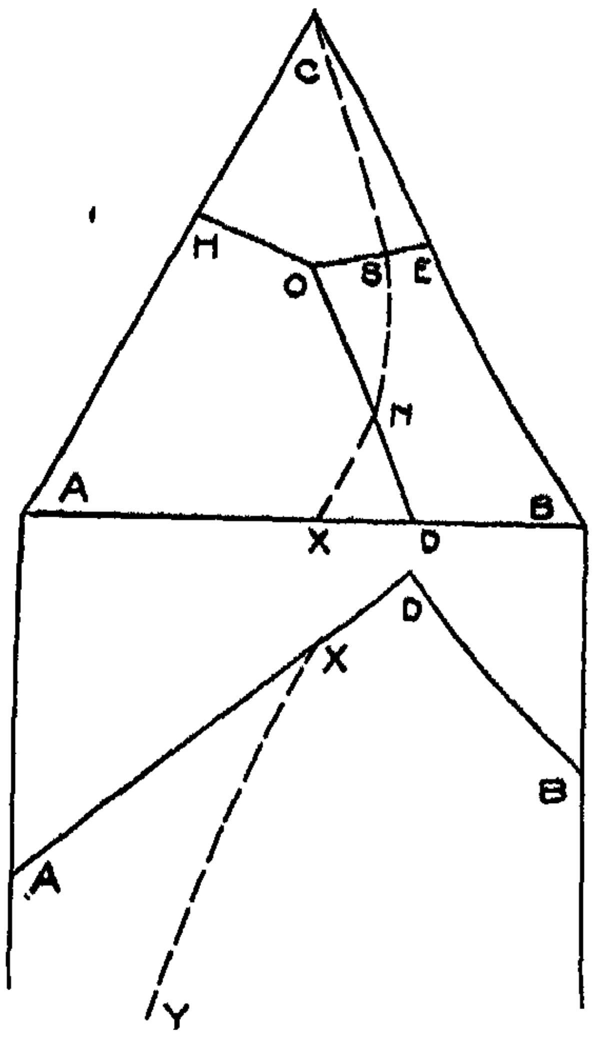

Fig. 2

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[1] Jour. Phys. Chem. 2, 192 (1898).

The diagram for case *2b* would not differ radically from Fig. 2 and therefore is not given. The chief point is that if the equilibrium between the two modifications is displaced by addition of component C, the line YX may slant to the left instead of to the right. A distinction, which does not appear in the diagram, is that the displacement of the equilibrium may be sufficient to make the β modification stable at temperatures at which it would change into the α modification if the component C were not present.

The important point now is how far these theoretical predictions have been verified experimentally. Cases corresponding to Fig. 1 may be looked upon as normal and can probably be realized in the large majority of instances. Carveth[1] found that acetone does not displace the equilibrium between α and β acetaldoxime towards the side of the β modification; more than that his experiments did not show. It seems safe to assume that the diagram for benzaldoxime and water would correspond to one of the three types presented in Fig. 1.

At least one case is known which comes under *1b*, the dibenzoyl acetone or acetyldibenzoyl methane, $(C_6H_5CO)_2HC.COCH_3$, studied by Claisen.[2] From the second paper[3] it seems clear that the instable modification melts at about 85°, the stable modification at about 110°, while the temperature of the stable triple point is about 101–102°. If the melt be heated above 110° and then cooled suddenly, the crystals are found to consist very largely of the instable form. This shows that, with rising temperature, the equilibrium is displaced toward the side of the less stable form. In other words, this latter changes into the more stable modification with evolution of heat. The addition of another component gives us at once a case coming under *1b*. While Claisen has not studied the subject from the point of view of the Phase Rule, he has made some interesting observations on the action of fifty percent aqueous alcohol. I quote his words, with

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[1] Jour. Phys. Chem. 2, 166 (1898).

[2] Liebig's Annalen, 277, 184 (1893); 291, 25 (1896).

[3] Not referred to in my first article. Jour. Phys. Chem. 2, 143 (1898).

the prefatory comment that he calls the instable form the α modification and the stable form the β modification.[1]

"The α compound changes quantitatively into the β form if we dissolve it in boiling fifty percent alcohol and allow the solution to cool *slowly*. Consequently the β modification can be recrystallized unchanged from hot fifty percent alcohol; if we cool the solution *suddenly* by placing it in a freezing mixture or by pouring into ice water, the precipitate contains nearly ninety percent of the α compound. I am not able to offer an explanation of this remarkable behavior." As a matter of fact, the explanation is an easy one to find on the basis of Duhem's theory. In the solution we have equilibrium between the α and the β modification, the amount of the former being relatively large. If we cool slowly, the α modification changes over as the β crystals precipitate and the final result is pure β. If however we cool the solution suddenly, it becomes supersaturated with respect to both modifications and both precipitate. On longer standing the less stable form changes over into the other. Claisen found also that a solution in hot absolute alcohol precipitated a mixture of the two forms on cooling. This mixture contained about sixty-seven percent of the α modification. Although not so stated, I gather from the context that the rate of cooling in this case was gradual but not so gradual as in the first experiment with aqueous alcohol. This intermediate behavior is what would be expected under the circumstances. It seems probable that the rate of change is less in absolute than in aqueous alcohol though there are not data enough to establish this satisfactorily.

One case is known in which there is reversal of stability without the nature of the solvent being of much importance. Benzilorthocarboxylic acid, $C_6H_5CO.CO.C_6H_4COOH$, occurs in two modifications, one yellow and the other white.[2] The white or β modification melts at 125–130° and changes slowly into the yellow or α modification melting at 141.5°. The two modifica-

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[1] Liebig's Annalen, 291, 30 (1896).

[2] Graebe. Ber. chem. Ges. Berlin, 21, 2003 (1888); 23, 1344 (1890).

tions have the same molecular weight. By crystallizing at low temperatures, the yellow form can be converted into the white modification. Some experiments made in my laboratory by Mr. Soch have shown that the yellow crystals become white on standing, even when no solvent is present. Since the yellow form is stable at 100° and the white at 20°, it is clear that there must be an inversion point somewhere between these two temperatures. This is now being investigated.[1]

As yet, I have not succeeded in finding any authenticated case in which the solvent forms no compound with the two modifications and yet reverses the stability. Displacement of equilibrium occurs. The recent experiments of W. Wislicenus[2] show this clearly. In no case, however, can one be certain that a reversal of stability has occurred. According to Beckmann the high melting form of *p*-anisaldoxime does not change over in boiling alcohol;[3] but there is nothing to show that alcohol makes the other form instable. In the same paper Beckmann states that β benzaldoxime liquefies very rapidly in presence of traces of alcohol or water while benzene seems to have no effect. Here again, it is more than probable that we are dealing with a very low reaction velocity rather than with a change of stability. Similarly, Claisen[4] found that dibenzoyl acetone could be recrystallized without difficulty from ligroïn or benzene; but he would certainly have made more than a passing reference if he had observed a quantitative change of the less stable into the more stable form. It is much the same with all the other instances which I have yet come across. It must, however, be kept in mind that the most favorable conditions for such a trans-

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[1] Some of Mr. Soch's measurements of the freezing-points show that Graebe's statements are not entirely accurate. From Graebe's papers one would certainly place benzilorthocarboxylic acid under 2*a*. As a matter of fact, the equilibrium phenomena are very different and much more complicated. The real analogy is with sulfur. The statements in the text have been allowed to stand in order to emphasize the unreliability of the data compiled by people who were working without hypotheses to guide them.

[2] Liebig's Annalen, 291, 147 (1896).

[3] Ber. chem. Ges. Berlin, 30, 1680 (1890).

[4] Liebig's Annalen, 291, 30 (1896).

formation are that the less stable form shall change into the more stable with absorption of heat and we have, as yet, no experimental knowledge of any such case except, perhaps, in the two forms of benzilorthocarboxylic acid.

In this paper there has been given a discussion of the conditions under which reversal of stability does and does not take place, on adding another component which forms no compounds with the two modifications. In this discussion it has been brought out that Duhem's theory is able to offer a simple explanation of what few facts are known and to predict many phenomena which have not yet been observed. In the third paper of the series I shall take up the question of reversal of stability when compounds are formed.

Cornell University

NEW BOOKS

Vorlesungen über theoretische und physikalische Chemie. *By J. H. van 't Hoff. Part I, Chemical Dynamics; 15 × 23 cm; pp. xii and 252. Braunschweig: F. Vieweg und Sohn, 1898. Price: paper 6 marks.*—To those who are lecturing physical chemistry, the first point of interest in a book is always the question of classification. The opening sentence of the preface is a little disappointing, though probably not intended to be taken too seriously. "Owing to the arbitrariness inherent in every classification, the really important point is to make such a choice that it will be clear where everything belongs." The great reputation of van 't Hoff is due to the fact that he has seen relations where other people did not see them. In other words, he has been a leader in the rearrangement and classification of the heterogeneous masses of facts which some people call chemistry. He has brought order out of chaos in so many different fields that it was not unreasonable to hope that his general presentation of the whole field of physical chemistry would emphasize points of view which had been overlooked heretofore. It has not seemed to him worth while to do this.

The general order is to be: Part I, Chemical Dynamics; Part II, Chemical Statics; Part III, Relations between Properties and Constitution. "The logical advantage, that is thus obtained, is that no hypothesis in regard to the nature of matter needs to be made at first and that nowhere in Part I do we introduce much more than the conception of molecules. It is in Part II that the atomistic hypothesis first becomes prominent together with the complicated, allied problems of structure. At the end comes the still very obscure problem of the relations between one substance and another." This classification is excellent as far as it goes, and the reviewer is much pleased to find that reaction velocities are treated in their proper place—after chemical equilibrium. It should be noticed, however, that this is the merest outline of a classification and that it is easy to see where everything belongs because there is practically only one place for everything.

Before passing to a consideration of the book itself, the reviewer would like to call attention to the following passage, p. 4: "There is no denying the modern tendency to develop the pure thermodynamic conception to the gradual exclusion of the molecular view, a proceeding which is justified by the hypothetical character of the latter. For all that, the latter is still necessary and, in accordance with it, we shall express the chemical equilibria by a symbol showing graphically what we imagine in regard to the mechanism of the reaction."

Under chemical equilibrium there are two main divisions, the external and the internal phenomena. The subheads for the first division are: physical and chemical equilibrium phenomena in one-, two-, three- and four-component systems. This is really the qualitative and quantitative study of invariant, monovariant and divariant systems. The subheads for the second division are homogeneous equilibrium, heterogeneous equilibrium and general conclusions. This is really the application of the mass law to polyvariant systems.

This classification needs only to be accentuated to be excellent. The phase rule is not emphasized sufficiently in the first part and the question of variance is entirely ignored in the second part. These two omissions may seem unimportant but they change the character of the book. Instead of being a brief but coherent exposition of physical chemistry, the volume gives us a series of pictures, connected by a running comment. One feels that the single phenomena interested the writer more than the general development of the subject.

The last half of the volume is devoted to a study of reaction velocity, the subdivisions being reaction velocity and equilibrium, reaction velocity at constant temperature, influence of temperature, influence of pressure, reaction wave.

The chapter on the influence of the solvent on the reaction velocity will be read with interest by every one for it is the most complete treatment to be found anywhere. The results, of course, are mostly negative; but a clear statement of our ignorance is always the preliminary step to dispelling that ignorance. The reviewer is a little sceptical as to the real importance of viscosity, though that seems to be the direction in which most people are working.

Some of the novelties in the book are the complete pressure-temperature diagram for a salt and water, p. 34; the diagram for ether and water, p. 39; the question of the non-existence of intermediate hydrates, p. 57; the use of the term "half-electrolyte" for weak acids and bases, p. 112; the discussion of false equilibrium, p. 208.

The book is a valuable contribution to scientific literature. It will prove itself what the author wished it to be, "a help to those who wish especially to learn the latest achievements of physical chemistry." *Wilder D. Bancroft*

Leçons de Chimie générale.—*By P. Schützenberger. Edited by O. Boudouard. 15 × 24 cm; pp. viii and 586. Paris: O. Doin, 1898. Price: paper 10 francs.*—This volume contains the lectures on general chemistry delivered by Schützenberger at the *Collège de France*. He had always intended to publish them and, after his death, they were edited by his former assistant, Boudouard. The headings of the fifteen chapters are as follows: 1, Chemical Phenomena; 2, Chemical Equilibria; 3, Volume and Weight Relations for Compounds; 4, Determination of Equivalents and of Atomic Weights; 5, Classification of the Elements; 6, Gases and Liquids; 7, Solutions; 8, Molecular Diffusion; 9, Cryoscopy; 10, Boiling-points; 11, Refractive Index; 12, Molecular Volumes; 13, Spectrophotometry; 14, Thermochemistry; 15, Stereochemistry.

This makes a fairly well-rounded course though open to the criticism that the mass law and reaction velocity phenomena have received relatively less attention than they deserve. It must be remembered, however, that these lectures were intended to give the student a general view of the subject rather than to teach him physical chemistry. If one remembers the attitude of the majority of French chemists towards the modern theories, this book must be taken as a great advance. It is true that Schützenberger looks upon the electrolytic dissociation theory as a passing fad; but, on the other hand, he devotes less than nine pages to thermochemistry. There can be no doubt but that M. Boudouard has acted wisely in preparing these lectures for the press. It is to be hoped that the book may have a large sale in France.

Wilder D. Bancroft

The Arrangement of Atoms in Space.—*By J. H. van't Hoff. Second revised and enlarged edition. Translated and edited by Arnold Eiloart. 13 × 19 cm; pp. xi and 211. London: Longmans, Green & Co., 1898. Price: cloth $1.75.*—This book is a fraud. It purports to be a translation of a book written in 1894 by van 't Hoff and it is not. It is based on a book written by van 't Hoff in 1894; but it has been rewritten by some one—presumably the translator and editor—and brought down to 1897, without there being anything to show which parts are due to van't Hoff and which to some one else. It is quite probable that the translator believes that the interpolated passages and pages would have been put in by van 't Hoff if he had rewritten the book in the fall of 1897; but that does not help him at all. Square brackets are always at the service of the zealous editor. The translation, in its present form, is valueless as a document, though serviceable enough as a compilation.

Wilder D. Bancroft

Ordinary Differential Equations, with an introduction to Lie's theory of the group of one parameter. *By James Morris Page. 13 × 19 cm; pp. xviii and 226. New York: The Macmillan Company, 1897. Price: cloth $1.25.*—From the beginning, the study of differential equations has been to a great extent a search after more or less ingenious devices for integrating special classes of equations. Methods that would serve in special cases were soon discovered, but, so diverse were they in character, that for a long time it seemed as if there could be no bond of union between them. It is one of Lie's claims to distinction to have shown that these apparently unconnected methods are in reality embraced in one general theory.

For ordinary differential equations of the first order in two variables, the fundamental theorem in Lie's theory is the following: if a one-parameter group of transformations under which the differential equation is invariant be known, or rather, if the infinitesimal transformation of the group be known, then an integrating factor can at once be written down, and thus the integration of the equation can be effected by a quadrature. Of course, this amounts simply to a restatement of the problem; for the difficulty to be overcome consists now in finding a group of transformations for which the equation is invariant.

If a group of transformations be given, it is possible to establish a general formula for all the equations that are invariant under the group. Theoretically, this is admirable, for by making a sufficiently large list of groups and the corresponding invariant equations it would be possible to integrate a great variety of equations. Practically, however, the formulas are so involved that, except in the case of the simplest groups, it is very difficult to apply them. The equations belonging to these groups are the equations for which methods of integration have long been known: for example, the homogeneous and the linear equation;

and the integrating factors furnished by the theory are the same as those in use.

Although the most important of Lie's results were obtained twenty-five years ago they have not yet had much effect upon the writers of textbooks. The only books that treat the subject from his point of view are his *Vorlesungen über Differentialgleichungen*, published in 1891, and the book before us. This book gives in a small compass and in clear outline the main features of the theory as presented in the *Vorlesungen*; the heaviness and prolixity of the original have been avoided, and instead of giving all the known proofs of each theorem, the simplest and most direct has usually been chosen.

Chapter I consists of the usual description of the genesis and the geometrical interpretation of the ordinary differential equation in two variables. Chapter II discusses the simultaneous system of ordinary differential equations, the equivalent partial differential equation, and their geometrical interpretation. These are subjects that are not usually discussed until much later on, but their introduction at this point is necessary for the presentation of the subsequent theory in its most elegant form. In Chapter III the fundamental theorems in Lie's theory of the one-parameter group are given, and these are employed in Chapter IV to explain the connection that exists between the infinitesimal transformation of a group and an integrating factor of the corresponding differential equation. Chapter V contains Lie's geometrical interpretation of the integrating factor, and its application to parallel and to isothermal curves. Chapter VI gives the usual methods for the integration of equations of the first order but not of the first degree. It also contains a very simple method, due to the author, for finding the singular solution when a group is known under which the equation is invariant. Chapters VII and VIII are devoted respectively to the equations of Riccati and of Clairaut, and to total differential equations in three variables. Chapters IX and X take up ordinary differential equations of the second order and of the m-th order, and Lie's methods are employed to show that in certain cases the order of the equation can be diminished by unity. Chapter XI contains the usual discussion of the linear differential equation with constant coefficients, and also the application to the general linear equation of the methods given in the preceding chapter. Finally, Chapter XII gives a treatment of the simultaneous system, first by the ordinary methods and then by the methods of the group theory.

This book is not to be recommended to one who wishes quickly to acquire dexterity in the integration of equations; for it is necessary to read the first four chapters, almost half of the book, before integrating a single equation. But it is sure to give pleasure as well as information to anyone whose interest in mathematics is not confined solely to its practical applications. The first four chapters are especially interesting, for they have a continuity that is lacking in other parts of the work.

Paul Saurel

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry

One-Component Systems

The tension of mercury vapor between 0° C and 100° C. *L. Pfaundler. Wied. Ann.* **63**, *36* (*1897*).—Measurements of the tension at 15° (0.00081 mm), 56.3° (0.01801 mm) and 98.8° (0.26305 mm). Dry air was passed first through a saturating vessel containing glass wool impregnated with mercury and heated in a vapor-bath, next through an absorption tube loosely filled with silver leaf and finally through a gas meter or into a calibrated gasometer. In each experiment at least 100 mg of mercury was evaporated.

The results agree well with Hertz's interpolation formula, but not with that of Hagen. *W. L. M.*

Remarks on the equation of state. *M. Thiesen. Wied. Ann.* **63**, *329* (*1897*).—Van der Waals's equation cannot stand strict examination from any point of view, even if temperature functions be introduced in place of the two constants; no more can the hypothesis that, for constant volume, the pressure is a linear function of the temperature. Certain other assumptions commonly made—viz: that the energy at constant volume is a linear function of the temperature or of the pressure—are shown not to hold for the case of water near its maximum density; consequently they cannot be regarded as general laws.

"In this paper I have examined several forms of the equation of state ... which are supported by the most obvious hypotheses of the kinetic theory ... and have found that they are not valid for all liquids .... If however we let them drop, it will hardly be possible to arrive at forms for the equation which are definite enough to be of practical value. Substantial progress in this department at the present time is only to be expected from accurate measurements impartially handled." *W. L. M.*

The densities of carbonic oxide, carbonic anhydride and nitrous oxide. *Lord Rayleigh. Chem. News*, **76**, *315* (*1897*).—The observations were carried out by the method and with the apparatus described in Proc. Roy. Soc. 53, 134 (1893). The carbon dioxid was prepared from hydrochloric acid and marble, the nitrous oxid from ammonium nitrate and from the commercial article purified by dissolving in water, while the carbonic oxid was prepared by three methods, viz: (a) from potassium ferrocyanid and sulfuric acid; (b) oxalic and sulfuric acids; (c) sodium formate and sulfuric acid. It was free from hydrogen.

The following summary gives the densities of the various gases relatively to air, as determined by the author (the last figure is of little significance):

Air free from H_2O and CO_2	1.00000
Oxygen	1.10535
Nitrogen and argon (atmospheric)	0.97209
Nitrogen	0.96737
Argon	1.37752
Carbonic oxid	0.96716
Carbonic anhydrid	1.52909
Nitrous oxid	1.52951

W. L. M.

On the dissociation of nitrogen peroxid. *K. Schreber. Zeit. phys. Chem.* **24**, *651* (*1897*).—In 1885–1886 E. and L. Natanson published a series of very careful determinations of the densities of nitrogen peroxid at various temperatures and pressures; they compared the results of their observations with the theoretical formulas of Gibbs and of Boltzmann and came to the conclusion that these formulas did not fit their experiments.

Swart then (1891) endeavored to lessen this discrepancy between theory and experiment by assuming that the gases NO_2 and N_2O_4 did not obey the simple gas laws, and by employing van der Waals's equation in place of the latter in the deduction of the theoretical formulas. This complicated the calculations immensely, but did not lead to the desired result.

In the present paper, the author shows that the uncertainties caused by unavoidable experimental errors, are greater than the differences between the two theoretical formulas or between either of them and the Natanson results.

If in the thermodynamical formula

$$K = \frac{(\text{conc } NO_2)^2}{\text{conc } N_2O_4} = \frac{T}{p}\, a.e^{-b/T}$$

[a and b constants, T absolute temperature, p pressure, K equilibrium constant, e base of the nat. logs.] the concentration of NO_2 and of N_2O_4 being expressed in terms of the densities, d and D of the mixture and of pure N_2O_4 respectively, the equation becomes

$$K = \frac{4(D-d)^2}{D(2d-D)} = \frac{T}{p}\, a.e^{-b/T}$$

If f_1 be the error in the determination of d, and F_1 the error in K caused thereby, then by introducing $d + f_1$ and $K + F_1$ in the above equation and rearranging

$$V_1 = \frac{F_1}{K} \cdot \frac{d}{f_1} = \frac{D - d + f_1 (1 - D/2d)}{(d + \frac{D}{2})(\frac{D}{d} - 1)^2 + f_1 (\frac{D}{d} - 1)^2}$$

V_1 being the relation which the percentage error in K bears to the percentage error in d to which it is due.

The coefficients of f_1 in the expression on the right, may vary between 0 and 1/2, and 0 and 1 respectively; consequently for observations in which the difference between d and its limiting values D and D/2 is much greater than f_1, it is allowable to set $f_1 = 0$ in the expression in question, giving

$$V_1 = \frac{2d^2}{(2d-D)(D-d)}.$$

Similarly with the error F_2 caused by an error f_2 in D.

$$V_2 = \frac{F_2}{K} \cdot \frac{D}{f_2} = \frac{d^3}{D(D-d)(2d-D)} = \frac{V_1}{2} \cdot \frac{d}{D}.$$

From a comparison of the various series of observations, the author feels justified in assuming an average probable error of one-third percent in the Natanson determinations of *d*. The calculation of D from atomic weights, etc., involves an uncertainty of at least one-tenth percent. From these values for f_1 and f_2 he calculates $F_1 + F_2$ for each determination of K in Natanson's table; *in more than one-half of the forty-seven cases the probable error in* K *exceeds ten percent, in one case 153 percent.*

He next selects those experiments from which K may be calculated with a probable error not exceeding 10 percent, and shows that the isotherm itself, and its dependence on the temperature, may be expressed within the limits of experimental error by the thermodynamical equation given above, which serves also to calculate the heat of dissociation. Finally Berthelot and Ogier's figures for the specific heat of nitrogen peroxid are subjected to analysis; they may be regarded as the sum of the specific heats of the two gases plus the heat of dissociation. *W. L. M.*

Two-Component Systems

The vapor tensions of dilute aqueous solutions at zero. *C. Dieterici. Wied. Ann.* **62**, *616* (*1897*).—A glass funnel 7 cm in diameter was closed air-tight by a glass plate 0.08 mm in thickness, to the center of which a weight of fifteen grams was attached. The instrument when provided with mirror and telescope serves as a delicate manometer (indicating differences of 0.0003 mm Hg between the pressures on either side of the glass diaphragm) and was employed to determine the tensions of dilute solutions of NaCl, H_2SO_4, dextrose, etc.

The greatest difficulty in the way of obtaining accurate measurements lies in the impossibility of attaining absolute equality of temperature in the solutions compared. One five-hundredth of a degree corresponds to approximately 0.001 mm Hg, *i. e.* to 12 percent of the vapor-tensions of a decinormal aqueous solution of a non-electrolyte (at zero). The depression of the freezing-point for the same solution on the other hand is 0.184° consequently an uncertainty of 1/500 degree can cause an error of but little over one percent in the freezing-point determination.

The author's vapor-tension measurements, as far as they go, are in good qualitative agreement with Loomis's and Ponsot's determinations of the freezing-points of the same solutions. *W. L. M.*

On the freezing points of dilute sulfuric acid. *W. Hillmayr. Monatshefte für Chem.* **18**, *27* (*1897*).—According to recently published determinations by R. Pictet, the freezing-points of certain solutions of sulfuric acid in water lie *above* zero; a maximum freezing temperature of + 4.5° was observed for 1.78 percent acid. Repetition of these experiments by the author shows that these results must be regarded as altogether erroneous; the freezing-point is in every case below zero, and the molecular depression is about twice that calculated by Raoult's rule for $H_2SO_4 = 98$.

"If we set $m = 98/2 = 49$, and calculate the freezing-points, we obtain the following data [Table] which, with exception of the last number, agree fairly well with the experimental results. Despite this we can hardly assume that in the dilute acids the molecule H_2SO_4 is present, quite apart from the difficulty of accounting for the half molecular weight. ... The assumption that the hydrate is dissolved that makes the freezing-point curve a straight line [viz: $H_2SO_4 + 10H_2O$], is not in agreement with Raoult's rule."

Judging from these utterances, it seems that the author has never heard of the hypothesis of electrolytic dissociation. *W. L. M.*

The vapor tensions of hydrates which remain transparent on efflorescence. *G. Tammann. Wied. Ann.* 63, *16* (*1897*).—All crystals whose vapor-tensions have hitherto been measured, become opaque on losing water, with formation of an anhydrous salt or of a lower hydrate. As the two components, salt and water, thus exist in three phases, vapor, hydrate and salt (or vapor and two hydrates) the system is monovariant, and to each temperature corresponds a certain vapor-tension, independent of the relative quantities of the three phases present.

Certain of the zeolites, however, lose water when heated, but retain their transparency and are able to absorb the water again and return to their initial state. The system: (zeolite, vapor) must consequently be regarded as divariant, and the vapor-tension ought to vary with the quantity of water retained by the mineral. This conclusion the author finds verified by experiments on chabazite, heulandite, and desmine; similarly with magnesium platinocyanid.

"After long search I believe that in the zeolites I have found a material suitable for the construction of semipermeable cell walls. The precipitation-membranes, even when deposited on earthenware, are, as is well known, so little resistant that it is difficult to carry out measurements of osmotic pressure by their aid. In the zeolites, on the other hand, we possess a resistant material, which is permeable for water although perhaps not very readily; and which has the property, essential for such 'walls,' of assuming the vapor-tension of any solution with which it is brought into contact." *W. L. M.*

The transition temperature of a solid solution. *V. Rothmund. Zeit. phys. Chem.* 24, *705* (*1897*).—At temperatures below its melting-point and above 46.9° C tetrabrommethane exists as crystals of the regular system; below 46.9° however as monoclinic crystals. Owing to the rapidity with which the change from one modification to the other takes place, the transition temperature can be conveniently determined in Beckmann's freezing-point apparatus. The crystals are suspended in water above 47° and allowed to cool slowly; when the reaction takes place the thermometer rises a few tenths just as in a freezing-point determination.

The purer the tetrabrommethane, the higher the transition point; if the tetrabrommethane be dissolved in alcohol, tetrachlormethane added, and the whole poured into water, the transition point of the resulting crystalline mass (which contains chlorin) may be as much as five degrees below that of the pure substance. The author finds that the 'lowering of the transition point, is proportional to the amount of tetrachlormethane added; he assumes that the two substances unite to form a 'solid solution' and shows that if this be the case, the ratio of the solubilities of tetrachlormethane in the two modifications of tetrabrommethane is independent of the concentration, in other words, that the molecular weight of the 'dissolved' tetrachlormethane is the same in both 'solid solvents.' *W. L. M.*

A means of recognizing a good cryoscopic method. *A. Ponsot. Comptes rendus,* 124, *1227.*—In a good cryoscope, there should be as little difference as possible between the true 'water value' of the apparatus and its apparent water value—including heat generated by stirring, and by solidification of the supercooled solution, and that lost to the cooling jacket during the experiment. This condition is satisfied by the author's newest models, and, to a less degree, by those of Raoult.

W. L. M.

Poly-Component Systems

Equilibrium in systems of three components, where two liquid phases may appear. *Second paper. F. A. H. Schreinemakers. Zeit. phys. Chem.* 22, *515* (*1897*).—In each bitangent plane passing through a point P on the ordinate of one of the apices of the basal triangle (1, 597) there lies a triangle whose angles are formed by P and the two points of contact with the potential surface. The author classifies these triangles and the planes in which they lie by the relation which the bases of the triangle bear to the binodal curve; and discusses the relative order and positions of the various classes of planes for the special case that the binodal curve consists of one continuous closed loop.

Next follows an analytical treatment of the tangential cone (from P to the potential surface) contributed by Prof. H. A. Lorentz. If the surface contain a fold, there are, in general, three cones possible from each point; the direction of their concavities and the projections of the curve of contact between cone and surface are considered in full.

The paper closes with a short discussion of the less stable portions of the isotherms, and of cases in which the fold in the potential surface is cut by one of the three perpendicular planes which bound the figure, and where, in consequence, the projection of the binodal curve ends in two conjugate points on one of the sides of the basal triangle.

Before taking up the cases of two solid components, binary and ternary solid phases, and three liquid phases, the author promises experimental illustrations of the isotherms hitherto discussed. *W. L. M.*

Equilibrium in the system: water, sodium chlorid, succinonitrile. *F. A. H. Schreinemakers. Zeit. phys. Chem.* 23, *417* (*1897*).—Between 55° and 18° succinonitrile N and water W can form two coexisting liquid phases which at 55° become identical (critical phase) and at 18° are saturated with N. At 42° the two solutions have the same specific gravity, and the curious phenomenon is presented, of two solutions, formed of the same components and having the same specific gravity, but not mixing.

Solid N is thus at 18.5° in equilibrium with two solutions, one containing 2.5 and the other 72 mol.-percent N; at temperatures from 18.5° ot 54.5°

(the melting-point of pure N) with but one, containing more than 72 percent N, and at temperatures below 18.5° (to −1.2° the cryohydratic point) with a solution containing less than 2.5 percent N. These relations are illustrated *by a diagram in which Oy gives mols. N in 100 mols. solution, and Ox* the temperature.

Next follows an account of the various states of equilibrium in the three-component system W, N and salt S, graphically represented first by a double diagram [Ox temperature, Oy mol. N in 100 mol (N + W), $O'y'$ mol. S in 100 (W + S)] then by a solid figure in a prism, whose triangular base gives the composition of the solutions and the z axis the temperature; sections in the xy plane of this latter figure—isotherms—are drawn and discussed in the light of the author's previous papers (see above, and 1, 597). This case differs from those taken up in the theoretical papers, *first* in that between certain limits two solid phases are possible, viz: S and N, and *second* in that between 18.5° and 55.5° the binodal curve cuts one side of the basal triangle in two points.

W. L. M.

Equilibrium in the systems ether-water, and ether-water-malonic acid. *E. A. Klobbie. Zeit. phys. Chem.* 24, *615* (*1897*).—Analyses of the two layers formed in mixtures of ether and water, between the temperatures −4° and +95°, and determinations of the solubility of malonic acid in water and in ether form the first part of the paper. In contrast with its solubility in water, the solubility of malonic acid in ether is intermediate between that of oxalic and that of succinic acid.

The system ether-water-malonic acid was studied at 15° the results are given in tables and in a triangular diagram, on which one curve gives the compositions of the coexisting liquid phases [projection of the binodal curve], and a second the solubilities of malonic acid in mixtures of ether and water [projection of the tangential curve from a point above the malonic acid apex of the basal triangle].

As water and ether alone can form two coexisting liquid phases at 15°, the binodal curve cuts the side of the triangle opposite the malonic acid apex. It is neither cut nor touched by the tangential curve. *W. L. M.*

Application of the mass law to the equilibrium between β-naphtol and picric acid in solution in benzene. *B. Kuriloff. Zeit. phys. Chem.* 24, *697* (*1897*).—The solubility of β-naphtol-picrate NP in benzene is much greater than its solubility in saturated solutions of β-naphtol N or of picric acid P. Hence it must be assumed that the NP in solution is largely dissociated into N and P. This conclusion is confirmed by freezing- and boiling-point determinations.

The values of the dissociation constant, calculated from the solubilities of NP in benzene to which varying quantities of N or of P has been added, lie between 2767 and 4013. *W. L. M.*

The exchange of bromin for chlorin in aromatic compounds. *R. Wegscheider. Monatshefte für Chem.* 18, *329* (*1897*).—On heating with conc. hydrochloric acid to 200°–240°, *s*-tribromanilin is partially converted into *s*-trichloranilin; the reaction is reversible, conc. hydrobromic acid at the same temperature replacing the chlorin in *s*-trichloranilin by bromin. On the other hand, *s*-tribrombenzonitrile, *s*-tribrombenzoic acid, and perhaps also chlor-*s*-tribrombenzene are not acted on by hydrochloric acid.

The action of cuprous chlorid in hydrochloric acid solution on *s*-tribromanilin is to replace bromin by hydrogen, and to a less extent by chlorin.

The paper contains a résumé of previous work on the replacement of chlorin by bromin, etc., in organic compounds. *W. L. M.*

Osmotic Pressure and Diffusion

On reciprocal diffusion of electrolytes in dilute aqueous solutions, and in particular on diffusion against the fall of concentration. *U. Behn. Wied. Ann.* **62**, *54* (*1897*).—The apparatus consisted of two vessels, each of 0.75 liter capacity, placed vertically one over the other, and communicating by an opening 5 mm in diameter through a glass plate 2 mm thick; the whole was immersed in a vessel of water and kept in a constant temperature room. The solutions experimented with were: 1, HCl *n*/10, against LiCl *n*/10; 2, HNO_3 *n*/10, against $AgNO_3$ *n*/10; 3, $AgNO_3 < n/10$ [0.05 to 0.09 *n*], against a solution *n*/10 with respect to $AgNO_3$ and *n* with respect to HNO_3.

The results proved to be qualitatively in accordance with the requirements of Nernst-Planck's theory of diffusion—in particular the theory predicts and the experiments shewed a diffusion of Ag in (3) against the fall of concentration—quantitatively however the agreement was very imperfect; the discrepancies are ascribed to convection currents. *W. L. M.*

The motivities of dissociated and non-dissociated molecules. *H. Euler. Wied. Ann.* **63**, *273* (*1897*).—The diffusion coefficients D of non-electrolytes in water are, in first approximation, reciprocally proportional to the square roots of their molecular weights $\sqrt{m}$; though in the case of organic substances with heavy molecular weights the product $D\sqrt{m}$ is less than for the diatomic gases.

This rule holds for Cl_2, Br_2 and I_2 in H_2O, in C_6H_6 and in Cl_4, whereas the *electrolytic* rates of transport of the ions Cl′, Br′ and I′ are almost identical. The author seeks to explain the absence of any "influence of the mass" in this case by means of "the hypothesis of the hydration of the ions." An experimental paper on diffusion is promised. *W. L. M.*

Velocities

On esterification. *R. Wegschneider. Monatshefte für Chem.* **18**, *629* (*1897*).—The literature dealing with relations between chemical constitution and esterification is reviewed and found to be fairly in accordance with the following generalizations—first published in 1896:

1. By the action of alcoholic iodids on the acid salts of unsymmetrical dicarbonic acids, the stronger carboxyl (i. e. that with the greater electrical dissociation constant) is attacked.

2. By the action of alcohols on the anhydrids of unsymmetrical dicarbonic acids the stronger carboxyl is attacked.

3. The progress of the formation of esters from acids and alcohol in presence of hydrochloric acid does not depend on the strength of the acids.

4. The progress of the formation of esters from acids and alcohol in presence of hydrochloric acid, and that of the saponification of the esters by alka-

lies, are governed by the chemical constitution of the acids (V. Meyer's rules).

5. This [viz : 4] can be accounted for by the assumption that intermediate addition products are formed.

Experiments on the esterification of hemipinic acid, $C_6H_2.(COOH)_2.(OCH_3)_2$, and of *s*-tribrombenzoic acid by methyl alcohol, with or without addition of sulfuric acid, are described ; in the case of the acid first named, the reaction is complicated by the formation of an anhydrid. *W. L. M.*

Inflammability of thin layers of explosive gases. *F. Emich. Monatshefte für Chem.* 18, *6* (*1897*).—Measurements of the length of the shortest sparks capable of producing explosion in mixtures containing hydrogen and oxygen. Between thin platinum wires covered with glass except at the point, the minimum length of spark for $2H_2 + O_2$ is 0.22 mm. This value was obtained whether moist or dry [with H_2SO_4] gas was experimented with, and is practically identical with the width of the narrowest layer of gas in which the explosion can propagate itself.

A succession of sparks of length insufficient to cause explosion, nevertheless brings about the formation of water, recognized by the deliquescence of a crystal of calcium chlorid.

A mixture of *equal volumes* of H_2 and O_2 is the most inflammable ; addition of either O_2 or H_2 increases the length of spark necessary to induce ignition, similarly with addition of N_2 or CO_2, diminution of pressure or rise (!) in temperature. *W. L. M.*

Electromotive Forces

Transformation of the zinc sulfate in the Clark element. *W. Jaeger. Wied. Ann.* 63, *354* (*1897*).—At low temperatures zinc sulfate crystallizes with seven mols of water, above 39° with six. This point is marked by an angle in the curve of solubility of zinc sulfate in water, and by a corresponding change in the temperature coefficient of the Clark cell.

Cells containing $ZnSO_4.6H_2O$ may be cooled to zero, and may be kept for weeks without formation of $ZnSO_4.7H_2O$; addition of a crystal of the latter however effects the transformation at once. At zero, the E. M. F. of the 'abnormal' cell is 0.015 volt less (i. e. about one percent less) than that of the normal Clark cell. *W. L. M.*

On galvanic "precipitation" cells. *R. Lorenz. Zeit. Elektrochemie*, 4, *305* (*1898*).—By a "precipitation" cell is meant one in which an insoluble salt forms at the anode, the electrolyte not being a salt of the anode metal. The cell studied in most detail was $Zn \mid ZnO_2H_2 \mid NaCl \mid Cu_2O \mid Cu$. The electromotive force varies a good deal ; but the author seems to think that the cell is nearly as good as the Cupron cell. As was to have been expected, the irregularities are chiefly at the anode. Other cells were also made up with cadmium, magnesium and iron as anodes. *W. D. B.*

On the electrocapillary phenomena. *H. Luggin. Zeit. Elektrochemie*, 4, *285* (*1897*).—An elementary lecture on Helmholtz's theory of the change of the surface-tension with the polarization. *W. D. B.*

Photoelectric behavior of salts. *J. Elster and H. Geitel. Wied. Ann.* 62, *599* (*1897*).—Certain minerals, and salts colored by exposure to the cathode rays, acquire peculiar photoelectric properties in that a static negative electric charge communicated to them is dispersed much more rapidly in sunlight than in the dark. The authors find that the same holds true for NaCl and KBr when colored by heating in potassium vapor (Cf. Giesel, 1, 534), but not when colored by admixture of Prussian blue. *W. L. M.*

On magnetic susceptibility and atomic magnetism. *C. Jäger and St. Meyer. Wied. Ann.* 63, *83* (*1897*).—Determinations, by a modification of Quincke's manometric method, of the magnetism of water and of aqueous solutions of the chlorids, sulfates and nitrates of iron, cobalt, nickel and manganese. A short account of the results only is given.

In contrast to previous observers, the authors find that the diamagnetic properties of water decrease with rise in temperature. In the solutions studied, the magnetism depends only on the quantity and nature of the metal present, the nature of the electronegative ion has no appreciable influence. The atomic magnetisms of nickel, chromium, cobalt, iron and manganese stand very closely in the proportion 2, 3, 4, 5, 6. *W. L. M.*

Electrolysis and Electrolytic Dissociation

Studies on the electrolytic separation of cadmium and zinc, zinc and cobalt, antimony and tin. *A. Waller. Zeit. Elektrochemie*, 4, *241* (*1897*).—Cadmium can easily be separated from zinc by electrolysis of an oxalate solution at 80–85° provided the potential difference does not exceed the decomposition value of cadmium by more than 0.3 V. Some experimental data are given which confirm this statement; but, curiously enough, the actual potential difference is not given. This method is said to give the cadmium as a coherent film while the zinc can be precipitated by electrolysis after the solution has been concentrated and had tartaric acid added to it. The objection to separating cobalt and zinc by electrolysis of a tartrate solution is that cobalt oxid precipitates at the anode. This can be prevented by adding sodium hydroxid and hydroxylamin at the anode. Similar but less satisfactory results are obtained by adding potassium iodid instead of hydroxylamin.

The separation of antimony and tin can be effected by electrolysis of a sodium sulfid solution. The best results were obtained with a cold solution and a potential difference of 0.65 V. This part of the work has been criticised severely by Ost, Zeit. Elektrochemie, 4, 279. *W. D. B.*

Studies on the electrolytic separation of copper from silver, mercury or arsenic. *N. Revay. Zeit. Elektrochemie*, 4, *313*, *329* (*1898*).—This is a repetition, in the Aachen laboratory, of the work done in Leipzig by Freudenberg, Zeit. phys. Chem. 12, 97 (1893). In nitric acid solution silver can be separated from copper when the potential difference at the electrodes does not exceed 1.4 V. The silver precipitates in the best shape at 70°. When too little acid has been added, a temporary formation of silver peroxid is noticed at the anode. Freudenberg states that a potential difference of 1.7 V is necessary when precipitating silver from a cyanid solution. Revay finds that silver can be precipitated with potential differences as low as 1.1 V depending on the concentration. He also finds that under some circumstances copper will precipitate at

1.8 V instead of first at 2.3 V as given by Freudenberg. With increasing concentration of copper the decomposition value decreases so that it is only possible to get complete precipitation of silver when the solution contains relatively little copper.

The separation of mercury from copper in mixed chlorid and sulfate solution is not feasible because the mercury will not cling to the cathode. In nitric acid solution no result was obtained because, for some unexplained reason, the potential difference at the electrodes was not made greater than 1 V. In a cyanid solution the same difficulty occurs as with silver and copper; no separation is possible when the ratio of copper to mercury exceeds twenty-six percent. [The effect of varying the absolute concentration of the potassium cyanid seems not to have been considered.]

From a mixture of copper sulfate and potassium arsenate it is easy to precipitate pure copper because the arsenic is not present as cation. The potential difference should be 1.5 V. With a nitrate solution there is danger of some arsenic being precipitated. From an ammoniacal solution copper precipitates pure under a potential difference of 1.1–1.3 V. *W. D. B.*

Electrolytic separation of copper from nickel, cobalt, iron and zinc for technical purposes. *B. Neumann. Zeit Elektrochemie,* 4, *316, 333* (*1898*).—Starting with an alloy of copper with nickel, cobalt, iron or zinc as anode, it is possible by electrolysis to precipitate most of the copper at the cathode. It is not possible, by electrolysis, to precipitate all the copper because there comes a point where the precipitate no longer forms a coherent film. The presence of a large excess of free acid is disadvantageous. The copper precipitated at the cathode is not a measure of the amount dissolved at the anode because the other metals in the alloy react with the dissolved copper salt. The statement that iron can be precipitated from the solution by passing in air is said to be very inexact. *W. D. B.*

On the electrolytic preparation of perchloric acid and its salts. *F. Foerster, Zeit. Elektrochemie,* 4, *386* (*1898*).—Working with a fifty percent solution of sodium chlorate, a current density of 8.3 amp/dm^2 and a potential difference of 4.5 V, a ninety-eight percent yield of sodium perchlorate was obtained. With potassium chlorate the yield was not so good. In acid solutions, the same reaction takes place but the chlorate is reduced to a certain extent at the cathode. In alkaline solutions the yield is bad and for this reason, it is not possible to prepare perchlorates directly from the alkaline chlorids. *W. D. B.*

Behavior of the chlorids of platinum on electrolysis. *F. Kohlrausch. Wied. Ann.* 63, *423* (*1897*).—Nothing is known of the electrochemical equivalent of platinum, nor of the quantity electrolytically precipitated from solutions under definite conditions. The present preliminary investigation yielded the following results:

1. In solutions of H_2PtCl_6 between platinum electrodes, a grey deposit is formed on the cathode, which on heating loses weight and turns dull white. If the loss in weight be ascribed to hydrogen, and an equivalent quantity of electricity be subtracted from the total which has passed the solution, each milligram of platinum deposited corresponds to about 1/44 ampere minute; whence follows a valency of 2 or 3 (instead of 8) for the platinum.

The anode remains unchanged in weight; i. e. is not affected by the electrolytic chlorin.

2. In solutions of $PtCl_4.5H_2O$, for small current densities (up to 1/40 amp. per sq. cm) the weight of the cathode remains unaltered; it is consequently safe to assume that no platinum is deposited primarily. With greater densities the phenomena are the same as with H_2PtCl_6; a calculation similar to that just indicated gives the valency 4.

At the anode oxygen is evolved; after some time however, during which the solution has become darker orange in color and improved in conductivity (formation of H_2PtCl_6), the oxygen is replaced by chlorin. The author points out that these relations can be accounted for by assuming the existence of $PtCl_4O$ ions; the question must be decided by measurements of the ratio of transport. *W. L. M.*

Measurements of the temperature of electrolytes at the surfaces of very small electrodes. *P. Richarz and W. Ziegler. Wied. Ann.* 63, *261* (*1897*).—Into a test-tube 12 mm in diameter and 7 mm long were introduced, as electrodes, a cylinder of platinum foil which covered the whole inner surface of the tube, and a platinum wire 16 or 18 mm long and 0.35 mm (in another experiment 0.1 mm) thick. The tube was surrounded by ice, a current passed, and the temperature of the electrolyte (20 percent H_2SO_4 or 20 percent HNO_3) determined in the immediate neighborhood of the smaller electrode by means of a thermo-couple.

The temperature rose rapidly with the current until finally the boiling-point of the electrolyte was reached (3 to 7 amperes). The authors point out the errors which this rise in temperature may introduce into determinations of galvanic polarization. *W. L. M.*

On the supposedly active state of gases prepared by electrolysis. *F. Winteler. Zeit. Elektrochemie,* 4, *342* (*1898*).—Mixtures of hydrogen and chlorin, prepared electrolytically, often explode spontaneously in the voltameter, while Bunsen has shown that such mixtures, containing hydrochloric acid as they do, explode much less readily when removed from the cell than mixtures of pure hydrogen and pure chlorin. This abnormal explosive power in the voltameter is ascribed by the author to the catalytic action of the electrodes, due to their power of absorbing hydrogen. *W. D. B.*

Movements brought about by the electric current. *F. Braun. Wied. Ann.* 63, *324* (*1897*).—If two electrolytic solutions be separated by a membrane capable of imbibition (e. g. bladder) and a current be passed from one to the other, one of the electrolytes (depending on the direction of the current) will be introduced into the membrane. As, in general, the tension of the membrane depends on the nature of the liquid imbibed, the tension, and consequently the curvature, if the membrane be curved, will be affected by the current; if the tension be increased by a current in one direction it will be decreased by a current in the opposite direction.

The author describes a simple apparatus by means of which these movements may be studied, and suggests that certain biological phenomena are due to this cause. *W. L. M.*

Hemipinic and papaverinic acids. *A. Kirpal. Monatshefte für Chem.* 18, *461* (*1897*).—Measurements at 25° of the electrolytic conductivity of aqueous solutions of hemipinic, metahemipinic and papaverinic acids and of the mono-methyl ethers of the two last named. *W. L. M.*

Dielectricity and Optics

On the behavior of the dielectric constant and of the refractive index in the magnetic field. *K. R. Koch. Wied. Ann.* 63, *132* (*1897*).—Measurements with Zehnder's interferential refractor showed that the refractive indices (and consequently the dielectric constants) of various solids, liquids and gases, compressed (500 atm) or otherwise, were unaffected by magnetic fields of 30,000 units and more in strength. *W. L. M.*

The absorption of electric waves in electrolytes. *A. Eichenwald. Wied. Ann.* 62, *571* (*1897*).—In order to test the accuracy of Maxwell's theory connecting absorption and conductivity, the author has determined the quantities in question, by a modification of Zeeman's method, for solutions of NaCl and H_2SO_4 of various concentrations; wave lengths, 5.5 meters and one meter.

The measurements are in full accord with the theory: the discrepant results of Zeeman are discussed. *W. L. M.*

Difference in behavior between the electric and the magnetic vibrations in Hertz's waves. *K. Waitz. Wied. Ann.* 63, *234* (*1897*).—Preliminary observations on the motion of electricity induced by Hertz's waves in copper, nickel, iron, sulfuric acid of various concentrations, certain salt solutions, water, alcohol, and acetic acid.

The current induced by the *electric* vector of the Hertz's waves decreases regularly with decrease in the electric conductivity of the substances experimented on; this is not true of the current induced by the *magnetic* vector.
W. L. M.

The spectra of oxygen, sulfur and selenium. *C. Runge and F. Paschen. Chem. News,* 76, *255* (*1897*).—"Two years ago Prof. Paschen and I showed that the spectrum of helium consisted of six so-called series, which may be arranged in two sets of three, each set resembling very closely the spectrum of one of the alkali metals. From this fact we drew the conclusion that helium probably consisted of two elements, one element corresponding to each of the two sets. Since then we have made an investigation of the spectrum of oxygen as it is exhibited by the electric current passing through a vacuum tube containing oxygen, when no spark gap or Leyden jar is interposed in the circuit; and we have found that this spectrum of oxygen closely resembles that of helium. ... There is [consequently] about as much spectroscopic evidence for the duplex nature of oxygen as there is for the duplex nature of helium. ... Under analogous conditions sulfur and selenium emit a spectrum very similar to the set of the first three series [of oxygen]. ... It is strange that it should be possible to find new spectra of bodies so well known as sulfur and selenium; and we can perhaps infer from this fact that many of the lines which astronomers observe in the spectra of the sun and of the stars, the origin of which is not known, may after all belong to well-known elements." *W. L. M.*

On the relation between contraction and specific rotation of optically active solutions, I. *R. Pribram and C. Glücksmann. Monatshefte für Chem.* 18, *303* (*1897*).—The specific rotation $[\alpha]_D$ of aqueous solutions of nicotine at 20° decreases with decrease in the concentration of the solution, reaches a minimum at 5 percent nicotine, then increases slightly. When the results are plotted (Ox = percent nicotine, Oy = rotation) there is a slight discontinuity in the curve [corresponding to an error of less than one percent in the compositions of the solutions !] at 72 percent nicotine. The density of aqueous nicotine solutions and likewise the contraction on mixing nicotine with water reaches a maximum for 69 percent nicotine. Hein's cryoscopic measurements gave 'normal' molecular weights for nicotine only in solutions containing 0,3 percent or less. *W. L. M.*

On the relation between contraction and specific rotation of optically active solutions, II. *R. Pribram and C. Glücksmann. Monatshefte für Chem.* 18, *510* (*1897*).—According to Rimbach, Zeit. phys. Chem, 16, 671 (1895) the specific rotation $[\alpha]_D$ of aqueous solutions of rubidium tartrate (64 percent to 10 percent salt) is a linear function of the concentration. The large optical apparatus at the disposal of the authors enabled them to carry out measurements with much more dilute solutions (1.2 percent to 10 percent). When their results are plotted (Ox = percent salt, Oy = $[\alpha]_D$), the curve turns to the right under 10 percent, becoming straight again below 5 percent; consequently the values obtained by extrapolation from Rimbach's measurements, and employed in calculating the electrolytic dissociation of the tartrate solutions, are erroneous.

As in the case of nicotine, the alteration in density is parallel to that in optical properties. *W. L. M.*

Crystallography, Capillarity and Viscosity

The surface-tension of water and of certain aqueous solutions, determined by the method of ripples. *N. E. Dorsey. Phys. Rev.* 5, *170*, *213* (*1897*).—The author has shown great ingenuity and skill in perfecting Rayleigh's method of ripples for measuring surface-tension. Among other things it was found necessary to make measurements at least four centimeters from the tuning fork, as otherwise the apparent wave-length was a function of the distance from the fork. No care seems to have been taken with the chemical side of the problem. While pure water was poured into the vessel for the readings, the apparatus had previously been rinsed with tap water. The salts used were not purified in any way and the zinc sulfate, p. 227, seems to have been phenomenally impure. Measurements were made with zinc sulfate, sodium and potassium chlorids, sodium and potassium carbonates. The surface-tension increases with increasing concentration, according to the formula $T_r = T_w + KC$, where T_r is the surface-tension of the solution, T_w the surface-tension of pure water, C the concentration of the solution, and K a constant, varying with the nature of the salt. The author has shown that satisfactory measurements can be made in this way; but his own data are valueless, owing to his extraordinary carelessness.

W. D. B.

THE TRANSFERENCE NUMBER OF HYDROGEN

BY DOUGLAS MCINTOSH

Transference numbers are usually determined according to the method of Hittorf[1] by electrolyzing a solution and measuring the change of concentration at the anode or cathode. This method is applicable in all cases; but the experimental errors are large. The method of Helmholtz is not applicable in all cases; but seems to have very distinct advantages wherever it can be used.

When two cells of the type

$$\mathrm{Zn} \mid \mathrm{ZnSO_4Hg_2SO_4} \mid \mathrm{Hg}$$

are connected, mercury to mercury, the effect of their action is to bring the two zinc sulfate solutions to the same concentration. Helmholtz[2] has shown that the electromotive force of such a 'concentration cell without diffusion' can be expressed in terms of the concentrations of the cells, together with the relation obtaining between concentration and vapor pressure; he has shown, further, that the electromotive forces of the allied 'concentration cells with diffusion' can be computed from the same quantities, together with the transference number of the anion of the dissolved electrolyte; and, finally, that the ratio of these two electromotive forces, at any same temperature, is this transference number. His reasoning is essentially as follows:

Let ψ denote the free energy of a solution containing m_1 mass-units of water and m_2 of salt; and let the relative mass $m_1/m_2 = h$ of the water be known as the dilution-value of the solution. We seek the rate of change, with changing concentra-

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[1] Ostwald. Lehrbuch, II, 594.

[2] Ges. Abh. I, 840; II, 979.

tion, of the electromotive force π of a cell containing this solution, — *i. e.* the derivative $d\pi/dh$; that it may be integrated between the two dilution-values of the concentration cell. To find this function, the work-equivalents imparted in the reversible electrolytic addition of unit mass of salt to the solution must be equated with the corresponding change $\partial\psi/\partial m_2$ of the free energy of the latter, and the resulting expression be differentiated with respect to h.

Writing f for the free energy of that mass, of the solution, that contains unit mass of salt,— whereby f becomes a function of h alone for the isothermal changes here considered, — we have as initial equation

$$\psi = m_2 f, \tag{1}$$

whence

$$\frac{\partial\psi}{\partial m_2} = f(h) + m_2 \frac{df}{dh} \frac{\partial h}{\partial m_2}$$

$$= f - h \frac{df}{dh}.$$

since $h = m_1/m_2$, and therefore $\partial h/\partial m_2 = -h/m_2$. Now, when q mass-units of salt are brought into solution by unit current in unit time, the quantity of electric work-equivalents added to the solution in the dissolving of unit mass of salt is $-\pi/q$. So

$$\pi = -q\left(f - h\frac{df}{dh}\right),$$

whence

$$\frac{d\pi}{dh} = qh\frac{d^2f}{dh^2}, \tag{2}$$

or, for the electromotive force between two cells having the dilution values h_1 (dilute) and h_2 (concentrated),

$$\pi_1 - \pi_2 = q\int_{h_2}^{h_1} h\frac{d^2}{dh^2}f(h)\cdot dh. \tag{2a}$$

Helmholtz evaluates this integral, in terms of the vapor pressures of the two solutions, by showing that

$$\frac{d^2f}{dh^2} = v\frac{dp}{dh},$$

and then expressing p and v, the pressure and the specific volume of the vapor, as functions of h. Here the volume is, of course, regarded as a function $v[p(h)]$.

The above concentration cell, when arranged to act with diffusion, would be

$$\mathrm{Zn}\,|\,\mathrm{ZnSO_4}, h_1\,|\,\mathrm{ZnSO_4}, h_2\,|\,\mathrm{Zn},$$

in the working of which the migration velocities u and v of the cation and the anion must be considered. When an equivalent of metal dissolves in one side of this cell, with passage of the quantity of electricity E, the quantity $E\frac{u}{u+v}$ migrates to the other side, leaving an increase of $E\frac{v}{u+v}$. This same quantity of the cation is lost by the other side: for one equivalent of metal falls out there and $E\frac{u}{u+v}$ arrives by migration. Of the anion, the quantity $E\frac{v}{u+v}$ migrates of necessity from the second side to the first, to balance the increase of the cation at the latter place. An addition of electric work-equivalents to either solution is, therefore, accompanied by an addition of $\frac{v}{u+v}$ mass-units of salt where 1 was added in the case previously considered; so this electric work, $\pi_1 - \pi_2$ for unit quantity, assumes a $\frac{v}{u+v}$-fold value, and in place of equation (2*a*) we must write

$$\pi_1 - \pi_2 = \frac{v}{u+v}\int_{h_2}^{h_1} h\frac{d^2}{dh^2}f(h)\cdot dh. \qquad (2b)$$

It is apparent, therefore, that the ratio of the two electromotive forces (2*b*) and (2*a*) is the quantity $v/(u+v)$, the transference number of the anion. So far as I can see at present there are but two tacit assumptions involved in this equation. The first is that the solute shall be non-volatile under the conditions of the experiment. The second is that the transference number of the anion is the same in the two solutions.

The equation of Helmholtz has been tested experimentally by Moser.[1] With $ZnSO_4100H_2O$ and $ZnSO_4800H_2O$, the ratio of the electromotive forces was 0.64, while Hittorf found 0.636 by the direct method, and Kohlrausch obtained 0.65. With $ZnCl_2100H_2O$ and $ZnCl_2750\ H_2O$ the ratio was 0.71, while Hittorf found 0.70. These two instances suffice to show the accuracy of the method, and it is rather surprising that it has not been used more frequently when one considers that two measurements of the electromotive force are all that are necessary and that it is not even essential to know the concentrations of the solutions.

Practically all the work on the transference numbers of the acids has been done by Hittorf. Large and unexpected variations occur for small changes of concentration and these must be due, in part, to experimental error. While it has been proved for many electrolytes that the transference numbers change with the concentration, it is very improbable that the variations can ever be as large as some of the data for the acids would lead one to suppose. The experiments of Nernst and Loeb[2] — perhaps the most carefully performed research on this subject — show that, with many substances, the transference number changes very little with the concentration; as can be seen from the following table for silver nitrate:

Table I

Temp	Conc	$\frac{v}{u+v}$	Temp	Conc	$\frac{v}{u+v}$
20°	0.1043	0.528	0°	0.025	0.538
26	0.0521	0.524	26	0.0105	0.524
26	0.025	0.522	26	0.0105	0.521

At the suggestion of Prof. Bancroft I have attempted to determine the transference numbers for hydrogen in different

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[1] Sitzungsber. Akad. Wiss. Wien, 92, 652 (1885); 94, 115, (1885).
[2] Zeit. phys. Chem. 2, 948 (1888).

acids by the Helmholtz method, using gas electrodes. A gas cell consisting of hydrogen over two concentrations of acid is apparently quite similar to the concentration cells studied experimentally by Moser. Platinum strips touch the surface of the acid and form a hydrogen electrode after being saturated with hydrogen. This is really a hydrogen electrode because it has been shown experimentally that the electromotive force does not change when the platinum is replaced by another conductor having the property of occluding hydrogen. That the hydrogen electrode in an aqueous solution of an acid is completely reversible has been shown by Le Blanc.[1] We should therefore expect that the ratio of the electromotive forces of the cells $Pt_H | c_1HCl | c_2HCl | Pt_H$ and $Pt_H | c_1HCl | Hg_2Cl_2Hg | Hg_2Cl_2c_2HCl | Pt_H$ should give the transference number for the anion. This arrangement is open to the criticism that hydrochloric acid is a volatile solute and that the Helmholtz formula does not necessarily apply to this case. To this objection there are two answers to be made. With dilute solutions, the partial pressure of hydrochloric acid can certainly be considered as practically though not theoretically zero. If the formula is inapplicable to this case, entirely different results should be obtained when sulphuric acid and mercurous sulphate are substituted for hydrochloric acid and mercurous chloride.

Apparatus. — The apparatus used was similar to that of Peirce[2] and of Smale.[3] The glass cylinders used for holding the various gases were from 30 cm to 40 cm long and about 3 cm in diameter. Several electrodes were used in each cylinder and were kept in place by elastic bands. To set up the apparatus, the lower end of the cylinder was placed in a beaker containing the electrolyte; the air was removed by suction and then the gas was passed in by means of a bent tube ending in a capillary point and reaching to the top of the cylinder.

The connections between the electrolytes in the cells with diffusion were made by siphons plugged with filter paper, or by

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[1] Zeit. phys. Chem. 12, 333 (1893).

[2] Wied. Ann. 8, 98 (1879).

[3] Zeit. phys. Chem. 14, 577 (1894).

means of moistened yarn—the latter method proving very satisfactory.

The electrodes were of platinum and had a surface of about 2 cm^2 and making them somewhat larger or smaller had no perceptible effect on the electromotive force. Platinum wires were welded to the electrodes and fastened to copper wires. These latter were adjusted in small glass tubes so that only platinum came in contact with the gas and the electrolyte. Since variable and unsatisfactory results were obtained with unplatinized electrodes, they were platinized[1] by making them cathodes in a platinic chloride solution to which a little lead acetate had been added, the current being furnished by an accumulator. Since platinum black absorbs both chlorine and platinic chloride, the electrodes were then made cathodes in a solution of sulphuric acid, the current passing for about an hour. The electrodes were kept in boiling water for several hours until no two showed a difference of potential when connected with a galvanometer. They were left in boiling water until needed, so as to prevent absorption of oxygen. If burned off in the blast-lamp they absorb much less gas and do not prove so constant.

Gold electrodes were also tried and proved to be much like unplatinized platinum. On covering them with a thick coating of palladium black, from a palladium chloride solution, they were much improved, but still inferior to the platinum electrodes, although Böttger[2] found them very satisfactory. The measurements were therefore made entirely with platinum electrodes.

The measurements were made by the Poggendorff compensation method, using either a Lippmann upright electrometer or a galvanometer as the zero instrument. With the electrometer, measurements could be made to 0.0005 V and with the galvanometer to half of this, an accuracy quite sufficient in view of the other sources of error. Two resistance boxes of 1100 and 10,000 ohms were used and the various resistances were checked. As working element a Leclanché cell proved very satisfactory.

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[1] Lummer and Kurlbaum. Verh. phys. Ges. Berlin, 14, 56 (1895); Kohlrausch. Wied. Ann. 60, 315 (1897).

[2] Zeit. phys. Chem. 24, 253 (1897).

It gave an electromotive force of about 1.51 V and varied but 0.03 V in several months. It was compared before each set of measurements with a standard Clark that agreed exactly with one from the Imperial German Institute. Its value was taken as $1.4336 + (15 - t)0.0011$ V. A cupron cell of 0.7 V was also available as working element. It was checked against a cell[1] $Cu \mid CuSO_4Hg_2SO_4 \mid Hg$, this latter being in turn compared with a Clark cell. The electromotive force of the copper-mercury standard cell was taken as 0.361 V at 17°. All measurements were made at the ordinary temperature, about 18° C.

Hydrogen electrodes.—The hydrogen was made from pure zinc and sulphuric acid, and freed from impurities by passing through potassium permanganate, potassium hydroxide and water. This gives the same results as electrolytically prepared hydrogen.[2] The hydrogen was stored in a large balloon flask over water that had been freed from air by boiling.

The acids used were bought as chemically pure and were all found to be free from impurities excepting the hydrobromic acid and the hydriodic acid, the first of which contained free bromine and the second free iodine. These two acids were purified by distillation in a current of hydrogen. The solutions were made up to the given concentrations with a possible error of about one-fourth of one percent, greater accuracy than this being superfluous.

Since the measurements varied from time to time, a large number of observations were made and each value given in the following table is the mean of a series. The maximum variation was about 0.0015 V. In Table II are given the results for hydrogen concentration cells with diffusion, the electrolytes being hydrochloric, hydrobromic, hydriodic, sulphuric and oxalic acids. Under column I are given the concentrations expressed in liters per reacting weights; under II the values found by Smale[3] and under III my own determinations.

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[1] Jour. Phys. Chem. 2, 185 (1898).

[2] Glaser. Zeit. Elektrochemie, 15, 355 (1898).

[3] Zeit. phys. Chem. 14, 577 (1894).

Table II

Hydrogen concentration cells with diffusion

I Conc	II Smale	III Found	I Conc	II Smale	III Found
Hydrochloric acid			Sulphuric acid		
1 : 10	0.0186	0.0183	1 : 10	0.0108	0.0092
1 : 100	0.0338	0.0350	1 : 100	0.0172	0.0187
1 : 1000	0.0549	0.0544	1 : 1000	0.0259	0.0289
10 : 100	0.0170	0.0183	10 : 100	0.0097	0.0097
10 : 1000	0.0359	0.0360	10 : 1000	0.0172	0.0193
100 : 1000	0.0210	0.0216	100 : 1000	0.0081	0.0102
Hydrobromic acid			Oxalic acid		
1 : 10	0.0194	0.0196	1 : 10	....	0.0060
1 : 100	0.0367	0.0364	1 : 100	....	0.0126
1 : 1000	0.0606	0.0571	1 : 1000	....	0.0230
10 : 100	0.0192	0.0204	10 : 100	....	0.0084
10 : 1000	0.0409	0.0417	10 : 1000	....	0.0135
100 : 1000	0.0186	0.0197	100 : 1000	....	0.0111
Hydriodic acid			Hydriodic acid		
1 : 10	....	0.0183	10 : 100	....	0.0178
1 : 100	....	0.0355	10 : 100	....	0.0350
1 : 1000	....	0.0573	100 : 1000	....	0.0184

In the experiments on the hydrogen concentration cells without diffusion, a U-tube, containing mercury, the mercurous salt of the acid as depolarizer and the two concentrations of the acid, was interposed between the two solutions surrounding the hydrogen electrodes. Other metals than mercury might have been taken without changing the electromotive force, as was predicted by Ostwald and verified experimentally by Goodwin.[1]

The mercurous salts were all made in the same general way as the mercurous[2] iodide. One hundred and twenty-five grams of air-dried mercurous nitrate were dissolved in two liters of water containing 20 cc nitric acid. Fifty grams of dissolved potassium iodide were added to the clear liquid, drop by drop, stirring vigorously the while. After running in the potassium iodide the liquid was shaken vigorously for fifteen minutes so as to maintain the closest contact between the precipitate and the mother-

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[1] Zeit. phys. Chem. 13, 577 (1894).

[2] Jour. Pharm. Chem. (6) 6, 612, (1897).

liquor, the precipitate changing from greenish-yellow to a much brighter color. The liquid was then left in the dark for twenty-four hours and well shaken at intervals. After that, the precipitate was washed ten times by decantation with two liters of water each time; washed on a filter-paper and dried in an air-bath at 50°. The product is a yellow salt of much the same color as lead chromate. No indications of decomposition were noticed with any of the mercurous salts in spite of the fact that no particular care was taken to preserve them from the light.

In Table III are given the data for hydrogen concentration cells without diffusion and the transference number of the anion as obtained by the method of Helmholtz from the ratio of the electromotive forces in Tables II and III. In Table IV are given Hittorf's data[1] and, under sulphuric acid, three measurements by Wiedemann,[2] these latter being marked W. There are no direct measurements for oxalic acid.

Table III

Hydrogen concentration cells without diffusion

Conc	E.M.F.	$\frac{v}{u+v}$	E.M.F.	$\frac{v}{u+v}$	E.M.F.	$\frac{v}{u+v}$
	Hydrochloric acid		Hydrobromic acid		Hydriodic acid	
1 : 10	0.1174	0.156	0.1218	0.161	0.1029	0.178
1 : 100	0.2253	0.155	0.2208	0.164	0.2246	0.158
1 : 1000	0.3394	0.160	0.3644	0.157	0.3500	0.164
10 : 100	0.1132	0.162	0.1281	0.159	0.1242	0.158
10 : 1000	0.2295	0.157	0.2750	0.151	0.2314	0.143
100 : 1000	0.1328	0.163	0.1266	0.156	0.1116	0.165
	Mean	0.159	Mean	0.158	Mean	0.161
	Sulphuric acid		Oxalic acid			
1 : 10	0.0575	0.160	0.0402	0.149	....	....
1 : 100	0.1120	0.167	0.0850	0.148	....	....
1 : 1000	0.1789	0.162	0.1303	0.176	....	....
10 : 100	0.0558	0.174	0.0510	0.165	....	....
10 : 1000	0.0984	0.196	0.0746	0.181	....	....
100 : 1000	0.0555	0.184	0.0706	0.157	....	....
	Mean	0.174	Mean	0.163		

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[1] Pogg. Ann. 106, 337 (1859).

[2] Ibid, 99, 177 (1856).

Table IV

Conc	$\frac{v}{u+v}$	Conc	$\frac{v}{u+v}$	Conc	$\frac{v}{u+v}$
Hydrochloric acid		Hydrobromic acid		Sulphuric acid	
0.38	0.193	0.7	0.178	0.533	0.174
1.34	0.168	Hydriodic acid		2.3	0.177
3.00	0.161	0.61	0.201	9.62	0.212
5.21	0.171	15.2	0.258	15.9	0.206
11.77	0.218	Sulphuric acid		0.54	0.176W
78.1	0 210	0.055	0.400	0.89	0.189W
....	....	0.14	0.288	3.61	0.176W

These figures show that the transference numbers hold together very well but are considerably lower than Hittorf's values. It seems probable from the measurements with the gas cells that the transference number varies little, if at all, when the dilution changes from one to one thousand liters. The values obtained from the gas cells cannot be considered as right. Kohlrausch[1] has given 63 as the most probable value for the migration velocities of chlorine and iodine as ion at infinite dilution and 18°. From the conductivity measurements, the migration velocity of bromine as ion must also be 63, while sulphate is probably 67. Taking these figures and the mean values for the transference numbers from Table III, we find for the migration velocity of hydrogen, 333 in HCl, 336 in HBr, 328 in HI, 318 in H_2SO_4. The mean is 328, while Kohlrausch's value is 290. The most probable value for the transference number of hydrogen in the three halogen acids is 0.823 and for the transference number of the anion 0.177. It is clear that, for some reason, the Helmholtz equation is not applicable to these cells. The volatility of the solute can hardly be the cause of the error, so that the volatility of the hydrogen and its solubility in water would seem to be the chief points in which a hydrogen electrode differs from a zinc or a copper electrode. It is hoped that the development of this idea may form the subject-matter of a second paper.

Although it was not within the scope of this paper to con-

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[1] Wied. Ann. 50, 385 (1893).

sider the application of Nernst's theory of electromotive forces[1] to the gas cells, it seemed a pity not to utilize the data obtained to their fullest extent and the values for the gas cells with and without diffusion have therefore been calculated, taking 290 for the migration velocity of hydrogen and 63 for the migration velocity of the halogen. The values for the dissociation have been taken from Kohlrausch.[2] The results for the cells with diffusion are given in Table V. In the second column are the values calculated by Smale,[3] who does not state what numbers he took for the migration velocities. In the third column are the values calculated from Kohlrausch's figures. In the remaining columns are the experimental data for the three halogen acids. In Table VI are the calculated and experimental values for the cells without diffusion.

Table V

Conc	Smale	Calc	HCl	HBr	HI
1 : 10	0.0172	0.0190	0.0183	0.0196	0.0183
1 : 100	0.0367	0.0372	0.0350	0.0364	0.0355
1 : 1000	0.0568	0.0555	0.0544	0.0571	0.0573
10 : 100	0.0188	0.0199	0.0183	0.0204	0.0178
10 : 1000	0.0379	0.0397	0.0360	0.0417	0.0350
100 : 1000	0.0190	0.0188	0.0216	0.0197	0.0184

Table VI.

Conc	Calc	HCl	HBr	HI
1 : 10	0.1073	0.1174	0.1218	0.1029
1 : 100	0.2101	0.2253	0.2208	0.2246
1 : 1000	0.3136	0.3394	0.3644	0.3500
10 : 100	0.1124	0.1132	0.1281	0.1242
10 : 1000	0.2243	0.2295	0.2750	0.2314
100 : 1000	0.1062	0.1328	0.1266	0.1116

If we compare the mean of the values for the three halogen acids with the calculated values, it will be seen that the cells without diffusion give uniformly higher values than the theo-

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[1] Zeit. phys. Chem. 4, 129 (1889).

[2] Wied. Ann. 26, 196 (1885).

[3] Zeit. phys. Chem. 14, 577 (1894).

retical, while the cells with diffusion give, as a rule, slightly lower values than those calculated. The percentage as well as the absolute variation is much smaller for the cells with than for the cells without diffusion.

Having the hydrogen electrode made up, it seemed worth while to measure the electromotive force of the cell formed by combining it with a normal calomel electrode. The calomel electrodes were made from carefully purified material and were compared by checking one against the other. Those used agreed to within two millivolts. The data are given in Table VII.

Table VII

Hydrogen and calomel electrodes

Conc	HCl	HBr	HI	H_2SO_4	$H_2C_2O_4$
1	0.313	0.312	0.325	0.340	0.355
10	0.358	0.356	0.361	0.365	0.381
100	0.396	0.401	0.410	0.401	0.408
1000	0.436	0.455	0.461	0.439	0.433

It was thought that it might be possible to gain some information as to the reason for the low values for the transference number of the anions, as given in Table III, by studying the behavior of cells with chlorine electrodes. If we have the two combinations $Pt_{Cl} \mid c_1 HCl \mid c_2 HCl \mid Pt_{Cl}$ and $Pt_{Cl} \mid c_1 HCl \mid Pt_H \mid c_2 HCl \mid Pt_{Cl}$, the ratio of the two electromotive forces should give the transference number of hydrogen. For this reason some measurements were made with chlorine electrodes. Owing to the limited time at my disposal, I was not able to study the matter as thoroughly as I should have wished and the results can only be considered as preliminary.

Chlorine electrodes.—The apparatus was similar to that used for hydrogen. The hydrochloric acid was saturated with washed chlorine, made from manganese peroxide. Platinum electrodes were used and the cell was measured after standing twenty-four hours carefully protected from the light. The current flows in the opposite direction to that of the hydrogen cell, through the cell from the concentrated to the dilute solution.

In Table VIII are the data for the chlorine concentration cells with and without diffusion, together with the transference number for hydrogen. The cells without diffusion were not measured directly as reversed cells. The single cells were measured and the values for the double cells obtained by subtraction. The electromotive forces of the cells $Pt_H | HCl | Pt_{Cl}$ are 1.368 V for normal hydrochloric acid, 1.486 V for tenth-normal hydrochloric acid and 1.555 V for hundredth-normal acid.

Table VIII

Chlorine concentration cells

Conc HCl	With diffusion	Conc HCl	With diffusion	No diffusion	$\frac{u}{u+v}$
0.2 : 1	0.1180	1 : 10	0.1032	0.118	0.874
0.2 : 10	0.2177	1 : 100	0.1315	0.187	0.703
0.2 : 100	0.2543	10 : 100	0.0411	0.069	0.596

It will be noticed that the transference number varies enormously. This is not surprising because the measurements are very difficult to make and exceedingly unsatisfactory when made. Even if the variations in the transference number were due entirely to experimental error, the mean of the three measurements is 0.724, which differs widely from the most probable value, 0.823. The discrepancy may be due to the action of chlorine on the electrode, the electrolyte, or the water. On the other hand, it is a curious coincidence, though possibly nothing more, that 0.724 is about eighty-eight percent of 0.823, while the mean of the values for hydrochloric acid in Table III, 0.159, is about eighty-eight percent of 0.177. In other words, the found value seems to be the same percentage of the calculated values in the two cases. This point will be examined more carefully in the future.

Incidentally the chlorine electrodes were measured against the normal calomel electrode. The values are 0.957 V for five-normal hydrochloric acid, 1.064 V for normal, 1.138 V for tenth-normal and 1.160 V for hundredth-normal acid.

Bromine electrodes. —A few measurements were made with bromine and iodine electrodes for concentration cells with diffusion. The bromine and iodine cells were made up in test-tubes, the various solutions being left with an excess of bromine or iodine for several days. They were shaken from time to time. Except when the electromotive force of a cell was being determined, the solutions were carefully protected from the light. The platinum electrodes were saturated with bromine or iodine by electrolyzing normal solutions of the acids with the platinum electrodes as anodes.

The bromine concentrations were determined at 21° by adding a measured portion of the solution to an excess of potassium iodide and titrating with sodium thiosulphate, using starch as an indicator. The iodine concentrations were determined by titration with sodium thiosulphate.

The values for the bromine concentration cells with diffusion and for the bromine electrode against the normal calomel electrode are given in Table IX, the concentration of the bromine in the solutions being given in grams per liter.

Table IX

Bromine concentration cells

Conc HBr	With diffusion	Conc HBr	Conc Bromine	Calomel electrode
1 : 10	0.112	1	207.20	0.817
1 : 100	0.249	10	45.93	0.918
1 : 1000	0.266	100	39.24	1.023
10 : 100	0.127	1000	34.81	1.062
10 : 1000	0.162			
100 : 1000	0.031			

Since the concentration of the bromine varies greatly, no measurements were made of the hydrogen electrode against the bromine electrode. A few experiments were made with iodine cells having different iodine concentrations,[1] the results of which are given in Table X, the iodine concentrations being grams per liter.

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[1] Theoretically, this is analogous to a hydrogen electrode under varying pressures.

Table X

Concentration cells with iodine

Conc HI	Conc Iodine	Cell	E.M.F.
1	153.40	1 : 1(a)	0.049
1(a)	17.21	1 : 1(b)	0.075
1(b)	3.20	1(a) : 1(b)	0.028
10	13.02	10 : 10(a)	0.037
10(a)	1.73	10 : 10(b)	0.050
10(b)	0.32	10(a) : 10(b)	0.015

Iodine electrodes. — Saturated solutions of iodine in various concentrations of hydriodic acid were arranged as concentration cells with diffusion and as an iodine electrode against the normal calomel electrode. The results are given in Table XI, the iodine concentrations being grams per liter.

Table XI

Iodine concentration cells

Conc HI	With diffusion	Conc HI	Conc Iodine	Calomel electrode
1 : 10	0.0679	1	153.40	0.239
1 : 100	0.1224	10	13.02	0.302
1 : 1000	0.1928	100	0.83	0.363
10 : 100	0.0604	1000	0.26	0.451
10 : 1000	0.1197			
100 : 1000	0.0829			

Berthelot[1] has shown that a compound $KInI_2$ exists in solution. This was confirmed by Le Blanc and Noyes[2] who showed from the conductivity and freezing-point phenomena, that this compound changed, with increasing dilution, into potassium iodide and iodine — the conductivity at infinite dilution having about the same value as potassium iodide in water. It is therefore not improbable that compounds such as $HBrnBr_2$ and $HInI_2$ are formed. It would, of course, be impossible to apply the Helmholtz formula to measurements with the bromine and iodine

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[1] Ann. Chim. Phys. (5) 21, 375 (1880).

[2] Zeit. phys. Chem. 6, 397 (1890).

electrode until more is known about the conditions prevailing in the solutions.

I take this occasion to express my thanks to Professors Bancroft and Trevor for their advice and assistance.

The general results of this investigation are:

1. The Helmholtz method of determining transference numbers is not applicable to gas cells.

2. It is probable that the source of error is to be found in the solubility of the electrode in the electrolytic solution.

3. It is probable that the transference number for hydrogen in hydrochloric acid does not change with the dilution between normal and thousandth-normal solutions.

Cornell University

SINGLE DIFFERENCES OF POTENTIAL

BY HECTOR R. CARVETH

The progress of scientific electrochemistry has been so rapid in the past decade that it is not surprising to learn that a school of physical chemists regards the problem of the voltaic cell as already solved, and thinks that future work along this line will be merely corroborative in its nature. Recent literature has shown, however, that the adherents of this school may not be thoroughly consistent in their doctrine, and that whatever may be (and certainly are) the triumphs of the modern electrochemical view, it is necessary that there be eliminated from it any inconsistency which impairs its general usefulness. The adherents of this successful theory claim that the electromotive force of any ordinary chemical combination may be predicted with a fair degree of accuracy. This is done by adding up the single differences of potential in a cell, all of which, the theory claims, are capable of formulation, and one of calculation.

It thus appears that in the first place it must be known where differences of potential are to be observed in a cell, and secondly, what are their intensities. The total electromotive forces of a cell may be considered as composed of four single differences of potential which are located at the boundary surfaces of metal$_1$ | metal$_2$, metal$_2$ | electrolyte$_2$, electrolyte$_2$ | electrolyte$_1$ and electrolyte$_1$ | metal. The intensity at the first-mentioned contact surface is so small as to be ignored.[1] With regard to the other three potential differences, it may be said that no simple mathematical formula was given for their calculation until the appearance of the Nernst classic[2] in 1889. Since the Nernst

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[1] Ostwald. Lehrbuch II, 919.

[2] Zeit. phys. Chem. 4, 129 (1889).

theory has as its basis the theory of osmosis, it is evident that its application holds rigidly only in so far as the so-called 'law of osmotic pressure' holds, namely for dilute solutions. When restricted to these, experiments show that the theory is able to predict and to explain results very satisfactorily. By use of it alone, however, the difference of potential at the contact surface metal | electrolyte while capable of formulation, cannot be calculated. It is here that another theory has been introduced in order to supply the missing link.

That the two theories should be merged together is not unexpected. But by this procedure many abnormalities have been produced, for which no satisfactory explanation can be given. In a recent article[1] Nernst has called attention to the fact that the two theories cannot both be correct, while Taylor[2] in a dissertation presented in June, 1896, had arrived at similar conclusions.

The object of this research is to examine the theories of today with respect to single differences of potential, directing attention more particularly to the several methods which claim to determine the actual value at the surface, electrode | electrolyte, and from theoretical considerations and results obtained by use of one of these methods, to attempt to answer the question, "Do these methods give the true potential difference?"

The history of single potential differences is most intimately connected with the change of surface-tension of mercury. The relation existing between the two was not discovered, however, until many years after the announcement of the fact that the electrical condition of a mercury surface exercises a determining influence on its surface-tension. To the investigation of the phenomenon many scientists applied themselves with little or no success, until, by a very careful research, Lippmann showed that the surface-tension at the surface, mercury | sulfuric acid, is a constant function of the electromotive force of polarization at that surface, that when the surface of mercury is polarized by

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[1] Wied. Ann. 58, Beilage, (1896).

[2] Jour. Phys. Chem. 1, 1 (1896).

hydrogen it contracts until a certain electromotive force is reached, and that when this is further increased, expansion takes place. He plotted his results using as abscissas the different electromotive forces applied, as ordinates the surface-tension expressed in arbitrary units, and thus obtained a curve which consisted of a rising and a falling branch, and which approached the symmetry of a parabola. The practical application of Lippmann's discoveries appears in the electrometer that bears his name and is so extensively used in the measurement of electromotive forces.

Lippmann had thus shown that the intensity of the polarizing current had a decided effect on the surface-tension of mercury; other experiments performed by him showed that the reverse phenomenon could take place, viz., that by changing the surface-tension it was possible to produce changes in the electromotive forces. It is to these experiments that is due the mathematical treatment which was given the subject by Helmholtz[1] and of which the introduction only is here translated.

"Now in dealing with polarized mercury surfaces we have to do with a much more complicated process, since the electricity present in electrolytes has, according to Faraday's law, taken with it ponderable ions of the electrolyte. But the treatment of the subject just given may be generalized in a way which has already been used by Lippmann, in which it is necessary merely to make the supposition that the forces under whose influence the double layers are formed may be conservative forces, and that the variations produced are thus *perfectly reversible*. The actual occurrence of the reversibility of this process has been to a great extent proved at the same time by the researches of Lippmann."

Making use of the supposition above given, Helmholtz derived the formula

$$\frac{\partial T}{\partial P} = -\epsilon,$$

where ∂T is the differential of the surface-tension of the mer-

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[1] Wied. Ann. 16, 30 (1882).

cury, ∂P is the differential of the potential and ϵ is the amount of electricity per surface unit, forming the charge of the ions of the electrolyte.

Consideration of this formula shows that when the mercury is at its greatest surface-tension, it should show no difference of potential against the electrolyte, and Helmholtz concluded that such a result would be reached if one allowed mercury to fall in a fine stream into an electrolyte. Under his direction, König[1] examined the surface-tension of mercury in a few solutions; he found that while the absolute value of the surface-tension of mercury was *not* the same for all solutions, the surface-tension of mercury dropping into a solution was actually of the same value as the maximum obtained when it was polarized in the same solution. The theory was thus able to explain all the phenomena known at that time; and, although Helmholtz himself did not draw attention to the fact, there was a deduction to be drawn from his conclusion which has since influenced electrochemical views to a great extent. It was Ostwald[2] who showed that the conclusions of Helmholtz should lead to a knowledge of the single difference of potential between metal and electrolyte, since by the Helmholtz theory the dropping mercury could have no difference of potential against the electrolyte into which it fell, and that hence any electromotive force observed with such a combination as

dropping mercury | electrolyte | metal

should give the single difference of potential, electrolyte | metal.

Important as this work appears, and so simple its execution, the results obtained by its use have not been so uniform as to be considered satisfactory. Such at least must be said of the work of Ostwald, Exner and Tuma, Pellat, Moser and Miesler. It was Paschen who, in 1890, after studying carefully the phenomena of polarized mercury surfaces, directed his attention to dropping mercury electrodes, coming finally to the conclusion that the lack of uniformity in the results of other observers was

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[1] Wied. Ann. 16, 1 (1882).

[2] Zeit. phys. Chem. 1, 583 (1887).

caused by their not having the flowing mercury assume its greatest tension. This error[1] he claimed to have eliminated by having the flowing mercury 'break' just as it entered the surface of the electrolyte.

The results he obtained by this method of dropping mercury he compared, and found to agree remarkably well with results obtained by the polarization method as first used by Lippmann (see Table II on page 306). This method is regarded as the exact converse of the dropping mercury method. The mercury and electrolyte are put into a capillary electrometer and then the mercury is polarized by known electromotive forces until it attains its maximum of surface-tension. According to the Helmholtz theory, the electromotive force which must be applied at this point is equal, with reversed sign, to the potential difference of mercury | electrolyte.

In practice, the usefulness of this polarization method is impaired by the following disadvantages: —

(*a*) It is exceedingly difficult to ascertain when the maximum of surface-tension has been attained, more especially with dilute solutions. To find the maximum, it is hence necessary to resort to interpolation curves.

(*b*) With some electrolytes, mercury either does not move at all, or moves so very little as to render the method useless. This is the case when mercury is in contact with a solution of a soluble mercury salt where the current in passing through causes decomposition at the electrodes.

(*c*) The method is obviously inapplicable when mercury comes into contact with salts of silver, platinum or palladium.

The dropping mercury method should obviate the objection (*a*); while the proper variation of the method should allow the other two disadvantages to be overcome. If then it were found that this method actually fulfilled the conditions imposed in order that the Helmholtz theory might be strictly applicable, we should have here what Paschen thought he had — a beautiful experimental method of finding single differences of potential

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[1] Wied. Ann. 41, 42 (1890).

between metal and electrolyte or electrolyte and electrolyte. Values have been obtained, however, which can be explained only by the assumption that the mercury on entering the solution is not completely deprived of its charge. Instances of this are to be found in Paschen's[1] measurements with zinc and cadmium amalgams, when the flowing amalgam played into solutions of zinc sulfate, magnesium sulfate, magnesium chlorid and cadmium bromid. In these cases the investigator drew attention to the fact that the amalgams could no longer be considered as entering the electrolyte without a difference of potential. If then, in some cases, the failure of the method is only too obvious, while in the remaining cases no proof is adduced to show that the flowing mercury does actually attain the maximum of tension,[2] it is not surprising that the significance of the measurements made by both of these methods (since they agree fairly well with each other) should be doubted, and another theory given to explain the presence of these electromotive forces.

This theory, which was first advanced by Warburg[3] and afterwards[4] strongly supported on theoretical grounds, was based on his discovery that when mercury was in contact with solutions of electrolytes, such as H_2SO_4, $MgSO_4$, NaCl, KCl, etc., containing oxygen from the air, compounds of mercury were produced. Ostwald,[5] Paschen[6] and others have also observed the solubility of mercury in H_2SO_4 containing oxygen, and it is not improbable that such solubilities may be observed with almost every electrolyte. Accordingly in an electrometer holding mercury and sulfuric acid, the latter containing oxygen, there will always be present some mercurous sulfate. The passage of a current through the electrometer will cause decomposition of the latter electrolyte. The mercury precipitating at the cathode will render the mercurous sulfate solution there more

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[1] Wied. Ann. 43, 568 (1891).
[2] Paschen. Wied. Ann. 41, 205 (1890).
[3] Wied. Ann. 38, 321 (1889).
[4] Ibid. 41, 1 (1890).
[5] Zeit. phys. Chem. 3, 354 (1889).
[6] Wied. Ann. 43, 568 (1891).

dilute, while at the anode the concentration of the salt is increased. Now, if at any moment before the maximum tension is reached, the current is suddenly disconnected, and the electrometer is not short-circuited on itself, the latter will, on being connected with a sensitive galvanometer, indicate a current running in a direction exactly opposite to the polarizing current previously applied. From the standpoint of the Helmholtz theory, this is the charge from a condenser; but the Warburg theory regards it as a concentration element produced by

$$\text{Hg} \mid \text{dil } Hg_2SO_4 \mid \text{conc } Hg_2SO_4 \mid \text{Hg}.$$

To establish the Warburg theory, it was absolutely necessary to show that the surface-tension of mercury or of amalgams could be affected by other means than a polarizing current—viz: by the nature of the solution with which it was in contact. G. Meyer[1] has performed experimental work in this direction. He determined, by Lord Rayleigh's method, the surface-tension of mercury or amalgam, when there was added to the electrolyte with which it was in contact a salt of mercury or of the metal contained in the amalgam. In most cases this had the effect of decreasing the surface-tension of the mercury or the amalgam. With some, however, such as HgCu in caustic soda or potassium cyanid, HgZn in sulfuric acid, magnesium sulphate, sodium hydroxid and chlorid, and HgCd in sulfuric or hydrochloric acids, the addition of the salt of the metal contained in the amalgam did not effect the surface-tension and in all these cases the ascending part of the surface-tension polarization curve was lacking. The absence of this part of the curve in these cases is not explained by the Helmholtz theory since it deals with polarizable electrodes only; the Warburg theory ascribes the *decrease* of surface-tension to the formation of amalgam.

Since mercury in the presence of a salt of mercury cannot attain its maximum surface-tension, we have according to the Warburg theory when we polarize mercury in an electrometer until the mercury reaches its maximum tension, a combination, Hg | electrolyte | solution of mercurous salt | Hg, whose electromo-

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[1] Wied. Ann. 53, 845 (1894).

tive force gives the intensity opposing polarization. Thus, in addition to the single potential difference Hg | electrolyte which the upholders of the Helmholtz theory regard as the only one present, there should also be present the two—electrolyte | solution of mercurous salt, and solution of mercurous salt | mercury—the latter of which will be regarded by very few scientists as negligible.

With an ideal dropping mercury electrode, one should have an element similar to the one in the electrometer, since the mercury in falling thus assumes its greatest tension; hence the experimental result that both methods give (at times) the same values may be explained just as well by one as by the other theory. But does such an ideal electrode exist? Consider from the Warburg point of view the case of mercury flowing into potassium chlorid. There is formed here caustic potash (shown by alkaline reaction) and mercurous chlorid. The presence of the latter prevents the mercury from assuming its maximum tension. If we measure this at any time after it has been running an indefinitely short time, we are actually measuring

Hg | dil Hg salt | conc Hg salt | Hg

and not Hg | $KClHg_2Cl_2$ | Hg. The formation of the mercurous chlorid and its effect on the flowing mercury can certainly not be ignored in this case. Considering the case from the standpoint of the double-layer theory, one notes, bearing in mind that Hg in KCl was found by Göuy[1] to have a lower surface-tension than Hg in KOH, and that the mercury in dropping into KCl is continually changing its maximum of surface-tension as the composition of the solution into which it falls changes, that it is not connected with the electrolyte without a difference of potential. In the face of facts such as the above, it appears unreasonable to introduce as the value of the normal potassium chlorid electrode (Hg | Hg_2Cl_2KCl in normal solution) 0.560 volt, when according to either of the theories, this is *not* the value of the single potential difference of Hg | KCl. It would be just as reasonable to introduce the value of Hg | KBr = 0.49 since this value has been

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[1] Comptes rendus, 114, 211 (1892).

found by several observers. But if then we make such a combination as[1]

$$Hg \mid Hg_2Cl_2KCl(1) \mid KBr(1)Hg_2Br_2 \mid Hg$$

we should expect an electromotive force not much more than 0.07 volt, since the Nernst-Planck theory would allow us to neglect the potential difference at the surface of the two electrolytes. But the electromotive force actually found is (roughly) 0.14 volt. By making use of the double-layer idea, it should be found that the dropping electrode measurements always err (if at all) by giving too low values, because the mercury can hardly be considered as passing beyond its maximum of surface-tension. If then $Hg \mid KBr = 0.49$, and the potential difference between the solutions be equal to zero, the value found for $Hg \mid KCl$ must be too low. A consideration of other similar cases serves to confirm the conclusion that there is at present no justification for regarding even one potential difference, metal | electrolyte, as known. If only one of these were known, and the Nernst-Planck theory were accepted as true, all other values could be calculated readily therefrom.

That a knowledge of the values of true single differences of potential will be of great importance, especially theoretically, may readily be granted. From them may be deduced clearer ideas as to the solution-pressures of metals, temperature coefficients of certain types of cells, heats of ionization of the elements, etc. In this as in so many other branches, Ostwald has been the pioneer; but whether the values which he and many others assume as known definitely are true values, is the subject considered in this paper.

Unsatisfactory as the condition of the theoretical side of the subject appears, it seemed advisable to attempt further measurements by means of the dropping mercury method, comparing where possible the results obtained with those of other investigators. Attention has been directed more especially to the measurement of metals in solutions of their salts, since a con-

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[1] The figures after the chemical formula are used throughout this paper to denote the number of liters in which 1 grm mol weight is dissolved.

sideration of the combinations of this type will probably lead to more definite conclusions than a discussion of cells with irreversible electrodes.

Apparatus and material used.—In the description of his apparatus, Paschen drew attention to the necessity of performing the work of measurement by means of dropping mercury electrodes in a place free from jarring or other disturbance. In the work here described, no such effect was noticed at all, all due precautions having been taken at the beginning to obviate such. In the room placed at my disposal by Professor Bancroft, the (unused) fume cupboard had a stone floor which had been built into the wall, and hence was not disturbed by any motion or jarring in the room. On this floor was built a wooden platform which had an area outside of fume cupboard of about 0.6 sq. m. (100 cm by 60 cm). This was sufficiently large to hold all the apparatus required in the measurements. The electrode from which the mercury flowed was supported by clamps attached to an iron bar about 130 cm in length, which in its turn was attached to the side of the fume cupboard.

The electrodes for the dropping mercury varied in length from 80 cm to 200 cm. The one finally adopted consisted of 150 cm of glass tube of about 12 mm diameter, to the lower end of which was fused 10 cm of capillary tube (1 mm bore). This was connected to the tip by double rubber tube, the latter being securely wired to the glass tube. The tip was made by drawing out capillary tubes; diameters of different tips ranged from 0.2 to 0.05 mm. The greater number of the measurements were made with a tip of diameter 0.12 mm (calculated) which, with a pressure of 150 cm of mercury, gave a stream breaking about 8 mm below the tip. A wire pinch-cock over this rubber served to stop the flow of mercury when the electrode was not in use. This has several advantages over a stop-cock, which was discarded entirely after the former method had been tried. They are:

(1) It allows rapid change of tips.

(2) There is less danger of spilling mercury.

(3) Electrical connection between the flowing mercury and the platinum connection of the drop electrode is assured.

This platinum wire was fused into the wider part of the tube, and thus formed the terminal connection on the sides of the dropping mercury.

For a number of the measurements first taken, a platinum wire fused into the vessel receiving the falling mercury served as the other terminal, and thus formed electrical connection with the mercury there. As this method was somewhat inconvenient, it was soon given up. Accordingly in all the measurements given in this paper, the fallen mercury plays no part. The diagram shows the method used. The mercury falls from the drop electrode into a funnel, which is so made that it discharges mercury as rapidly as it flows in. This stream of mercury breaks just as it enters the surface of the electrolyte in the funnel, and thus when once the adjustment is made, the apparatus is self-regulating. The electrolyte in the funnel is connected by a siphon with a half-cell. The latter consists of a metal which forms the other terminal, and the solution of an electrolyte. Since these half-cells may be readily connected or disconnected without disturbing to any extent any other part of the apparatus, it is possible to make a considerable variety of measurements quite rapidly. There is, moreover, the advantage that they may be used repeatedly so that one knows he is always measuring the same half-cell, whereas if it is made up and then used immediately, it does not usually have the same value it finally attains. In all cases examined, the metals stood in the electrolytes some time before a measurement was taken.

In obtaining pure mercury, great trouble was taken. Two methods were used, both of which gave excellent results. The first was the ordinary method of shaking the mercury with dilute sulphuric acid and a few drops of potassium dichromate, and then washing it thoroughly with dilute nitric acid and water. The other method was the one in use in the gas laboratories here. The mercury is allowed to remain under sulfuric acid and mercurous sulfate in the separating funnel for some time. In this way a very pure mercury is obtained, which when washed thoroughly was ready for use. In all cases, the mercury after passing through the funnel was again cleaned if the surface appeared the least tarnished.

The copper, nickel, zinc, cadmium and lead electrodes used in the half-cells were in round sticks about 4 mm diameter and 5 cm long. The first two metals had been prepared electrolytically, and were quite pure. The zincs were carefully amalgamated before using. The cadmium electrodes (from Eimer & Amend) were always, like the other electrodes, given a bright surface before being put into the solution. The lead electrodes were made by reduction of pure lead oxid. The platinum electrodes had been previously platinized.

Especial care was taken with regard to the purity of the alkali halid salts. The sodium and potassium chlorids, and the potassium bromid were precipitated by hydrochloric or hydrobromic acids, the former two salts three times, the latter once. They were then fused. Tests showed no trace of impurities. The barium and magnesium chlorids, potassium iodid and potassium sulfate were each recrystallized twice, as were also copper sulfate and nitrate. All the nickel, cadmium, and zinc salts used, zinc sulfate excluded, were taken from the museum and subjected to no further treatment. The zinc sulfate was exceptionally pure, being the same as was used in making my Clark cells.

The mercurous chlorid,[1] bromid, iodid, sulfate and oxid which were used as depolarizers were made by precipitating from mercurous nitrate, washing rapidly and carefully, and, when possible, drying. When drying was not resorted to, the precipitates were carefully washed by a solution of same material as that in which the measurement was to be made. The hydrochloric and sulfuric acids and the ammonia were quite pure. In none of the solutions (with the exception of potassium chlorid) was especial care taken to make weighing or titrations

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[1] The statement is frequently made that mercurous chlorid darkens on exposure to the light; but the product of the writer is now unaltered in color, although it was made over fifteen months ago and has since been standing on an open shelf of the laboratory, but not in the sunlight.

closer than one percent, since the method of measurement could in no case detect an error so small.

Measuring apparatus.—Two Clark cells were made up; they were carefully compared with a Reichsanstalt, and found to differ from it by less than a millivolt. One was used as a working standard, the other reserved for comparison. At no time while measurements have been taken, has a variation from each other of 0.002 volt (referred to the temperature of 15°) been observed. The Leclanché working cells were very constant. The electromotive force of individual cells varied from 1.46 to 1.53 volts. The fluctuations in the daily measurements for a month did not exceed 0.01 volt, and for a day 0.002 volt. As it was frequently necessary during a measurement to have the cell closed for five minutes on a resistance of 1000 ohms, or a little more, preliminary measurements were made by means of a Weston voltmeter of 200 ohms internal resistance, in order to examine the effect on the electromotive force of the cell. The following are the readings:—

	p. m.	volts	
At start:	3.53	1.460	Cell now put on 1100 ohms external resistance.
	3.56	1.461	
	3.59	1.461	
	4.05	1.461	
	4.10	1.460	
	4.20	1.459	

This showed that the electromotive force of the cell remained quite constant, even with so low a resistance, for a time very much longer than was ever required in making a measurement.

The general arrangement of the apparatus is indicated by the diagrams, Figs. 1 and 2. Here DE is the dropping mercury electrode; HC the half-cell; 1, 2, and 3 are switches that are always thrown in for each measurement with the dropping electrodes; 4 is a switch used only in throwing in C, the standard Clark element, for purposes of comparison. E is an ordinary Lipp-

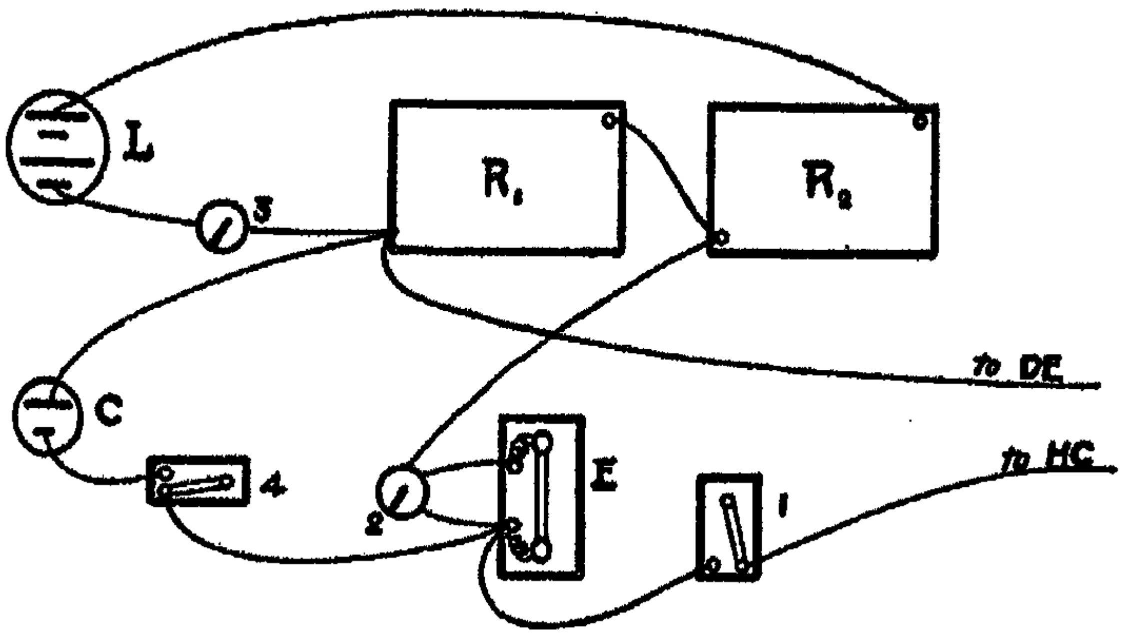

Fig. 1

mann electrometer, L the Leclanché working element, while R_1 and R_2 are the resistance boxes.

In using the Lippmann electrometer by this method difficulties are frequently to be met. They are not of such a nature however as to preclude its use, although Palmaer[1] seems to have been unable to use it in his measurements because its polarization capacity was greater than that of the cell being measured. The objection is overcome by the use of the half-cells, with depolarizer always present.

Two resistance boxes each of 1110 ohms were used in making the measurements. The readings on the electrometer were made by the zero method, and in the concentrated solutions (e. g. normal) could be taken as accurately as 0.001 volt. With the more dilute solutions such a degree of accuracy seems impossible, and notwithstanding the greatest care taken, the readings may possibly be incorrect to the extent of 0.008 volt in the case of hundredth-normal solutions. In making the measurements, the electrode tip was first adjusted so that the mercury might break just at the surface of the electrolyte. By using different switches (1 and 2) the terminals were connected directly to the electrometer, and the tip adjusted so that the mercury in the electrometer just moved slightly. Then switch (3) was thrown in, and the measurement made in the usual manner.

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[1] Zeit. phys. Chem. 25, 265 (1898).

This method of using the electrometer as an indicating instrument requires that it should always be short-circuited on itself when not in use. In this respect at least, too great care in its use cannot be taken.

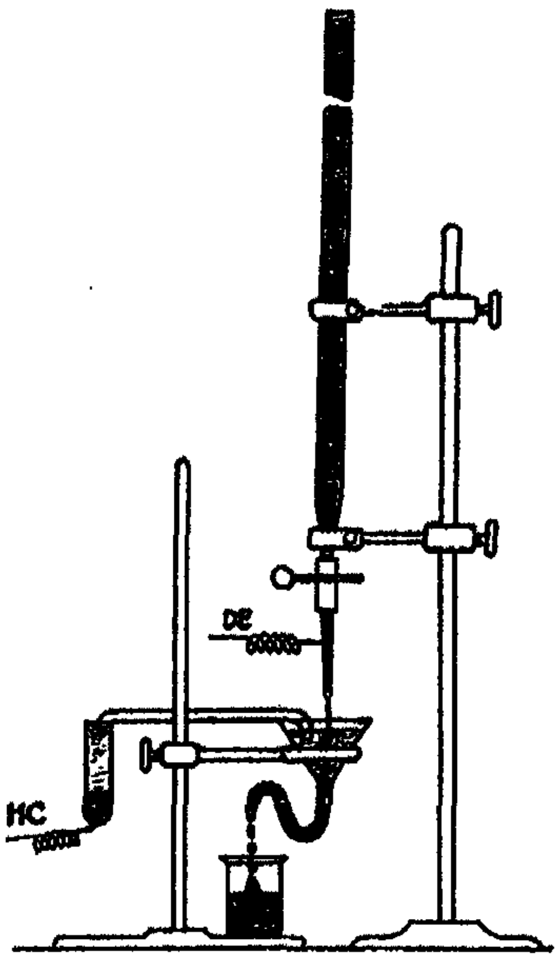

Fig. 2

Preliminary measurements.—The results of Paschen's experiments with electrodes of varying lengths, and tips of varying rates of discharge appeared at first sight somewhat strange, but a repetition of them leads to their confirmation. There was found for every electrode height a minimum diameter of the capillary tip, and hence a minimum flow below which the measurements did not agree when the other conditions were kept alike as far as possible. But when these so-called "critical" heights had been determined, it was found that the same values were obtained whether one used an electrode 80 cm long, which gave a stream of mercury 2 mm long before breaking, or one of 175 cm giving a 35 mm stream, or of any intermediate values of heights of electrodes or lengths of streams. The 8 mm stream with which many of the measurements were taken was so chosen merely because it served better to keep the electrolyte in the funnel at the constant level.

The values obtained by having the mercury break below the surface of the electrolyte, and by having the tip itself dip below the surface, were also of interest. In the latter case one could, by making the mercury flow in a stream of large cross-section and from low pressures, obtain, e. g. with Hg | HCl | S[1] or

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[1] S is used throughout the paper to denote the dropping mercury—in conformity with the nomenclature used by the first German investigators (Strahl-electrode).

$Hg \mid H_2SO_4 \mid S$, values approaching zero. By decreasing the cross-section, and increasing the pressure, the value was raised. A brief statement of the facts observed would be that almost any value may be observed which ranges from zero up to that maximum which is obtained by having the mercury break just at the surface. (We are here dealing with the case of $Hg \mid$ electrolyte $\mid S$.) Similar results seem to have been obtained by Paschen,[1] although he does not draw especial attention to them.

It was found by the writer that it was possible to obtain fairly constant readings when the mercury broke below the surface of the electrolyte. Two illustrations are given to show this. The mean value for $S \mid KCl(1) \mid KCl(1)Hg_2Cl_2 \mid Hg$ was found to be 0.560 volt. This is the average of a great number of observations of which the extreme variation from the mean was 0.003 volt. The electrode tip was then adjusted to break below the surface of the solution so that on three different occasions it gave the values 0.514, 0.519, 0.523 volt respectively. The normal electrode was then replaced by different metals in solutions of their salts, and the combination $S\ KCl(1) \mid$ metallic salt $(2) \mid$ metal, measured. Knowing the electromotive force of the whole cell, $Hg \mid Hg_2Cl_2KCl(1) \mid$ metallic salt$(2) \mid$ metal, we should be able by subtracting the two numbers obtained in the measurements to obtain a constant number for the value

$$S\ KCl(1) \mid KCl(1)Hg_2Cl_2 \mid Hg.$$

This is shown in the following table: —

Table I

	A. E.M.F. of whole cell	I	Ia	II	IIa	III	IIIa
$ZnCl_2$,Zn	1.057	0.546	0.511	0.539	0.518	0.535	0.522
$ZnSO_4$,Zn	1.079	0.575	0.504	0.559	0.520	0.557	0.522
$Zn(Ac)_2$,Zn	1.083	0.574	0.507	0.558	0.525	0.555	0.528
$CuSO_4$,Cu	0.019	0.540	0.521	0.535	0.516	0.539	0.520
$Cu(NO_3)_2$,Cu	0.047	0.566	0.519	0.561	0.514	0.564	0.517
		Mean	0.512	Mean	0.521	Mean	0.522

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[1] Wied. Ann. 41, 50 (1890).

In column A are given the electromotive forces of the whole cell, Hg | Hg_2Cl_2KCl(1) | metallic salt(2) | metal, copper being cathode when it was used, and zinc anode when it was used. In columns I, II and III are found the values of S KCl(1) | metallic salt(2) | metal, the electrode tips being adjusted to different positions in the three cases, but always having the same adjustment for one series. Ia, IIa and IIIa give the values for S KCl(1)Hg_2Cl_2Hg which should be found, in case the sum of the values S KCl(1) | metallic salt(2)metal and S KCl(1) | KCl(1)Hg_2Cl_2 | Hg were equal to the value of the whole cell as given in column A. These three columns are therefore obtained by subtraction of columns I, II and III, respectively from A. For the same adjustment of the electrodes was actually found for S KCl(1) | KCl(1)Hg_2Cl_2Hg in

Ia 0.514 in place of 0.512
IIa 0.519 in place of 0.521
IIIa 0.523 in place of 0.522

The variations are easily explained by the slight jarring of the electrode clamps when changing one half-cell for another. This is clearly proved by noting the way in which the variations from the mean value occur. In the case of measurements where the mercury broke just as it met the surface of the liquid it was found possible to make adjustments better than in the experiments here indicated. The table given above is the shortest one of a number made with potassium and hydrogen chlorid, in dilutions of 1, 10 and 100 liters; but it shows clearly the points to be illustrated — that by preserving like conditions in the adjustment of the breaking point of the mercury one may repeatedly obtain the same value for S | electrolyte | metal, and also that, as would be expected, the sum of S | $electrolyte_1$ | $electrolyte_1$ | $metal_1$ and S | $electrolyte_1$ | $electrolyte_2$ | $metal_2$ is equal to the electromotive force of the whole cell

$metal_1$ | $electrolyte_1$ | $electrolyte_2$ | $metal_2$.

Other experiments were made to ascertain if the absolute value of S | KCl Hg were the same as when a depolarizer was present. Other electrolytes were also used in place of potassium chlorid. The results proved that if the measurement were taken after the mercury had remained for some time in the electrolyte, and when it was perfectly quiet, the same electromotive force might be observed as when the depolarizer was present. The results were, however, very variable, and so it was thought advisable not merely to use a depolarizer, but always to allow the half-cell when made up to remain some time before being measured. The following table allows of a comparison being made between the results obtained by Paschen in two ways—B by the drop electrode, C by polarization method, while under A stand my own measurements obtained as absolute values.

Table II

	A	B	C		A	B	C
HCl(1)	0.557	0.560	0.561	HBr(0.9833)	....	0.459	0.501
HCl(10)	0.605	0.551	0.553	HBr(10)	....	0.470	.494
HCl(100)	0.659	0.584	0.622	HBr(100)	....	0.488	.528
KCl(1)	0.560	0.539	....	KI(1)	0.412	0.400	....
KCl(10)	0.593	0.553	....	KI(10)	0.455	0.412	0.426
KCl(100)	0.620	0.584	....	KI(100)	0.497	0.412	....
NaCl(1)	0.557	0.556	....	K_2SO_4(2)	0.922	0.670–0.734	
NaCl(10)	0.593	0.557	0.560	K_2SO_4(20)	0.897	0.700–0.745	
NaCl(100)	0.626	0.590	....	K_2SO_4(200)	0.812	0.720–0.743	
$BaCl_2$(2)	0.584	0.555	....	H_2SO_4(1–6)	0.975	0.934	....
$BaCl_2$(20)	0.615	0.553	....	H_2SO_4(1)	0.931	....	....
$BaCl_2$(200)	0.639	0.586	....	H_2SO_4(2)	0.921	0.818–0.853	
$MgCl_2$(2)	0.582	0.547	....	H_2SO_4(10)	0.875	....	....
$MgCl_2$(20)	0.600	0.548	....	H_2SO_4(20)	0.868	0.797–0.824	
$MgCl_2$(200)	0.624	0.580	....	H_2SO_4(100)	0.818	....	....
KBr(1)	0.490	0.483	0.488	H_2SO_4(200)	....	0.818–0.834	
KBr(10)	0.542	0.493	0.494				
KBr(100)	0.584	0.505	0.509				

Discussion.—The first glance shows that the values given in A and B do not agree any too well. It would indeed be a matter of surprise if two investigators working on this subject should obtain values agreeing at all well, for probably in few other fields of physico-chemical measurement is there present, at least with our present imperfect apparatus, such scope for personal error. An attempt was made to eliminate this by repeating the observations from three to ten times. At dilutions of one liter, the variations from the average were 0.002 volt. At dilutions of 100 liters, variations were 0.008 volt. But where the chance of the variation comes in is in the adjustment of the 'breaking' point of the mercury. From the measurements in A it might seem as if the adjustments regulated by the use of the electrometer to detect the passage of a current were more sensitive than the method employed by Paschen. This, however, is not claimed, although it is by no means impossible. Other conditions at present unknown, may have caused the variations. The latter are most apparent in dilute solutions, where the difficulties of measurement are greater than in the more concentrated. The fact that the values found by me for dilutions of 100 liters vary from those obtained by the polarization (capillary electrometer) method, counts for little, since in these solutions it is extremely difficult to ascertain where the maximum of surface-tension actually is. If the very careful measurements of Paschen on this subject[1] are right, it would indicate either that some conditions under which he worked were different from mine, or else that the values obtained by me were those corresponding to different parts of the *descending* branch of the polarization curve after it had passed through its maximum of surface-tension. From the standpoint of either the Helmholtz or the Warburg theory, this latter conjecture must be discarded as impossible. A test of the former by repetition of the polarization measurement could not be attempted, the apparatus at my disposal not being sufficiently sensitive to read with the accuracy obtained by Paschen, viz., 0.1 mm. It is probable that the presence of the depolarizer in the combinations measured by me had a very considerable influence, and that a repetition of the measurements by the polarization method, with depolarizer present, would give values different from those obtained by Paschen. This, however, must remain an open question at present.

In opposition to the results of Paschen it would appear that *both* anion and cation have an effect. The effect of the anion

[1] Wied. Ann. 43, 579 (1891).

may be observed especially between potassium chlorid, bromid, iodid and sulfate. KCl(1) = 0.560, KBr(1) = 0.490, KI(1) = 0.412, K_2SO_4(2) = 0.922. The effect of the cation is not so apparent from the previous table, but is shown well by the following: —

$CuSO_4$(2) | Hg = 0.200 K_2SO_4(2) | Hg = 0.922.

The effect of concentration appears from column A to be more regular than is apparent in column B. In all cases (with one exception, HCl) where attention was paid to this subject, regularity was found — either with increasing concentration the electromotive force increased else it decreased. Thus with sulfuric acid a case of the former may be observed and with sodium chlorid, a case of the latter. Hydrochloric acid, according to Paschen's[1] measurements, seems to give a decreasing value as the solution becomes more dilute, passes through a minimum and then again increases. The following results obtained by myself confirm this: —

S | HCl(0.1)	Hg_2Cl_2 | Hg	0.645	S | HCl(1)	Hg_2Cl_2 | Hg	0.557
S | HCl(0.125)	Hg_2Cl_2 | Hg	0.631	S | HCl(10)	Hg_2Cl_2 | Hg	0.605
S | HCl(0.2)	Hg_2Cl_2 | Hg	0.609	S | HCl(100)	Hg_2Cl_2 | Hg	0.659
S | HCl(0.5)	Hg_2Cl_2 | Hg	0.590			

It is thus very apparent that the effect of varying the concentrations of different electrolytes is not always regular. In the light of our present knowledge, it is not possible to say which are 'normal' or which are 'abnormal' cases.

A number of measurements were also taken for combinations of this type: —

S metallic salt | metallic salt | metal.

In the following table, the figures at the head of the column denote the number of liters in which one gram-molecular weight of the metallic salt is dissolved, while the results obtained are given in the columns. The arrow points toward the cathode.

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[1] Wied. Ann. 41, 54 (1890).

Table III

		(2)	(20)	(200)
$\overrightarrow{\text{Cd}\,\vert\,\text{CdCl}_2}$ S	....	0.170	0.258	0.309
$\text{Cd}\,\vert\,\text{CdBr}_2$ S	....	0.136	0.165	0.218
$\text{Cd}\,\vert\,\text{CdI}_2$ S	....	0.113	0.128	0.157
$\text{Cd}\,\vert\,\text{CdSO}_4$ S	....	0.248	0.335	0.362
$\text{Cd}\,\vert\,\text{Cd(NO}_3)_2$ S	....	0.132	0.249	0.283
$\overrightarrow{\text{Ni}\,\vert\,\text{NiCl}_2}$ S	....	0.125	0.250	0.239
$\overrightarrow{\text{Ni}\,\vert\,\text{Ni(NO}_3)_2}$ S	....	0.156	0.249	0.274
	(1)	(2)	(20)	(200)
$\overrightarrow{\text{Zn}\,\vert\,\text{ZnCl}_2}$ S	0.514	0.526	0.585	0.639
$\text{Zn}\,\vert\,\text{ZnBr}_2$ S	0.460	0.468	0.513	0.582
$\text{Zn}\,\vert\,\text{ZnSO}_4$ S	0.645	0.653	0.685	0.734
$\text{Zn}\,\vert\,\text{Zn(Ac)}_2$ S	0.630	0.634	0.649	0.695
$\overrightarrow{\text{Cu}\,\vert\,\text{CuSO}_4}$ S	0.010	0.019	....	....
$\text{Cu}\,\vert\,\text{Cu(NO}_3)_2$ S	0.056	0.024	....	....
$\overleftarrow{\text{Pb}\,\vert\,\text{Pb(NO}_3)_2}$ S	0.121	0.101	0.105	....
$\overleftarrow{\text{Pb}\,\vert\,\text{Pb(Ac)}_2}$ S	0.170	0.125	0.159	....

In this table also may be noticed the change of the electromotive force produced by changing the concentrations, as well as that produced by the variation of the anion. The effect of increasing the concentration of the zinc and cadmium salts is to cause the electromotive force to fall quite regularly; similarly for copper sulfate and nickel nitrate. The lead salts apparently pass through a minimum in the same manner as hydrochloric acid, while nickel chlorid seems to pass through a maximum.

The effect of variation of the concentration may also be shown by figures gathered from Paschen's measurements[1] with $ZnSO_4$ and Zn. In column A are given the specific gravities of the solutions at the (conjectured) temperature of 18°. In column B are given the values found for $\text{Hg}\,|\,\text{ZnSO}_4\,|\,\text{Zn}$. (All the electromotive forces in this table are expressed in terms of Daniell cell.) In column C are given the values which he obtained for $\text{S ZnSO}_4\,|\,\text{Hg}$. In column D may be found the values of

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[1] Wied. Ann. 41, 63, 66, 179 (1890); 43, 570, 571 (1891).

S $ZnSO_4$|Zn, either given directly by Paschen's measurements (observed) or calculated from the two previous columns by subtraction of the value given under C from that in B (calculated).

Table IV

A Spec. gr	B Hg | $ZnSO_4$ | Zn	C S $ZnSO_4$ | Hg	D S $ZnSO_4$ | Zn	
1.054	....	....	0.5876	Observed
1.163	....	....	0.5699	"
1.305	1.157	0.598	0.559	Calculated
1.316	1.224	0.681	0.543	"
1.40	1.150	0.607	0.531	"
1.403	1.240	0.709	0.531	"
1.406	....	....	0.5358	Observed
1.409	1.170	0.639	0.531	Calculated
1.433	1.167	0.640	0.527	"
1.456	....	....	0.519	Observed

It is to be observed from this method of arranging the results of Paschen that the concentration effect is, with zinc sulfate at least, a very regular one, and shows that in this case the low electromotive force is to be observed in the most concentrated solutions.

If the values found above in Table III give the actual potential difference between a metal and a salt of the metal, a comparison with those predicted by the Nernst theory should allow us to see whether there were agreement between the observed and predicted values. According to this theory the potential difference between a metal and a solution of its salt may be thus formulated

$$\pi_1 = \frac{0\ 0002\mathrm{T}}{n_1} \log \frac{\mathrm{P}}{p_1} \qquad (1)$$

where P is a pressure function depending on the nature of the electrode, and p_1 denotes the osmotic pressure of the metallic ions in the solution. Accordingly, if there are chosen two isohydric solutions of different salts of a metal, the term p_1 and hence also the potential difference between metal and the solution of the salt of the metal will be the same for each solution. Now equimolecular solutions of zinc chlorid and zinc bromid are practically isohydric in respect to the zinc ions; but it will be observed (Table III) that the values given by the dropping mercury method for the potential differences $Zn|ZnCl_2$ and $Zn|ZnBr_2$ differ very considerably—the difference varying from 0.054–0.072 volt with changing concentration. Similar results are obtained when any of the other values given in Table III are examined in this way.

If in place of choosing isohydric solutions, one chooses differently concentrated solutions of the same salt, the pressure p will vary in a way which may be determined by conductivity measurements, and for a solution of different concentration from the one used in equation (1) may be called p_2. The difference of potential between the electrode and this solution will be

$$\pi_2 = \frac{0.0002\,T}{n_e} \log \frac{P}{p_2}. \qquad (2)$$

The difference between the two single potentials at the electrodes will be

$$\pi_2 - \pi_1 = \frac{0.0002T}{n_e} \log \frac{p_1}{p_2} \qquad (3)$$

Inserting for p_1 and p_2 values corresponding to normal and tenth-normal solutions, and for n_e the valency of the metals used (in this case two) it is found that at ordinary temperatures

$$\pi_2 - \pi_1 = \frac{0.0002 \times (273 + 17)}{2} = 0.029 \text{ volt}. \qquad (4)$$

The table which is now to be given contains values which may determine whether this formula holds. In the first column are denoted the metal and its salt; in the column (2)—(20) are given values obtained by subtraction of the values given in column (20) from those in column (2) of the same table; in the column (20)—(200) are given values obtained by subtraction of the values given in column (200) from those in column (20).

Table V

	(2)—(20)	(20)—(200)		(2)—(20)	(20)—(200)
Cd | $CdCl_2$	0.088	0.051	Zn | $ZnCl_2$	0.059	0.054
Cd | $CdBr_2$	0.029	0.053	Zn | $ZnBr_2$	0.045	0.069
Cd | CdI_2	0.015	0.029	Zn | $ZnSO_4$	0.033	0.049
Cd | $CdSO_4$	0.087	0.027	Zn | $Zn(Ac)_2$	0.015	0.048
Cd | $Cd(NO_3)_2$	0.117	0.034	Pb | $Pb(NO_3)_2$	0.020*	0.004
Ni | $NiCl_2$	0.125	0.011*	Pb | $Pb(Ac)_2$	0.055*	0.034
Ni | $Ni(NO_3)_2$	0.093	0.025			

It is to be observed from the table that in all cases except the ones marked with the asterisk, the difference of potential is in the same direction as the theory requires. Where, however in one column the numerical value seems to agree with the theoretical one (equation 4) as closely as the experimental error would allow, the value in the other column diverges considerably from what it should be. Speaking generally, we must therefore conclude that the dropping electrode does not give the values which the Nernst solution-pressure theory would require.

If from Table II a table is prepared in a similar manner, irregular results such as appear in the last table would be found present; but it must be pointed out that the values obtained for HCl, KBr and KI in dilutions of 1, 10 and 100 liters, approximate values required by the Nernst theory. Thus arranging the table in exactly the same way as Table V.

Table VI

	(1)—(10)	(10)—(200)
Hg | Hg_2Cl_2, HCl	0.052	0.054
Hg | Hg_2Br_2,KBr	0.052	0.042
Hg | Hg_2I_2,KI	0.043	0.042

The value as predicted by the Nernst theory is

$$\pi = 0.058 \text{ volt.}$$

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* Values marked with asterisk denote currents running in other directions.

Hydrochloric acid shows the best agreement with the theoretical value, but this and the other values given above are in my opinion to be regarded as accidental so far as the Nernst theory is concerned. Reference need only be made to the table (III) where it is to be noted that if drop electrode values be regarded as true single differences of potential, a solution containing 5 gram-mols of HCl per liter will have approximately the same potential against the electrode as a solution containing 0.1 gram-mol of HCl; which can hardly be accepted as a fact.

Whoever upholds the correctness of the view that single differences of potential may be determined by means of dropping mercury electrodes, must necessarily assume that the contact surface of two electrolytes is the seat of a potential difference, whose value may by no means be neglected. This follows directly from the consideration of any combination such as,

$$\mathrm{Zn}\,|\mathrm{ZnSO_4}(2)\,|\mathrm{CuSO_4}(2)\,|\mathrm{Cu},$$

whose value was found on measurement to be 1.098 volts. By dropping electrodes we found $\mathrm{Zn}\,|\overrightarrow{\mathrm{ZnSO}}_4(2) = 0.653$, and the same method gave for $\overleftarrow{\mathrm{CuSO}}_4(2)\,|\mathrm{Cu} = 0.019$. Whence it follows that at the contact surface of $\mathrm{ZnSO_4}(2)|\mathrm{CuSO_4}(2)$ there must exist a potential difference of $(1.098 - 0.653 + 0.019)$ volts, *i. e.* 0.464 volt. Selection of any other values from Table III will illustrate the same point. Further emphasis is given this fact by the following table of values, where the normal electrode side of the cell has been retained throughout, but the electrolyte into which the mercury fell was varied.

In the table, N. E. is used to represent the normal electrode half-cell. In all cases, except with the solution of copper sulfate and nitrate, the mercury of the normal electrode was cathode.

Table VII

S $\mathrm{KCl}(1)$ |N.E.	0.559	S $\mathrm{Cd(NO_3)_2}(2)$ |N.E.	0.549
S $\mathrm{CdCl_2}(2)$ |N.E.	0.555	S $\mathrm{ZnCl_2}(2)$ |N.E.	0.530
S $\mathrm{CdBr}(2)$ |N.E.	0.595	S $\mathrm{ZnSO_4}(2)$ |N.E.	0.426
S $\mathrm{Zn(Ac)_2}(2)$ |N.E.	0.449		
S $\mathrm{CuSO_4}(2)$ |N.E.	0.036		
S $\mathrm{Cu(NO_3)_2}(2)$ |N.E.	0.068		

Here instead of all the values coming out 0.559 as would be expected if there were no potential differences between the solutions, they fluctuate very much, and in the case of copper sulfate, actually change sign. One is then forced to ask the question: Is it probable that between solutions of approximately the same concentration such enormous potential differences may be considered present? Since, for obvious reasons, no direct experimental test of this can be given at present, it is necessary to obtain an opinion on this subject from a consideration of the phenomena at the surface of the two liquids. This is exactly what Nernst had to do before it was possible for him to reach his conclusions in respect to the electromotive force present at the contact surface of liquids. In support of his views, we have much evidence, both experimental and theoretical; in support of the idea that there exist large potentials at the boundary surface of electrolytes, there is no evidence at all, save such as is based on this method of determining single differences of potential.

So-called irreversible electrodes.—The question has often been raised as to whether a cell containing one electrolyte and two electrodes of different chemical nature has a perfectly definite value. Measurements with cells of this type have been made by Ostwald, Bancroft, Braun, Oberbeck and Edler, Paschen, Taylor and others. A summary of some of the measurements (this Journal 1, 9, 1896) shows that the results agree with each other none too well. An attempt was made by the writer to repeat these measurements, but as it was found too tedious and unprofitable to sit down and wait varying periods of time to allow such combinations to come to a maximum,[1] the following plan suggested itself. In the measurement of a combination of such a type as Zn | KCl | Cd, if there were any variation in the electromotive force caused by the lapse of time, this would probably be caused by the variations at both electrodes. Measurements at different times would thus always show the sum of the effects, whereas it is always desirable to examine the single variations when this is possible. Accordingly use was made of the potas-

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[1] Taylor. Jour. Phys. Chem. 1, 3 (1896).

sium chlorid, mercurous chlorid, mercury electrode, which had been found by Coggeshall[1] to give very constant results. The cell was then made up, *e. g.* $Hg|Hg_2Cl_2KCl(1)|KCl(1)|Zn$, the two vessels, each of which held one electrode, being connected by a siphon as in previous experiments. Then another metal was measured against the normal electrode, *e. g.* $Cd|KCl(1)|KCl(1)Hg_2Cl_2|Hg$. The difference in the two measurements gives the value $Zn|KCl(1)|KCl(1)|Cd$ (calculated). The cells were measured immediately after setting up. The corresponding results are given under I. They were then measured 24 hours (II) and 48 hours (III) later. Under 'found' values are given those actually observed; under 'calculated' those obtained by subtraction of the potentials in question. These should agree; any disagreement rises from errors of measurement.

Table VIII

I

	Cd	Cu	Zn	Cd — Zn		Cd — Cu		Zn — Cu	
				found	*calc.*	*found*	*calc.*	*found*	*calc.*
$Hg|Hg_2Cl_2KCl(1)$	0.819	0.284	1.085	0.276	0.276	0.534	0.535	0.799	0.801
$Hg|Hg_2Cl_2KCl(10)$	0.832	0.255	1.170	0.338	0.338	0.577	0.577	0.915	0.915
$Hg|Hg_2Cl_2KCl(100)$	0.845	0.230	1.264	0.419	0.419	0.614	0.615	0.037	1.034

II

$Hg|Hg_2Cl_2KCl(1)$	0.810	....	1.119	0.310	0.309	....	....	....	....
$Hg|Hg_2Cl_2KCl(10)$	0.859	....	1.208	0.350	0.349	....	....	....	....
$Hg|Hg_2Cl_2KCl(100)$	0.890	....	1.247	0.358	0.357	....	....	....	....

III

$Hg|Hg_2Cl_2KCl(1)$	0.817	0.285	1.127	0.309	0.310	0.531	0.532	0.840	0.842
$Hg|Hg_2Cl_2KCl(10)$	0.855	0.205	1.135	0.279	0.280	0.650	0.650	0.928	0.930
$Hg|Hg_2Cl_2KCl(100)$	0.935	0.245	1.150	0.215	0.215	0.690	0.690	0.906	0.905

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[1] Zeit. phys. Chem. 17, 62 (1895).

Discussion.—The extreme irregularity of the results at once attracts attention. While other observers have found a maximum value for the combinations, it is found by this method (which should assuredly be a more accurate one) that even after two days have passed, the values are not yet definite and constant. That chemical action had taken place at the contact surface of metal | electrolyte was certain. If then such an action were so apparent as to be observable after a few hours, it is certain that it would be impossible to leave it out of a theoretical consideration of the subject, even if the metal had been in contact with the electrolyte only so long as would be required for the measurement. The conclusion then presents itself that in all measurements which have been made by this method, since they were made in an atmosphere containing oxygen, and in electrolytes containing oxygen, this oxidizing action must be present. The effect of the presence of oxygen on the electromotive force of cells was examined very carefully by Warburg,[1] whose results have been confirmed by Paschen.[2] Their results, however, seem to have been overlooked by later writers on the subject.

In giving the few and necessarily incomplete results above, the author wishes merely to insist that the claims of Warburg and Paschen are correct, *i. e.* that the oxygen of the air has an effect in causing a change in the electromotive force of a cell where irreversible electrodes are used. Before the cells given in the last table had been measured, the writer had made a large number of measurements with combinations such as S KCl | Cd; the table shows that the measurements should all vary with the time the electrolyte had been in contact with the electrode. Such of course was found, the measurements not agreeing from day to day. They were of importance only in the consideration of the question whether it was advisable to use reversible or the so-called irreversible electrodes in the half-cells when making measurements with the drop-electrodes.

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[1] Wied. Ann. 38, 321 (1889).

[2] Wied. Ann. 43, 568 (1891).

Comparison with Rothmund.—Among the many interesting measurements bearing on the question as to the relations between surface-tension and polarizing currents are those of Rothmund,[1] who determined the electromotive force necessary to polarize amalgams to their maximum. The electrolytes used were sulfuric and hydrochloric acids, containing dissolved in them an arbitrary amount of the salt of the metal contained in the amalgam. Having determined these maximum values by use of interpolation curves, he compared them with the values calculated from the whole cell, assuming Hg | H_2SO_4(2) = 0.926 and Hg | HCl(1) = 0.560. In the following table are collected under column "Polarization method" the results obtained when he made use of this interpolation-curve method; under column "Calculated" are to be found the results obtained, when he subtracted from the electromotive force of the whole cell the value he obtained by the polarization method for his normal electrode. Under the column "Drop-electrode" are to be found the values obtained by the writer when he made use of combinations such as S H_2SO_4(2) saturated with Hg_2SO_4 | H_2SO_4(2)Hg_2SO_4 | Hg.

Table IX

	Polarization method	Calc	Drop electrode
Hg | $Hg_2SO_4H_2SO_4$(2)	0.926	....	0.921
Hg | Hg_2Cl_2HCl(1)	0.560	....	0.560
Pb | $PbSO_4H_2SO_4$(2)	0.008	0.003	0.004
Cu | $CuSO_4$(100)H_2SO_4(2)	0.445	0.481	0.221
Zn | $ZnSO_4$(100)H_2SO_4(2)	—0.587	—0.546	—0.629
Cd | $CdSO_4$(100)H_2SO_4(2)	—0.079	—0.164	—0.280
Hg | HgI_2(100)KI(1)	0.437	0.157	0.120

In this table numbers after the chemical name represent the number of liters in which one gram-equivalent was contained. When no figures are given, a solution of the substance, saturated at 20° C, is denoted.

Of the seven cases here compared, it is to be seen that only in the first three do the values obtained by both methods agree

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[1] Zeit. phys. Chem. 15, 1 (1894).

at all. As to the other four cases, one method gives values about as near to the calculated as the other, and with neither method is there good agreement with that value. That the values given in Table IX represent single differences of potential can certainly not be maintained by the adherents either of the Helmholtz or of the Warburg theory. The former requires that the electrode shall be polarizable, and certainly a zinc amalgam in a solution of a zinc salt is not to be regarded as a polarizable electrode.[1] As previously stated, the Warburg theory does not regard these values as single potentials at all, but rather as a sum of several potential differences. To these measurements, therefore, regarded as determinations of single differences of potential, no importance can be attached.

This conclusion is strengthened by a closer consideration of the values which Rothmund considered as fully determined, *e.g.*

$$\mathrm{Hg}\,|\,\mathrm{H_2SO_4}(2) = 0.926$$
$$\mathrm{Hg}\,|\,\mathrm{HCl}(1) = 0.560.$$

When he formed the cell

$$\mathrm{Hg}\,|\,\mathrm{Hg_2SO_4H_2SO_4}(2)\,|\,\mathrm{HCl}(1)\mathrm{Hg_2Cl_2}\,|\,\mathrm{Hg}$$

he[2] found for its value 0.369 volt, whereas its value calculated from polarization was 0.366 volt. But if now in the place of using normal solutions of the acids, he had made use of tenth-normal solutions and applied values obtained from either the drop electrode or the polarization method, he would have calculated values (using the writer's values) of

$$0.868 - 0.605 = 0.261 \text{ volt},$$

or for hundredth-normal solutions,

$$0.818 - 0.656 = 0.159 \text{ volt},$$

whereas the values actually obtained will in each case be very much higher than these. The differences here observable cannot, if the Planck theory be accepted, be due to the potential

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[1] Compare with Le Blanc who disagrees (English edition Le Blanc's Electrochemistry, 214) and with Nernst (Jahrbuch der Electrochemie, 1, 38 (1894)), who thinks it probable that on polarizing zinc amalgam the zinc is dissolved until there is left a surface of pure mercury.

[2] Meyer found for this combination 0.407 volt.

difference at the boundary surfaces of the two acids. From the consideration of this case, we must therefore draw one of two conclusions:

(*a*) The Helmholtz theory is applicable here in the case of normal sulfuric and hydrochloric acids, the amount of mercurous salt being so small as to be left out of consideration entirely.

(*b*) By some coincidence not explained by the Helmholtz theory, the values obtained for Hg| H_2SO_4(2) and Hg|HCl(1) by both the polarization and the dropping mercury method add up to give the electromotive force of the cell, whereas if other dilutions of these acids be used, the values agree no longer.

Conclusion (*a*) cannot be correct since the presence of *any* mercurous salt is sufficient to exclude the mercury in this case from being classed as a polarizable electrode to which alone the Helmholtz theory applies. That it may under certain experimental conditions be polarized is also true, but the fact that the disturbing influence exerted by the presence of the salt is not definitely known certainly prevents a rigid application of this theory. The second conclusions seem the more probable.

Since therefore the results of Rothmund may not be explained by the theory which they are given to support, and do not agree with the results predicted by this theory when one employs for the determination of these values the other method which is supported by this theory, grave doubts must be cast upon their being true single potential differences.

The work of Luggin[1] has been directed toward an examination of the two theories which attempt to explain the relation existing between electromotive force and surface-tension. His method consisted in polarizing mercury in an electrolyte until it had reached its maximum surface-tension, and in then measuring it against a normal electrode. The Helmholtz theory would require that in these cases almost the same potential should be observed, no matter what the electrolyte was. Experimentally Luggin found values which could not fulfil this requirement in its strictness, but so many regularities were found that it is cer-

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[1] Zeit. phys. Chem. 16, 677 (1895).

tain the chemical theory alone cannot account satisfactorily for the alteration of the surface-tension.

It is an easy step to pass from the conclusions of Luggin to the explanation that the Helmholtz theory does hold, but that exceptions are found where other and secondary influences may also affect the surface-tension. Under such a category must be placed the influence exerted by the salts of the metal or amalgam polarized. It may be found possible to discover the experimental conditions which must prevail in order that the Helmholtz formula may apply. One of these will of course be that the change of surface-tension energy into electrical energy shall be completely reversible. Another has been recently indicated by Wiedeburg,[1] who has shown that the formula holds only when a current does not pass when the mercury is polarized to its maximum. According to his view the values obtained are always higher than the true single differences of potential. Wiedeburg has also drawn attention to the fact that the measurements made with a view of testing the theories of today should be made under as simple conditions as possible.

The principal conclusion to be drawn from this paper is that neither on the ground of the Helmholtz theory, the Warburg theory nor that of Nernst[2] is there reason for regarding one single potential difference as known. Some of the conditions which must be observed before applying the Helmholtz theory have been noted. Cases where the dropping electrode gives values corresponding to the polarization method have been observed, as well as cases where a difference in the values occur. It has been found that the values obtained by the dropping electrode with different concentrations of the same electrolyte apparently follow in regular order; also that both the anion and the cation affects the values obtained. The solution-pressure formula of Nernst has been tested by use of the drop-electrode and found to hold approximately in a few cases, while in the great majority of cases it failed. The action of oxygen on the

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[1] Wied. Ann. 59, 744 (1896).

[2] Palmaer. Zeit. phys. Chem. 25, 265 (1898).

electrodes of irreversible cells has also been briefly examined, and the views of Warburg and Paschen thus substantiated. The main query of the paper, however—"Are the values given by the drop electrodes true single differences of potential" must be answered in the negative.

The writer wishes to express his warmest thanks to Professor Bancroft, both for the suggestion of the subject of investigation and for the assistance and encouragement he has given in carrying it to completion.

Cornell University

ACETONECHLOROFORM

FIRST PAPER

BY FRANK K. CAMERON AND H. A. HOLLY

In a series of investigations upon the reactions between acetone and alkyl halids in the presence of alkalies, acetonechloroform was discovered by Willgerodt.[1] By bringing together acetone and chloroform, and adding powdered potassium hydroxid to the cooled mixture in small portions at a time, allowing to stand until the reaction was completed, and fractioning the fluid products, a white solid was obtained from the higher boiling portions, which bore a striking resemblance in smell and general appearance to camphor. It was purified by recrystallization and sublimation and its properties noted. A detailed description of the substance will be given below. Analysis and a vapor-density determination corresponded to a composition indicated by the formula $(CH_3)_2CO.CHCl_3$. Further study of the compound by Willgerodt,[2] and other investigators working with him, established the constitution of the substance. It is trichlortrimethyl carbinol, $(CH_3)_2C.CCl_3OH$, or a derivative of tertiary butyl alcohol. Willgerodt describes it generally as trichlorid of acetonic acid or oxyisobutyric acid. It is more commonly known as acetonechloroform.

In the distillation of the products from which acetonechloroform was obtained was a portion which on fractioning boiled approximately constant as 170°, remained fluid on cooling if kept

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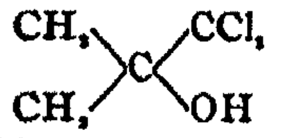
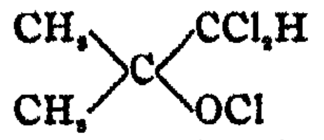
[1] Ber. chem. Ges. Berlin, 14, 2456 (1881).

[2] Ibid. 15, 2305 (1882); 16, 1585 (1883); Jour. prakt. Chem. [2] 37, 361 (1888); [2] 39, 283 (1889); [2] 41, 515 (1890).

from moisture, and which had the same composition as acetonechloroform. If poured into water or allowed to come into contact with moist air, it rapidly changed into the solid acetonechloroform, from which it was not possible to obtain it again. It was at first supposed to be a polymer of the solid variety, or an instable physical modification of it. But Willgerodt and Geneiser[1] finally decided it to be an isomer, and by ingenious though inaccurate reasoning, based on its supposed analogy to the acetone-hydrocyanic acid addition-product of Bredt[2] ascribed to it a formula. The relative orientation of the two compounds was indicated thus:



Solid acetonechloroform



Liquid acetonechloroform

The reactions of the liquid modification with reagents were in all essential features the same as those of the solid, and Willgerodt and Geneiser assume that under the conditions of these reactions it first undergoes a molecular rearrangement. Wherein the reactions of these two compounds may differ and the probable reasons therefore will be presently noted. With a view to establishing more fully the nature of these two compounds and their interrelations, this investigation was undertaken.

The material was prepared as directed by Willgerodt and Geneiser. A fractional separation by distillation under diminished pressure was found to be impracticable from the choking of the condenser tubes with the solid substance. The liquid variety was refractioned several times. In every case, some solid material came over at the beginning of the distillation. A portion of the liquid variety was distilled into a dried specimen vial, into which a stream of dried carbon dioxid was constantly passing. The fraction boiled at 165–167°. A few crystals formed in the neck of the vial and were washed into it with the liquid and the vial sealed by drawing out the neck to a capil-

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[1] Jour. prakt. Chem. [2] 37, 361 (1888).

[2] Ber. chem. Ges. Berlin, 15, 2306 (1882).

lary tube. This specimen was labelled A, and at room temperature (about 25° C) was a clear nearly colorless liquid, containing a few crystals.

Another portion of the liquid variety distilling at 170°-171° was distilled into a vial, so arranged that a considerable space about it was filled with carbon dioxid, carefully dried by passage through a column of sulfuric acid. This specimen was labelled B, and was a perfectly clear, colorless liquid, containing at no time, any trace of solid matter. The two specimens, A and B, were now cooled to −4°. In A there was a further deposition of crystals, but the entire mass would not solidify. In B no change appeared. Both vials were then placed in a mixture of solid carbon dioxid and ether. The contents of both solidified, A rapidly, B rather slowly. After staying at this temperature some time, both specimens were brought to room temperature again, melting over a wide range of temperature, and appearing to have undergone no change. They were then submerged in a bath at 55° for 72 hours, the crystals in A entirely dissolving, but reappearing on cooling. When brought to ordinary temperature again, neither specimen appeared to have changed. Assuming the presence of two modifications in either specimen, it seemed impossible to displace the equilibrium through a temperature range of at least 140° C.

The two vials were then opened and weighed portions of their contents poured into about equal volumes of water, the whole brought just to boiling, by which a very small portion volatilized. On cooling, the solid formed was filtered, washed with cold water, quickly dried and weighed. For specimen B which was supposed to be very pure, we give the figures: 14.95 g oil yielded 12.90 g of the solid, or 86.3 percent, leaving out of consideration the water known to be present in the crystals. Therefore at least 13 percent of the original material remained in the filtrate. This filtrate was brought into a narrow vessel, and potassium carbonate added; it first became milky, and then separated into two layers, the upper being quite small, a yellowish liquid having the smell and general appearance of acetone. It evaporated over night, leaving a few crystals of the solid acetonechloroform floating on the surface of the remaining liquid. The amount of acetone separating was too small to make possible a more positive identification.

Anhydrous solid acetonechloroform was then prepared by heating the material in a distilling bulb, with an oil bath at 75°, and under diminished pressure. By this process, water and some crystals of the material sublimed into the condenser tube. When no more water appeared to come off, the bulb was attached to another condenser tube without jacket, and the material distilled. It practically all distilled at 166.4° to a beautiful colorless liquid, which solidified on cooling to a mass bearing a striking resemblance to camphor which has been fused. It melted at 91°–92° and solidified at the same point.[1] 14.5 g of this anhydrous material was weighed into a distilling bulb and 2.2 g of purified acetone added. The solid completely dissolved at 25°. The solution was then distilled, the temperature rising rapidly to 163° and but a few drops of the material distilling. The temperature then rose slowly to 166.4°, the major portion of the substance distilling as a clear, colorless liquid, which did not solidify even at 4°. The thermometer remained constant at 166.4°, the remainder of the material distilling at that temperature and solidifying at once in the condenser tube. It melted at 91°–92°. The liquid distilling at 163°–166° poured into water or exposed to moist air yielded a solid melting at 78°–79°. It appeared to be liquid acetonechloroform in everything but its boiling-point. About 40 g of solid acetonechloroform was placed in a distilling bulb and moistened with water. On distillation the thermometer rose rapidly to 98°. Water and a portion of the material sublimed at this temperature. The temperature rose slowly to 110°, more and more rapidly to 135°, and then at once to 169°, and the greater portion of the material came over at 170°–171°, the temperature finally rising to 174°. A repeti-

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[1] This melting-point determination was made after the usual manner, in a capillary tube. Subsequent melting-point determinations of the same material taken in larger quantities and in the more accurate manner described in this paper, did not confirm the statement made above. Another illustration of the little value of such determinations when made in the conventional way.

tion of this experiment with very pure materials gave practically all the material distilling at 170–171°. It appeared that acetonechloroform retained readily appreciable quantities of acetone and water at its boiling-point, and with the latter there is probably a mixture with a maximum boiling-point. From these experiments we concluded that *liquid acetonechloroform did not in fact exist*, but that the supposed compound is a mixture of solid acetonechloroform with acetone and water. All the known phenomena observed in connection with the substance confirms this view. In its conduct towards reagents in general, as has been pointed out, it behaves in the same way as the pure solid, but being, as Willgerodt has said "a little less reactive." This statement is purely qualitative, and is undoubtedly justified by the main reactions being more or less disguised by the reactions of the acetone and water present. The only reagent towards which there was a notable difference in the conducts of the two substances was phosphorus pentachlorid,[1] where the same products were obtained, but accompanied in the case of the liquid variety, by a very volatile substance which attacked the mucous membrane. It is well known that some of the chlorin derivatives of acetone possess this property, and its presence in this case is not therefore surprising, granted our premises. The gradual darkening of the liquid on standing in the light can be accounted for by the action of traces of hydrochloric acid on the acetone. That these traces of hydrochloric acid are present is shown by the fact that the liquid acetonechloroform is acid enough to redden litmus, as was noticed by Willgerodt and Geneiser,[2] and, further, the fact also noticed by them, that whenever the solid acetonechloroform was distilled with water, the water is always slightly acid owing to the formation of oxyisobutyric acid. Its greater activity as a poison is due to the fact of its being in solution in acetone, in which it is marvelously soluble even when considerable quantities of water are present. Any discussion of the

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[1] Willgerodt and Geneiser. Jour. prakt. Chem. [2] 37, 361 (1888).

[2] Jour. prakt. Chem. [2] 37, 364 (1888).

formula proposed is superfluous in view of the facts just presented.

Acetonechloroform is a white crystalline solid, readily soluble in most organic solvents to a very remarkable extent. It is not appreciably soluble in cold water, but fairly so in hot water. Its melting-point when free from water lies above 97° and probably near this figure, but when obtained from solutions containing water or standing exposed to the air for a time it shows melting-points from 76° to 82°. By crystallizing from solvents insoluble in water, by distillation or sublimation, the melting-point is raised. It burns with a greenish flame. Small particles thrown on water rotate violently as does camphor under the same conditions. In general appearance the substance, especially when cooled from a molten magma, very strongly resembles camphor. It has the same characteristic odor, and apparently in as intense a degree. This smell to a faint extent is said to be characteristic of the mother substance trimethylcarbinol. Acetonebromoform, prepared by Willgerodt[1] in an analogous way, has as intense an odor but more like pepper. It is readily volatile with steam. It volatilizes very readily with volatile solvents, when left in open vessels, and the dried material evaporates fairly rapidly at ordinary temperature, so that weighing must be made in closed vessels. It dissolves in and is decomposed by strong nitric or sulfuric acid, and with the latter gives off hydrochloric acid. According to Willgerodt[2] it materially increases the deposition of metallic silver, from a solution of silver nitrate and aniline in water. On standing in contact with an ammoniacal silver nitrate solution, a gray powder is deposited. A vapor-density determination by Willgerodt, according to the method of Hofmann, indicated the formula $(CH_3)_2CO.CHCl_3$; calculated, 88.5; found, 88.7. Determinations of the molecular weight in benzene were made by the freezing-point and boiling-point methods and in acetone by the boiling-point method. By freezing-point method, apparatus of Beckmann:

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[1] Willgerodt. Ber. chem. Ges. Berlin, 14, 2458 (1881).

[2] Willgerodt. Ibid. 14, 2455 (1881).

Solvent: Benzene

[K = 49.0]

g solvent	g solute	Δ	mol. wt.
18.075	0.1094	0.174	171
	0.2646	0.414	173
	0.4107	0.635	175
	0.5591	0.829	183

At infinite dilution 169
Theoretical 176

By boiling-point method, apparatus of Orndorff and Cameron:[1]

Solvent: Benzene

[K = 26.6]

g solvent	g solute	Δ	mol. wt.
122.75	1.0584	0.127	182
	2.0765	0.240	190
	3.0351	0.352	189
	4.1014	0.465	194
	5.0029	0.551	198

At infinite dilution 179
Theoretical 176

Solvent: Acetone

[K = 16.7]

g solvent	g solute	Δ	mol. wt.
114.55	1.9910	0.157	190
	3.9297	0.307	192
	5.4232	0.427	190
	6.6791	0.536	189
	7.9054	0.633	187

At infinite dilution 190
Theoretical 176

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[1] Orndorff and Cameron. Am. Chem. Jour. 17, 517 (1895).

Experiments were made to determine the proportions in which the reagents would give the best yields of acetonechloroform, and to try and obtain an insight into the reaction by which it is formed.

To a mixture of 200 g acetone and 400 g chloroform were added little by little 400 g of pulverized caustic potash, in such a way as to require about 48 hours to complete the operation. The reacting materials were in a balloon flask of about 3 liters capacity, which was kept in a cooling bath of snow and water and frequently shaken. The contents gradually assumed a yellow pulpy appearance, and towards the end of the reaction they became quite dark. The flask which was closed by a rubber stopper bearing a tube with capillary opening was then allowed to stand for two days longer in a bath of cold water. The contents were then poured on a filter, the liquid portion drawn off with the aid of the pump, and the solid washed several times with acetone and chloroform. It was found in previous experiments that some alkali was always to be expected in the filtrate, which would decompose the acetonechloroform on distilling. The liquid and washings were therefore brought into a large separating funnel and washed several times with water, whereby probably but a small amount of the desired material was lost, and then transferred to a distilling flask. On distilling, the temperature rose gradually to 110° acetone, chloroform, and water coming over. From 110° on the temperature rose rapidly, the operation was then interrupted, the contents of the flask poured into a relatively large amount of cold water, and the flask washed out with a small quantity of acetone, which was added to the water. The acetonechloroform at once separated as a crystalline mass, but slightly colored. After standing over night it was filtered, pressed dry and weighed; yield 21.4 g. The distillate below 110° gave no appreciable addition to this amount on refractioning.

This same process was repeated starting with 100 g acetone, 400 g chloroform and 100 g pulverized caustic potash. It required about a day to introduce all of the potash. The contents of the flask were not appreciably colored at the end. They were allowed to stand for three days before being filtered, distilled, etc.; yield 21.4 g acetonechloroform. A third experiment starting with 200 g acetone, 400 g chloroform and 100 g potash was carried on at the same time and in the same manner as the one last described. The contents of the flask at the end were very slightly colored yellow; yield 60.8 g of acetonechloroform, perfectly white and in quite pure condition. The solid filtrate, after being washed with acetone and ether, was dried and weighed 110 g. It contained a small amount of potassium carbonate and some organic material, probably salts of organic acids. Analysis[1] of the material showed about 98.5 percent of potassium chlorid. In comparison with the other experiments, the yield in this last case was most noteworthy, being nearly three times as much. The product also was much cleaner and contained relatively much less organic matter. The proportions suggested by Willgerodt and Geneiser are in near agreement with the results of this experiment, but the use of somewhat less potash and longer standing than they advise, is indicated.

The formation of acetonechloroform was attempted by heating the constituents in sealed tubes at various temperatures from 150° to 250°, but unsuccessfully, as had already been found by Willgerodt. The introduction of potassium bisulfite did not produce an apparent modification of the results. In every case there was considerable charring. Chloroform, water and a volatile constituent containing chlorin were the products. By suspending the material in a sealed vial in an oil bath at 150° the charring was avoided but no formation of acetonechloroform was detected. Heating acetonechloroform in sealed tubes resulted in charring of the contents, dependent on the temperature and time of heating. On cooling, the contents of the tubes were found to be under diminished pressure as was also noted by Willgerodt. In one case the tube was heated to 400° and the charring was found to be quite complete, but a very small amount of crystalline substance presenting an entirely different

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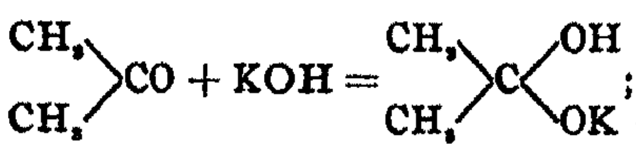
[1] Kindly made for us by Mr. C. A. Soch.

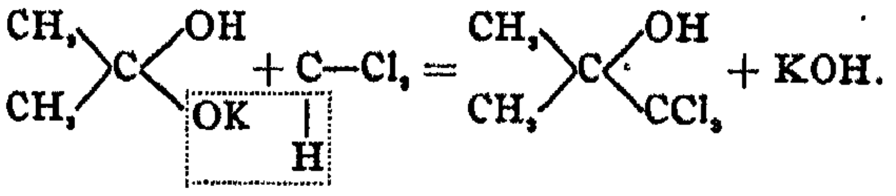
appearance from acetonechloroform was obtained. It could not be examined farther however. Acetonechloroform in a sealed vial was suspended in an oil bath at 170° for some hours without change. On being kept at 205° for three hours, it darkened somewhat, but entirely solidified on cooling, and showed no change which could be studied. The mechanism of the reaction by which acetonechloroform is obtained is not obvious. It is not, in view of these experiments, an addition-product in the ordinary acceptance of that terminology and its usual name therefore is ill-advised.

The simplest reaction and the one which seems to have the greatest probability may be expressed in two stages, thus:



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CO + KOH = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>C\left<\begin{matrix}OH\\OK\end{matrix}\right.$$

; but this being instable reacts at once,



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>C\left<\begin{matrix}OH\\OK\end{matrix}\right. + \underset{H}{\underset{|}{C}}-Cl_3 = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>C\left<\begin{matrix}OH\\CCl_3\end{matrix}\right. + KOH.$$

The potash seems to be reacting here as a catalytic agent. In favor of this view is the fact that a better yield is obtained when a relatively small amount of potash is used. This potash is gradually removed by action on the chloroform, giving potassium chlorid, formate and water, but under the conditions given this decomposition is relatively slow. A proof of this view is not now possible, but will be the subject of a future investigation.

One, two or all the chlorin atoms can be substituted by aromatic radicles[1] by the Friedel-Craft's reaction. With caustic alkali it is readily converted into oxyisobutyric acid and the barium salt[2] of the acid has been prepared and analyzed. With phosphorus pentachlorid[3] it forms chlorisobutyric acid chlorid, as well as other substances needing further investigation. It has

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[1] Willgerodt and Geneisėr. Jour. prakt. Chem. [2] 37, 365 (1888).

[2] Willgerodt. Ber. chem. Ges. Berlin, 15, 2305 (1882).

[3] Jour. prakt. Chem. [2] 37, 365 (1888).

been reduced to trimethylcarbinol by nascent hydrogen.[1] From these reactions its constitution is undoubted; it is indicated by the formula $(CH_3)_2:C.OH.CCl_3$. When crystallized from water or solvents containing water, or even if allowed to stand exposed to the moisture of the air, the crystals contain water. Willgerodt[2] finally obtained crystals by distilling with steam, and recrystallizing from aqueous alcohol and ether which melted at 81°–82° and gave on analysis the following figures: .

	Found	Calculated
C	25.54	25.0
H	4.59	4.29
Cl	56.8 57.17 57.3	57.1

which indicate the formula $2[(CH_3)_2.C.CCl_3.OH] + H_2O$. This formula had presumptive evidence in its favor from the fact that trimethylcarbinol itself is said to form a hydrate[3] of the composition $2(CH_3)_3C.OH + H_2O$. Analysis for chlorin by the method of Carius gave us figures indicating a composition varying from one to two molecules of water to one of acetonechloroform. Therefore the following method was used to determine this point.

A round bottom flask was fitted with a cork containing a slit in the side. The cork was bored to fit a test-tube, and the test-tube was in turn fitted with a stopper containing a thermometer. The test-tube was partially filled with a weighed amount (about 10 g) of the anhydrous compound, the thermometer put in place with its bulb well down in the tube so as to be covered when the material melted, and the whole tube fitted into the bulbed flask, which was partially filled with water to a convenient amount. Four such pieces of apparatus were arranged

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[1] Willgerodt and Dürr. Jour. prakt. Chem. [2] 39, 283 (1889).

[2] Willgerodt. Ber. chem. Ges. Berlin, 16, 1585 (1883).

[3] Butlerow. Liebig's Ann. 162, 229 (1885).

and into the test-tubes were run from a burette, amounts of water calculated to correspond to 1/2, 1, 1 1/2, and 2 molecules per molecule of acetonechloroform. In each case the same phenomena were observed. The apparatus was heated until the substance had entirely melted. *Two liquid layers were formed.* On cooling the thermometer would fall until a little below 75°. Crystals having started to form it would rise to 75.2° and remain constant until the second liquid phase had disappeared. We thus obtained the quadruple point for solid, two solutions, and vapor, which we had already obtained by a previous experiment for that purpose. But we were forced to the conclusion that our supposed anhydrous material really contained water, or the substance contained less than 1/2 molecule of water of crystallization. The existence of a hydrate then became questionable and was answered by the following experiment:

A convenient quantity of dehydrated substance was placed in such an apparatus as the one just described, with the addition of wire stirrers run through slits in the sides of the corks. The apparatus was heated until the substance melted and then allowed to cool. As soon as crystals began to form, they were churned into a slush by the stirrer, and then a few drops of water would be added from a pipette with long capillary stem. The freezing-point was lowered; the crystals immediately dissolved. This process was repeated until a mixture was obtained which both melted and froze sharply at 75.2°. This was the lowest point reached. On the addition of more water, *the freezing-point did not rise*, but a second liquid layer separated. The fall of the freezing-point was regular, and the existence of a quadruple point between 75.2° and 92° was answered negatively. Consequently, *no hydrate exists.* Attempts to remove the water and raise the melting-point by subjecting it to great pressure between folds of filter paper were unavailing. By sufficiently strong pressure the substance was so driven into the films of fine Swedish filter paper as to make it almost impossible to separate it mechanically, but specimens so treated showed no elevation of the melting-point.

An attempt to accurately determine the melting-point of the substance was made in the following way: A test-tube with side arm, such as is used in the Beckmann freezing-point apparatus, was fitted with a thermometer, and by means of the side arm attached to a Chapman filter-pump, with the usual intervention of a Bunsen flask. The tube was partially filled with the substance, sufficient when melted to cover well the bulb of the thermometer. It was then surrounded by a hot water-bath. The temperature of the bath was raised, the melting-point and freezing-point of the substance noted, and then the aspirator would be put in operation for awhile, the bath being kept a little below the melting-point of the substance. In the early part of the operation a fairly large amount of water and substance sublimed into the upper portions of the tube. By repeating the operation, we finally obtained a substance which melted a little above 97° and all solidified before reaching 96°, apparently an approximately pure product. It absorbed moisture so rapidly however, that it was considered inexpedient to attempt an analysis.

It would appear from these facts that the substance does contain water, and in varying amounts. That the water cannot be detected or eliminated by mechanical means. That it is not present to form a hydrate. Therefore it is probably present to form a solid solution. Similar cases have recently been reported by Tammann,[1] who investigated certain of the zeolites. He found that heulandite, desmin, and chabezite, when fully hydrated, contained more water than could be accounted for by the accepted formula, that they lost water regularly over a very wide range, and no inversion point could be detected. The crystals remained throughout clear and transparent. Acetone-chloroform presents additional features in forming two liquid solutions with water and this subject we will investigate at once.

From the work here recorded we conclude:

I. The existence of but one acetonechloroform, a white crystalline solid, a derivative of trimethylcarbinol.

II. The substance is not a simple addition-product, and can-

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[1] Wied. Ann. 63, 16 (1897); Zeit. anorg. Chem. 15, 318 (1897).

not be resolved into its original constituents by direct means.

III. The substance forms no definite hydrate.

IV. The temperature of the quadruple point for solid, two solutions and vapor in the system acetonechloroform-water, is 75.2.

V. The melting-point is near, but above 97°, and in all probability perfectly anhydrous material has not yet been obtained.

VI. The system acetonechloroform and water seems to present the remarkable case of a solid solution and two liquid solutions.

Further investigation of conclusions V and VI will be described in a subsequent communication.

We would here record our acknowledgment of the courtesy of Professor W. D. Bancroft, to whose suggestions the success of the investigation is largely due.

Cornell University, March, 1898.

NEW BOOKS

The Principles of Chemistry. *By D. Mendeléeff. Translated from the sixth Russian edition by George Kamensky, and edited by T. A. Lawson. Vol. I; 15 × 22 cm; pp. xviii and 621. Vol. II; 518 pp. New York: Longmans, Green & Co., 1897. Price: cloth $10.00.*—In the first chapter of the first volume the author discusses water and its compounds. This leads to a consideration of the components of water—hydrogen and oxygen—and then to a study of ozone and hydrogen peroxid. The law of definite and multiple proportions is introduced at this point. Next come nitrogen and air, followed by a chapter on the compounds of nitrogen with hydrogen and oxygen. The laws of Gay-Lussac and of Avogadro are then in order and serve as a basis for the conceptions of molecules and atoms. The application of these new views to the compounds of carbon with hydrogen, oxygen, and nitrogen forms here a very natural digression. The tenth chapter is devoted to sodium chlorid, hydrochloric acid and Berthollet's laws, which latter are stated accurately and not in the customary crude form. A discussion of the halogens comes next, and is followed by chapters on the alkali metals, on spectrum analysis, on the metals of the alkaline earths, and on the valency and specific heats of the metals.

The second volume opens with the grouping of the elements, and the periodic law. The remaining elements are considered in the following order; zinc, cadmium, and mercury; boron, aluminum, and the analogous metals of the third group; silicon, and the other elements of the fourth group; phosphorus, and the other elements of the fifth group; sulfur, selenium, and tellurium; chromium, molybdenum, tungsten, uranium, and manganese; iron, cobalt, and nickel; the platinum metals; copper, silver, and gold. In an appendix are given a lecture on chemical affinity, a lecture on the periodic law, and a paper on argon, this last written in 1895.

This classification is a very simple one. The skeleton is, water, air, salt, and the periodic law. While one can easily pick flaws in such an arrangement, it is hardly worth while to do so. No one would claim high merits for it and yet it is by no means bad. The chief difficulty comes where one would expect it to come,—in the first chapter. Curiously enough, it is one that is not a necessary consequence of the arrangement selected. If the first chapter had been on water only instead of on water and its compounds, the book would have been much better. The discussion of solutions and of cryohydrates is entirely out of place, quite apart from any question as to its correctness. Inorganic chemistry—and organic chemistry for that matter—is primarily a study of elements and compounds; the study of solutions and of equilibrium phenomena comes at a different time.

This work of Mendeléeff's, with its mass of detail, is very interesting to the student who looks forward as well as backward. One fact stands out clearly from every page of the two volumes; our knowledge of inorganic chemistry is qualitative and not quantitative. Our textbooks should be entitled Qualitative Inorganic Chemistry. Not only is there no book on quantitative inorganic chemistry but there are as yet few data on which to base such a work. Mendeléeff's book abounds with such statements as "loses CO_2 at high temperatures," "decomposes above 500°," "the reaction does not take place in the cold," etc., etc. These are qualitative statements but they express the facts as known. The quantitative inorganic chemistry of the future will be a very different science from the so-called inorganic chemistry of the present. Stortenbeker's work on the equilibrium between iodin and chlorin is a study in quantitative inorganic chemistry, and it stands practically alone. Its importance as the dawn of a new era has not yet been recognized by a single inorganic chemist. The future textbook of quantitative inorganic chemistry will consist chiefly of diagrams and tables.

Coming back to Mendeléeff's treatise, it is necessary to say a few words in regard to the style. The author had such a wealth of material at his disposal that he was puzzled how to get it all in. Consequently he tried a compromise. One-third to one-half of the book is text and the remainder is footnotes. From the preface we learn that the book is both an elementary and an advanced treatise. The elementary student is to read the text. The man who wishes to know more about the subject is to go back and struggle through the footnotes. By many people this has been considered one of the merits of the book. The reviewer does not admire this folding-bed style. When a man starts to write a book, he should make up his mind what sort of a book he wishes to write and then write that to the best of his ability. A book that tries to be two different things cannot be a real success. The elementary student does not want the footnotes at all; the advanced student wants them in the text. He objects to having the continuity of his thoughts broken by continual digressions. An author puts into a footnote statements and comments that he is unable to work into the text. Numerous footnotes mean an inability to master the subject.

Reference has been made twice in this review to the wealth of material contained in the two volumes. It is indeed a pleasure to note the many interesting minor facts that the author has succeeded in bringing together in what is, after all, a small work. It is not too much to say that every chemist should own a copy of this book. No one can fail to profit by a study of it and it is probable that everyone who reads it will be impressed by the fact that a knowledge of Russian is already indispensable to the man of science. The translation has been well done, barring a phenomenal tendency to misplace adverbs.

Wilder D. Bancroft

Spectrum Analysis. *By John Landauer. Authorized English edition by J. Bishop Tingle. Octavo; pp. x and 213. New York: John Wiley & Sons, 1898. Price: cloth $3.00.*—The appearance of Dr. Tingle's translation of Landauer's book will be welcomed by American teachers as at last giving them an English textbook which may be used for class and laboratory instruction in this important but greatly neglected field.

The first chapter of the work is devoted to the history and bibliography of spectrum analysis, and there then follow chapters upon the physical properties of light, spectroscopes, spectroscopic instruments for special purposes, spectroscopic adjuncts, emission-spectra, spectra of the elements, absorption spectra, the solar spectrum, other celestial bodies.

If the book is intended for the instruction of students of chemistry, as is stated in the translator's preface, it is greatly to be regretted that "There has been no attempt to treat the subject exhaustively, but rather to indicate the more salient points of theory, etc., leaving it to the teacher to complete and expand them at his own discretion." It is exactly that characteristic of this and other English works upon spectrum analysis that has prevented the general introduction of the subject into the curriculum of many a department of chemistry in American colleges. What is needed is not instruction in the *theory* of spectrum analysis, but instruction in the methods of using it in chemical analysis and investigation. An understanding of the theory of spectrum analysis and of the principles involved in the construction of the spectroscope should, of course, be possessed by every chemist, and can easily be obtained from the courses in physics offered in our colleges or from many of the textbooks of physics. A book intended for chemists should describe the methods of using the spectroscope in chemical work, but unfortunately Landauer gives us almost no such information. For example, a chapter is devoted to the spectra of stars, comets, aurora borealis, etc., while quantitative spectroscopic analysis is scarcely mentioned and the important work of De Gramont upon the Direct Spectroscopic Analysis of Minerals is almost completely ignored. From these and other shortcomings it is therefore evident that, while the book is an improvement upon its predecessors, it is far from being a satisfactory guide for the chemist.

Dr. Tingle is to be congratulated upon the excellence of his translation, which is clear and accurate. One of the very few mistakes observed is the misleading inversion which causes the well-known Krüss constant, "Dunkelheitsmaximum," to appear as "minimum of brightness." *L. M. Dennis*

Quantitative Chemical Analysis by Electrolysis. *By Alexander Classen, in collaboration with Walter Löb. Authorized translation by W. H. Herrick and B. B. Boltwood. 15 × 23 cm; pp. xii and 301. New York: John Wiley & Sons. Price: cloth $3.00.*—The last German edition has been noticed so recently (1, 569) that it is scarcely necessary to do more than to congratulate the translators on the speed with which they have done their work. The English edition differs from the German in that the Special Part of the former edition has been retained and revised. This increases the size of the book; but it also increases its usefulness. The English version is markedly superior to the original, in that the translators have added an elaborate index, thus doubling the value of the book. *Wilder D. Bancroft*

Théories de l'Électrolyse. *By Ad. Minet. (Encyclopédie des Aide-Mémoire.) 12 × 19 cm; 175 pp. Paris: Gauthier-Villars et Fils, 1898. Price: paper 2.50 francs, boards 3 francs.*—This little book is a distinct improvement over the other three by the same author (1, 674; 2, 57, 197). The first part is devoted to the general laws of electrolysis, the second to a discussion of the modern theory of solutions and the dissociation theory, while some electrolytic constants are given in the third section. The second part of the book is much more up to date than is usually the case in this series. The weak point in the volume is the treatment of decomposition values, it being stated that these can be calculated from the heats of reaction. *Wilder D. Bancroft*

Experimental Untersuchungen über Zersetzung und Verbrennung von Kohlenwasserstoffen. *Habilitationsschrift. By F. Haber. 18 × 26 cm; 116 pp. München: R. Oldenbourg, 1896. Price: 1.50 marks.*—This pamphlet is divided into two distinct parts, the first dealing with the decomposition of hydrocarbons by heat, the second with combustion experiments. When studying the effect of temperature the vapor or gas was passed through a heated tube. With hexane there was no decomposition at 500°. At 600° the chief products are methane, amylene, propylene, ethylene, and benzene (about five percent). The primary reaction seems to be the splitting off of methane with formation of amylene or propylene and ethylene. At 940° the chief products are methane, ethylene, and tar. About seven percent of benzene is formed and three percent of charcoal. At 1200° the products are charcoal, methane, and hydrogen. Very little acetylene is formed at any temperature.

At 940° trimethylethylene gives tar, methane, ethylene, and benzene, the primary reaction being apparently the splitting off of methane. At 1060° there is a good deal of charcoal, and naphthalene is found in the tar.

These data are more valuable for technical than for purely scientific purposes owing to the uncertainty as to the question of equilibrium. It is also a pity that the mere suggestion of a reversible reaction produces much the same effect upon the author as waving a red rag before a bull. While it is quite possible that Berthelot may have been carried away by enthusiasm and thus led to assume the existence of many very hypothetical reactions, there seems to be no reason for going to the other extreme and assuming that none of the reactions of hydrocarbons at high temperatures are reversible.

The second part of the pamphlet is essentially technical in its scope, though the experiments on the efficiency of gas burners is of value—more especially since the results obtained appear to be in flat contradiction with the beliefs that prevail in many laboratories. *Wilder D. Bancroft*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry

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General

The conditions requisite for attaining maximum accuracy in the determination of specific heats by the method of mixtures. *F. L. O. Wadsworth. Am. Jour. Sci.* 4, *265* (*1897*). — In the method of mixtures the body whose specific heat is to be determined is first raised to a known temperature, then immersed in a known quantity of water and the rise in temperature of the water noted. In practice the following quantities must be determined: weight of substance and of water, water value of calorimeter and contents, initial temperature of substance, and initial and maximum temperature of calorimeter. The sources of error in determining each of these quantities, the means adopted to avoid these errors, and the effect of each on the final result are subjected to a mathematical investigation, from which it appears that: —

"The greatest possible care should be taken in reading temperatures, and since the errors of these readings are much greater than any others likely to be committed, it is advisable to use:

(*a*) A small amount of water in the calorimeter, i. e. a small calorimeter.

(*b*) A large amount of metal [whose specific heat is to be determined], having a maximum surface for given weight; sheets or wire.

(*c*) As high an initial temperature as can be conveniently attained."

Finally, the calorimeter should be surrounded by a water jacket, maintained at a constant temperature, which is higher than the initial temperature of the water in the calorimeter; formulas are given for finding that temperature of the jacket for which the maximum temperature attained by the calorimeter is the same as though no radiation whatever took place. A simple mechanism (car and trap) is described and illustrated, for introducing material quickly into the calorimeter without splashing or loss of heat. *W. L. M.*

One-Component Systems

The species of isomerism in the homologous series of the paraffins. *S. M. Losanitsch. Ber. chem. Ges. Berlin,* 30, *1917* (*1897*). — "Cayley has calculated the possible number of isomeric paraffins by means of certain analytical figures. I have sought out the various kinds of isomerism for each paraffin by introducing into the main normal carbon chain, one or more, smaller or larger, similar or dissimilar, normal or branched, side groups. … In this manner it is possible not only to find with ease the number of possible isomers, but to classify them." The paper is accompanied by a table extending to $C_{23}H_{47}$.

W. L. M.

On the problem: To find the number of isomeric paraffins of the formula C_nH_{2n+2}. *F. Herrmann. Ber. chem. Ges. Berlin*, 30, *2433* (*1897*). — The author indicates a method of calculation and classification simpler than that adopted by Losanitsch (see above); he also points out certain numerical errors in the results of the latter. *W. L. M.*

Regularities in the boiling-points of isomeric aliphatic compounds. *N. Menschutkin. Ber. chem. Ges. Berlin*, 30, *2784* (*1897*). — Rules connecting the boiling-point with the length of the main carbon chain, and with the number, nature and position of the side chains. Tables are given of the boiling-points of the eight amyl alcohols, their iodhydrins, acetic esters, and amins, and the corresponding capronic acids, $C_5H_{11}COOH$; also for certain butylene compounds, and for fourteen of the hexyl alcohols. The "amplitude," i. e. the interval between the boiling-points of the highest and the lowest boiling isomer, increases with the molecular weight, and is greater for the alcohols than for any other class. *W. L. M*

The conduction of heat in rarefied gases. *M. Smoluchowski, Ritter von Smolan. Wied. Ann.* 64, *101* (*1898*). — A cylindrical glass vessel containing a thermometer and the gas under investigation (air or hydrogen) was heated until the thermometer showed a certain high temperature, then suddenly plunged into ice-water, and the rate noted at which the thermometer fell. The loss of heat by the thermometer may be referred to: 1, convection currents; 2, radiation; 3, conduction by the gas. The first of these diminishes rapidly with diminution of pressure, the second depends on the form and nature of the surface of the thermometer and may be eliminated by special experiments, leaving the third to be determined by difference. The results can be expressed by Poissan's equations, only if a sharp fall in temperature — as much as seven degrees in one case — be assumed between the gas and the solid [thermometer] from which it receives the heat. *W. L. M.*

Preliminaries to a study of the determination of vapor densities at extreme degrees of heat. *V. Meyer and M. v. Recklinghausen. Ber. chem. Ges. Berlin*, 30, *1926* (*1897*). — Attempts to prepare infusible apparatus for use at 2000°–3000°. Magnesia proved to be a suitable material, but a satisfactory gas-proof glaze has not yet been discovered. *W. L. M.*

Two-Component Systems

The theory of solutions. *B. Pawlewski. Ber. chem. Ges. Berlin*, 30, *2805* (*1897*). Reply to criticisms of a former paper. The melting-points of mixtures of two organic compounds follow (in first approximation) Blagden's law; the only exception so far met with by the author being the case of mixtures of *p*-dibrombenzene with *p*-chlornitrobenzene. In this case the author is "unable to explain the irregularities observed," but does not appear to have looked for dimorphous forms, mix-crystals, addition compounds, etc.

W. L. M.

On metallic precipitates. *F. Winteler. Zeit. Elektrochemie,* 4, *338* (*1898*). — Referring to Förster's experiments on the precipitation of nickel at 50°-90° (2, 70), the author calls attention to the fact that palladium, platinum, iron, nickel, copper, and other metals absorb hydrogen, and expresses the opinion that the good results obtained by Förster at high temperatures are due to the fact that comparatively little hydrogen is absorbed by nickel under these conditions. *W. D. B.*

Poly-Component Systems

Further observations on the evolution of oxygen gas upon reduction. *K. Frenzel, S. Fritz and V. Meyer. Ber. chem. Ges. Berlin,* 30, *2515* (*1897*). — In order to avoid the possibility of formation of hydrogen peroxid, experiments were carried on in the dry way; the behavior of potassium permanganate, of silver oxid, and of the peroxids of potassium, lead, and barium with air, hydrogen, carbonic oxid, and carbon dioxid was studied at different temperatures. The evolution of oxygen, where any was observed, may be accounted for plausibly by reference to the probable chemical reaction involved; in some cases it is due to rise of temperature caused by oxidation, and consequent decomposition of the oxidizing agent. *W. L. M.*

'Active' oxygen. *W. P. Jorissen. Ber. chem. Ges. Berlin,* 30, *1951* (*1897*). — A short discussion of the various theories of the formation of 'active' oxygen. (See 1, 514.) *W. L. M.*

Velocities

On aliphatic carbon chains. *N. Menschutkin. Ber. chem. Ges. Berlin,* 30, *2775* (*1897*). — The velocity constants for the etherification of ten aliphatic alcohols by acetic anhydrid, and for the reactions between fifteen aliphatic monamins and allyl bromid are given; and their dependence on the constitutional formulas are discussed. *W. L. M.*

Influence of the side chains on the distribution of the velocities of reaction in the benzene ring. *N. Menschutkin. Ber. chem. Ges. Berlin,* 30, *2966* (*1897*). — In the reactions between allyl bromid and the three toluidins, the velocity is greatest for metatoluidin and least for orthotoluidin (*m, p, o*). For the reaction between dipropylamin and the three nitrobrombenzenes, the order is *o, p, m*. For bromalkyl and the chloranilins (also for caustic soda and the tolylsuccinimids) *p, m, o*. Finally the degree of electrolytic dissociation of the chlor- and of the oxy-benzoic acids decreases in the order *o, m, p*. The paper also contains velocity constants for reactions involving various tri- and tetra-derivatives of benzene. *W. L. M.*

Dynamic investigation of the formation of the azo dyes, II. *H. Goldschmidt and F. Buss. Ber. chem. Ges. Berlin,* 30, *2075* (*1897*). — The theoretical connection between the rate of the reaction and the strength of the acid was tested by experiments on the reactions of diazobenzenesulphonic acid, and the chlorid, acetate, mono-, di-, and tri-chloracetates of diethylanilin. The experimental method was the same as in the first paper (1, 612). *W. L. M.*

Hydrolytic dissociation. *H. Ley. Ber. chem. Ges. Berlin,* 30, *2192*

(*1897*). (*Preliminary notice*). —The author is engaged on measurements of the rate of inversion of cane sugar by dilute solutions of various salts at 100°, with a view to calculating the degree of their hydrolytic dissociation. In the case of aluminum chlorid the dissociation increases notably with the dilution; aluminum sulfate gives smaller constants for equivalent dilutions. The influence of neutral salts (KCl) on inversion, and of the temperature on hydrolysis, are also under investigation. *W. L. M.*

On the circumstances which affect the rate of solution of zinc in dilute acids, with especial reference to the influence of dissolved metallic salts. *J. Ball. Jour. Chem. Soc*, 71, *641* (*1897*).—Two series of experiments, on the effect of soluble sulfates in sulfuric acid solutions and of soluble chlorids in hydrochloric acid solutions, respectively.

Addition of magnesium and aluminum salts had very little effect on the rate at which the zinc was dissolved (determined by measuring the hydrogen evolved); the salts of Cr, Mn, Fe, Pb, Sn, Ag, Cu, Au, Pt, Co, Ni accelerate the reaction, nickel salts producing the greatest effect, those of the other metals approximately in the order given.

"It is remarkable that in some of these cases — amongst them that of highest acceleration — no precipitation of reduced metal could be noticed, so that although the observed action may have been in all cases the result of a reduction of metal from the added salt, the *amount* of metal so reduced had, at any rate, only a subordinate value in determining the amount of acceleration. ... Whilst the addition of a mere trace of the salt to the pure acid solution produced a large acceleration, this effect became proportionally less and less for further additions." *W. L. M.*

The rates of oxidation of gases by liquids. *V. Meyer and E. Saam. Ber. chem. Ges. Berlin*, 30, *1935* (*1897*).—The gases were shaken with permanganate solution in a graduated tube. Every five minutes the tube was opened under permanganate solution and the volume of the remaining gas noted. Propane and isobutane were unaffected by shaking for an hour with five percent permanganate; ethylene and acetylene on the other hand were instantly oxidized; while with hydrogen, carbonic oxid, methane and ethane the reaction progressed at a measurable rate. The results are given in tabular form, with no attempt at representing them by formulas. *W. L. M.*

Electromotive Forces

The theory of galvanic polarization. *A. Oberbeck. Wied. Ann.* 63, *29* (*1897*). —In reply to Streintz's assertion, that determination of the polarization in an original circuit is impossible, the author points out that for very weak and for very strong polarizing currents the problem has already been solved. His treatment of the polarization produced by currents of intermediate strength leads to results already obtained by Wiedeburg. *W. L. M.*

Experiments on the discharge of electricity from points. *S. Arrhenius. Wied. Ann.* 63, *305* (*1897*). — The reaction produced by the electric wind from needle-points in various gases and vapors was measured by means of a torsion balance. The ratio (of reaction to current) decreases with the current, and is less when the points are negative than when they are positive. With negative points in all gases and vapors examined, and with positive points in ethylene, acetone, ether, and carbon bisulfid, the ratio in question increases more rapidly than the pressure of the gas; while for positive points in hydrogen, oxygen, carbon dioxid, methane, and air, it is proportional to the pressure and approximately proportional to the square root of the density. *W. L. M.*

Electrolysis and Electrolytic Dissociation

A source of error in calculating the heat of dissociation of electrolytes. *J. J. van Laar. Zeit. phys. Chem.* 24, *608* (*1897*).—In the earlier applications of the mass law to liquid systems, it was customary to define the concentration of a constituent as the number of grams of that constituent in one liter of the solution,—'volume concentrations.' Planck then introduced his 'numerical concentrations' or ratios between the 'number of molecules' of each constituent and the total number of molecules in the system. This definition is, naturally, somewhat elastic, and van Laar is of the opinion that in calculating the 'total number of molecules' the degree of 'association' of the solvent should be taken into consideration.

As the association of the solvent varies with the temperature as well as with the degree of dissociation of the electrolyte, the simple formulas proposed by Arrhenius for calculating the heat of dissociation must be replaced by others, which are given. *W. L. M.*

The electrolytic preparation of iodoform. *F. Foerster and W. Mewes. Zeit. Elektrochemie,* 4, *268; Jour. prakt. Chem.* (*2*) 56, *353* (*1897*).—Elbs and Herz (1, 71) used a porous cell and found that it was unnecessary to pass in carbonic acid at the anode. The authors dispense with the porous cell and surround the cathode with parchment paper. Since caustic potash will diffuse rapidly through paper, it is advisable to neutralize it with carbonic acid. This may seem a disadvantage; but it is more than counterbalanced by the slight resistance of the paper.

An attempt to account for the beneficial effect of potassium carbonate and the deleterious effect of caustic potash is made; but is absolutely unintelligible. The position of the authors seems to be this: Presence of potassium carbonate is beneficial because it is necessary to form hypoiodites in the solution; presence of caustic potash is deleterious because it converts iodin too rapidly into hypoiodite and then into iodate. This seems reasonable but the matter is obscured by the statement (probably a slip) that presence of caustic potash does not affect the amount of iodate formed.

Under the most favorable conditions a ninety-seven percent yield of iodoform is obtained; but this yield dropped nearly one-half when a continuous production of iodoform was attempted. *W. D. B.*

The electrolysis of sodium chlorid. *R. Lorenz. Zeit. Elektrochemie,* 4, *247* (*1897*).—LeBlanc found 1.95 V as the decomposition value for sodium chlorid solutions when the electrodes are smooth platinum points. In actual practice a potential difference of 2.1—2.3 V is necessary. This discrepancy disappears when one remembers that after the first moment, the actual cell is $Pt \mid Cl_2 \mid NaCl \mid NaOH \mid H_2 \mid Pt$. The (calculated) electromotive force of this combination is 2.23 V with *n*/10 NaOH. By surrounding the electrodes with parchment paper, it was found possible to get as high as 2.18 V for the decomposition value of sodium chlorid solutions. *W. D. B.*

Our knowledge and theories of the electrolytic formation of persulfuric acid. *F. Richarz. Ber. chem. Ges. Berlin*, 30, *1826* (*1897*).—A claim for priority. *W. L. M.*

Dielectricity and Optics.

The optical constants of sodium. *P. Drude. Wied. Ann.* 64, *159* (*1898*).—According to the author's experiments on the reflection of polarized light, the least refractive power among the metals is possessed by sodium; next follows an alloy of sodium with potassium, and then silver. The velocity of light in molten sodium is approximately 220 times as great as in air. *W. L. M.*

The molecular refraction of dissolved salts and acids, Part II. *J. H. Gladstone and W. Hibbert. Jour. Chem. Soc.* 71, *822* (*1897*).—"Additional data in answer to two of the questions in the last paper:—Has a salt the same molecular refraction whether it be in the crystallized state or in solution? and, How far is refraction change dependent on the solvent used?"

Dufet has proposed a method by which the refractive indices of crystals with more than one optical axis may be calculated; in the case of seventeen salts the molecular refraction thus calculated is almost identical with that in aqueous solution.

A diagram is given showing the refractive indices of solutions of hydrochloric acid in water and in seven organic solvents (alcohols and ethers); a second diagram and a table furnish similar data for nitric acid and for a number of salts.

"Our growing conviction is that neither the salt nor the solvent really change in specific refraction, but that by their interaction some new product results. ... We hope soon to be in a position to say something more definite as to the nature of this *tertium quid*, and especially as to the relation which it bears to the change in electrical conductivity of the solutions examined. *W. L. M.*

A new means of increasing the angle of rotation. *P. Walden. Ber. chem. Ges. Berlin*, 30, *2889* (*1897*).—The action of oxygen compounds of boron, arsenic, antimony, molybdenum and tungsten in increasing the rotatory power of optically active solutions, is far surpassed by that of uranyl salts in alkaline solution. Experiments with twelve active acids, however, show that the action of uranyl salts is confined to acids whose formulas contain at least one free hydroxyl group. *W. L. M.*

Reciprocal transformation of optical antipodes, II. *P. Walden and O. Lutz. Ber. chem. Ges. Berlin*, 30, *2795* (*1897*).—*l*-brom, and *l*-chlor-succinic acids with silver oxid give *l*-malic acid; heated with alcoholic ammonia, on the other hand, they give rise to *d*-amino-succinic acid, which on boiling with baryta water gives off ammonia and is converted into the barium salt of *d*-malic acid. *W. L. M.*

Theory of anomalous electric dispersion. *P. Drude. Wied. Ann.* 64, *131* (*1898*). — An extension of the theory of anomalous optical dispersion to the case of extremely broad absorption bands. Comparison between the calculated and observed values of the index of absorption shows fair agreement.
W. L. M.

A theoretical study of elastic bodies and light. *P. Glan. Wied. Ann.* 63, *230* (*1897*).—Modification of the mathematical treatment for light of very short wave length. Spring's measurements of the coefficients of extinction of white light in water, ligroïn, methyl ethyl, and amyl alcohols, are compared with the theoretical values. *W. L. M.*

Crystallography, Capillarity and Viscosity

Connection between the crystallographical characters of isomorphous salts and the atomic weight of the metals contained. A comparative crystallographical study of the normal selenates of potassium, rubidium and caesium. *A. E. Tutton. Jour. Chem. Soc.* 71, *846* (*1897*). — Determinations of the solubility (in water at 12° C), and of the crystallographical and optical relations, and densities, of the crystals and of certain of their solutions in water. Special precautions had to be taken because of the highly hygroscopic nature of the salts, especially of cesium selenate.

"The difference in the nature of the elements of the same family group, which is manifested in their regularly varying atomic weights, is also expressed in a similar regular variation of the characters of the crystals of an isomorphous series of salts, of which these elements are the interchangeable constituents."
W. L. M.

A relation between the electrical, chemical and geometrical properties of crystals. *J. Beckenkamp. Wied. Ann.* 61, *597* (*1897*).—According to prevalent crystallographic theories, the rhombic holohedral crystals, like all others with a center of symmetry, ought to exhibit none of the phenomena of pyroelectricity. Arragonite and baryte however, which are usually considered to belong to this group, are markedly pyroelectric and moreover give abnormal figures on etching.

The author seeks to bring these properties into connection with their regular deviation from 'true' geometric form (law of rational indices) by means of an electrochemical theory of the growth of crystals. *W. L. M.*

Specific cohesion and surface-tension of freezing gold. *A. Heydweiller. Wied. Ann.* 62, *694*, *700* (*1897*).—From the shape and dimensions of a drop of solidified gold, about 99.5 percent pure, the author finds that the specific cohesion of pure gold in contact with air at 1070° (the melting point of gold) is 6.90 mm, while its surface-tension at the same temperature is $\alpha = 62.4$ mg/mm when the density is taken as 18.1. These results do not agree with those of Quincke. The cause of this discrepancy is to be found in Quincke's measurements. With increasing diameter the height of a drop passes through a maximum value. This was not reached with gold, and yet Quincke calculated his results as if he were dealing with drops of an infinite diameter. *W. D. B.*

MOLECULAR WEIGHTS OF LIQUIDS

BY CLARENCE L. SPEYERS

Consider the equation

$$\frac{n_1}{n_2 + n_1} = \frac{p - p'}{p}$$

in which n_1 is the number of grammolecules of one constituent of a homogeneous mixture, n_2 the number of grammolecules of the other constituent, p the vapor-pressure in the pure state of that constituent to which n_2 refers, p' the vapor-pressure of the same constituent after the other constituent has been mixed with it.

We shall consider a mixture of two liquid constituents miscible in all proportions, and apply the above equation to determine the molecular weights of the liquid constituents. We have only to consider each constituent separately, changing n_1 into n_2, as each constituent in turn becomes the constituent to which p and p' refer. This idea is in essence due to Nernst.[1]

Unfortunately we have very few data available for this purpose, the vapor-pressures of homogeneous liquid mixtures are generally given as the sum of the vapor-pressures of the constituents, the partial pressures not being given. Linebarger has made some investigations[2] in this direction which will answer our purpose. Likewise some experiments of Raoult[3] can be turned to account, but outside of these I cannot find anything.

I repeat what we need from Linebarger's article, giving the number of molecules of each constituent in 100 mole-

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[1] Zeit. phys. Chem. 8, 110 (1891).

[2] Jour. Am. Chem. Soc. 17, 615, 690 (1895).

[3] Zeit. phys. Chem. 2, 353 (1888).

cules of the mixture. The values in parentheses are either the temperatures of the observations or the vapor-pressures in mm Hg of the pure constituents at the given temperatures.

C_6H_5Cl and C_6H_6 (34.8°)

C_6H_5Cl pct mols	C_6H_6 pct mols	v. p. C_6H_5Cl (20.3)	v. p. C_6H_6 (145.4)
15.18	84.82	1.7	124.6
29.08	70.92	6.6	101.3
65.06	34.94	12.3	51.3
79.21	20.79	19.1	27.9

C_6H_5Cl and C_7H_8 (34.8°)

C_6H_5Cl pct mols	C_7H_8 pct mols	v. p. C_6H_5Cl (20.3)	v. p. C_7H_8 (46.8)
18.96	81.04	4.3	38.2
41.82	58.18	8.1	27.6
76.71	23.29	17.5	8.2

C_6H_5Br and C_6H_6 (34.8°)

C_6H_5Br pct mols	C_6H_6 pct mols	v. p. C_6H_5Br (8.0)	v. p. C_6H_6 (145.4)
30.33	69.67	2.6	103.1

$CHCl_3$ and C_6H_6 (34.8°)

$CHCl_3$ pct mols	C_6H_6 pct mols	v. p. $CHCl_3$ (289.2)	v. p. C_6H_6 (145.4)
16.97	83.03	39.6	123.5
50.53	49.47	130.7	74.3
59.47	40.53	162.2	59.2

$CHCl_3$ and C_7H_8 (34.8°)

$CHCl_3$ pct mols	C_7H_8 pct mols	v. p. $CHCl_3$ (289.2)	v. p. C_7H_8 (46.8)
28.74	71.26	64.7	34.4
60.43	39.57	160.9	19.5

CCl_4 and C_6H_6 (34.8°)

CCl_4 pct mols	C_6H_6 pct mols	v. p. CCl_4 (169.4)	v. p. C_6H_6 (145.4)
7.21	92.79	14.5	135.4
18.68	81.32	32.5	125.5
28.00	72.00	60.0	105.0
50.19	49.81	91.3	75.6
63.88	36.12	103.1	54.5
77.89	22.11	117.6	31.8

CCl_4 and C_7H_8 (34.8°)

CCl_4 pct mols	C_7H_8 pct mols	v. p. CCl_4 (169.4)	v. p. C_7H_8 (46.8)
30.69	69.31	51.5	37.0
53.85	46.15	78.3	22.3
60.00	40.00	99.1	19.4
91.87	8.13	155.1	4.5

CCl_4 and $C_6H_5NO_2$ (34.8°)

CCl_4 pct mols	$C_6H_5NO_2$ pct mols	v. p. CCl_4 (169.4)	v. p. $C_6H_5NO_2$ (1.16)
5.37	94.63	18.9	1.3
50.73	49.27	113.9	6.2
73.54	26.46	141.5	5.6
95.21	4.79	167.6	2.3

The following data are from Raoult:[1]

$C_{10}H_{16}$ and $(C_2H_5)_2O$ (16.2°)

$C_{10}H_{16}$ pct mols	$(C_2H_5)_2O$ pct mols	v. p. $(C_2H_5)_2O$ (377) + $C_{10}H_{16}$ (< 4)
5.9	94.1	354
12.1	87.9	332
23.4	76.6	294
35.5	64.5	255
47.9	52.1	212
64.5	35.5	159

$C_6H_5NO_2$ and $(C_2H_5)_2O$

The temperature of observation was 16.0°. I have recalculated for 16.2° by taking the ratio of the vapor-tension of pure ether at 16.0° to the vapor-tension of pure ether at 16.2° and multiplying each vapor-tension by this ratio. The quantity so obtained was substituted for the vapor-tension given by Raoult.

$C_6H_5NO_2$ pct mols	$(C_2H_5)_2O$ pct mols	v.p $(C_6H_5)_2O$ (377) + $C_6H_5NO_2$ (< 4)
6.0	94.0	356
17.9	82.1	324
35.5	64.5	280
53.2	43.8	237
71.83	24.1	167
82.23	16.0	133

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[1] l. c.

$C_6H_5NH_2$ and $(C_2H_5)_2O$ (16.2°, raised from 15.3°)

$C_6H_5NH_2$ pct mols	$(C_2H_5)_2O$ pct mols	v. p. $(C_2H_5)_2O$ (377) + $C_6H_5NH_2$ (4)
3.8	96.2	361
7.7	92.3	344
14.8	85.2	319
20.5	79.5	302
49.6	50.4	217
68.7	31.3	152

$C_6H_4(OH)CO_2CH_3$ and $(C_2H_5)_2O$ (16.2°, raised from 14.2°)

$C_6H_4(OH)CO_2CH_3$ pct mols	$(C_2H_5)_2O$ pct mols	v. p. $(C_2H_5)_2O$ (377) + $C_6H_4(OH)CO_2CH_3$ (4)
1.1	98.9	364
2.1	97.9	364
4.8	95.2	351
9.2	90.2	334
15.1	84.9	318
23.2	76.8	297
49.0	51.0	220
77.0	23.0	132
85.0	15.0	107

$C_6H_5CO_2C_2H_5$ and $(C_2H_5)_2O$ (16.2°, raised from 11.7°)

$C_6H_5CO_2C_2H_5$ pct mols	$(C_2H_5)_2O$ pct mols	v. p. $(C_2H_5)_2O$ (377) + $C_6H_5CO_2C_2H_5$ (4)
4.9	95.1	357
9.6	90.4	345
27.1	72.9	283
53.0	47.0	201
75.5	24.5	113
94.4	5.6	46.8

The following data are again from Linebarger:[1]

$HC_2H_3O_2$ and C_6H_6 (35°)

$HC_2H_3O_2$ pct mols	C_6H_6 pct mols	v.p. $HC_2H_3O_2$ (26.5)	v. p. C_6H_6 (146)
8.21	91.79	3.5	140
18.85	81.15	6.4	129
43.39	56.61	10.5	117
50.52	49.48	13.2	106
56.39	43.61	14.0	103
59.59	40.41	14.9	97.6
61.04	38.96	15.3	97.3
62.88	37.12	16.4	96.0
78.61	21.39	18.4	72.7
83.87	16.13	22.3	59.3

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[1] l. c.

$HC_2H_3O_2$ and C_6H_6 (20°)

$HC_2H_3O_2$ pct mols	C_6H_6 pct mols	v. p. $HC_2H_3O_2$ (11.7)	v. p. C_6H_6 (75.6)
59.59	40.41	6.6	48.7
83.87	16.13	9.1	33.0
97.88	2.12	11.4	6.2

$HC_2H_3O_2$ and C_7H_8 (35°)

$HC_2H_3O_2$ pct mols	C_7H_8 pct mols	v. p. $HC_2H_3O_2$ (26.5)	v. p. C_7H_8 (47.2)
59.57	40.43	15.0	31.8
70.48	29.52	17.4	28.5
88.50	11.50	22.2	16.7

Let us consider the liquid mixtures, C_6H_5Cl with C_6H_6, C_6H_5Cl with C_7H_8, C_6H_5Br with C_6H_6. Their vapor-pressures and molecular percentage compositions are plotted in Fig. 1. The vapor-pressure of C_6H_6 must be multiplied by 2, as indicated. To mark the points of observation taken from the above tables, I have used the signs •, x, ◉, o, in the various plottings.

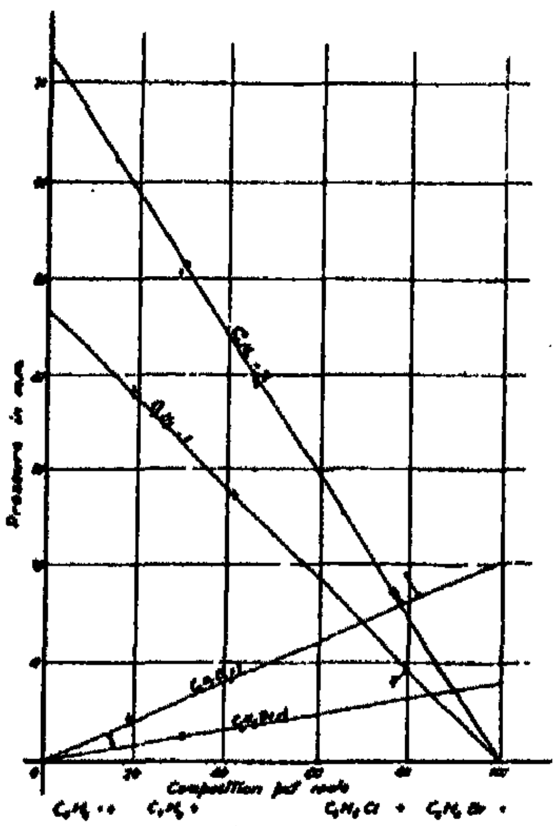

Fig 1

It will be noticed that C_6H_6 is a constituent of two different mixtures, one with C_6H_5Cl and the other with C_6H_5Br, and that its vapor-pressure is equally depressed by equal numbers of molecules of C_6H_5Cl and C_6H_5Br. So C_6H_5Cl and C_6H_5Br in solution have the same degree of association. Moreover, since the vapor-pressure plot is a straight line, it agrees with the equation

$$\frac{n_1}{n_1 + n_2} = \frac{p - p'}{p}$$

which is the equation of a straight line when $n_1 + n_2$ and p are both constant. So the degree of association of C_6H_5Cl and

C_6H_5Br in liquid mixture with C_6H_6 is to be considered unity, for we cannot assume that a substance either associated or dissociated does not change its association either positively or negatively when its concentration is changed.

The same thing seems to be true for C_6H_5Cl; so whenever a vapor-pressure plot is a straight line, we shall claim that the other constituent of the mixture (with C_7H_8) has the normal molecular weight.

Also for C_6H_6 and C_7H_8 with C_6H_5Cl and C_6H_5Br the same thing seems to be true. The molecular weights of these four substances are normal.

The curves for the mixtures of $CHCl_3$ with C_6H_6 and with C_7H_8 are not so simple, Fig. 2.

The curves would indicate that $CHCl_3$ might have a normal molecular weight in C_6H_6, but as it evidently has not a normal molecular weight in C_7H_8 the indication is that it has not a normal weight in C_6H_6. Let us put down some molecular weights taken from these curves.

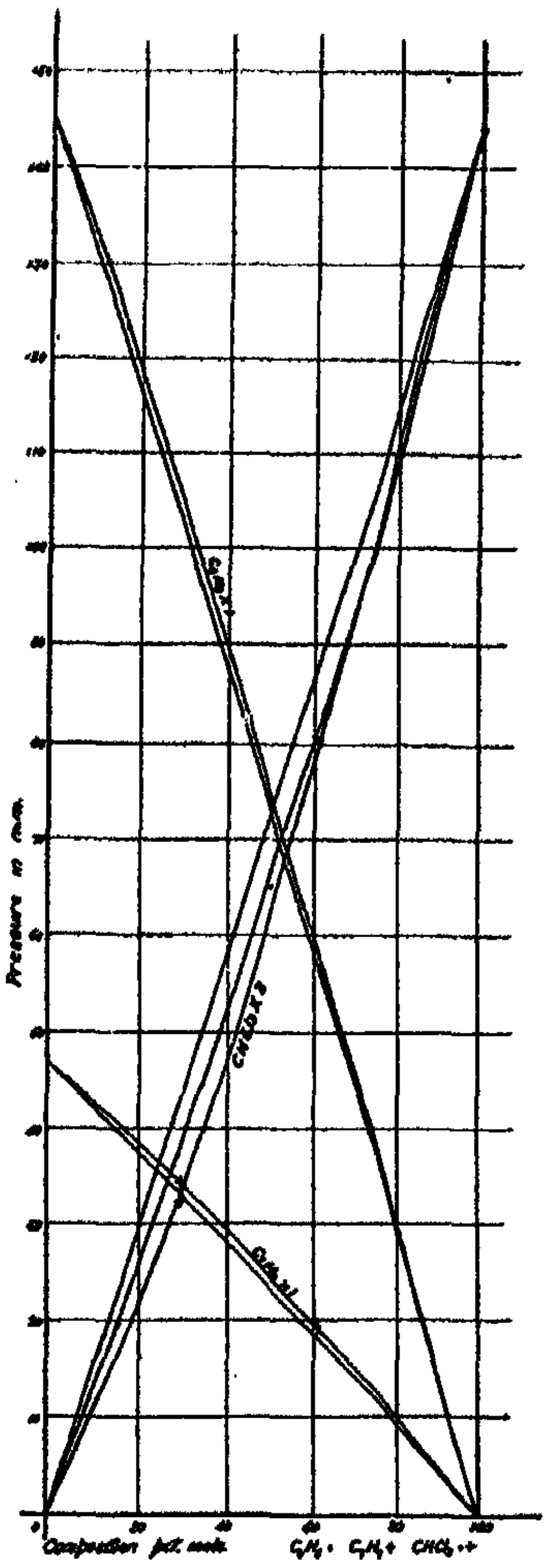

Fig 2.

$CHCl_3$ and C_6H_6 (34.8°)

$CHCl_3$ pct mols	C_6H_6 pct mols	v. p. $CHCl_3$ (289.2)	v. p. C_6H_6 (145.4)	Mol wt	
				$CHCl_3$	C_6H_6
10	90	26.2	132.5	136	70.2
30	70	79	103.6	127	68.4
50	50	134	74.2	124	67.3
70	30	192	43.9	120	66.0
90	10	254	14.9	122	63.4

$CHCl_3$ and C_7H_8 (34.8°)

$CHCl_3$ pct mols	C_7H_8 pct mols	v. p. $CHCl_3$ (289.2)	v. p. C_7H_8 (46.8)	Mol wt	
				$CHCl_3$	C_7H_8
10	90	21.4	42.7	138	66.1
30	70	67.8	33.8	134	65.7
50	50	125.8	24.6	132	70.8
70	30	192	14.9	130	77.9
90	10	257	5.2	134	81.6

Consider the molecular weight of the benzene first. Its value starts considerably below the normal value for benzene and drops continuously to the end. That is, when dissolved in chloroform, benzene behaves as if it were dissociated. A similar behavior is noticed for toluene except that, in this case, the molecular weight of toluene rises as its concentration diminishes. This is probably due to the meagre data available for plotting and is not to be taken seriously. All we may conclude, and that to my mind is very assured, is that if the curves are true representations of the vapor-pressures of chloroform in mixture with benzene and toluene, benzene and toluene are dissociated in such mixtures. That benzene and toluene are dissociated in this way, I do not see how we can believe and accordingly I prefer to think that these curves do not represent the true vapor-tensions of chloroform with benzene and toluene.

The experiments seem to have been very carefully made by Linebarger, so any error of observation I think we may safely consider out of the question. I do think, however, there are several chances for errors in the method. One, pointed out by Linebarger himself, is the failure of vapor in a rather concentrated state to behave according to Avogadro's law. In the case of chloroform, indeed, Linebarger shows that its vapor-pressure can come out 3 percent lower than the vapor-pressure found by Regnault. This would be fully sufficient to explain the apparent dissociation with benzene and toluene. Another chance would be a chemical reaction of chloroform producing substances varying from $CHCl_2C_6H_6$ to $CH(C_6H_6)_3$ with benzene and similar compounds with toluene. These substances remaining chiefly in solution would diminish the vapor-pressure of the chloroform. If any of them volatilized, the chlorin in them would be caught of course by the calcium oxid, but being calculated to chloroform, too little would be subtracted from the total loss in weight of the bulbs, and the difference between the total loss in weight of the bulbs and the chloroform volatilized being attributed to the benzene or toluene volatilized, a vapor-pressure too high would be assigned to benzene and toluene. Since benzene and toluene do react with chloroform in the presence of aluminum chlorid, I see no reason against assuming that they react somewhat without aluminum chlorid. The curve for benzene in a mixture of chloroform with benzene, and the curve for toluene in a mixture of chloroform with toluene are also to my mind impossible for according to these curves either the molecular weight of chloroform does not change on dilution, although above the normal molecular weight, or else it increases on dilution. Another possibility is this, that the molecular masses of benzene and toluene in a saturated vapor state at ordinary temperatures are a little above the normal. Consequently if the normal values were used the vapor-pressures would come out too high. See method of calculation used by Linebarger.[1]

Let us pass on to consider CCl_4 with C_6H_6, CCl_4 with C_7H_8, and CCl_4 with $C_6H_5NO_2$.

CCl_4 and C_6H_6 (34.8°)

CCl_4 pct mols	C_6H_6 pct mols	v. p. CCl_4 (169.4)	Mol wt CCl_4	Mol wt C_6H_6
10	90	22.2	153	106.0
30	70	60.0	"	99.8
50	50	87.8	"	83.9
70	30	109.6	"	61.3
90	10	139.8	"	40.9

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[1] l. c.

CCl_4 and C_7H_8 (34.8°) Normal molecular weights

CCl_4 and $C_6H_5NO_2$ (34.8°)

CCl_4 pct mols	$C_6H_5NO_2$ pct mols	v. p. CCl_4 (169.4)	v. p. $C_6H_5NO_2$ (1.16)	Mol wt CCl_4	Mol wt $C_6H_5NO_2$	m/m_0[1]
10	90	33.2	2.0	..	270	2.20
30	70	79.0	4.0	..	251	2.04
50	50	112	6.0	..	239	1.94
70	30	137	6.1	..	224	1.82
90	10	159	2.7	..	209	1.70

The curve for carbon tetrachlorid in the mixture with benzene is so peculiar that again we must attribute its form to some error in the method. See Fig. 3. I cannot at all believe that this waving line represents the real vapor-pressure of carbon tetrachlorid, particularly since in the mixture with toluene the carbon tetrachlorid plot is a straight line. The vapor-pressure curve for carbon tetrachlorid in the mixture with nitrobenzene is such as to show that nitrobenzene is quite strongly associated. The curve for nitrobenzene in this mixture is extraordinary, but it is explained when we assign a higher molecular weight than the normal one to nitrobenzene vapor at ordinary temperatures.

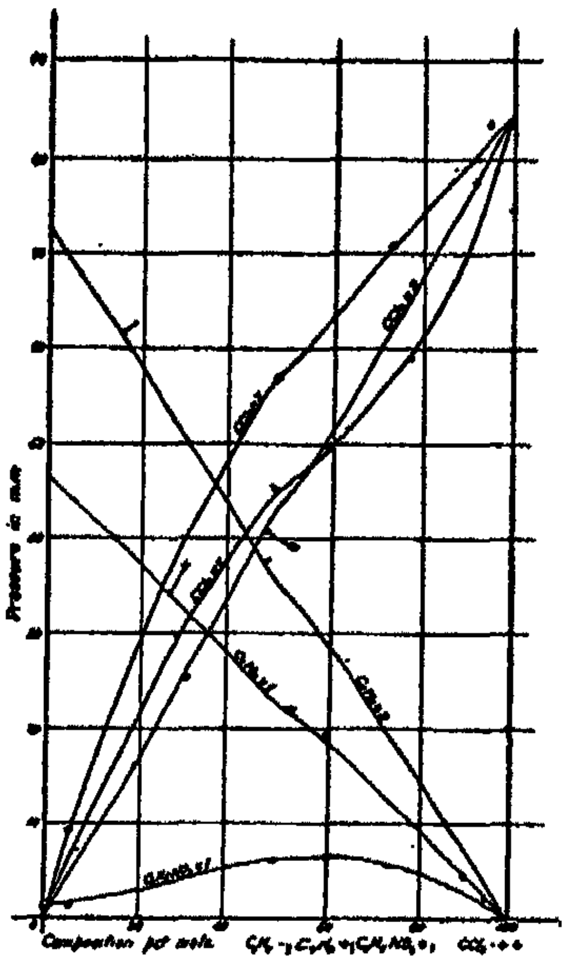

Fig. 3.

Let us pass on to the ether mixtures examined by Raoult,[2] changing the pressures to suit the temperature 16.2°

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[1] m is the observed molecular weight, m_0 is the normal molecular weight.

[2] l. c.

$C_{10}H_{16}$ and $(C_2H_5)_2O$ (16.2°)

$C_{10}H_{16}$ pct mols	$(C_2H_5)_2O$ pct mols	v. p. $(C_2H_5)_2O$ $C_{10}H_{16}$ (377)	Mol wt $C_{10}H_{16}$	*m*/*m*₀
10	90	338	132	0.97
30	70	273	153	1.12
50	50	208	167	1.23
70	30	138	183	1.35
90	10	52	196	1.44

$C_6H_5NO_2$ and $(C_2H_5)_2O$ (16.2°, raised from 16.0°)

$C_6H_5NO_2$ pct mols	$(C_2H_5)_2O$ pct mols	v. p. $(C_2H_5)_2O$ (377)	Mol wt $C_6H_5NO_2$	*m*/*m*₀
10	90	345	148	1.20
30	70	294	187	1.52
50	50	245	228	1.85
70	30	180	262	2.13
90	10	77.6	287	2.34

$C_6H_5NH_2$ and $(C_2H_5)_2O$ (16.2°, raised from 15.3°)

$C_6H_5NH_2$ pct mols	$(C_2H_5)_2O$ pct mols	v. p. $(C_2H_5)_2O$ (377)	Mol wt $C_6H_5NH_2$	*m*/*m*₀
10	90	333	78.2	0.84
30	70	274	106	1.14
50	50	216	125	1.34
70	30	148	140	1.50
90	10	59.2	156	1.68

$C_6H_4(OH)CO_2CH_3$ and $(C_2H_5)_2O$ (16.2°, raised from 14.2°)

$C_6H_4(OH)CO_2CH_3$ pct mols	$(C_2H_5)_2O$ pct mols	v. p. $(C_2H_5)_2O$ (377)	Mol wt $C_6H_4(OH)CO_2CH_3$	*m*/*m*₀
10	90	333	128	0.84
30	70	280	188	1.24
50	50	226	227	1.49
70	30	161	264	1.74
90	10	67.6	299	1.97

$C_6H_5CO_2C_2H_5$ and $(C_2H_5)_2O$ (16.2°, raised from 11.7°)

$C_6H_5CO_2C_2H_5$ pct mols	$(C_2H_5)_2O$ pct mols	v. p. $(C_2H_5)_2O$ (377)	Mol wt $C_6H_5CO_2C_2H_5$	*m*/*m*₀
10	90	340	153	1.02
30	70	274	171	1.14
50	50	212	193	1.29
70	30	148	226	1.51
90	10	63.2	272	1.81

We see that in mixtures with ether the other constituent is associated more or less; I do not think that the apparent dissociation in some of the mixtures at the beginning is real. Unfortunately the method used by Raoult did not allow him to get the partial pressures of each constituent, so we are in the dark as to the molecular weight of the ether. The vapor-pressure of the other constituent is not more than the error of the method, so that the vapor-pressure of the whole mixture as given may be taken as that of the ether alone.

Let us pass on to mixtures of acetic acid and benzene and toluene, taken again from Linebarger.[1]

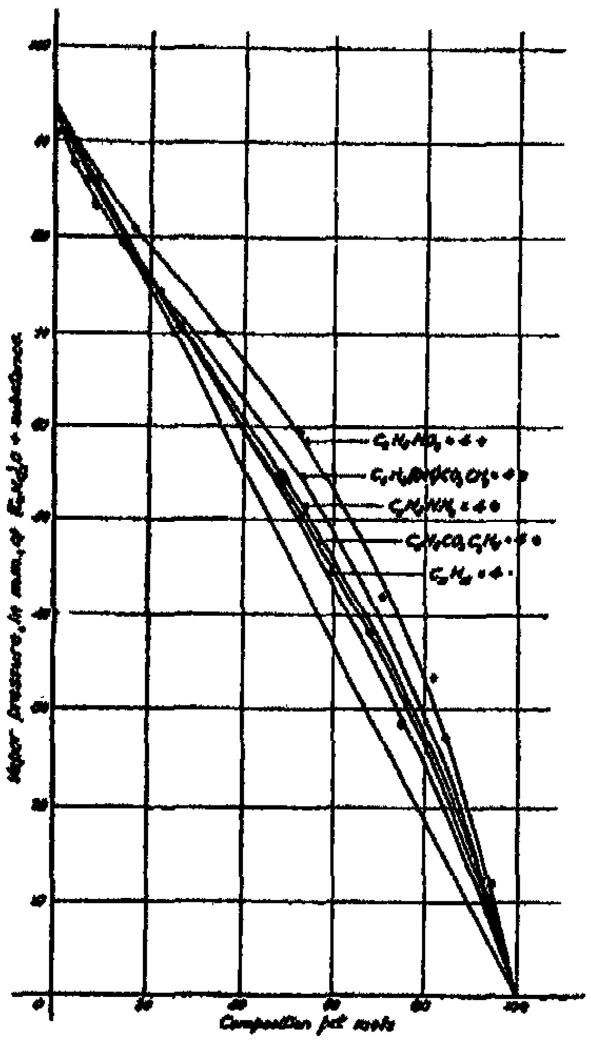

Fig. 4 – $(C_2H_5)_2O$ mixtures.

$HC_2H_3O_2$ and C_6H_6 (35°)

$HC_2H_3O_2$ pct mols	C_6H_6 pct mols	v. p. $HC_2H_3O_2$ (26.5)	v. p. C_6H_6 (146)	Mol wt $HC_2H_3O_2$	Mol wt C_6H_6	m/m_0
10	90	2.8	140	156	78	2.60
30	70	8.0	127	172	"	2.87
50	50	13.2	109	177	"	2.95
70	30	18.1	85.8	199	"	3.32
90	10	23.0	45.0	241	"	4.02

$HC_2H_3O_2$ and C_6H_6 (20°)

$HC_2H_3O_2$ pct mols	C_6H_6 pct mols	v. p. $HC_2H_3O_2$ (11.7)	v. p. C_6H_6 (75.6)	Mol wt $HC_2H_3O_2$	Mol wt C_6H_6	m/m_0
10	90	1.3	71.3	111	78	1.85
30	70	3.7	62.3	120	"	2.00
50	50	6.1	53.4	144	"	2.40
70	30	8.4	43.2	187	"	3.12
90	10	10.7	24.8	264	"	4.40

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[1] l. c.

$HC_2H_3O_2$ and C_7H_8 (35°)

$HC_2H_3O_2$ pct mols	C_6H_6 pct mols	v. p. $HC_2H_3O_2$ (26.5)	v. p. C_7H_8 (47.2)	Mol wt $HC_2H_3O_2$	Mol wt C_7H_8	m/m_0
10	90	2.8	44.9	130	92	2.17
30	70	8.0	39.8	138	"	2.30
50	50	13.2	34.4	161	"	2.68
70	30	18.1	28.6	.215	"	3.58
90	10	23.0	14.9	249	"	4.15

We see that acetic acid is strongly associated in benzene and toluene, in harmony with the results of Ramsay.[1] See Fig. 5. But for nitrobenzene our results and those of Ramsay are different. We find a molecular weight of more than twice the normal weight for pure nitrobenzene, whereas he gets about 1.1 times the normal weight. Nevertheless it seems to me that the results of this method, due essentially to Nernst, are far more reliable than the surface-tension method of Ramsay, for it has a firm theoretical basis, whereas the method of Ramsay seems to be altogether empirical since the theoretical development of Eötvös does not appear reliable; at least Ramsay rejects it, preferring to take the empirical equation by itself.

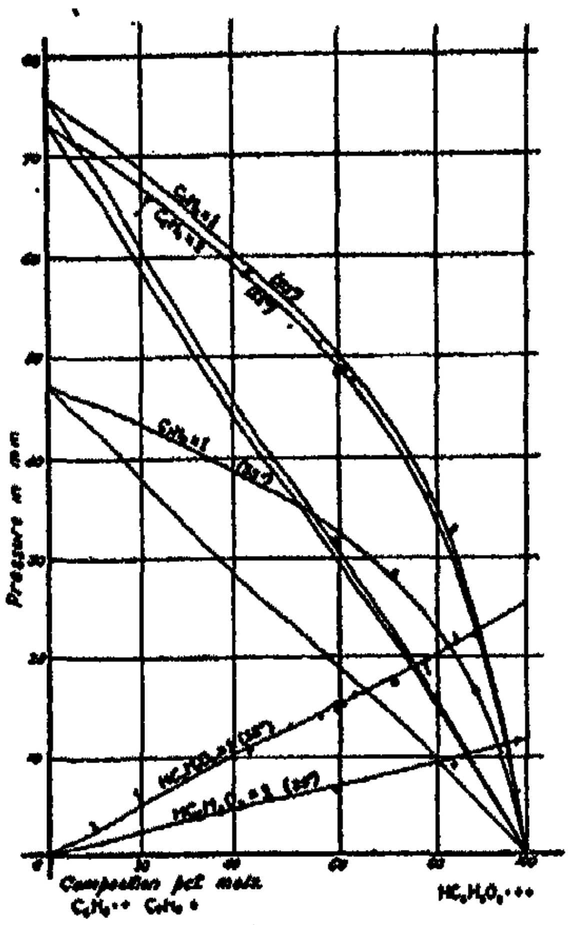

Fig. 5.

The molecular weight of pure nitrobenzene will be found to be different according to whether we use a mixture with ether or with carbon tetrachlorid. Of course this result is to be attributed to some error which is very easily found on looking back to the data. For nitrobenzene and carbon tetrachlorid we have four observations only. Of these one is at each critical

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[1] Jour. Chem. Soc. 63, 1089 (1893).

part of the curve, namely near the ends, but one of these data is so far from the curve that passes through the other three that it is not reliable. For the mixture of nitrobenzene and ether, there are six observations, but none of them in the critical part of the curve, namely at the end where the concentration of the nitrobenzene is 90 grammolecules and upward.

Similarly for the mixture of acetic acid with benzene and with toluene, at 35°. The number of observations in the benzene mixture is very satisfactory, but the number in the toluene mixtures is altogether unsatisfactory. Only three observations are given and only one in a critical place. So that I do not think we should expect the molecular weights so obtained to agree well. All we should say is that pure acetic acid is considerably associated, likewise pure nitrobenzene, in fact most of the liquids considered.

In regard to the excellent results Linebarger got from his plots of acetic acid mixtures for the molecular weights of acetic acid in benzene and toluene I may say that I was unable to recover them though using the same size of section paper. I have not his skill in plotting. The best I could do without forcing the steel rule, was to plot the curves given in the figure, the data were too few and too irregular for reliable curves.

With this idea of association of liquids in mind, let us consider some vapor-pressure curves. Let $n_1 + n_2 = 100$.

B is associated in A. Let us assume first that a liquid which is associated at all, has a higher molecular weight in the pure state than in a mixture with some other liquid. So when B is mixed with A, the molecules of B are simpler the poorer the mixture is in B. So the curve which shows the vapor-pressure of A for increasing quantities of B is depressed less at the beginning than at the end, and is concave towards the axis of abscissæ, being higher throughout than would follow from the equation above supposing that B did not associate, Curve I, Fig. 6. For instance, carbon tetrachlorid in the mixture with nitrobenzene.

Assume now that B is less associated in the pure state than in a homogeneous liquid mixture, and let the molecule be simple in the pure state. This gives a curve for the vapor-pressure of A that is at first, at least, concave towards the axis of abscissæ and lies throughout its course above the straight line given by the vapor-pressure of A according to the rule of mixtures. The vapor-pressure curve of B approaches this straight line somewhere in its course but does not touch it until the 100 mark is reached. The curve would be somewhat like II though perhaps at no time convex to the concentration axis. I know of no example of such a curve.

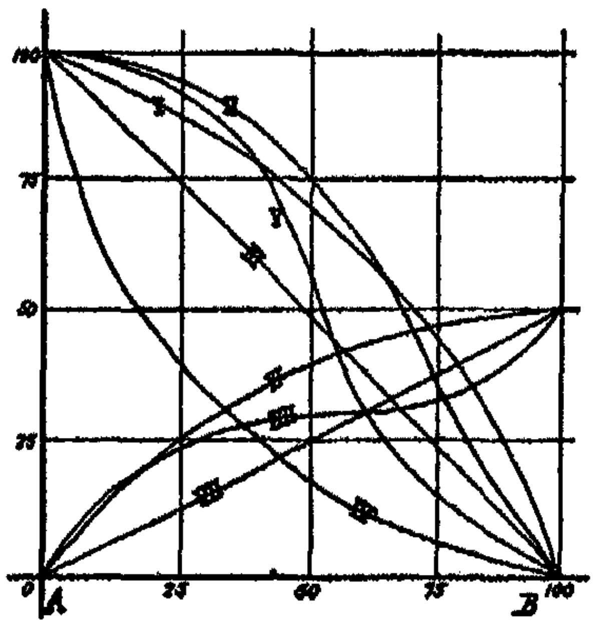

Fig. 6.

B is not associated in A. The plot of the vapor-pressure of A is a straight line, III. For instance, benzene in the mixture with acetic acid or with any other liquid.

B is dissociated in A. In this case, the depression is greater than the normal depression so that the vapor-pressure curve for A lies below the straight line, giving a curve something like IV, though perhaps in a part of its path concave to the axis of abscissæ. There are many such liquid mixtures, but I have not been able to find any data for the partial pressures of the constituents with the exception of sulfuric acid with water. But in this case we are troubled with chemical action between water and sulfuric acid. Otherwise this mixture would give particularly interesting results, for sulfuric acid seems to be strongly associated in the pure state, but is strongly dissociated in aqueous mixtures. For such cases we should have a curve like V. The reasons have already been given why we should not consider the carbon tetrachlorid curve in the mixture with nitrobenzene to belong to this class of curves.

Suppose one constituent of a liquid mixture has a vapor-pressure according to curve I and the other constituent a vapor-pressure curve according to curve VI. We find that the vapor-pressure curve of the mixture should be like curve I of Fig. 7.

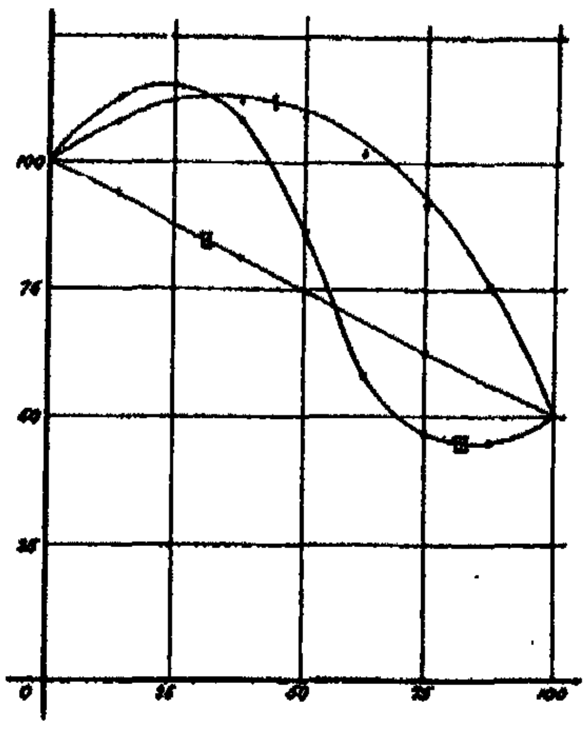

Fig 7

Suppose one constituent of a liquid mixture has a vapor-pressure according to curve III, and the other constituent a vapor-pressure curve according to curve VII. We find that the vapor-pressure of the mixtures should be a straight line II, Fig. 7.

Suppose one constituent of a liquid mixture has a vapor-pressure according to curve V, and the other constituent according to curve VIII. We find the vapor-pressure curve of the mixture should be like III, Fig. 7.

There is no need of further explanation. We easily see how to account for the vapor-pressure curve of any mixture by association or dissociation of the constituents as given by the fundamental equation

$$\frac{n_1}{n_1 + n_2} = \frac{p - p'}{p}.$$

Rutgers College, March 20, 1898

MOLECULAR WEIGHTS OF LIQUIDS

Second Paper

BY CLARENCE L. SPEYERS

Consider a mixture of two liquids not miscible in all proportions. Express the composition of the mixture in grammolecules of constituents per 100 grammolecules of the mixture.

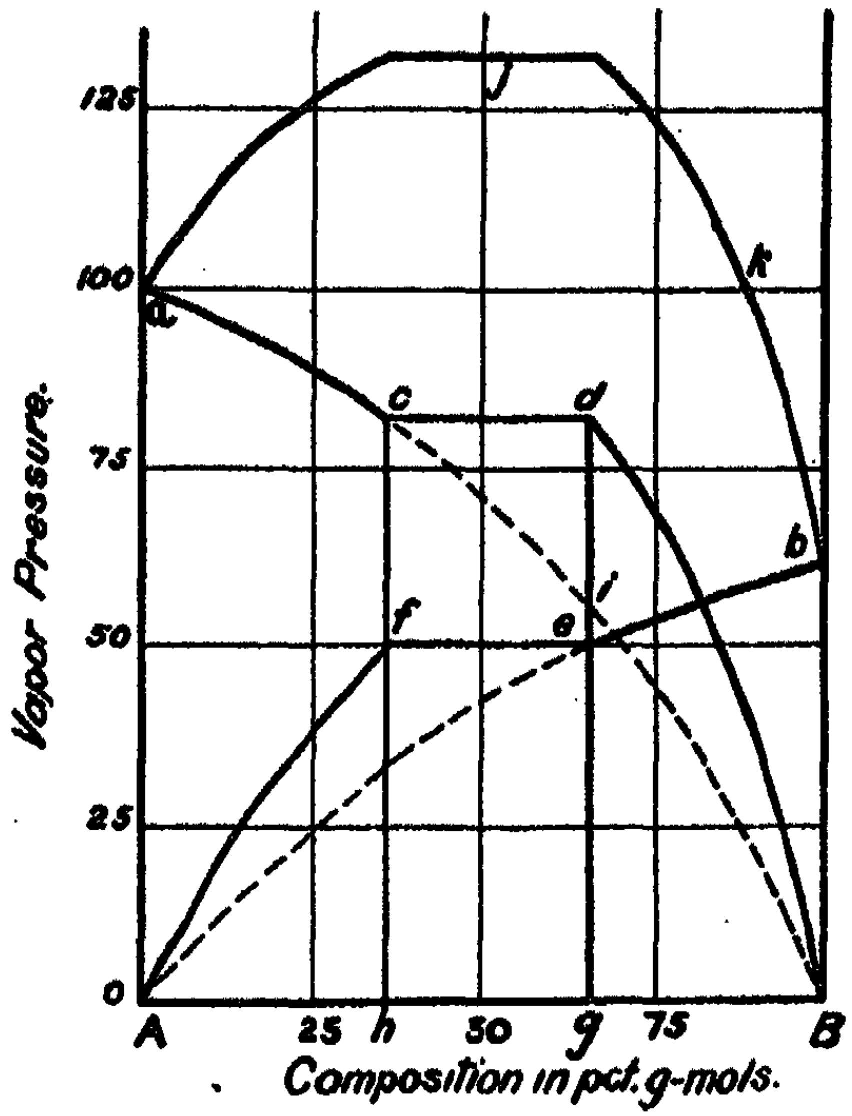

FIG. 1.

Let pure A have a vapor-pressure denoted by the ordinate A*a*; let pure B have a vapor-pressure denoted by the ordinate B*b*, Fig. 1. The temperature is constant.

As B is added to A, the vapor-pressure of A decreases in some way, say according to curve *ac*. At *c*, which is some certain point varying with the mixture and the temperature, another phase appears, for the liquids are not miscible in all proportions. On further addition of B, this new phase increases at the cost of the first phase. On continued addition of B the first phase finally disappears entirely.

The vapor-pressure of A in the two phases is the same, but the quantity of B in the new phase is greater than in the first phase. Consequently, the composition of the new phase is represented by *d* to the right of *c* and on a level with it.

On further addition of B we get the unbroken curve *d*B for the vapor-pressure of A in the mixture after the first phase has disappeared. Similarly, when A is added to B, the vapor-pressure curve of B is *bef*A.

It is evident that *c* and *f* lie on the same ordinate and that *e* and *d* likewise lie on the same ordinate.

Had a new phase not appeared at all, the vapor-pressure of A in a mixture corresponding to the composition denoted by *d* would have been *gi*. But as the second phase disappears, the vapor-pressure of A in the second phase is greater than *gi*. Hence B in the second phase has a molecular weight greater than B in the first phase has.

So the separation of a second phase in a mixture of liquids shows the sudden formation of more complex molecules on the part of one constituent. Similarly, when A is added to B.

It would seem therefore that when two phases are formed in a liquid mixture, a sudden increase in the molecular weight of each constituent is indicated. Curve *ajkb* is the vapor-pressure curve of a mixture whose constituents have the vapor-pressure curves considered above.

Rutgers College, March 26, 1898

BENZILORTHOCARBOXYLIC ACID

BY C. A. SOCH

Benzilorthocarboxylic acid, $C_6H_5CO.CO.C_6H_4COOH$, occurs in two modifications, one white and the other yellow.[1] Determinations in acetic acid showed that the two have the same molecular weight. In alcohol, in fifty percent aqueous alcohol, and in chloroform, the yellow crystals are said to be about twice as soluble as the white. The yellow modification melts at 141.5°, while the white form melts at 125°–130° and changes over to the yellow form. This is exactly what should happen in case the two modifications existed in equilibrium in the melt.[2] The yellow modification would then be the more stable and the white the less stable form. On the other hand Graebe states that the white form can be obtained by crystallization at ordinary temperatures, even when starting from the yellow crystals. This could be interpreted in one of two ways. The white crystals might be more stable at low temperatures and the yellow above 100°. If this were the case, there would necessarily be an inversion point somewhere between 20° and 100° which would be very interesting since no case is yet recorded of an inversion point for two substances which melt to different liquids. It was also quite possible that the reversal of stability might be due to the solvent, the white crystals being stable at ordinary temperature only in presence of certain solvents. There is nothing in Graebe's papers to enable one to distinguish between these two hypotheses. I have not been able to find any mention of the white crystals changing into the yellow at ordinary tem-

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[1] Graebe and Juillard. Ber. chem. Ges. Berlin, 21, 2003 (1888); Graebe. Ibid, 23, 1344 (1890).

[2] Bancroft. Jour. Phys. Chem. 2, 143 (1898).

peratures nor of the reverse reaction. At the suggestion of Professor Bancroft I have studied the conditions of equilibrium for the two modifications.

In preparing the acid I first made benzilidenephthalid and then α-orthodesoxybenzoincarboxylic acid according to the directions of Gabriel and Michael.[1] This latter substance was converted into benzilorthocarboxylic acid according to Graebe's method. It was found that the yellow modification does change into the white form at ordinary temperatures but so slowly that the change might easily be overlooked. This is probably the reason that Graebe did not mention the fact. To determine the inversion temperature some of the white modification, together with a trace of the yellow crystals, were sealed in a glass tube, the yellow crystals being added to guard against a persistence of a metastable state. In another tube was placed some of the yellow modification together with a trace of the white crystals. The third and fourth tubes differed from the first and second in having a little chloroform added. It was thought that this would increase the reaction velocity[2] and possibly change the inversion temperature. Only the first of these two anticipations was realized. At 50° the yellow modification changes to the white while the reverse reaction takes place at 75°. The inversion temperature was next found to lie between 60° and 70°. It was not possible to bring these limits nearer together without spending more time on the question than it was worth, since the change takes place very slowly near the inversion temperature. The temperature of the triple point may be taken as 65° ± 3°.

The rate of change in the tubes containing chloroform was roughly twice as great as in the dry tubes. In one experiment at 75° only the lower part of the tube was in the bath and some of the yellow solid sublimed into the cooler end, precipitating as white needles.

The next point was to determine the changes of equilibrium at higher temperatures in order to see whether they met the requirements of Duhem's theory. I have succeeded in confirming

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[1] Ber. chem. Ges. Berlin, **11**, 1017 (1878); **18**, 3470 (1885).

[2] Reicher. Recueil Trav. Pays-Bas, **2**, 246 (1883).

all the results obtained by Graebe in regard to the freezing-points though, at one time, I was misled by a rather unfortunate phrase of his into believing that my results did not agree with his. In the first paper[1] Graebe says that if the white crystals are heated to 115° they become yellow and then melt at 141.5°. In the second paper[2] he says: "The white modification becomes liquid at 125°–130° but, after long heating at this latter temperature, solidifies to the yellow form." This was taken to mean that the melting-point of the white modification could easily be determined and that the change to the yellow crystals was slow at this temperature. As a matter of fact it was found that on heating the white crystals they became yellow at about 110°–115° and melted at 141.5°. The rate of change was so great that the white crystals changed entirely into the yellow before the melting-point of the former could be reached. Since the yellow crystals melt at 141.5°, but begin to freeze at a lower temperature, there must be two modifications in equilibrium in the melt. Under these circumstances it seemed probable that the second liquid modification was a third, hitherto unknown, form. This seemed the more probable because a similar case had already been realized with sulfur.[3] The white crystals would then correspond to rhombic sulfur, the yellow to monoclinic sulfur, and the unknown modification to the insoluble sulfur.[4] Subsequent investigation showed that this view was wrong and it must be withdrawn. Graebe's results are right with the exception that he has overestimated the time necessary for the change. As has been said, it was found impossible to get a melting-point for the white crystals in the ordinary way. By plunging the capillary tube containing the white crystals into a bath heated to 125°–130° the crystals melted entirely and then solidified immediately to the yellow modification. This shows that the melting-point of the white crystals is about 130°, possibly a little higher, and

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[1] Ber. chem. Ges. Berlin, 21, 2003 (1888).

[2] Ibid, 23, 1344 (1890).

[3] Duhem. Zeit. phys. Chem. 23, 193 (1897).

[4] Cf. Bancroft. Jour. Phys. Chem. 2, 254 (1898).

that the temperature of the stable triple point is certainly above 130°.

Experiments were then made to determine the effect of the initial temperature of heating upon the apparent freezing-point. Some of the acid was placed in a thin-walled glass tube and heated in a sulfuric acid bath. One thermometer was placed in the melt and another in the bath. The test-tube with its contents was heated to a definite temperature, kept there for awhile and then allowed to cool in the bath. The contents of the tube were stirred vigorously with the thermometer and the temperature noted at which the crystals began to appear. This is not an ideal arrangement because there is undoubtedly a change of equilibrium while the system is cooling in the bath. Having but a small quantity of the acid at my disposal, sudden cooling did not seem advisable since the error due to supercooling would probably exceed the error due to the change of equilibrium. Since the error is a real one, the relation between the initial temperature of heating and the apparent freezing-point is qualitative and not quantitative. The following results were obtained:

1. Heated to 141°–142°. Crystals began to appear at 128° and the temperature remained constant at 127.5° while the liquid was solidifying.[1] In a second experiment crystals began to appear at 128° and the mass was solid above 126°.

2. Heated to 160°. Crystals began to appear at 120° and the mass solidified at 119.5°. In a second experiment the solidification temperature was 118.5°.

3. Heated very gradually, keeping the temperature of the bath and the tube as nearly equal as possible. The contents of the tube melted at about 132°. Raised the temperature to 173°–174° and then allowed to cool. Crystals began to appear at 110° and the thermometer rose to 112°, remaining constant there.

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[1] Since it is impossible, under the circumstances, to tell when the last trace of liquid disappears, this is to be taken as a statement of the facts as they appear to be. It is neither believed nor asserted that the temperature really remains constant until the last drop of liquid has disappeared.

4. Heated to 180°. Crystals began to appear at 115° and the thermometer rose to 115.5°.

5. Heated to 190°. Crystals began to appear at 118° and the temperature rose to 118.8°.

6. Heated to 200°. Partial decomposition, the mass freezing at 114°.

All the facts observed are in harmony with Duhem's theory as applied to stereoisomers.[1] The melting-point of the yellow modification is 141.5°, that of the white crystals about 130°. The temperature of the stable triple point is about 132°, the phases being yellow crystals, solution and vapor. The temperature of the instable eutectic point is 110°–112°, probably about 112°. With rising temperature, the equilibrium is displaced to the side of the white modification. The theory foresees the possibility of the freezing-point being lowered and then raised by raising the initial temperature of heating and this has been realized experimentally. The freezing-point is 127° when the system is heated to 142°, 119° after heating to 160°, 112° after heating to 173°, 115.5° after heating to 180°, 118.8° after heating to 190°. These last two points undoubtedly represent a solution saturated with respect to the white modification. No attempt was made to show this experimentally because the rapidity with which the white modification changes to the yellow at these temperatures precluded all hopes of a successful result unless one worked with a very large quantity of the acid. To show the presence of the white modification in the melt I heated some of the acid to 180° and then cooled it very suddenly. On examining the mass under the microscope both yellow and white crystals could be seen. The experiment above 190° shows nothing because the acid had begun to decompose.

While all these facts are very satisfactory, there is one point that, at first sight, seems not to be right. The white crystals change at about 115° to the yellow modification, though the theory as developed would lead one to expect that, at all temperatures between 112° and 130°, the white crystals should

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[1] Bancroft. Jour. Phys. Chem. 2, 143 (1898).

liquefy and then solidify in the yellow form. The explanation of this seeming anomaly is probably that the rate of change of solid into solid is so rapid at this temperature that the intermediate state of solution does not appear, provided no solution be added. This in itself is not improbable. It is known that the rate of change of solid into solid increases as the temperature rises above the inversion point. In this particular case the temperature is some fifty degrees above that at which the two solid modifications are in equilibrium. It is known also that very often a new phase does not appear when it should and that metastable states can be realized experimentally. While this behavior of the white crystals at 115° is very interesting, there is nothing in it to necessitate a modification of the theory. It is to be noticed that although at 125°–130° the rate of change of solid into solid is necessarily greater than at 115°, the tendency to form a solution is also more marked and it is therefore not surprising that we get a passing formation of solution at these temperatures.

One interesting conclusion can be drawn from the experimental data, in regard to the heat of transformation of the two modifications. Above 65° the yellow modification is the more stable and therefore it is formed from the white with absorption of heat. On the other hand, it has been shown that, above 132°, the equilibrium is displaced with rising temperature to the side of the white modification and therefore the change of this latter into the yellow form at these temperatures must be accompanied by evolution of heat. From this, it is safe to conclude that there is some temperature between 65° and 132° at which the heat of transformation is zero.

While the object of this investigation was to study the equilibrium phenomena for pure benzilorthocarboxylic acid, I wish to call attention to a point bearing on the preparation of the acid. Graebe found that he obtained both forms by rapid crystallization from chloroform but only the white crystals when crystallization took place slowly. At any given temperature there would be equilibrium between the two modifications in the solution. If the chloroform evaporated very slowly, the equilibrium would continually be restored and only the form stable at that temperature would separate. If the chloroform were evaporated rapidly then the change of one form into the other might not keep pace with the loss of solvent and both kinds of crystals would separate, as was found experimentally by Graebe.

The general results of this paper are:

1. The white modification of benzilorthocarboxylic acid is stable below 65°.
2. The yellow crystals are stable between 65° and 132°.
3. The temperature of the instable eutectic point is about 112°.
4. Raising the initial temperature of heating first lowers and then raises the apparent freezing-point.
5. The percentage of the white modification in the melt increases with rising temperature.
6. At some temperature between 65° and 132° the heat of transformation is zero.

Cornell University

ANALYSIS OF AQUEOUS ALCOHOL

BY CHESTER B. CURTIS

Alcohol and water are miscible in all proportions; so also are alcohol and toluene; water and toluene, however, are practically nonmiscible. The last two components form colorless liquid layers when allowed to stand, but give a milky turbidity when thoroughly shaken. If a definite quantity of aqueous alcohol be taken, the amount of toluene that must be added in order to produce a cloudiness increases as the amount of water in the alcohol decrease. The foregoing facts are here correlated into a method of determining the percentage purity of alcohols containing water, by titrating with the third component, toluene. This principle was first used by Tuchsmidt and Follenius[1] in determining saturation points for carbon bisulphide in aqueous alcohol of known strengths.

In a paper "On Ternary Mixtures," Bancroft[2] pointed out that, owing to the unpleasant properties of carbon bisulphide, the choice had been unfortunate; and he suggested the use of chloroform, benzene, or toluene in its stead. The experiments carried on by the writer proved the advantage of toluene over both chloroform and benzene. It is easily obtained pure, and does not decompose in the light, an objectionable feature of pure chloroform. It is difficult to separate thiophene as an impurity from benzene, since both boil at nearly the same temperature. Fractional distillation in this case is useless, and the sulphuric acid method is tedious. There being a difference of thirty degrees between the boiling-points of thiophene and toluene there is no difficulty in separating these two liquids by distillation.

Moreover, aqueous alcohol of whatever percentage above 85, the minimum limit of the accompanying table, required ap-

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[1] Ber. chem. Ges. Berlin, 4, 583 (1871).

[2] Phys. Rev. 3, 130 (1895).

proximately twice as much toluene as benzene for saturation, making the titration with toluene much the more sensitive method.

A few tests were made for the purpose of determining what effect thiophene would have when present in benzene. As it was found by Waddell[1] in his work on "Benzene, Acetic Acid and Water" that the presence of thiophene had no effect whatever, it seemed of interest to ascertain its deportment towards alcohol and water. So far as I could observe, the results were identical whether the benzene contained thiophene or was free from it.

Pure substances were used in the following tests. The toluene was rectified by drying over calcium chloride to remove traces of water and alcohol, then distilled. Only that portion coming over between 110° C and 111° C was used. Various methods were employed for obtaining the highest grade alcohol. Commercial "absolute" alcohol was boiled for several hours with quicklime in a flask provided with a return condenser, then left for twelve hours over anhydrous copper sulphate. This product was superior to that obtained from the same alcohol treated first with sodium, and then with aluminum amalgam, and also better than that dried by copper sulphate alone. After treatment with lime, this product was not improved by standing over copper sulphate.

The purified alcohol gave a pycnometer test of 99.9 percent, and though possessing the odor characteristic of high grade alcohol gave no perceptible reaction with calcium carbide[2] until after long standing.

Method of Work.—Mixtures containing approximately 85, 86, 89, 92, 93, 94, 96, 97, 98, 99, and 99.9 percent of alcohol were made from the purest sample and distilled water, the weight being accurate to three decimal places. From these mixtures of known percentage 10 cc. portions were measured with an accurately calibrated pipette, and each portion diluted with 1 cc. of water. Toluene was added from a burette and titration

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[1] Jour. Phys. Chem. 2, 233 (1898).

[2] Yvon. Jour. Pharm. Chem. (2) 7, 100 (1898).

was carried on in test-tubes or thin-walled 60 cc flasks. The liquids, taken up at ordinary room temperature, were cooled to 0° C by a bath of ice and salt.

This particular constant temperature, while as convenient as any other, also possesses the advantage of requiring the minimum amount of toluene for the titration. The temperature was read from a Gerhardt thermometer graduated to tenths, which was used as a stirrer, the lower part of the mercury bulb being protected by rubber tubing. The solution must be stirred constantly as the end-point is approached, since the reaction is sensitive within a range of two-tenths degree centigrade and five drops of toluene. Even a slight excess of the latter causes the cloudiness to appear from 0.2° to 0.5° above zero.

In every case the end-point was determined by the appearance of the milky turbidity. Before this is reached the mixture containing less than ninety percent alcohol becomes hazy on addition of toluene as the end-point is neared; those above ninety percent in alcohol become slightly bluish, this color becoming more pronounced and giving a display of shades resembling fluorescence as the higher grades of alcohol are used.

With the amount of toluene recorded below, each 10 cc. portion became milky at 0° C. From these data the accompanying curve was plotted. Two series of measurements were made from mixtures containing the percentages of alcohol by weight recorded in Table I. Each sample was a 10 cc. portion diluted with 1 cc distilled water.

Table I

Series I			Series II		
No.	pct alcohol	cc toluene	No.	pct alcohol	cc toluene
1	86.14	3.6	1	85.2	3.40
2	89.00	4.7	2	92.07	6.6
3	92.13	6.65	3	93.86	8.5
4	94.60	9.75	4	96.22	13.5
5	98.30	20.2	5	97.83	18.6
6	99.40	25.4	6	98.82	22.8
7	99.9	27.5	7	99.9	27.5

The two curves[1] plotted from these data are identical.

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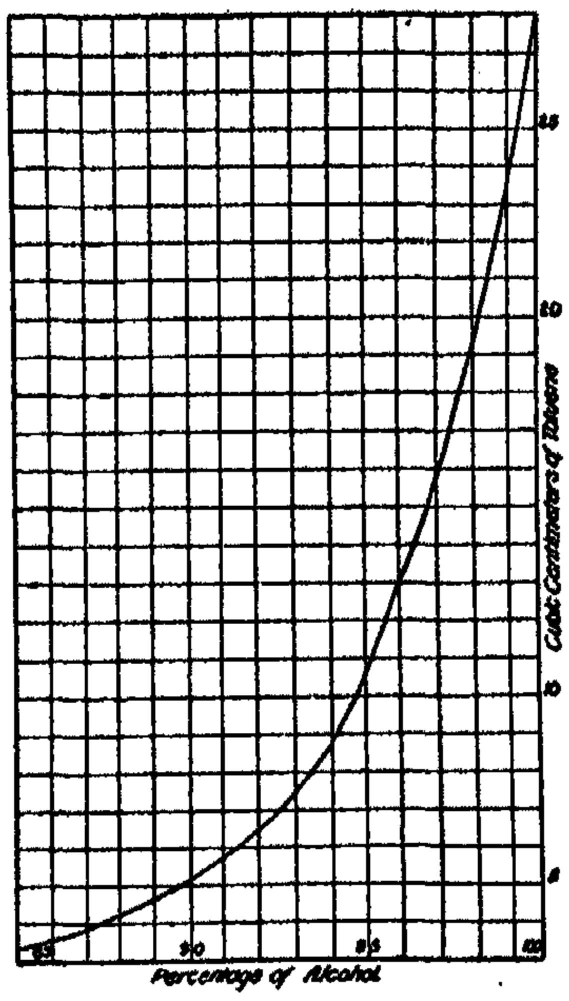
[1] Drawn by Mr. R. C. Taylor, College of Civil Engineering.

The following table constructed from the curve shows the amounts of toluene for alcohols differing by one-half percent from 85 to 100. As before, each sample is 10 cc alcohol plus 1 cc. water.

Table II

pct	cc	pct	cc	pct	cc	pct	cc
85.0	3.40	89.0	4.70	93.0	7.50	97.0	15.75
85.5	3.49	89.5	4.95	93.5	8.10	97.5	17.45
86.0	3.58	90.0	5.20	94.0	8.70	98.0	19.40
86.5	3.70	90.5	5.40	94.5	9.55	98.5	21.50
87.0	3.90	91.0	5.80	95.0	10.60	99.0	23.70
87.5	4.05	91.5	6.15	95.5	11.70	99.5	25.85
88.0	4.25	92.0	6.55	96.0	12.90	100.0[1]	28.00
88.5	4.48	92.5	7.00	96.5	14.25		



To determine the percentage of alcohol (above 85 per cent) in a mixture containing water, pipette off 10 cc of the solution, dilute with 1 cc water; add toluene until the mixture clouds and clears at 0° C. The percentage of alcohol is read as the abscissa of that point on the curve, of which the ordinate is the number of cc toluene added. Alcohol, commercially called absolute, tested by pycnometer proved 99.37 percent; by the toluene method 99.40 percent. The same alcohol after treatment with sodium, and again treated with aluminum amalgam, still proved by the toluene method 99.40 percent. Ordinary (or so-called 95 percent) alcohol gave a pycnometer test of 90.90 percent; by the toluene method 90.80 percent.

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[1] By extrapolation.

The same alcohol purified by lime gave a pycnometer test of 99.55 percent and a toluene test of 99.63 percent. Incidentally this shows the advantages of lime over sodium or aluminum amalgam as a drying agent.

The accuracy of this method is greater as the purity of the alcohol increases. This is shown both by the pitch of the curve and the following table.

Table III

pct alcohol	cc toluene	Ratio
85–90	1.8	1
90–95	5.4	3
95–100	17.4	9.66

In other words the delicacy of the test is three times as great in the second third, and nearly ten times as great in the last third of the curve as in the first.

But even near the lower limits the percentage can be read to hundredths with accuracy. It is evident that this method gives as accurate results as the pycnometer test and possesses the advantage of obviating the well-known difficulties attending the latter.

The method is simplicity itself and the process rapid compared with the pycnometer test.

If one has many tests to make, the Ostwald[1] device of the siphon burette clamped to the toluene bottle will prove a valuable time saver, as well as a great convenience.

Cornell University, April, 1898

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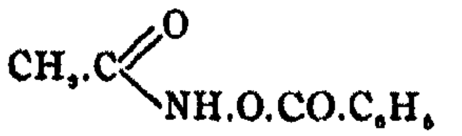
[1] Physicochemical Measurements, 88 (1894).

THE BENZOYL ESTER OF ACETHYDROXAMIC ACID

BY FRANK K. CAMERON

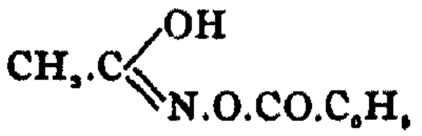
The benzoyl ester of acethydroxamic acid was obtained by Jones[1] as a product of the reaction between sodium isonitroethane and benzoyl chlorid. For purposes of identification, it was also obtained from the reaction between benzoyl chlorid and acethydroxamic acid, prepared according to the directions of Miolati.[2] The ester obtained by each method presented properties similar in all respects, and these have been noted.

If ligroin be added to the mother-liquor obtained by the crystallization of the substance from ether, another compound is precipitated, isomeric with the first. This isomer on standing is gradually but completely converted into the first modification. The melting-point of the ester of acethydroxamic acid is 99°, that of the isomer 70°. This latter compound Jones regards as a probable ester of acethydroximic acid, the relative orientations of the molecules being indicated thus:



$CH_3.C\begin{matrix} /\!/O \\ \backslash NH.O.CO.C_6H_5 \end{matrix}$

Ester of acethydroxamic acid



$CH_3.C\begin{matrix} /OH \\ \backslash\!\backslash N.O.CO.C_6H_5 \end{matrix}$

Ester of acethydroximic acid

In this paper, for the sake of convenience, the ester of the hydroxamic acid will be designated as the α compound, the ester of the hydroximic acid as the β compound.

Bancroft[3] has recently indicated the way in which the theory of "permanent changes," developed by Duhem,[4] may be applied to such a case as is presented by these isomers, and experimental

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[1] Am. Chem. Jour. 20, 5 (1898).

[2] Ber. chem. Ges. Berlin, 25, 700 (1892).

[3] Jour. Phys. Chem. 2, 143 (1898).

[4] Zeit. phys. Chem. 22, 545; 23, 193, 497 (1897).

work in illustration thereof has been in progress in this laboratory during the past year. At the time of the appearance of Dr. Jones's article, the contents of Professor Bancroft's paper had been communicated to me. On calling the attention of the former gentleman to the points involved, he most courteously responded by placing at my disposal what specimens of the ester were then available.

The material was in two parts, the first being the ester of the hydroxamic acid, in large well-formed, perfectly clear crystals; the second part consisted of perfectly white opaque crystals of the hydroxamic ester, which had been formed by the conversion of the hydroximic compound on standing. In all other respects both portions seemed to be identical.

A melting-point determination was made in the conventional way. The substance was ground fine in an agate mortar, placed in a capillary tube, and the tube sealed. It melted very sharply between 98° and 99°. On allowing to cool slowly, it did not recrystallize, but on reaching the ordinary room temperature it appeared as a very viscous liquid, which would not become crystalline, even on the most violent shaking or tapping of the tube. It was further cooled to 4°, then in a freezing mixture of ice and hydrochloric acid, and finally allowed to remain for about two hours in a slush of solid carbon dioxid and ether, without the slightest appearance of any tendency to crystallize. The tube was then brought to the room temperature, opened and the contents touched with a platinum wire. Crystals commenced forming, and gradually spread through the entire mass. The experiment was repeated, using a tube of about 4 mm diameter. The substance again cooled to a viscid state, but by touching with a wire, or dropping in a crystal, the entire mass gradually crystallized.

A melting-point apparatus was then arranged as follows: A pear-shaped flask, containing a convenient amount of sulfuric acid.[1] Into this was fitted an ordinary test-tube by a cork con-

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[1] In the majority of melting-point determinations ordinary cottonseed oil will be found to make a very satisfactory bath. As in the case here described, it was desirable to use a substance which absorbed and lost heat very slowly, concentrated sulfuric acid was chosen.

taining a slit in the side. A cork was fitted to the test-tube, somewhat loosely. This cork carried the thermometer and was provided with a slit in the side through which moved a stirrer consisting of a stout platinum wire, with a loop at the end. The substance under investigation was placed in a small test-tube, this introduced into the larger tube, and prevented from touching the bottom by a small cork. The thermometer was so adjusted, that the bulb would be covered by the melted material. After a few preliminary experiments the material was heated to 103°, it melting entirely at 98°-99°. It was then cooled rapidly by drawing the outer tube from the bath, and immersing in a stream of water from the tap. The mercury in the thermometer fell rapidly to 80°, when crystals began to form. It rose immediately to 93° and then fell slowly. The tube was returned to the bath and heated again. The material all melted at 98°-99°. The temperature was carried to 107°. Cooling as before, crystals began to appear at 83° and the temperature rose at once to 92°. The experiment was then repeated, but keeping the melt at 108°-110° for twenty minutes. On cooling, crystals appeared at 87° and the temperature rose to 91°. The experiment was repeated again, the platinum stirrer being used more vigorously. Crystals appeared at 88° and the temperature rose to 92.7°. The material was then heated at 140°. In a few minutes small bubbles began to pass through the liquid, which also showed signs of discoloring. It was promptly cooled to about 83°, crystals appeared and the temperature rose at once to 88°.

The last experiment was repeated, the material being held at 140° for a very few minutes. On cooling, crystals appeared at 82°-83° and the temperature rose to 88°.

The material was then heated to 96°-97° for about an hour, a large part of it melting, but it had become considerably discolored, so further experiments in this direction were abandoned. The amount of the ester at my disposal was unfortunately quite small, being less than a cubic centimeter when melted, so that considerable difficulty was experienced in working with it in the manner described. The temperatures here recorded are believed to be approximately correct, nevertheless. These results are presented graphically in Fig. 1.

A (99°) is the melting-point of the α modification; B (70°) the melting-point of the β modification; X (between 93°–97°) the stable triple point of the system, the so-called "natural" freezing-point; Y (110°) and W (140°) represent the temperatures respectively to which the system was heated and the corresponding equilibrium concentrations; while Z (93°) and V (88°) are the respective points of solidification of the mixture when suddenly cooled. The point D (65°–66°) at which the β modification would appear as solid phase was determined by experiments which will be described presently. The line XW for concentration-temperatures in the liquid phase slopes to the right as indicated.

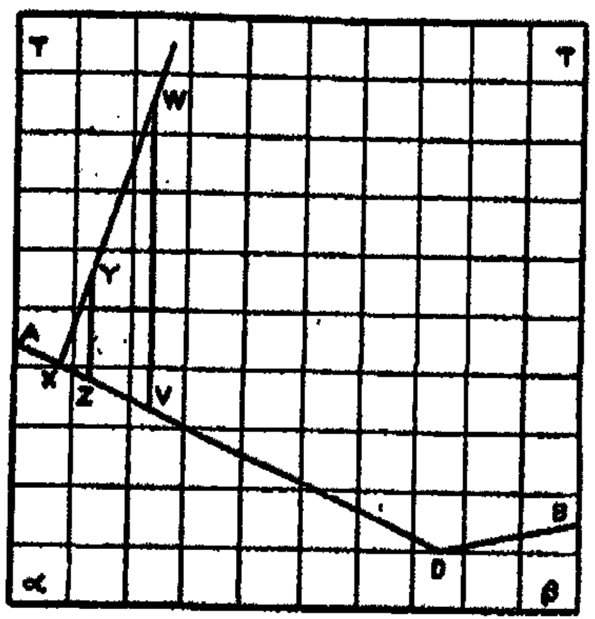

Fig. 1.

The substance which had become slightly discolored as described above was purified by recrystallization from ether. From a portion of this purified material melting at 98°–99° a concentrated ethereal solution was prepared. To this solution ligroin was added, the whole strongly cooled and shaken. It became milky at once, and in a few minutes a quantity of fine white crystals separated. These were pressed between filter-paper until dry and no odor from the mother-liquor remained. A melting-point determination was then made in the usual manner. The crystals were observed to soften below 69°; at 84° nearly all had liquefied, but the last trace of crystals did not disappear before 90°. Evidently the substance was a mixture of the two isomers and by suitably modifying the method just described any desired quantity of the β compound could be obtained. These phenomena are readily explicable. Both modifications exist in the solution and, under definite conditions, in definite concentrations. By allowing the crystals to separate slowly, there is time for the β compound to change to the α modification, and the latter is precipitated. Successive crystallizations in this manner will yield each time the α modification more or less pure. If however the equilibrium conditions be displaced suddenly as by the addition of the ligroin or sudden great cooling, there will not be time for the conversion of the β to the α modification, and the solvent being supersaturated with respect to both modifications, the β compound will be deposited together with more or less of the α. The relative amount of one isomer separating with the other is thus entirely a question of the control of the conditions in each particular case. Strictly analogous to the one here described is the case of the isomeric modifications of acetyldibenzoyl methane, studied by Claisen,[1] for which he has given fairly complete data, and for which an explicit explanation has been given by Bancroft.[2]

The crystallography of one modification, as determined by Zirngiebl is published by Jones,[3] and attempts were made to obtain the corresponding data for the other modification for the purpose of confirming the results here presented.[4] On account of the small amount of material at my disposal this was not possible and no crystallographic data were obtained sufficiently definite to warrant any conclusions therefrom. Repeated precipitations were made, from ether solutions by ligroin; from chloroform solutions by benzene; from boiling toluene solutions by sudden cooling in a mixture of crushed ice and concentrated hydrochloric acid. From all these methods it was sometimes possible to select crystals which melted at 70°, crystals which melted at 99°, and mixtures without a definite melting-point, which began to soften at about 66°. By repeated experiments with these mixtures the eutectic point was determined, and found to be probably a little above 65°.

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[1] Liebig's Annalen, 277, 184 (1893); 291, 25 (1896).

[2] Jour. Phys. Chem. 2, 252 (1898).

[3] Am. Chem. Jour. 20, 7 (1898).

[4] For assistance in these attempts, I wish to acknowledge the courtesy of Professor A. C. Gill of the Department of Mineralogy in this University. The results of Zirngiebl were confirmed.

The following conclusions may now be drawn:

I. Both modifications exist in the liquid phase.

II. The α, or less fusible, modification is the stable one at ordinary temperatures.

III. Crystals of the β modification can be obtained by dissolving the α compound and precipitating the ester suddenly from solution.

IV. The equilibrium concentration changes with the temperature.

V. The α modification is converted into the β modification with absorption of heat.

VI. By raising the temperature of the system and cooling rapidly, the point of solidification may be brought below the stable triple point. It is not possible to realize the eutectic point in this manner, because of decomposition of the substance.

VII. The eutectic point of the system was shown to be below 66° and is near 65°.

VIII. The temperature of the stable triple point is about 95°.

Cornell University

BOILING-POINT CURVE FOR BENZENE AND ALCOHOL

BY E. F. THAYER

Relatively few pairs of liquids are known, giving mixtures with minimum or maximum boiling-points. In order to add to our knowledge of such cases, it seemed desirable to study a series of systems made up of pairs of the more common organic liquids. In this paper are presented the results obtained for benzene and alcohol.

The benzene was prepared in the following way: A quantity of the material, distilling between 79.5° and 80.5°, was kept for a week in contact with concentrated sulfuric acid and shaken frequently. The acid was drawn off from time to time and fresh portions added. The benzene was then distilled, using a Hempel column. The first and last fourths were discarded. Practically all the liquid—including the discarded portions—passed over within half a degree. The alcohol (originally ninety-five percent) was kept for a week in contact with quicklime. It was then distilled from the lime and kept for a week over dehydrated copper sulfate, being shaken from time to time. It was then decanted and distilled, using a Hempel column. It was distilled within three-tenths of a degree; but the first and last portions were discarded.

A mixture of benzene and alcohol containing 52.3 percent of benzene was subjected to fractional distillation. The solution began to distil at 66.7° and the temperature rose gradually to 78°. The last portion appeared to be quite pure alcohol. The lower boiling portions were fractioned repeatedly until a solution was obtained which boiled constantly at 66.7° under a barometric pressure of 737 mm of mercury.

The composition of the mixture with the minimum boiling-point was determined optically with a Pulfrich refractometer. The solution contains approximately 66.5 percent of benzene.

The boiling-point curve was determined in the following way: An apparatus was arranged similar to that used by Orndorff and Cameron[1] in the boiling-point method for the determination of molecular weights. The stopper was of cork and fitted quite closely. At no time was there any evidence of leaking. A small Alleyn condenser was used. Instead of a Beckmann differential thermometer, one of the ordinary type was used; it was graduated to degrees, but with so large a scale that tenths could be estimated readily. A weighed amount of benzene was introduced into the apparatus and boiled rather vigorously for half an hour. The thermometer and barometer readings were noted, a weighed amount of alcohol added and the new boiling-point determined. Alcohol was added in successive portions until the solution contained less than sixty percent of benzene. The flask was then emptied and the same method followed, starting with pure alcohol and adding benzene. In Table I are given the percentage benzene in the solutions, the boiling-points, and the corresponding barometric readings in millimeters of mercury.

Table I

Comp	Temp	Bar	Comp	Temp	Bar
100.00	79.5°	736.9	67.15	66.9°	735.8
95.18	70.8	728.5	59.21	67.1	735.3
93.87	69.6	728.5	44.45	67.5	732.9
92.64	68.8	728.5	35.11	68.4	732.9
85.28	67.6	736.3	27.14	69.8	732.9
76.00	67.1	736.0	15.86	72.1	732.9

The general relations are shown more clearly in the concentration-temperature diagram, Fig. 1. The left hand ordinate represents one hundred parts of benzene. In drawing this curve, it was of course assumed that the pressure was constant. It was

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[1] Am. Chem. Jour. 17, 517 (1895).

not possible to apply corrections for variations in pressure, but any error introduced from this source is probably inappreciable. It was not deemed worth while to recalculate the data so as to represent reacting weights per hundred reacting weights of solution.

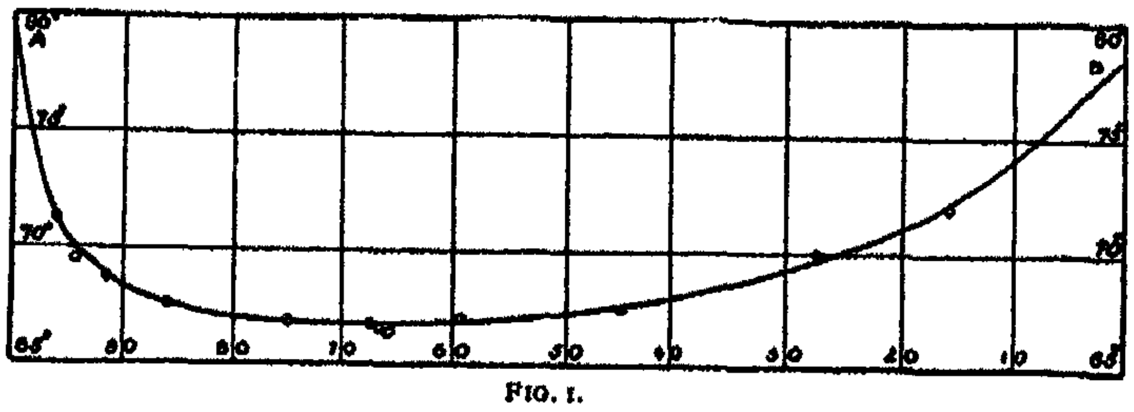

FIG. 1.

To have done this would merely have displaced the curve somewhat to the left and, in this particular case, formula weights are not a bit more rational than grams, judging from the abnormal freezing-point depressions of alcohol in benzene and from the surface-tension of alcohol. The first addition of alcohol to benzene lowers the boiling-point a great deal; then comes a nearly horizontal curve followed by a rise at the alcohol end which is somewhat less steep than at the benzene end.

In a second paper I hope to communicate results obtained with mixtures of acetone and chloroform. The work described in this paper has been done under the supervision of Dr. Frank K. Cameron.

Cornell University

NEW BOOKS

Das Princip der Erhaltung der Energie, und seine Anwendung in der Naturlehre. *By Hans Januschke. 16 × 24 cm; pp. x and 455. Leipzig: B. G. Teubner, 1897. Price: cloth 12 marks.*—There can be but little doubt that the actual results of our study of physical science consist essentially in a more or less exact knowledge of the relations that measurable quantities bear to one another. A treatise designed to present the facts of physical science in general should, therefore, be concerned with these relations themselves, together with the working method or methods by means of which they have been discovered. Of such methods the most significant at present is, unquestionably, the energy theory. The procedure of the energy theory consists, as everyone knows, first in seeking the work-equivalents of physical manifestations, and then in asserting the constancy of the algebraic sum of all amounts of work and of work-equivalents that undergo change in any process considered. This assertion of conservation rests, of course, upon the principle of the excluded perpetual motion, which we recognize in its turn as nothing other than a simple expression of the ultimate scientific postulate that definite relations do subsist among the measurable parameters whose changes determine physical phenomena. A further element of the energy theory is, to be sure, the determination of the potential, and therefore of the corresponding quantity-coordinate, of any given work-equivalent,—*i. e.*, in brief, the 'potential theory'. According to this, an ideal exposition of the outlines of physical science must either show, in historical order, how the energy principle, whether consciously or unconsciously applied, has reached its several results; or it must first describe and justify the method itself, and thereupon detail in some logical order the actual applications of it that have been made.

Januschke, in his *Princip der Erhaltung der Energie*, has followed the latter, or more deductive, plan; and it may be said that he has made a brave and praiseworthy attempt to give a connected account of the real facts of physical theory. In his own words:

> "Im vorliegenden Buche sollen Geltung und Anwendung des Energie-principes in allen Gebieten der Naturlehre dargethan werden. Es geht aus vieljährigen Studien über die Verwendung des genannten Principes für den höheren Unterricht hervor [he is Director of the *Oberrealschule* in Teschen], nämlich aus dem Bestreben, mit Hilfe des Principes nach einem einheitlichen Plane sowohl die einzelnen Erscheinungen eindringlicher zu behandeln, als auch den Zusammenhang derselben möglichst innig zu gestalten."

In the working out of this plan the author has enlivened his text by the addition of considerable interesting and well stated historical information; and he has simplified things by using the calculus notation freely, although without introducing any extended analytical developments. Of the 450 pages of the book, 104 are devoted to the dynamics of solids; 20 pp each to the dynamics and statics of liquids and of gases respectively; 69 pp to what are unfortunately termed 'molecular forces', — namely cohesion, elasticity, capillarity, and osmotic pressure; 63 pp to heat; 133 to electricity and magnetism; and 22 to light. Although the book is not a treatise on physical chemistry proper it is interesting throughout to the physical chemist, and this is particularly true of the extended chapters on the 'molecular forces', on heat, and on electric currents (really electrochemistry). One-component systems are treated in some detail in the chapter on heat; polycomponent systems, on the other hand, are not given anything like due consideration.

The disappointing feature of the work is the author's weak grasp of the three great ideas upon which the energy theory is built: the idea of the relativity of physical phenomena; that of the potential, and of the corresponding quantity-coordinate, of each work-equivalent; and the conception that 'bodies' are complexes of sense-elements. Regarding the first of these points, the author's vague idea that "The problem of natural science is to gain an understanding of natural phenomena" (p. 9) contrasts unfavorably with, for instance, Mach's 'The aim of all [physical] research is to ascertain the mode of connection of the sense-elements that constitute bodies' (1, 500), — whereby, of course, it is understood that these modes of connection are to be expressed in terms of the physical parameters that are determined by — are functions of — the sense-elements. If the author had been clear on the second point he could not have classified forces, tensions, and pressures, with thermodynamic temperatures, electric potentials, etc., as 'intensity factors'; for these are not the same kind of thing at all, — the former are forces, the latter are true potentials. He could not have fallen into this difficulty had he perceived the fundamental distinction between work and work-equivalents, — the one being the product of a force into a change of space, the other the product of a potential into the change of a quantity-coordinate. And his antiquated metaphysics, finally, (the third point) is exemplified by the naive and helpless remark that "The *permanent*,[1] sense-affecting part of the things about us we term ... *matter* or *substance*; spatially limited matter is called *body*" (p. 2). Is this irresponsible metaphysical ghost 'matter' never to be banished from among us? And why should physicists, of all people, be the ones to cling so tenaciously to a crude and outworn materialism? Physics, and chemistry with it, have to do with bodies, — they do not have to do with 'matter'. We may say of our author, however, and we say it gratefully, that he "makes no use of Ostwald's view that energy is a real agent."

Notwithstanding the weakness of the author's fundamental scientific ideas, the general plan of his book is fairly good, and the details are, on the whole, clearly and sensibly put. As a work for general reference, and as a presentation of what might almost be called the physics of physical chemistry, it cannot but prove a useful book.

J. E. Trevor

Die Energetik, nach ihrer geschichtlichen Entwickelung. *By Georg Helm. 15 × 23 cm; pp xii and 370. Leipzig: Veit und Comp., 1898. Price: paper 8.60 marks.*—In the course of the vigorous discussion of the new 'ener-

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[1] The italics are the author's.

getics', carried on in Germany in 1895–96, chiefly by Helm, Boltzmann, and Ostwald, Helm announced that he had in preparation a comprehensive work on the historical development of the energy theory. This long awaited book is now out, and its appearance will unquestionably be greeted with a wide-spread interest. To allow the author himself to speak first for it, we print his preface entire, reserving for our next issue a detailed examination of the body of the text.

> "Although produced in the midst of strife, this book is not a polemic. The quieting influence of the years that have passed since the excitement of the Lübeck days brings warrant that its pages will treat quietly of the acquisition and outgrowing of opinions, and of the struggle for truth and for recognition of error.
>
> "In a few places, particularly in Part VI, it will be noted, — indulgently I hope, — from the halting of the book, that it comes from battle. In these places appear discussions that correspond in extent neither to the difficulty of the questions considered, nor to their influence. Not as in the remainder of the book could the allotment of space here be governed solely by an estimate of the value and import of the investigations presented; the writing had to be done with a view to defense.
>
> "One guiding idea, however, is supreme throughout the book: Energetics, as it has developed from the days of Robert Mayer to our own, is in its homogeneity of character a unique kind of comprehensive knowledge of nature. Errors and excrescences have indeed appeared at all stages of its development, as is also true of much that finds general acceptance to-day. But he who has an appreciation of historical development understands that useful growths and those that require to be pruned away are alike produced by the same forces. The book registers protest, therefore, against regarding either single branches or temporary misconceptions as constituting the true energetics — as its opponents have sought to do. This creation of thought must be looked upon as a whole, and indeed as a great advance in our understanding of natural phenomena."

J. E. Trevor

Thermochimie, *Donnérs et Lois numériques. By M. Berthelot. Tome I: Les Lois numériques; 17 × 24 cm; pp xvii and 737. Tome II: Les Données expérimentales; 878 pp. Paris: Gauthier-Villars et Fils, 1897.* —The first volume deals with the numercial laws and general principles of thermochemistry, the second contains the tabulated data. In the first volume the headings of the chapters are: the principle of maximum work and the entropy; the specific heats; on certain positive characters of the chemical elements as deduced from thermochemistry; heats of formation referred to the same state; on some general formulas expressing relations between the chemical mass of the elements and the heat of formation of their compounds; isomerism; on substitutions in inorganic chemistry; on the formation of salts; on the formation of hydrates; hydrocarbons; alcohols; aldehydes; organic acids; thermochemistry of the nitrogen compounds.

The second volume is not an interesting one to read but it is the more valuable of the two for reference. The data are tabulated under the main heads: metalloids; metals; organic compounds. An enormous amount of work has been done by Berthelot and his assistants in calculating and arranging this mass of material. In the past one has had to hunt through the literature for particular data, with absolutely no certainty as to whether any given heat effect had or had not been measured. This volume is very satisfactory in that it is very complete. This work of Berthelot's is valuable also because it shows what the thermochemists have not done. They have studied an enormous number of systems superficially; but they have not studied a single one in detail. The recent criticism by Duhem is sound. We have here an exposition of thermochemistry as it has been studied, not as it should be studied.

Since this work is really a second edition of the *Mécanique chimique*, it is a matter of interest to note what part the principle of maximum work plays in the book. The first chapter is given up to a half-hearted defense of the principle. It is shown that practically all types of reactions must be excluded; it is admitted that the conclusions drawn from the free energy doctrine are always right and that those drawn from the principle of maximum work are right only when they agree with the results of thermodynamics; and, finally, it is stated that "*whether we consider the quantity of heat* Q *or the quantity* $Q - T(S_a - S_b)$, it will always be a consideration of the final and initial states which will determine the possibility of a direct reaction." Even the bitterest opponent of the principle of maximum work should be satisfied with this surrender. It is expressed diplomatically but it is complete and unconditional.

Wilder D. Bancroft

An Elementary Course in Integral Calculus. *By Daniel Alexander Murray. 14½ × 21 cm; pp. xiv and 288. New York: American Book Co., 1898. Price: cloth, $2.00.* — In this book integration is defined in the only proper way, that is, as a summation, and it is then shown that to evaluate the sum in question, in any particular case, it is necessary to find the anti-derivative of some function. The fundamental formulas are then deduced, and are applied in finding areas of plane curves and volumes of surfaces of revolution. These four chapters contain as much of the subject as most persons, not mathematicians or engineers, ever find occasion to use. The rest of the book follows the conventional lines, with chapters on rational, irrational, trigonometric, and exponential functions, successive integration, geometrical and mechanical applications, approximate integration, integral curves, and differential equations. One novelty to be noted is the derivation of the so-called reduction formulas by means of undetermined coefficients. As a practical method this is eminently satisfactory, but as a proof it can hardly be accepted as satisfying. The usual proof is deemed too difficult for the average student and is accordingly relegated to the appendix, which also contains a short but serviceable table of integrals.

The distinguishing feature of the book is the thoroughness and clearness with which the fundamental ideas are explained. No one who studies it should carry away with him the usual but erroneous view that the integral calculus is at best only a peculiarly dismal algebraical exercise. For those whose object is practical this is perhaps the best textbook that has yet appeared.

Paul Saurel

The Principles of Theoretical Chemistry with Special Reference to the Constitution of Chemical Compounds. *By Ira Remsen. Fifth Edition. 14 × 20 cm; pp. iv and 326. Philadelphia: Lea Brothers and Co., 1897. Price: cloth, $2.00.*—As indicated in its title the object of this work is "to point out as clearly as possible the reasons for accepting the prevailing views in regard to constitution, to show that these views are not merely products of the imagination, but that they are the legitimate results of a profound and comprehensive study of chemical phenomena, and that they are the simplest views possible if we accept as the basis of speculation the atomic theory."

By thus limiting the scope of his treatise, and in particular by omitting all thermodynamic discussion, and condensing to the utmost all matter relating to the recent advances in physical chemistry, the author has been able to present a selfcontained and connected account of the most characteristic branch of distinctively chemical theory. And whether one considers the great practical services rendered to organic chemistry by the theories of constitution, or their almost total want of connection with the recent work in general chemistry, it can hardly be denied that the subject is much better discussed in a volume to itself than — as is the case in one well-known work — in a chapter wedged between 'the theory of solutions' and 'the action of mass'.

The book begins with the laws of definite and multiple proportion, "the fundamental laws of chemistry", leading to the conception of atoms; next come the investigations of Gay-Lussac, and the molecular theory, a short chapter (5 pages) on the determination of molecular weights in solution, then atomic heat, isomorphism, and finally the periodic law.

What is logically the second division of the work is introduced by a long chapter on valency, in which the evolution of that conception is traced to its present state; a definition of the 'constitution or structure of chemical compounds' follows, and the remaining two hundred pages (except thirteen on chemical affinity) are devoted to full discussions of the constitution of various classes of compounds, organic and inorganic, and to the connection between chemical constitution and properties of compounds. *W. Lash Miller*

A Treatise on Magnetism and Electricity. *By Andrew Gray. In two volumes, Vol. I, 16 × 23 cm; pp. xv and 479. New York: The Macmillan Co., 1897. Price: $4.50.* — The subjects of the chapters are: permanent magnetism; magnetic intensity and magnetic induction; terrestrial magnetism; magnetism of an iron ship and compensation of the compass; elementary phenomena and theory of electrostatics; steady flow of electricity in linear conductors; general dynamical theory; motion of a fluid; elementary facts and theory of electromagnetism; induction of currents; dynamical theory of current induction; general electromagnetic theory; the voltaic cell; thermoelectricity. At first sight it would seem as if this book contained little that would interest the chemist; but a closer inspection shows the incorrectness of such a view. The chapters on the elementary phenomena and theory of electrostatics, on the elementary facts and theory of electromagnetism, and on induction of currents contain many things that the chemist should know; while the chapters on the steady flow of electricity in linear conductors, on thermoelectricity, and on the voltaic cell, contain matter that is quite as important to the chemist as to the physicist. The chapter on the voltaic cell is one of the poorest in the book; but the reason for this appears to be that the more interesting phenomena are to be treated in the second volume.

The general style of the book is so good that one is grieved to read, even in a quotation, about "the energy expanded in algebraically generating reversible heat." The typographical errors are few in number and consist chiefly of dropped letters. *Wilder D. Bancroft*

Practical Exercises in Electrochemistry. *By F. Oettel. Authorized translation by Edgar F. Smith. 13 × 17 cm; pp. vii and 92. Philadelphia: P.*

Blakiston, Son & Co., 1897. Price: cloth, 75 cents. — The German edition of this little book has already been reviewed (1, 429). In its new garb the book will be more useful than ever to English-speaking students and should find its way into every laboratory. *Wilder D. Bancroft*

Introduction to Electrochemical Experiments. *By F. Oettel. Authorized translation by Edgar F. Smith. 13 × 17 cm; pp. viii and 143. Philadelphia: P. Blakiston, Son & Co., 1897. Price: cloth, 75 cents.* — This is a translation of an earlier work by Oettel (1894). The book differs from the Exercises in Electrochemistry in that it is devoted almost exclusively to a discussion of apparatus. The headings of the chapters are: source, measurement, and regulation of current; arrangement of experiments; phenomena observed in electrolysis; preliminary experiments of an electrolytic process; practical part; tables. *Wilder D. Bancroft*

Thermodynamique. *By H. Pellat. 16½ × 25 cm; pp. iv and 312. Paris: Georges Carré et C. Naud, 1897. Price: paper, 12 francs.* — The latest addition that we have to chronicle to the list of treatises on general thermodynamics is made up from a course of lectures given by Pellat at the Sorbonne in the academic year of 1895–96, and edited for the press by Messrs. Duperray and Goisot. To bring out as strongly as possible the coherence of the subject the author has made it a point to omit all details not essential to the development of the main argument, to cast the exposition into deductive form, and to give considerable attention to important experimental data. In accordance with this plan he has omitted to give references to original sources, but he makes up in part for this omission by the addition of a number of brief biographical notes.

The book treats successively the energy theorem, the entropy theorem, and simple applications of both. Under the first head come thermometry, calorimetry and specific heats, the mutual convertibility of heat and work, the important determinations of the mechanical equivalent of heat, and a formal statement of the energy theorem. Under the second head we find Carnot's cycle, the thermodynamic scale of temperatures, the entropy function, and dissipation. The applications relate to the determination of temperatures, to fusion, compression, etc., to irreversible changes, ideal gases, the porous plug experiment, saturated vapors, and the various forms of heat engines. All this is fairly simple and clear, but it would probably be more so if the author had made use of Mach's researches on the history of the energy law, and on the significance of the thermodynamic temperature as a thermal potential. Gibbs's consideration of independently variable masses is omitted, as lying beyond the scope of the book, but the omission is compensated in some measure by appended notes on Massieu's characteristic functions, on the continuity of liquids and vapors, etc. The result, as a whole, is a simple and fairly well rounded treatment of general thermodynamics. *J. E. Trevor*

Science Abstracts: *Physics and Electrical Engineering. Issued under the direction of the Institution of Electrical Engineers and the Physical Society of London. Volume I, current numbers; 16 × 24 cm. London: Taylor and Francis, 1898. Price, to non-members, thirty-six shillings, post free, per annum.* — We are glad to call attention to this new enterprise. It appears to be a development of the series of reviews that was formerly published by the Physical Society of London in its Transactions. It is issued monthly under the direction of J. Swinburne, with collaboration of W. R. Cooper as sub-editor and under the general supervision of a committee appointed from the Physical Society and the Institute of Electrical Engineers. The list of abstractors comprises about forty well-known names, and this staff is being enlarged. The numbers for January, February, March, and April contain 470 abstracts, and we are assured that the monthly parts will be considerably expanded as time goes on. Physicochemical items appear, of course, under most of the heads under which the reviews are classified, and they make up pretty much all of the sections on 'Heat' and 'Electrochemistry and Chemical Physics.' As an index and critical digest of current work in physics, this admirably conducted journal deserves cordial support from English-speaking men of science.

J. E. Trevor

Die Fortschritte der Physik *im Jahre 1896, dargestellt von der physikalischen Gesellschaft zu Berlin. 52d year; Part II., Physics of the Ether; edited by Richard Börnstein. 16 × 23 cm; pp. xlix and 820. Braunschweig: F. Vieweg & Sohn, 1897. Price: paper 30 marks.* — The thoroughness and the comprehensive scope of the *Fortschritte der Physik* continue to be evident in the present Part II. for the year 1896. This large section (820 large octavo pages) of the year's output reports progress in light, heat, and electricity, the greater part of which is work of a physicochemical nature. Under the heading 'Light' is summarized the work of the year in refraction, dispersion, spectra, luminescence, rotation, and photochemical action; under 'Heat' are considered the energy and the entropy laws, the kinetic theory, expansion, thermochemical data, fusion, vaporization, and calorimetry; under 'Electricity' are assembled the very extensive researches in electrochemistry, besides the work in electricity and magnetism that has a more purely physical aspect. The value of these compact reviews of *all* the work done year by year in our special subjects and in those immediately related to them is hardly to be overestimated. *J. E. Trevor*

Monographieen aus der Geschichte der Chemie. *Edited by Georg W. A. Kahlbaum. I. Heft:* **Die Einführung der Lavoisier'schen Theorie, im Besonderen in Deutschland; Ueber den Anteil Lavoisier's an der Feststellung der das Wasser zusammensetzende Gase;** *by Georg W. A. Kahlbaum and August Hoffmann. 15 × 23 cm; pp. xi and 211. Leipzig: Johann Ambrosius Barth, 1897. Price: paper 4 marks.* — In founding this new periodical — the "Monographs" are to appear at irregular intervals depending on the supply of suitable articles — the editor hopes to provide a central organ for the results of independent historical research on chemical subjects, as well as for the numerous short articles, biographical and otherwise, at present published in pamphlet form or buried in the proceedings of local societies.

The initial number contains two articles, both by G. W. A. Kahlbaum and A. Hoffmann, "On the Introduction of Lavoisier's Theory, especially in Germany," and "On Lavoisier's Part in Determining the Gases of which Water is Composed." The first of these is devoted to the patriotic task of proving that the antiphlogistic theory gained ground in Germany at least as rapidly as in other countries — a more or less obvious proposition, which however appears to have been denied by Kopp. For non-Germans the interest of the paper lies in the voluminous extracts from writers of all nationalities, showing with what vigorous opposition the new system had to contend; opposition based mainly on conservatism and on ignorance of the theory opposed, but strengthened in many instances by personal, local, and sentimental considerations. That the same causes are still active in resisting scientific progress will hardly be questioned by those familiar with the evolution of physical chemistry in the last decade. The second paper, much the shorter of the two, goes to show that the celebrated founder of modern quantitative chemical research never brought his own quantitative experiments on the composition of water to a successful conclusion; and that in his publications on the matter he was only too apt 'to take the wish for the deed.'

The thoroughness with which the authors have worked up their subject is evidenced by citations from no less than 455 books and articles in the two papers. The "Monographs" ought to have a large circulation, and it is to be hoped that the 'irregular intervals' may not prove to be long.

W. Lash Miller

Popular Scientific Lectures. *By Ernst Mach. Third Edition; 14 × 20 cm; pp. ix and 411. Chicago: The Open Court Publishing Co., 1898. Price: cloth, $1.50; paper, 50 cents.* — It is an encouraging sign that a third edition of Mach's Popular Scientific Lectures has been called for. Since the issue of the first English edition (1, 170) three lectures have been added to the collection: On the Part Played by Accident in Invention and Discovery; On Sensations of Orientation; On Some Phenomena Attending the Flight of Projectiles;—and two historical appendices: A Contribution to the History of Acoustics; Remarks on the Theory of Spatial Vision. The first of the new lectures was Professor Mach's Inaugural Lecture at Vienna in 1895; the second presents his discovery of the function of the three semi-circular canals that lie in three mutually perpendicular planes in the labyrinth of the ear; and the third recounts the results of the recent very interesting photographic study of the head-waves of projectiles, and of the trains of vortex-rings that follow in their wake.

But the important characteristic of the work is the emphasis laid by its author upon the philosophical aspect of scientific knowledge. Nowhere is this aspect more clearly brought out than in the lecture on the Conservation of Energy. This investigation into the significance of the energy theory is one of the weightiest contributions ever made to physical science. Because of its fundamental importance and great scope, it should be studied and understood by everyone who pretends to a liberal education. If this were done, the civilized world would be the wiser and the happier for it; for nothing so clarifies one's ideas and brings a lasting sense of intellectual comfort, as a little common-sense understanding of what it is that we really know.

The astonishingly low price of the book makes it accessible to everybody. In issuing this admirable translation the Open Court Company is doing missionary work of a high order.

J. E. Trevor

Light, Visible and Invisible. *By Silvanus P. Thompson. 13 × 19 cm; pp. xii and 294. New York: The Macmillan Co., 1897. Price: cloth $1.50.* — This book reproduces a series of popular lectures given at the Royal Institution in 1896. In his Introduction the author says:

> "Two things are expected of a lecturer who undertakes a course of Christmas lectures at the Royal Institution. In the first place his discourses must be illustrated to the utmost extent by experiments. In the second, however simple the language in which scientific facts and principles are described, every discourse must sound at least some note of modernity, must reflect some wave of recent progress in science."

What with Roentgen rays and the color photography of Lippmann and of Ives the lecturer could certainly be at no loss to find his wave of recent progress. The note of modernity in his first lecture, on 'Light and Shadows', is a consistent treatment of geometrical optics as a description of wave motion. The result is clear, simple, and delightfully interesting. Nothing could be more satisfactory than the account given of the march of the wave front in reflection from plane and curved mirrors, and in refraction through prisms and lenses. The second lecture is on spectra and colors, and the third on polarization. Here the author says, emphatically:

> "Scientific men often fall into the habit of using long and difficult words to express very simple and easy ideas. The natural consequence is that people are often led to think that there is something difficult about a really easy subject, whereas the main difficulty is to understand the meaning of the words selected to describe it. The word 'polarization', used in optics, is one of these terms."

And then he goes ahead to make clear what the fundamental phenomena of polarization are; illustrating them, finally, with a number of beautiful experiments. Two lectures on the ultra-violet spectrum and on the infra-red spectrum come next in order. In the latter we find a brilliant account of the work of Hertz, in the course of which Thompson tells that he carried out practically the same experiments in 1876, getting sparks all over the room with a resonator when an induction coil was discharged. "But it never dawned upon me that these sparks were the evidence of electric waves crossing the space. That was Hertz's discovery." The closing lecture is on Roentgen light. Taking Roentgen's discovery as a text, the author says:

> "With such material and intellectual encouragements to research as surround the university professor in even the smallest of universities in Germany, what wonder that advancements are made in science? ... Perhaps some day London may have a university worthy of being mentioned beside that of Würzburg, which is eleventh only in size amongst the universities of Germany."

Truly the history of the last half century has made clear that academic freedom is indispensable in a university system that is to advance the interests of human knowledge.

More detailed information regarding optical theory appears in appendices to the several chapters. The author's simple style, and his firm grasp of the significant facts of his subject, have contributed to the making of a good and very interesting book.

J. E. Trevor

The Arrangement of Atoms in Space. *By J. H. van 't Hoff. Second revised and enlarged edition. Translated and edited by Arnold Eiloart. 13 × 19 cm; pp. xi and 211. London: Longmans, Green & Co., 1898. Price: cloth $1.75.* In a previous notice of this book (2, 258) the reviewer criticized the translator severely because the book purported to be a translation of the German edition of 1894 and yet was "brought down to 1897, without there being anything to show which parts are due to van 't Hoff and which to someone else." The reviewer has since been informed that van 't Hoff was consulted in regarded to the additions and alterations. While it seems to the reviewer that this fact should have been mentioned in a preface for the benefit of the reading public, it is a pleasure to be able to state that this English edition is valuable as a document, and that the adverse criticism in the original notice was due to the misleading title-page.

The main subheads in the present edition are: the asymmetric carbon atom; division of the active mixture and temperature of conversion; compounds with several asymmetrical carbon atoms; determination of the position of the radicals in stereomers; unsaturated carbon compounds; ring formation; numerical value of the rotatory power; stereochemistry of nitrogen compounds. There is also an appendix by Werner on the stereochemical isomerism of inorganic compounds. Among the additions in this edition are to be noted the work of Walden on the properties of racemic compounds, the recent papers of Kipping and Pope, the work of Fischer and Beensch on methyl mannosid, the work of Fischer on lyxose and arabonic acid, and the data of van Ekenstein, Jorissen, and Reicher, while a large proportion of the chapter on nitrogen compounds refers to work that has been done within the last few years.

Wilder D. Bancroft

A Manual of Quantitative Chemical Analysis. *By E. F. Ladd. 13 × 19 cm; pp. vi and 82. New York: John Wiley & Sons, 1898. Price: cloth $1.00.* — "This little manual is intended for the use of beginners in quantitative analysis, and is in no way designed for the use of the professional chemist."

Short general instructions (7 pages) are followed by 20 examples in gravimetric, 6 in volumetric, and 3 in electrolytic analysis, besides illustrations of the methods employed in analyzing ashes, soils, ores, sugars, starches, water, and urine. At the end of each section there is a series of questions on the reasons for the operations prescribed.

The book is well printed on good paper, the subscript numbers in the chemical formulas are however much too small to be read by any one who does not know them by heart. The proof-reader is no doubt responsible for the use of 'titre' in place of titration, and of 'voltmeter' for voltameter.

W. Lash Miller

Die Bedeutung der physikalischen Chemie für andere Wissenschaften. *By F. W. Küster. 15 × 22 cm; 19 pp. Göttingen: Vandenhoeck and Ruprecht, 1898. Price: paper 60 Pf.* — This is a reprint of Küster's Inaugural Lecture at Breslau. It asserts that the chemistry of the past collected new compounds, while the physical chemistry of the present collects general laws; and it remarks upon the bearing of the mass-law and the van 't Hoff-Arrhenius theory of solutions upon inorganic chemistry, mineralogy, organic chemistry, electrochemistry, physiology, and physics. The author assigns no role, significant or otherwise, to the phase rule.

J. E. Trevor

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry

General

Thermochimie. *P. Duhem. Revue des Questions Scientifiques,* 1897, *October.*—This is a reply to the first chapter of Berthelot's book of the same title (2, 350). Duhem shows the utter unsatisfactoriness of Berthelot's last stand in behalf of the "principle of maximum work." He then takes up Berthelot's career as a scientific man. He calls attention to the fact that Berthelot has been outwardly a most successful man. For years he has been the recognized head of the scientific world in France. Everything that a man can have in the present, Berthelot appears to have had. When we look at what he has accomplished we see another side of the matter. He has fought against and been vanquished by the modern organic chemistry. He has spent much time in trying to pass from chemical reactions to living matter and has failed. He has fought for thermochemistry and against thermodynamics. At all times during his life he has cast the whole weight of his authority against the truth. He, more than any one else, is responsible for the fact that France, once the leader in chemistry, is now years behind the rest of the world. The results of forty years of incessant labor are almost zero so far as the advancement of science is concerned and Berthelot will be remembered, if at all, only as a disturbing influence. This is a terrible arraignment and the sad part of it is that it is true.

W. D. B.

On the molecular velocity of liquids and its variation with the pressure. *G. Guglielmo. Rend. Accad. Lincei,* (*5*) 6, *II, 254* (*1897*).—The four points discussed are the variations in the molecular velocity due to external pressure, the relation between surface-tension and vapor-pressure, the change of freezing-point with the pressure, and osmose. We are told what assumptions are necessary in order to discuss these phenomena qualitatively from a kinetic point of view, but we are not told why we should make these assumptions at all.

W. D. B.

On a means of decreasing the harmful space in air thermometers. *G. Guglielmo. Rend. Accad. Lincei,* (*5*) 6, *II, 292* (*1897*).—The "harmful space" is in the tube connecting the manometer. If this tube be made very narrow, capillary phenomena are disturbing factors. The author eliminates these to a

great extent by making the tube conical at the end. Since the contact angle of mercury and glass is about 45° the surface will be practically plane if the pitch of the side of the cone be 45°. The paper contains an elaborate discussion of this device and of the probable error of the readings obtained by means of it.
W. D. B.

On a new form of Sprengel pump. *G. Guglielmo. Rend. Accad. Lincei,* (*5*), 6, *II, 324* (*1897*). — The apparatus is simplicity itself, consisting, as it does, of the fall-tube, the tube leading to the vessel to be exhausted, and a side-tube connecting with the mercury reservoir. The important feature of this pump is that the mercury is siphoned from the reservoir. A needle valve is used to check the flow of mercury. *W. D. B.*

A revision of the atomic weight of nickel. *T. W. Richards and A. S. Cushman. Proc. Am. Acad.* 33, *97; Chem. News,* 76, *284, 293, 307* (*1897*); *Zeit. anorg. Chem.* 16, *167* (*1898*). — The bromin in nickel bromid was weighed as silver bromid. The result was Ni = 58.69. *W. D. B.*

A revision of the atomic weight of cobalt. *T. W. Richards and G. P. Baxter. Proc. Am. Acad.* 33, *115* (*1887*); *Chem. News,* 77, *20, 30; Zeit. anorg. Chem.* 16, *362* (*1898*). —The bromin in cobalt bromid was weighed as silver bromid. The result was Co = 58.99. *W. D. B.*

The atomic weight of aluminum. *J. Thomsen. Zeit. anorg. Chem.* 15, *447* (*1897*). — A determination of the hydrogen evolved by the action of caustic potash on aluminum gives 26.992 as the most probable value for the combining weight of aluminum. *W. D. B.*

One-Component Systems

On the liquefaction of fluorin. *H. Moissan and J. Dewar. Comptes rendus,* 124, *1202; Bull. Soc. Chim. Paris,* (*3*) *17, 643, 929; Chem. News,* 75, *277* (*1897*). — Liquid fluorin boils at about — 185°. At this temperature it does not attack glass nor does it replace iodin in the iodids. Silicon, boron, carbon, sulfur, phosphorus, and iron do not become incandescent when cooled in liquid oxygen and then thrown into an atmosphere of fluorin. Above 180° fluorin acts upon benzene producing incandescence. When fluorin is passed into liquid oxygen a solid white precipitate is formed that decomposes explosively as the temperature rises. In capillary tubes in which liquid fluorin rises 3.55 mm, liquid oxygen rises 5 mm, alcohol 14 mm, and water 22 mm. The temperatures to which these experiments refer are not specified. *W. D. B.*

Determination of the relations of the specific heats of certain gases. *O. Lummer and E. Pringsheim. Wied. Ann.* 64, *555* (*1898*).—The gas, slightly compressed, was contained in a copper sphere of 90 liters contents, surrounded by ice and provided with a large tap opening to the atmosphere. The fall in temperature of the gas consequent on opening the tap was determined by measuring quickly the conductivity of a strip of platinum, 0.006 mm thick, suspended in the center of the sphere; and the relation $C_p/C_v = k$ was calculated in the usual manner. The results are:

Air	$k = 1.4025$	Carbon dioxid	$k = 1.2995$
Oxygen	$k = 1.3977$	Hydrogen	$k = 1.4084$

W. L. M.

A contribution to the study of oxygen at low pressures. *R. Threlfall and F. Martin. Chem. News, 76, 283 (1897).* — Sutherland has assumed (1, 511) that the peculiar behavior of oxygen when under less than 0.7 mm pressure was due to the formation of ozone. The authors have tested this hypothesis by passing oxygen under 0.4 mm pressure through a solution of potassium iodid and starch in glycerol. No trace of ozone could be detected and the authors conclude that not more than five hundred-thousandths of the oxygen is converted into ozone and that there is no reason to assume this amount of change.
W. D. B.

Formation and transformation of hylotropic-isomeric forms of matter *K. Schaum. Ber. chem. Ges. Berlin, 31, 126 (1898).* — Preliminary communication, induced by a paper of W. W. J. Nicol, Zeit. anorg Chem. 15, 397 (1897). The white and the yellow modifications of *m*-nitro-*p*-acet-toluid give rise to the same liquid on melting, and to identical solutions when treated with toluene.
W. L. M.

Reply. *F. Herrman. Ber. chem. Ges. Berlin, 31, 91 (1898).* — Losanitsch (2, 340) has made a mistake in addition. *W. L. M.*

Relations connecting the thermal constants of the elements. *N. Deerr. Chem. News, 76, 234 (1897).* — The thermal constants for a number of the elements are tabulated, with a view of testing the accuracy of the following empirical relations, put forward by various authors :

1. $TC \sqrt[3]{V} =$ constant
2. $TC =$ const
3. $\frac{LC}{S} =$ const
4. $\frac{TS}{L} =$ const
5. $\frac{AT}{LW}$ 4 const
6. $ALC \sqrt[3]{V} =$ const
7. $\frac{L}{TS} = \frac{1}{3}$

Here T denoted the absolute melting temperature, L the specific heat of fusion, S the mean specific heat from — 273° to T, C the mean coefficient of expansion between — 273° and T, and A, V, and W the atomic weight, atomic volume, and valence. In the relations 2, 3, and 4 the 'const' holds only for members of any one periodic group ; 4, 5, and 7 are identical ; the 'main idea' of 1 and 2 is the same ; 3 follows from a combination of 2 with 4, precisely as 6 is obtained by combining 1 with 7 and putting AS = 6.4. *W. L. M.*

Molecules and liquefaction heats. *P. J. Beveridge. Chem. News, 76, 264 (1897).* — The author assumes "in accordance with van't Hoff's theory of solutions" that the molecules of a liquid have the same energy of translation as if they belonged to a gas at the same temperature ; then, as on solidification 'the molecule becomes fixed in position', the molecular heat of liquefaction of a monatomic liquid (*e. g.* of a fused metal) must be equal to the total kinetic energy of a monatomic gas molecule at the same temperature, i. e. must be about 3 T calories. Eleven percent should be deducted from this number to allow for 'polymerization', and the latent heats so calculated agree [with a maximum variation of 50 percent] with the experimental values for fourteen metals. *W. L. M.*

Molecules and liquefaction heats. *N. Deerr. Chem. News*, 77, *35* (*1898*). —Beveridge's relation [see above] may be expressed symbolically by $\frac{ST}{AL}$ = const. Substituting 6.4/S for A this becomes TS = 2.1 L. Compare numbers 4 and 7 in the author's paper on 'thermal constants' above. *W. L. M.*

Regularities in the boiling-points of isomeric aliphatic compounds. *A. Naumann. Ber. chem. Ges. Berlin*, 31, *30* (*1898*). —The relations between structure and boiling-point discussed by Menschutkin (2, 341) are substantially the same as those published by the author in 1874. *W. L. M.*

Regularities in boiling-point, etc. *N. Menschutkin. Ber. chem. Ges. Berlin*, 31, *313* (*1898*). — The author points out in what respects his results differ from those of A. Naumann. *W. L. M.*

On some recent laws respecting the molecular volumes of liquids. *R. Nasini. Gazz. chim. Ital.* 27, *II*, *533* (*1897*). —Reviewed (2, 59) from Rend. Accad. Lincei, (5) 6, II, 175, 199 (1897.)

The molecular weights of solids. *J. Traube. Ber. chem. Ges. Berlin*, 31, *130* (*1898*). — The 'atomic volume' of the group CH_2, as determined from measurements of the specific gravities of seventeen pairs of solid substances, is roughly 16.7 [14.3 to 20.1]; for liquids it is 16.2. Consequently "the atomic volumes in all three states of aggregation are equal or almost equal."

The further assumption that the "molecular covolume" is the same for solids as for liquids, furnishes a means of determining the 'association' of solids. According to this definition, most solid organic compounds are bimolecular, salts 'consisting of' two ions bimolecular, and those consisting of three ions monomolecular. *W. L. M.*

Molecular weights of solids. *A reply to J. Traube. A. Fock. Ber. chem. Ges. Berlin*, 31, *506* (*1898*). — "To avoid misunderstandings, I must say that in my opinion it is not proper to speak of 'Traube's methods of molecular weight determination.' They are all — as Ostwald aptly puts it — but arguments from analogy, more or less veiled in mathematical form; and where there are no substances of analogous constitution available, whose molecular weights are known for certain, the methods fail." Traube's paper of the same title is discussed at length. *W. L. M.*

On the thermal conductivity of nitrogen peroxid. *G. Magnanini and G. Malagnini. Gazz. chim. Ital.* 27, *II*, *493* (*1897*). — Reviewed, (2, 65) from Rend. Accad. Lincei, (5) 6, II, 22 (1897).

Note on the heat of dissociation of iodin. *J. Sperber. Zeit. anorg. Chem.* 15, *281* (*1897*). — From considerations in regard to the "amplitude of the atoms" the author deduces 13.132 cal as the heat of dissociation of iodin. He is pleased to find that this agrees well with the number 14.265 calculated by Boltzmann. *W. D. B.*

Two-Component Systems

New tables for the specific gravities of solutions of sulfur in carbon bisulfid. *G. J. Pfeiffer. Zeit. anorg. Chem.* 15, *194* (*1897*). —The tables in the textbooks being wrong, the author has made a new set of measurements. After the work was finished, it was discovered that the ordinary tables would be right if they were changed to read "parts of sulfur per hundred parts of carbon bisulfid" instead of "parts of sulfur per hundred parts of solution." The data are tabulated correctly in the original paper by Macagno, and the mistake was due to the compiler of the first book of tables. *W. D. B.*

The influence of molecular association on the lowering of the freezing-point and on the osmotic pressure. *H. Crompton. Ber. chem. Ges. Berlin*, 30, *2720* (*1897*). **Osmotic pressure and electrolytic dissociation.** *J. Traube. Wied. Ann.* 62, *490* (*1897*). **Association or dissociation? A reply to Messrs. Crompton and Traube.** *H. Jahn. Ber. chem. Ges. Berlin*, 30, *2982* (*1897*). — The object of Jahn's vigorously worded article is thus stated by the author: "In writing the following lines I have no intention of entering into a controversy with the gentlemen named in the title. My only desire is, in the interest of my fellow workers, to present as briefly as possible the reasons which have led to the assumption that electrolytes in solution are more or less completely dissociated into their ions. ...

"If ever a theory has spread light over heterogeneous and widely separated subjects, it is the theory of electrolytic dissociation; and it seems to me that in attacking a theory that has so many successes to point to, one should go to work more cautiously and more modestly than has been the case in these two latest — and weakest — attacks upon it." *W. L. M.*

Osmotic pressure and electrolytic dissociation. *J. Traube. Ber. chem. Ges. Berlin*, 31, *154* (*1898*). — Recapitulation of the author's views on the subjects named in the title. *W. L. M.*

Reply to H. Jahn. *J. Traube. Ber. chem. Ges. Berlin*, 31, *160* (*1898*). — The author finds it "not difficult to demonstrate the complete failure of Jahn's attack. ... If I had asserted the existence of *stable* hydrates $NaCl.2H_2O$, Jahn would be right; but I assume continuous dissociation, and am even willing to assume that the period of separation of the ion-hydrates is greater than that of their union." *W. L. M.*

On freezing-point determinations carried out with dilute solutions and on their relation to the theories of solution. *R. Abegg. Wied. Ann.* 64, *486* (*1898*). — The sources of error in freezing-point determinations — depending on temperature of freezing mixture, rate of formation of ice, generation of heat by stirring, lag of thermometer, etc. — are enumerated, and their probable influence on the results of Jones, Loomis, Wildermann, Ponsot, and Raoult are discussed. Feezing-point determinations in which errors owing to the above-mentioned causes have been avoided, afford striking confirmation of the theories of van 't Hoff and Arrhenius. Dieterici's vapor-tension measurements (2, 262) are *not* in thermodynamic accord with the more accurate freezing-point determinations. *W. L. M.*

Contribution to the constitution of inorganic compounds, VII. *Alfred Werner. Zeit. anorg. Chem.* 15, *1* (*1897*). — Pyridin dissolves the halid salts of copper, zinc, cadmium and mercury, forming crystalline addition-products with most of them. The same is true of piperidin, in which the silver halid salts also dissolve readily. From an experiment with diphenylamin the boiling-point constant of pyridin was found to be 30.07 [30.51 if the first series be omitted]. Most of the salts gave values corresponding to the simplest formulas, cuprous chlorid being markedly high and mercuric iodid markedly low. One curious fact is that mercurous chlorid is decomposed partially by pyridin into mercuric chlorid and mercury.

In piperidin (K = 28.42) the cadmium gives normal values and the silver salts double values. In methyl sulfid (K = 18.5) cuprous chlorid is high and the other salts normal; in methyl sulfid (K = 32.32) cuprous chlorid and bromid are high; in benzonitrile (K = 36.5) only mercuric chlorid and mercuric iodid and silver nitrate were studied. All three were normal. *W. D. B.*

The valency of beryllium. *A. Rosenheim and P. Woge. Zeit. anorg. Chem.* 15, *283* (*1897*). — From experiments with *p*-toluidin, diphenyl, triphenylmethane and phenanthrene as solutes the authors obtained 30.7 as the boiling-point constant for pyridin. Two series of observations were made with beryllium chlorid. The first series gave 77.84 as the mean reacting weight, the second gave 81.2, while the value calculated for $BeCl_2$ is 79.77. *W. D. B.*

A new procedure for determining molecular weights by the boiling-point method. *W. Landsberger. Ber. chem. Ges. Berlin*, 31, *458* (*1898*). — The vapor of the boiling solvent is led into the solution, the temperature attained is noted and the solution is finally analyzed. The apparatus used is described and illustrated. As advantages of the new method the author enumerates the short time necessary for a determination, and the simplicity and cheapness of the apparatus employed; a disadvantage is the necessity for large quantities of solvent (100–250 ccm) — which is however recovered at the close of the experiment. The accuracy of the method is vouched for by numerous molecular weight determinations. *W. L. M.*

Occlusion of hydrogen and oxygen by palladium. *L. Mond, W. Ramsay, and J. Shields. Chem. News*, 76, *317* (*1897*). — Abstract of a paper read before the Royal Society. To be reviewed when the paper is printed.

Absorption of gases and liquids at various temperatures. *C. Bohr. Wied. Ann.* 62, *644* (*1897*). — The author advances a formula to represent the solubility of gases as a function of the temperature. Possibly owing to printer's errors, the relation in question is stated differently in different parts of the paper. *W. L. M.*

Experiments on the condensation and critical phenomena of some substances and mixtures. *J. P. Kuenen. Proc. Phys. Soc.* 15, *235* (*1897*). — Mixtures of carbonic acid and acetylene have critical temperatures between those for the pure gases. The rest of the paper consists of data in regard to acetylene and ethane, and of a general discussion of van der Waals's theory as applied to the mixture of gases already stated. The bulk of the paper has appeared in the *Zeitschrift für physikalische Chemie*, 2, 200, in an inverted order with some other matter added and without any cross-reference. Kuenen's work is very valuable, but that does not excuse his publishing a couple of papers in one place and then rearranging them to make other papers which are then published in another Journal. *W. D. B.*

The hydrates of magnesium platinocyanid and their solubility. *Hellmuth Baron Buxhoeden and G. Tammann. Zeit. anorg. Chem.* 15, *318* (*1897*).—The anhydrous salt is orange-red; the one with two of water white; the tetrahydrate green; the pentahydrate yellow, while there is one series of solid solutions, the crystals being red and transparent, and containing from 6.25 to 6.9 H_2O. The solubilities have been determined up to 100°. The cryohydric temperature is —4.12°; the quadruple point for the trihydrate and dihydrate comes at 87.5°. The pentahydrate can exist in equilibrium with the solution only in the neighborhood of 45°, but the limiting temperatures were not determined accurately, while the solubility curves are certainly wrong. At 19° the vapor-pressure of the solid solutions can vary continuously from 14.4 mm to 7 mm. (See 2, 263.) *W. D. B.*

On supersaturation and its dependence on crystalline form. *W. W. J. Nicol. Proc. Roy. Soc. Edinb.* 21, *473*; *Zeit. anorg. Chem.* 15, *397* (*1897*).—The author advances the thesis that an instable crystalline substance will always separate in case a solution supersaturated with respect to a stable form be evaporated still farther. The true part of this statement is that metastable forms often precipitate from supersaturated solutions; the new part of the statement is that supersaturation is possible only when solid metastable forms are possible. The valuable part of the paper is the experimental demonstration that metastable crystalline forms precipitate in many systems that had not previously been studied with care.

The author's grasp of the theoretical side of the subject is weak, as may be seen from his discussion in regard to potassium nitrate. Sodium nitrate increases the solubility of potassium nitrate, although no double salt is formed. It occurred to the author that this peculiar phenomenon was "probably due to the solubility of the unusual, hexagonal modification of potassium nitrate isomorphous with sodium nitrate being greater than that of the usual rhombic modification." It was then shown experimentally that when a small drop of concentrated potassium nitrate solution evaporates spontaneously, the potassium nitrate crystallizes at first in an instable form. To the author that seems sufficient. He overlooks entirely the fact that with the sodium and potassium nitrate solutions referred to above, we are dealing with stable and not with metastable states. He forgets, too, that he himself has shown that potassium nitrate does not crystallize from sodium nitrate solutions in a form isomorphous with sodium nitrate. *W. D. B.*

On the constitution of eutectic alloys. *G. Charpy. Séances. Soc. Phys. Paris*, 1897, *87*.—A microscopic study of the eutectic alloys of tin and bismuth and of silver and antimony shows that there are two phases present. (See 1, 740.) *W. D. B.*

My theory of water of crystallization, and calcium mesitylenate. *T. Salzer. Ber. chem. Ges. Berlin*, 31, *504* (*1898*).—The neutral calcium salts of all *m*- and *p*-substituted monobasic benzoic acids crystallize with at most three molecules of water; while the corresponding *o*-substituted acids unite with but two molecules of water. Anisic acid is an exception; and, perhaps, certain nitro-acids. *W. L. M.*

Formation of metallic sulfids by mechanical influences. *L. Franck. Bull. Soc. Chim. Paris,* (*3*) 17, *504* (*1897*). — Attention is called to the fact that sulfids of mercury, copper, iron, aluminum, magnesium, silver, and gold can be prepared by rubbing the powdered metal with sulfur. With aluminum and magnesium there was evolution of hydrogen sulfid even when the metals were apparently dry. *W. D. B.*

On the synthesis of organic substances by the electric discharge. *M. de Hemptinne. Bull. Acad. roy. Belg.* (*3*) 34, *269* (*1897*). — The distance between the walls often has a great influence upon the course of the reaction. With CO and H_2O, CO and CH_4, CO and C_2H_6, the best results are obtained when the walls are very close. With CO and H_2 the distance between the walls was not an important factor. Lowering the temperature often increases the yield. *W. D. B.*

Poly-Component Systems

Note on a curious lead salt. The double iodide of lead and potassium, $PbI_2 2KI$. *F. C. H. Brooks. Chem. News,* 77, *191* (*1898*). — The author has just discovered that lead and potassium iodids form a double salt. He hastens to inform the world of this fact. He makes the formula $PbI_2 2KI$ instead of PbI_2KI2H_2O as found by Herty and by Schreinemakers. *W. D. B.*

Aqueous solutions of salts with a common ion. *C. Hoitsema. Zeit. phys. Chem.* 24, *577* (*1897*).— Review of the principal cases of equilibrium in solutions of two salts with a common ion in the presence of the simple salts, double salts, complex salts, and mix-crystals respectively. *W. L. M.*

Racemism. *A. Ladenburg. Ber. chem. Ges. Berlin,* 31, *524* (*1898*). — Quinine forms a salt with pyrotartaric acid, which appears to be a compound of the *d* and *l* pyrotartrates. As, however, these two latter are not strictly enantiomorphous (quinine itself being optically active) the author suggests the term 'partial racemism' to distinguish this new class of double salts. The evolution of heat on mixing *d* and *l* coniin is again advanced as an argument for the existence of a [liquid] *r*-coniin. *W. L. M.*

The racemic transformation of ammonium bimalate. *J. H. van 't Hoff and H. M. Dawson. Ber. chem. Ges. Berlin,* 31, *528* (*1898*). — The view that the anhydrous crystals, sometimes deposited from solutions of racemic ammonium bimalate, $C_4H_5O_5NH_4$, consists of a mixture of *d* and *l* bimalate, and not of a 'modification' of the racemic salt, is advanced, and supported by experiments with tensimeter and dilatometer, and by melting-point and solubility determinations. *W. L. M.*

Observations on the hydrolysis of ferric chlorid. *W. Spring. Bull. Acad. roy. Belg.* (*3*) 34, *255* (*1897*). — Reviewed (2, 202) from Recueil Trav. Pays-Bas, 16, 237 (1897).

On hydrolysis and catalysis. *G. Platner. Elektrochem. Zeit.* 4, *218* (*1898*). — Magnesium dissolves readily in salt solutions with evolution of hydrogen. This is interpreted as showing that the salt is decomposed to a certain extent into acid and base. The addition of manganous chlorid to a solution of potassium chlorate and permanganate causes an evolution of oxygen. The author proposes using ferric sulfate, potassium chlorate, and manganese peroxid as a depolarizer. (See 1, 522.) *W. D. B.*

Action of potash on epichlorhydrin in presence of alcohols. *V. Zunino. Rend. Accad. Lincei,* (*5*) 6, *II, 348* (*1897*).—The author has made the dimethyl, diethyl, dipropyl, diallyl, and diisoamyl ethers of glycerol by the action of alcoholic potash on epichlorhydrin. The reacting weights of the first two ethers were determined in benzene solution by the freezing-point method. The values for the dimethyl ether decrease with increasing concentration, becoming approximately normal in the more concentrated solutions. The diethyl ether gives normal values, though the molecular lowerings as tabulated do not follow from the data. *W. D. B.*

Osmotic Pressure and Diffusion

Osmotic pressure. *A. H. Bucherer. Wied. Ann.* 64, *549* (*1898*).—Taking for granted, as experimental results, that:

(1) The work necessary for isothermal reversible removal of $n_0 - n_1$ g-mols of solvent, by osmotic means, from a solution made up of n_0 g-mols solvent and n g-mols dissolved substance

$$n\mathrm{RT} \log (n_0/n_1);$$

(2) PV = RT where P is the osmotic pressure and V the volume of solution containing one g-mol dissolved substance, the author deduces the expression

$$n/n_0 = \log (\pi/p) \qquad (9)$$

(where π represents the vapor-pressure of the pure solvent and p that of the solvent over the solution) and contrasts it with Raoult's empirical formula $(\pi - p)/\pi = n/\mathrm{N}$.

"It must however be granted that equation (9) is practically identical with Raoult's equation in the case of dilute solutions"—and as the premises of the author's argument are "taught by experience" only in the case of dilute solutions, his own results are not binding in any other case. *W. L. M.*

Velocities

Catalysis of methyl acetate by the salts of some bases with mixed properties. *G. Carrara and U. Rossi. Rend. Accad. Lincei,* (*5*) 6, *II, 219* (*1897*).—In a previous paper (2, 142) the authors determined the relative strengths of various bases by means of conductivity measurements. They have now supplemented these determinations by a study of reaction velocities, taking the hydrochlorid and hydrobromid of the different bases. *W. D. B.*

The rate of solution of solid substances in their own solutions. *A. A. Noyes and W. R. Whitney. Jour. Am. Chem. Soc.,* 19, *930* (*1897*).—Reviewed (2, 65) from Zeit. phys. Chem. 23, 689 (1897).

Note on the rate of dehydration of crystallized salts. *T. W. Richards. Proc. Am. Acad.* 33, *23* (*1897*).—Barium chlorid with two of water was placed in a desiccator over phosphoric oxid and the loss of weight determined as a function of the time. There is a sudden change in the rate of dehydration when the salt has the composition $BaCl_2H_2O$. The results are interesting as data but they should not have been published as illustrating anything new. The work of Guthrie on this same salt ought to have been mentioned, Phil. Mag. (5) **6**, 105 (1878), and the author appears to be entirely ignorant of the papers of Müller-Erzbach.

A table is also given for the relation between the specific gravities of sulfuric acid solutions and the vapor-pressures at different temperatures.

W. D. B.

Electromotive Forces

On some new forms of gas batteries and a new carbon consuming battery. *W. E. Case. Elec. Eng.* **24**, *209 (1897).* — With hydrochloric acid as electrolyte and carbon electrodes an electromotive force of 0.4–0.54 volts was obtained when one of the electrodes was saturated with chlorin. When carbon monoxid and chlorin were the gases at the electrodes, an electromotive force of 0.33 volt was observed. With marsh gas and chlorin, the electromotive force was 0.6–0.7 volt. From the context it is probable that the author is really talking about potential differences at the electrodes and not about electromotive forces.

W. D. B.

On the polarization capacity of very thin metallic foil. *G. P. Grimaldi and G. Platania. Nuovo Cimento*, (*4*) **6**, *277* (*1897*). — By means of an elaborate clockwork device it was possible to charge the foil for short but accurately measured periods of time, varying from one one-thousandth of a second upward. Experiments were made with gold foil having an average thickness of 94 mm $\times 10^{-6}$ and with sheet gold having a thickness of about 0.09 mm. The initial capacity for zero time is higher for the foil than for the sheets. On increasing the time of charging, the apparent capacity of the sheets increases much more rapidly than that of the foil and eventually exceeds the latter. The initial capacity of the sheet gold is estimated to be 14.2 microfarads per square centimeter of surface, that of the gold foil 19.4 mf/cm^2. The difference is attributed to a difference in the state of the surface. *W. D. B.*

On the decomposition of silver salts by pressure. *J. E. Myers and F. Braun. Proc. Phys. Soc.* **15**, *200* (*1897*). — When silver bromid is subjected to a pressure of 3000–5000 atmospheres between a silver and a platinum electrode, an electromotive force of about 0.08 V. was obtained. Increasing the pressure increased the electromotive force. The platinum was cathode. *W. D. B.*

On Hall's phenomenon in liquids. *F. Chiavassa. Nuovo Cimento* (*4*) **6**, *296* (*1897*). — The author's measurements confirm the conclusions of Bagard (**1**, 268, 386, 532 ; **2**, 73) as to the existence of Hall's phenomenon in liquids. The most valuable feature of the paper is the discussion of the effects produced by lack of homogeneity in the magnetic field. The ideal arrangement — not attained by Bagard — is absolute homogeneity. *W. D. B.*

On the photoelectric phenomena and the photographic process. *H. Luggin. Zeit. phys. Chem.* **23**, *577* (*1897*). — When one of two platinum electrodes covered with a silver halid salt is illuminated, a current is observed that passes through the solution to the dark electrode. This is called the normal photocurrent. If the illuminated electrode be polarized to some other potential than the natural one and the current density determined that is necessary to keep it at that potential, the relation $v - V = ib$ is found to hold approximately when the light is not too intense. Here v is the natural potential for the particular intensity and color of light under consideration, V is the artificially produced potential, i the current density [not current as the author has it] and b a constant. With too intense illumination, some reaction takes place producing a current in the opposite direction, called the solarization current by the author. The relation between the normal photocurrent and the normal behavior of photographic plates is pointed out and attention is called to the fact that the conditions that produce the solarization current are the same as those that cause reversed pictures on the developed negative. In addition the paper contains a lengthy and interesting discussion of many photochemical phenomena from a photoelectric point of view. *W. D. B.*

Electrolysis and Electrolytic Dissociation

New basis for determining the conductivities of electrolytes. *F. Kohlrausch, L. Holborn, and H. Diesselhorst. Wied. Ann.* 64, *417* (*1898*). — It has hitherto been customary to express the resistance of electrolytic solutions in terms of the Siemens mercury unit instead of the ohm; formulas are given for reducing to modern units the data furnished by the different groups of workers in this field, — the actual labor of calculation has already been carried out and the results are soon to be published.

Accurate determinations of the conductivities of certain standard solutions [H_2SO_4 maximum conductivity at 18°; $MgSO_4$ maximum at 18°; NaCl saturated; KCl *n*, *n*/10, *n*/50, and *n*/100] have been made for each degree between 0° and 36°; the results are tabulated, to be employed in standardizing conductivity cells. The following table gives the resistance in 'international ohms' of a one centimeter cube of KCl solution at 25°:

Conc.	*n*	*n*/10	*n*/50	*n*/100
Resistance	0.11180	0,01288	0.002765	0.001413

The *n* KCl was prepared by dissolving 74.555 grams of the salt, weighed in air, to one liter at 18°. *W. L. M.*

The unit of electrical resistance at the Imperial Institute, Charlottenburg. *W. Jäger and K. Kahle. Wied. Ann.* 64, *456* (*1898*). — An account of the methods employed at the *Physikalisch-technische Reichsanstalt* in preparing standard mercury resistances according to the definition adopted at the international electrical congress, Chicago, 1893. Five 'normal' tubes of various diameters have been constructed and measured independently, besides numerous copies in manganin and in mercury. Details are given of the measurement and calibration of the tubes, comparison of resistance, etc. *W. L. M.*

Contribution to the electrical resistance of solutions as a function of pressure and temperature. *Second Part. S. Lussana. Nuovo Cimento,* (*4*) 5, *441* (*1897*). — The water used had a conductivity of 34×10^{-10}. At 24° an increase of pressure causes a decrease of resistance amounting to 2×10^{-5} per atmosphere and per unit resistance. At 57° no change could be detected. With salt solutions increasing pressure means decreasing resistance, the effect being more marked the more dilute the solution. Since the rate of change with the pressure decreases with increasing pressure the author assumes that there will probably be some pressure beyond which increase of pressure involves increase of resistance. With each solution there is some temperature for which the resistance is independent of the pressure. In these experiments the pressure varied between one and one thousand atmospheres. (See 1, 698.) *W. D. B.*

On the calculation of the conductivity of aqueous solutionscontaining potassium and sodium sulphates. *E. H. Archibald. Trans. Nova Scotian Inst. Sci.* 9, *291* (*1897*). — It is shown that the conductivities of mixed potassium and sodium sulfate solutions can be calculated from the conductivities of the single salts with an accuracy of ± 0.3 percent until the concentration of each salt is half normal. (See 1, 135, 524). *W. D. B.*

Preparation of the primary carbonate of tetramincobalto carbonate. *A. Miolati. Rend. Accad. Lincei,* (*5*) 6, *II, 344* (*1897*). — From conductivity determinations of the salt $[Co(NH_3)_4CO_3]HCO_3$ it appears that $\Delta_{1024-32} = 19.73$. From this the author concludes that the salt in solution is the pyrocarbonate of tetramincobaltocarbonate, having the formula $[Co(NH_3)_4CO_3]CO_2.O.CO_2.[Co(NH_3)_4CO_3]$. *W. D. B.*

On the electrolytic behavior of some complex fluo- and fluoxy-salts. *A. Miolati and U. Alvisi. Rend. Accad. Lincei* (*5*) 6, *II, 376* (*1897*). — The salt $K_3(UrO_2Fl_5)$ dissociates into $3\,K^+$ and $(UrO_2Fl_5)'''$. The migration velocity of the trivalent anion is 62.7 — presumably at 25°. With the salt $(NH_4)_2SiFl_6$ there seems to be some hydrolytic dissociation. These conclusions are all based on conductivity measurements. *W. D. B.*

On the energy of some sulfonic acids of toluene and xylene. *P. Bonomi da Monte and A. Zoso. Gazz. chim. Ital.* 27, *II, 467* (*1897*). — Tolylsulfonic, *p*-toluenesulfonic, xylylsulfonic, and *p*-xylenesulfonic acids have practically the same conductivity and invert cane sugar at practically the same rate. The change of the dissociation with the concentration cannot be represented accurately by any formula, but Ostwald's dilution formula gives better results than the expressions of Rudolphi or of van 't Hoff. For the sodium salts, the formula of Rudolphi seems to be the best, though the van 't Hoff formula is only slightly more unsatisfactory. Very satisfactory reaction velocity constants were obtained. *W. D. B.*

On the energy of some bases with mixed properties. *G. Carrara and U. Rossi. Gazz. chim. Ital.* 27, *II, 505* (*1897*). — Reviewed (2, 142) from Rend. Accad. Lincei, (5) 6, 152, 208 (1897).

The electric conductivity of nitric acid. *V. H. Veley and J. J. Manley. Chem. News,* 76, *316* (*1897*). — Abstract of a paper read before the Royal Society. To be reviewed when the paper is printed.

On the color of the ions. *G. Carrara and A. Minozzi. Gazz. chim. Ital.* 27, *II, 455* (*1897*). — Anhydrous copper sulfate dissolves in absolute methyl alcohol and the dissociation appears to be greater than for the same volume concentrations in pure water. A comparison of the spectra of copper sulfate in the two solvents shows that these are identical as far as the position of the absorption bands is concerned; but the extinction coefficients are higher for the concentrated aqueous solutions than for the methyl alcohol solutions; while the reverse is true for dilute solutions. The authors believe that a specific coloring effect due to the solvent must be assumed. *W. D. B.*

Surface travel on electrolytes. *W. E. Fiske and W. D. Collins. Am. Jour. Sci.* (*4*) 5, *59* (*1898*). — Different lengths of saturated [temperature?] copper sulfate solutions were placed in series with the spark gap, the spark photographed and the number of half-oscillations noted. The operation was repeated with manganin or German silver wires substituted for the solutions. The results were then plotted with ohms as abscissas and half-oscillations as ordinates. Although the results vary greatly, it appears probable that the curves for the solutions lie below those for the wires, indicating surface travel in the electrolyte. While manganin and German silver wire behaved identically, an iron wire showed fewer half-oscillations. The experiments are to be repeated with an apparatus giving a much higher period. In these experiments the number of oscillations per second was 500,000. *W. D. B.*

Dielectricity and Optics

On the atomic index of refraction of fluorin. *F. Swarts. Bull. Acad. roy. Belg.* (*3*) 34, *293* (*1897*). — Using the formula of Lorenz, the author has calculated the atomic index of refraction of chlorin, bromin, and fluorin from the indices of refraction of organic compounds containing these elements. For chlorin the value is 5.9028 when calculated from saturated compounds and 6.001 when calculated from unsaturated compounds. For bromin the corresponding values are 8.762 and 8.759, while for fluorin they are 1.082 and 0.775. With bromin the values obtained from the saturated and unsaturated compounds are identical; with chlorin the difference is within the limits of the probable error, while with fluorin there is a difference of thirty percent between the two series. Though unable to explain this peculiar result, the author calls attention to an analogous fact that the replacement of bromin by fluorin in unsaturated compounds lowers the boiling-points much more than when the substitution is made in saturated compounds. *W. D. B.*

The refractivities of certain gases. *W. Ramsay and M. W. Travers. Chem. News*, *77*, *1* (*1898*). — Abstract of a paper read before the Royal Society. To be reviewed when the paper is printed.

Measurements of absorption and emission of water vapor and carbon dioxid, in the ultra red. *H. Rubens and E. Ashkinass. Wied. Ann.* 64, *584* (*1898*). — By means of a spectrometer with sylvine prism, the spectrum of a group of Bunsen burners was thrown on a specially constructed linear thermocouple, and the energy of radiation determined for wave lengths $\lambda = 9\mu$ and greater. The radiations from heated carbon dioxid and from water vapor were similarly studied and the results plotted. The measurements of absorption were carried out with the same apparatus, using a Zircon burner as source of light.

W. L. M.

Researches on optical activity. *L. Tchúgaeff. Ber. chem. Ges. Berlin*, 31, *360* (*1898*). — The author finds that in the higher members of a series of homologous derivatives of asymmetrical compounds, the 'molecular rotation' is constant, i. e. the specific rotation is inversely proportional to the molecular weight. In the case of the esters of menthol, this rule holds from the acetate up; with the esters of *l*-amyl alcohol from the butyrate. Six other series are quoted in support of the generalization. *W. L. M.*

Fluorescent compounds. *B. Pawlewski. Ber. chem. Ges. Berlin*, 31, *310* (*1898*). — Resorcinbenzëin, allofluorescëin, and benzylguayacol are organic, fluorescent bodies whose formulas do not contain the groups enumerated by R. Meyer (2, 208). Benzylchlorid and resorcin warmed on the water-bath give rise to a remarkably fluorescent substance. *W. L. M.*

Fluorescence and constitution. *R. Meyer. Ber. chem. Ges. Berlin*, 31, *510* (*1898*). — The constitutional formulas of the substances quoted by Pawlewski (see above) are not known. The author adds to his list of "fluorophoric groups" (2, 208) and describes a simple apparatus (small U-shaped Geissler's tube, filled with nitrogen at 3 mm pressure) for illuminating fluorescent liquids. *W. L. M.*

On the recent development of flame illumination. *H. Bunte. Ber. chem. Ges. Berlin*, 31, *5* (*1898*). — An address delivered before the German Chemical Society. The author ascribes the brilliancy of the Auer-Welsbach light to catalytic action of the ceria, causing intense local combustion and consequent elevation of temperature. The thoria which forms the greater part — 99 percent — of the mantle serves merely as a support for the particles of ceria. *W. L. M.*

Crystallography, Capillarity and Viscosity

Determination of the inner friction of a solid. *A. Heydweiller. Wied. Ann.* 63, *56* (*1897*).—By means of a column of mercury, menthol was pressed through a narrow passage in a glass tube, the rate measured at various temperatures and the inner friction η calculated in c. g. s. units.

For the solid state as for the liquid, $\log \eta$ is a linear function of the temperature; the decrease in η for one degree rise in temperature (solid menthol) reaches the extraordinary value of *twenty per cent!* The inner frictions of solid and liquid menthol at the melting-point stand approximately in the ratio of 10^{11} to one. *W. L. M.*

The surface-tension of gold. *G. Quincke. Wied. Ann.* 64, *618* (*1898*). — In 1869 the author found that the specific cohesion of gold was approximately the same as that of silver, of platinum, and of water. Heydweiller's contradictory results are ascribed to impurities in the gold experimented on by him. *W. L. M.*

BENZALDOXIME

BY FRANK K. CAMERON

The study of the equilibria between stereoisomers has been in progress in this laboratory for some time. In connection with this there have recently appeared descriptions of the acetaldoximes,[1] the benzoyl esters of acethydroxamic and acethydroximic acids[2] and of the benzilorthocarboxylic acids.[3] But there has not as yet appeared any description of a system in which the change from one modification to the other has been followed in a complete as well as systematic way. The benzaldoximes seemed to present a case, unusually well suited to such investigations, and furthermore possessed additional interest, in as much as no case had yet been studied in which the stable modification was the lower melting one. At the request of Professor Bancroft I have studied this system with the results here recorded.

Benzaldoxime exists in two modifications. The stable α modification melts at 34°–35°, and is capable of supercooling to a very remarkable degree without crystallizing. To it is usually assigned the "anti" formula according to the views proposed by Hantzsch and Werner. The instable β or "syn" modification melts at about 130° if the heating be sufficiently rapid. On long standing, much more quickly at higher temperatures, it is converted into the α modification. It does not display the phenomena of supercooling to anything like the same extent as does the α modification. α-Benzaldoxime was prepared according to the directions of Beckmann.[4] It was obtained as a heavy

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[1] Jour. Phys. Chem. 2, 159 (1898).

[2] Ibid. 2, 376 (1898).

[3] Ibid. 2, 364 (1898).

[4] Ber. chem. Ges. Berlin, 23, 1684 (1890).

oil, practically colorless. It was carefully dried over calcium chlorid, decanted and distilled under diminished pressure. During this operation I always found that some decomposition took place, so the material was further purified by crystallizing from ligroin (boiling between 50° and 70°). The product was then a clear, colorless oil at ordinary temperature, containing some crystals, which, on standing, gradually all solidified to large six-sided plates, perfectly colorless. These plates carefully freed from adhering mother liquid, melted sharply at 34°-35°. When melted even in comparatively large masses in test-tubes it most readily supercooled. Unless crystals were added the melt could be cooled to $-10°$ C without solidifying even when stirred vigorously. It was hoped from this fact that the equilibrium curve PX, Fig. 1, for the α and β modifications could be realized below the temperatures of the stable triple point of the system. This was undoubtedly accomplished. But the nature of the curve, as will presently be seen, deprived this phenomenon of any great interest in the case under investigation. The data for this equilibrium curve PX was obtained in the manner I have previously described.[1]

A stout test-tube was fitted with a rubber stopper carrying the thermometer, and sufficient material was introduced to cover well when melted the bulb of the thermometer. It was deemed desirable to have the stopper fit closely, as the benzaldoxime is measurably hygroscopic at ordinary temperatures. When the material had remained at the temperature and for the time desired, it was quickly brought to a temperature slightly below that at which it was expected it would solidify, a few crystals of the material would be introduced and the whole stirred vigorously. The thermometer would rise, fairly rapidly, and then remain stationary for a considerable length of time, while the material was becoming a more or less thick slush. This reading was taken as the true temperature of solidification. Great cooling and considerable time was required to bring the entire mass to a solid condition. Preliminary experiments showed that a con-

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[1] Jour. Phys. Chem. 2, 376 (1898).

siderable error was introduced into the reading of the temperature of solidification, depending on the amount of supercooling, and care was therefore taken to have it always as small as practicable. The results of the first series of determinations are here tabulated.

In the first column are given the temperature at which the substance was held until equilibrium was reached; in the second, the time; in the third, the temperature to which it was supercooled; and finally the temperatures at which solidification took place.

Initial temp	Time at initial temp	Temp of supercooling	F. Pt
18.5°	42.00 hrs	18.5°	26.5°
43.0	4.00	18.0	26.5
1.5	15.00	18.0	26.1
1.5	0.85	21.0	26.7
1.0	0.50	25.5	27.4
—2.0	0.75	26.3	27.7
—8.0	1.00	19.0	26.7
—7.0	1.50	24.5	27.1
21.5	15.00	26.0	27.6
21.7	72.00	26.0	27.7
60.0	1.00	23.5	27.3
60.0	0.35	26.6	27.7
110.0	1.00	24.5	26.4
102.0	1.60	27.0	27.2

With some freshly prepared material and working very carefully at various temperatures it was determined that the "natural" melting-point of the system was approximately 27.7° C. The *equilibrium concentration between the α and β modifications is independent of the temperature*, which Carveth found to be the case for acetaldoxime.[1] The curve PX is a straight line parallel to the temperature ordinate.

β benzaldoxime was prepared in the usual way. The α modification was suspended in ether, and dry hydrochloric acid passed in until the whole was thoroughly saturated and then allowed

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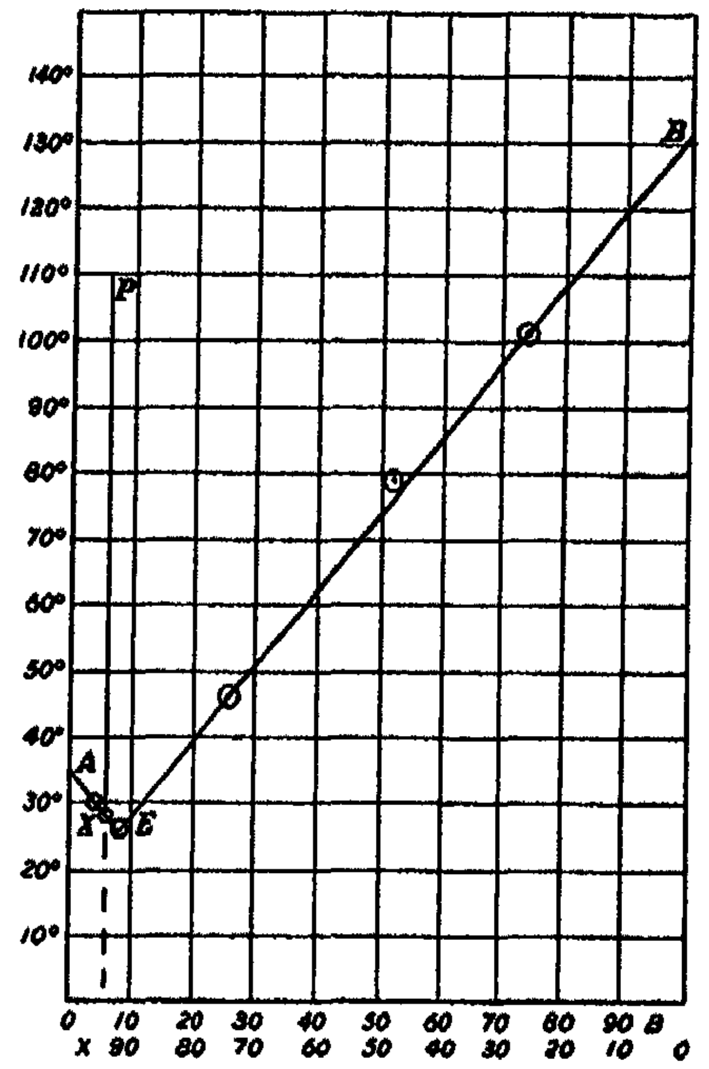
[1] Jour. Phys. Chem. 2, 162 (1898).

to stand for a short while. The β benzaldoxime hydrochlorid which separated was then added to a thoroughly cooled solution of sodium carbonate. It was found desirable to have crushed ice in the alkaline solution and to shake well after the addition of each portion of the oximehydrochlorid. The β benzaldoxime which separated as a pulpy solid was extracted with ether, and the solution evaporated on large watch-glasses. The residue was recrystallized from chloroform or benzene. Specimens of the β product when first prepared were found to melt at 132° apparently when very rapidly heated, but it is not certain that the melting-point is as high as this; it is probably nearer 130°.

A portion of the β product was arranged in a test-tube with a thermometer as described above for the α compound, and melted. It solidified at about 112°. Again heated up it melted near 114° and on cooling solidified at about 95°. This process was continued; melting at about 98°, solidified at 74°, melting at 76° solidified at 56°. At the lower temperatures the rate of inversion appeared to decrease rapidly, so the temperature was carried far beyond the melting-point and held for some time before cooling. The freezing-point continued to fall until about 26°. The β modification does not show the phenomena attendant on supercooling to anything like the same extent as does the α variety. But the amount of the α variety was so great in these lower melting mixtures that the readings were made with considerable difficulty. Theoretically it should be possible to carry the freezing-point down to the eutectic point and then have it rise again to the stable triple point of the system. I cannot definitely state that this was accomplished. By observing the temperature at which mixtures of the two modifications began to melt, it appeared that the eutectic point was 25°–26°. A closer determination was not possible. Pure specimens of both modifications were prepared and definite mixtures made up with approximate accuracy. They were heated rapidly and the melting-point observed. In each case as soon as all the material was melted it was at once cooled and the freezing-point noted, to check the reading. The determination of these points was attended with considerable difficulty, and in several cases where the observed melting-point and freezing-point differed widely, the readings were entirely abandoned as too doubtful to have any value. The figures given in the following table are believed to be approximately correct.

Grams α	Grams β	Percent α	Freezing-point
0.11	0.31	26.2	101°
0.31	0.32	49.2	79
1.15	0.41	73.7	46
1.55	0.14	91.7	26.2
1.72	0.09	95.0	28.6
2.65	0.11	96.0	30.0

The significance of these figures is better seen in the accompanying diagram. It would appear that the curves EA and EB are straight lines. The eutectic point and the stable triple



point of the system lie very close together. And this fact together with the difficulty in obtaining true temperature readings on account of the error introduced by supercooling (in this case a large one) made the exact determination of the point E impossible.

Attempts were made to obtain the β modification from the α variety. To a somewhat supercooled melt of the α product, crystals of the β modification were added, but on standing they gradually disappeared. Crystals of the β variety dropped into solutions of the α product in no case continued to grow, but always disappeared. But it should be noted, that the α product did not itself readily separate from solutions as a solid. Usually the solvent would evaporate leaving an oil, which would gradually solidify into crystals of the α modification. Mixtures of the two modifications dissolved in chloroform or ether would deposit mixtures of the two modifications if evaporated rapidly. The β modification is much the less soluble in benzene, and this fact has been used for its separation.

By reference to Fig. 1 it will be observed that the angle made by EA and the temperature ordinate is approximately the same as that made by EB with the temperature ordinate. In other words the lowering of the freezing-point of the α modification by the presence of a given percentage of the β isomer will be the same as the lowering of the freezing-point of the β form by the addition of the same percentage of the α crystals. The freezing-point constant k is thus the same for the two isomers. To have this true the heats of fusion of the two forms must stand in the ratio of the square of fusion temperatures expressed in the absolute scale. It seemed worth while to calculate these heats of fusion. The form of the van 't Hoff-Raoult formula generally used for this purpose is $\rho = \frac{2T^2}{\Delta T} \cdot \frac{n}{N}$, but while this is fairly satisfactory for dilute solutions in which n is very small relatively to N, it could not be expected to apply in the case under consideration. I have therefore used the other form of the formula $\rho = \frac{2T^2}{\Delta T} \cdot \frac{n}{N + n}$. Introducing the very plausible assumption that the two modifications of benzaldoxime are perfectly normal both in the vapor and in the liquid, this formula simplifies to $\rho_1 = \frac{2T^2}{\Delta T} \cdot \frac{g_1}{g_1 + g_2}$, where g_1 is the amount in grams of the form that crystallizes, and g_2 the amount in grams of the form that does not separate. The results for ρ_α and ρ_β as calculated by this formula are given below. The melting-point of the α modification is taken as 308° (35°C) and that of the β crystals as 404° (131° C). It is to be remembered that the temperatures given are only approximately correct, and also that the data refer to concentrated solutions.

g_α	g_β	ΔT	ρ_α	g_β	g_α	ΔT	ρ_β
1.55	0.14	8.8°	8.93	0.31	0.11	30.0°	14.3
1.75	0.09	6.4	7.25	0.32	0.31	52.0	15.5
2.65	0.11	5.0	7.55	0.41	1.15	85.0	14.2

In view of the difficulties of measurement, the agreement between the values of the heat of fusion as calculated from different temperatures is certainly interesting. If we take 14.3 as the heat of fusion for the β modification, the heat of fusion of the α form would be 8.3 if calculated on the assumption that the molecular depression of the freezing-point is the same in the two cases. The value 8.3 lies within the extreme values found for ρ_α, though it would have been more striking had it come out a little lower. While it is unsafe to generalize from one instance, the results here given make it an interesting question whether all pairs of stereoisomers, corresponding to the benzaldoximes have heats of fusion connected by the same relation.

The general results of this investigation may be summed up as follows:

1. Benzaldoxime exists in two modifications in the liquid phase as well as in the solid phase.
2. The stable modification has the lower melting-point.
3. The equilibrium composition in the liquid phase is independent of the temperature.

4. The stable triple point or "natural freezing-point" of the system is 27.7° C.

5. The composition of the mixture at the stable triple point is about 94 percent of the α modification.

6. The temperature of the eutectic point is between 25° and 26° C.

7. The composition at the eutecticpoint is about 91 percent of the α modification.

8. The curves EA and EB are apparently straight lines.

9. The molecular depression of the freezing-point is practically the same for the two isomers.

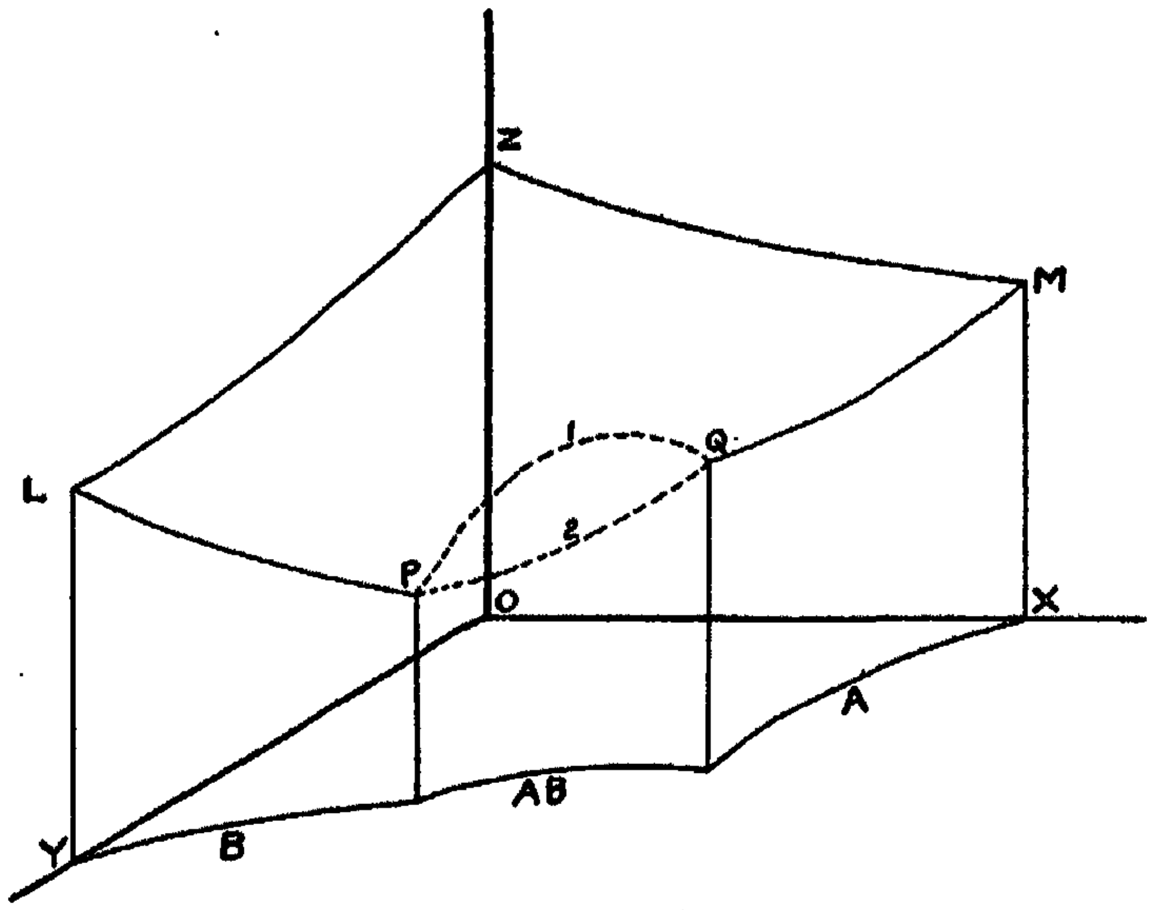
10. The course of the freezing-point curves can be represented with approximate accuracy by the van 't Hoff–Raoult formula when $n/N + n$ is substituted for n/N.

Cornell University, June, 1898

THE ISOTHERMAL PRESSURE-SURFACE IN THE CASE OF TWO SINGLE SALTS AND ONE DOUBLE SALT

BY F. G. DONNAN

The phenomena which occur on isothermal variation of the system whose components are water, A, B, where A and B are two single salts with a common ion, have been already investigated, and the discussion of the phenomena from the point of view of the solubility relations has been given by van 't Hoff[1] and by Bancroft[2] in easily accessible form. It may nevertheless be of some interest to reconsider the phenomena purely from the point of view of the pressure relations.



In the figure the concentration with respect to A is meas-

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[1] Vorlesungen über Bildung und Spaltung von Doppelsalzen, Leipzig, 1897.

[2] The Phase Rule, Ithaca, N. Y., 1897.

ured along OX, and with respect to B along OY. Vapour-pressures are measured along OZ. The curves in the *xy*-plane represent the usual typical solubility relations for the double salt AB and the two single salts A, B. OZ represents the vapour-pressure of pure water at the temperature in question, and the curves ZL, ZM are the vapour-pressure curves for pure solutions of B and A respectively, while the curves LP, PQ, QM are the saturation pressure-curves for B, AB and A respectively, that is to say, they give the pressures of solutions which are in equilibrium with B, AB, and A respectively. The general trend of the curves ZL, ZM, LP, and QM is evident from the law of lowering of vapour-pressure with increasing concentration and from the theorem that the vapour-pressure of a saturated solution is in general lowered by saturation with respect to a new substance.

One of the most important isothermal variations is the removal of water by evaporation. We shall consider in this case the motion of the point which represents at any given moment the vapour-pressure of the solution. For unsaturated solutions, i. e. for points lying on the pressure-surface, since the relative amounts of A and B cannot change, the motion is along a curve determined by the intersection of the pressure-surface with a vertical plane through OZ and the starting-point. On reaching a saturation-curve, the corresponding salt begins to precipitate and the motion now possesses only one degree of freedom, i. e. along the border curve. The direction is determined by the fact that the pressure cannot rise on isothermal evaporation of a system in equilibrium. On arriving at the point of intersection of two saturation pressure-curves, the next substance begins to precipitate. We have now two cases to consider, according as the curves in the neighborhood of the point of intersection lie entirely above or partly above and below this point. Supposing the curve PQ to have the form (2), then the former case occurs at P and the latter at Q. It is evident that on reaching such a point as P it cannot be passed, as any such motion would involve an increase of vapour-pressure. Hence the solution must dry up completely at P leaving a mixture of B and AB. A point of this sort has been termed an *end-point of crystallization.*[1]

Consider now the point Q. On arriving at Q, AB begins to precipitate. If we imagine any solid A present removed, the motion will be, from what has been said, along PQ in the direction Q2P. The solution does not therefore deposit A on further evaporation, and if the solid A be replaced the only effect will be to detain the point at Q until all the solid A has disappeared, after which the point will proceed down Q2P. It is evident that none of the saturation-curves LP, PQ, QM can possess a minimum, for this would involve the stoppage of the tracing-point on isothermal evaporation at these minima, which leads to obvious absurdities. The curve PQ may however under certain conditions possess a maximum point as in P1Q. Let us consider what the existence of such a maximum would involve. It could evidently be reached by isothermal evaporation only from the pressure-surface. Since on reaching points on PQ infinitely near it either to the right or left, the subsequent motion would be either towards P or Q, it is clear that on arriving exactly at the maximum point on PQ the tracing-point would remain stationary here on further isothermal evaporation, and the solution would evaporate down to pure double salt. This shows then that the curve PQ possesses a maximum for temperatures outside the *transformation-interval* of the double salt and in the region of complete stability in contact with water. The maximum on PQ corresponds in fact to a pure saturated solution of double salt, and the straight line $\frac{x}{y} = \frac{a}{b}$ in the xy-plane (where $\frac{a}{b}$ = ratio of components A,B in AB) cuts the solubility curve for AB in a point vertically under this maximum point. For temperatures within the transformation-interval the curve PQ will possess the form P2Q. If we imagine supersaturation with respect to one of the single salts

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[1] Van 't Hoff und Meyerhoffer, Untersuchungen über die Bildungsverhältnisse der Oceanischen Salzablagerungen, (V). Sitzungsber. Akad. Wiss. Berlin, XLVI, 1897.

to occur, we may suppose P2Q continued, and since in this case also the point corresponding to saturation with respect to pure double salt will be a maximum-point, it follows that if as in the figure the pressure at Q exceed that at P, then the line $\frac{x}{y} = \frac{a}{b}$ cuts the solubility curve for A. It likewise follows in this case that at the temperatures separating the region of complete stability and the transformation-interval, the curve PQ will touch a horizontal plane through Q.

With respect to the surface ZLPQM all that can be said is that for temperatures in the region of complete stability of the double salt it would appear to possess a saddle-shaped form.

The foregoing considerations show that the phenomena of isothermal evaporation are rendered immediately evident by means of the vapour-pressure surface, and can be fairly well considered by means of it alone.

THE MOLECULAR WEIGHT OF ORTHORHOMBIC, MONOCLINIC, AND PLASTIC SULPHUR IN NAPHTHALENE AND PHOSPHORUS, BY THE FREEZING-POINT METHOD

BY SAMUEL D. GLOSS

The many different investigations on the molecular weight of sulphur seem still to leave some room for question as to the values indicated for the different varieties. Thus, in the papers of Biltz,[1] Ramsay,[2] Biltz and Meyer,[3] Beckmann,[4] J. Hertz,[5] Helff,[6] Paterno and Nasini,[7] Schall,[8] and Orndorff and Terrasse,[9] I find only two instances in which comparison has been made between the different kinds of sulphur. Orndorff and Terrasse conclude that orthorhombic and monoclinic sulphur have the same molecular weight since there is no difference in the results obtained by the boiling-point method in carbon disulphide (B. P. 46°) and in benzene (B. P. 79.6°) *although only the ortho*rhombic variety crystallizes from the first and the monoclinic from the second.

Biltz also finds no difference between the orthorhombic and plastic varieties by the vapor-density method. It would seem more likely that differences might be discovered by methods ap-

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[1] Zeit. phys. Chem. 2, 920 (1888).
[2] Ibid. 3, 67 (1889).
[3] Ibid. 4, 266 (1889).
[4] Ibid. 5, 80 (1890).
[5] Ibid. 6, 358 (1890).
[6] Ibid. 12, 196 (1893).
[7] Ber. chem. Ges. Berlin, 21, 2153.
[8] Ibid. 23, 1704.
[9] Am. Chem. Jour. 18, 173 (1896).

plicable at low temperatures than by those involving a high temperature, as in all the vapor-density determinations. Accordingly in the following experiments the attempt has been made to compare the values obtained for the several varieties in some solvent which has a low freezing-point, and also dissolves large quantities of sulphur. Naphthalene was first tried, (F. P. 79.4°), and then phosphorus (F. P. 44.2°).

The orthorhombic sulphur was prepared by crystallization from carbon disulphide and the monoclinic from fusion. The plastic was made from the crystallized orthorhombic in the usual manner, by turning the melted sulphur into cold water. This was dried by absorbent paper, weighed and quickly used. The naphthalene, the commercial article, was simply melted and filtered.

The mixtures were melted in a large test-tube immersed in a beaker of water. They were allowed to cool slowly, with constant stirring, until solidification began, accompanied by rise of temperature, and the maximum reading of the thermometer was taken with the aid of a magnifying glass.

In the observations with naphthalene, a Beckmann thermometer was used, graduated to a hundredth of a degree. In the series with phosphorus a thermometer graduated to a tenth of a degree was used. An ordinary thermometer gave the temperature of the water, which was kept constantly stirred.

In naphthalene, orthorhombic and monoclinic sulphur dissolve readily, although the latter seems to leave a slight residue. Plastic sulphur dissolves very slowly. The precipitated and sublimed varieties dissolve so incompletely, except above 100°, that they were not used.

The freezing-point of naphthalene was determined by thirteen readings on the same sample, which gave results from 79.250° to 78.8°, the average is 79°.

Several readings were taken in each determination as shown in the following table:

	No. 4	No. 5	No. 6	No. 8
	1.60	1.34	1.58	1.38
	1.6125	1.34	1.59	1.39
	1.61	1.34	1.60	1.41
	1.62	1.3475		1.42
	1.605	1.3475		1.415
	1.64	1.3375		1.400
		1.355		1.425
		1.345		
		1.34		
Mean	1.616°	1.344°	1.59°	1.406°

The maximum variations in these four series are: 0.055°, 0.0175°, 0.02° and 0.045° respectively. A variation of 0.01° in the lowering for the solution of maximum concentration in this series, namely 2 g in 100 g of solvent makes a difference of 6.5 in the molecular weight. The repetitions of the freezing-point, on the same sample, also show that the solution does not change with any regularity by repeated heating and cooling. The constant for naphthalene, 69.4, is calculated by van 't Hoff's formula.

The molecular weights obtained in these four experiments, see Table No. 1, are 287 and 271 for the orthorhombic, 283 for the plastic, and 292 for the monoclinic. These results are practically identical for the three varieties of sulphur at concentrations of only one and two percent.

The values of Orndorff and Terrasse for concentrations between one percent and two and four-tenths percent, lie between 233 and 251. Hertz's value for two and four-tenths percent is 262.

In as much as plastic and monoclinic sulphur change rapidly at about 100°, it is possible that the change may take place before the substances go into solution at the freezing-point of naphthalene, (79°).

It was thought that the comparison might be more decisive in a solvent of lower freezing-point, and so phosphorus was next tried, (F. P. 44°). In these experiments the fusions were made under water instead of in an atmosphere of carbon dioxide, as in Helff's experiments. In weighing the sample of phosphorus it was first dried by absorbent paper, and then weighed in a beaker of water, the weight of which had been previously determined. On repeated heating and cooling of the mixture of phosphorus and sulphur, a white milky color is given to the water above it, evidently due to the separation of sulphur, and an evolution of hydrogen sulphide takes place. That neither of these reactions takes place rapidly enough to interfere appreciably with the results was shown by repetition on the same sample with a considerable interval of time. In calculating the results with sulphur in phosphorus, the constant used for phosphorus is the one given by van 't Hoff's formula, namely 384.

Orthorhombic and monoclinic sulphur are readily soluble in phosphorus. Plastic is slowly soluble and seems to leave a slight undissolved residue, like precipitated sulphur.

In this series the plan was adopted of dissolving first eleven percent of sulphur, which brought the freezing-point down to about 27°, when two portions of three percent each were added at this low temperature.

In the cases of monoclinic and plastic sulphur, a sample of the sulphur was kept in a tube along side of the one containing the mixture. It was thus seen that the sample did not change during the interval and at the temperature of the solution. Care was taken that the temperature during solution should not rise more than four or five degrees above the freezing-point. The freezing-point of the phosphorus alone was 44.1°.

The eleven percent portions of orthorhombic and monoclinic sulphur give for the molecular weight the following values See Table II:

Orthorhombic	Monoclinic
255	255
258	261
264	265
262	260
259	
253	
260	
259 average	260 average

These results show no difference in the molecular weight of orthorhombic and monoclinic sulphur as indicated by the eleven percent portions dissolved in phosphorus.

The three percent additions give the following values:

First three percent additions:

Orthorhombic	Monoclinic	Plastic
330	311	329
300	339	
316	284	
320		
—	—	—
317	311	329

Second three percent additions:

Orthorhombic	Monoclinic
356	320
274	355
307	325
281	
—	—
305	333

The average of the first and second portions is, for orthorhombic 311, for monoclinic 322. The one plastic gives 329. These results with the three percent additions are higher than any of Helff's results. They cannot be interpreted as indicating any difference in the molecular weight of the three kinds of sulphur, even at so low a temperature as 20° to 25°.

TABLE I[1]

Experiment number	Grams of naphthalene	Grams of sulphur	Concentration. Grams in 100 of solvent	Freezing-point	Lowering in degrees	Specific lowering	Molecular weight
4	10.0024	0.0998	0.998	1.616	0.241	0.2415	287
5	10.0000	0.2001	2.000	1.344	0.513	0.2565	271
6	20.000	0.2180	1.090	1.590	0.267	0.2450	283
8	20.000	0.3788	1.894	1.406	0.451	0.2380	292

[1] Experiments No. 4 and No. 5 are with orthorhombic sulphur.
" No. 6 is with plastic sulphur.
" No. 8 is with monoclinic sulphur.

TABLE II

Experiment number		Concentration. Grams in 100 of solvent	Freezing-point	Lowering in degrees	Specific lowering	Molecular weight
19	Orthorhombic sulphur	11.05	27.45	16.65	1.505	255
20	" "	11.06	27.60	16.50	1.490	258
21	" "	11.05	28.00	16.10	1.457	264
22	" "	11.00	27.95	16.15	1.468	262
23	" "	11.00	27.85	16.25	1.480	259
24	" "	11.00	27.35	16.75	1.520	253
27	" "	11.00	27.85	16.25	1.477	260
18	Monoclinic sulphur	11.60	27.45	16.65	1.505	255
25	" "	11.00	27.90	16.20	1.470	261
26	" "	11.00	27.70	16.40	1.450	265
28	" "	11.00	27.80	16.30	1.480	260
22	Orthorhombic sulphur	3.007	24.45	3.50	1.164	330
23	" "	3.00	24.00	3.85	1.280	300
24	" "	3.00	23.70	3.65	1.217	316
27	" "	3.00	24.25	3.60	1.200	320
25	Monoclinic sulphur	3.00	24.20	3.70	1.233	311
26	" "	3.00	24.30	3.40	1.133	339
28	" "	3.00	23.75	4.05	1.350	284
29	Plastic sulphur	3.00	24.30	3.50	1.166	329
22	Orthorhombic sulphur	3.00	21.20	3.25	1.080	356
23	" "	3.00	19.80	4.20	1.400	274
24	" "	3.00	19.95	3.75	1.250	307
27	" "	3.00	20.15	4.10	1.366	281
25	Monoclinic sulphur	3.00	20.60	3.60	1.200	320
26	" "	3.00	21.05	3.25	1.083	355
28	" "	3.00	20.20	3.55	1.183	325

The conclusion from this entire series of experiments is, that no difference is established between the molecular weights of orthorhombic, monoclinic, and plastic sulphur dissolved in naphthalene or in phosphorus.

This work was done in the chemical laboratory of Northwestern University.

Evanston, Ill., May 5, 1898.

THE VARIANCE OF THE VOLTAIC CELL

BY WILDER D. BANCROFT

Nernst has attempted to apply the phase rule to the voltaic cell.[1] After recalling the fact that "complete heterogeneous equilibrium can exist only when the number of phases exceeds the number of components by one" he proceeds in the following manner: "We can easily convince ourselves, by an example that the same rule holds good for a galvanic element. If we consider the Clark cell, for instance,

$$\mathrm{Hg}\,|\underset{\text{solid}}{\mathrm{Hg_2SO_4}}|\underset{\text{solution}}{\mathrm{H_2O} + x\mathrm{Hg_2SO_4} + y\mathrm{ZnSO_4}}|\underset{\text{solid}}{\mathrm{ZnSO_4}}|\,\mathrm{Zn}$$

we distinguish five different phases; the two metals, the two sulfates, and the saturated solution containing x and y parts of the two salts respectively. To construct this system we must have at least four components, Hg, Zn, H_2O, SO_4, and we therefore conclude that we have here a complete chemical equilibrium. Now we know, as a matter of fact, that for any definite temperature there is a corresponding definite electromotive force and that the phases are in equilibrium only when we introduce an opposing electromotive force of the same value. On the other hand, if the opposed electromotive force is greater or less than that of the cell for that temperature, the reaction, expressed by the equation $Zn + Hg_2SO_4 \rightleftarrows 2Hg + ZnSO_4$, runs to an end, i. e. until one of the phases is used up. During this reaction no phase changes in composition and we thus have all the criteria of a complete heterogeneous equilibrium."

This is interesting, instructive, and incorrect. When there is no vapor phase, the electromotive force of the cell in question varies both with the temperature and with the pressure. If

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[1] Theor. Chem. 560.

there is a vapor phase containing water alone and no air, the number of phases becomes six and Nernst's deduction leads to the untenable conclusion that, under these circumstances, the electromotive force is independent of the temperature. It is thus clear that Nernst's application of the phase rule is faulty.

The matter is stated correctly by Gibbs, though not in a very definite form.[1] In addition to the ordinary conditions of equilibrium, there is also the electromotive force. The variables are the n components, pressure, temperature, and electromotive force. It will therefore take $n + 3$ phases to constitute an invariant system. In the Clark cell under pressure, there are four components and five phases. Since seven phases constitute an invariant system in this particular case, we conclude that we are considering a divariant system. This is in accord with the experimental results because the electromotive force is not determined until the pressure and temperature are fixed. We can apply the rule that an electromotive force is to be considered as an added degree of freedom to all cells; but there are a great many cases in which other conditions must be introduced. For instance the cell $\mathrm{Zn}\,|\,\mathrm{ZnSO_4}\,|\,\mathrm{CuSO_4}\,|\,\mathrm{Cu}$ is not in equilibrium at all unless we consider the two solutions as separated by a membrane permitting diffusion only under electrical stress. This introduces another degree of freedom.[2] For the Daniell cell the number of phases necessary for an invariant system is $n + 4$. This way of looking at the matter necessitates considering the number of hypothetical walls and deciding whether each involves a limiting condition or a degree of freedom. If each case has to be considered by itself there is no advantage in applying the phase rule. It will therefore be advisable to attack the subject in a slightly different way. Let us consider the cell[3] $\mathrm{Zn}\,|\,\mathrm{ZnSO_4}\,\mathit{Hg_2SO_4}\,|\,\mathrm{Hg}$ as though it were divided into three distinct and isolated systems marked off by the vertical lines. As long as these subdivisions are kept entirely distinct the variance of the whole system will be the sum of the variances of the three

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[1] Trans. Conn. Acad. 3, 502 (1878).

[2] Cf. Trevor. Jour. Phys. Chem. 1, 349 (1897).

[3] Italics are used to denote solid salt.

subdivisions. They can be kept distinct by introducing an opposing electromotive force, and the variance of the system will therefore be the sum of the variances of the subdivisions or

$$V = \Sigma v. \qquad \text{(I)}$$

If we consider the cell as under uniform pressure and temperature, we reduce the variance by the number of independently variable pressures that are thereby eliminated. If m be the number of subdivisions in the system under consideration, the number of independently variable pressures that are eliminated is $m - 1$, since the one remaining uniform pressure is independently variable. The number of independently variable temperatures that are eliminated is also $m - 1$, so the variance of the whole system is

$$V = \Sigma v - 2(m - 1).$$

This may be written in a simpler form

$$V = \Sigma(v - 2) + 2. \qquad \text{(II)}$$

The variance of the whole system is equal to the sum of the variances of the subdivisions leaving out the pressure and temperature, plus the pressure and temperature of the system.

In applying this formula to different types of cells it will be best to begin with uniform pressure and temperature, and no vapor phase—

1. $\mathrm{Zn}|\mathrm{ZnSO_4}\mathit{Hg_2SO_4}|\mathrm{Hg} \quad V = 0 + 1 + 0 + 2 = 3.$

Since the electromotive force varies with the concentration, pressure and temperature, this system is trivariant. It should be noticed that adding copper wire to close the circuit increases the number of components by one, but also increases the number of phases by one, thus leaving the variance unchanged.

2. $\mathrm{Zn}|\mathrm{ZnSO_4}|\mathrm{CuSO_4}|\mathrm{Cu} \quad V = 0 + 1 + 1 + 0 + 2 = 4.$

The independent variables are the concentrations of the two solutions, the pressure and the temperature. If both solutions are saturated, the variance drops to two.

3. $\mathrm{Zn}|\mathrm{ZnSO_4}|\mathrm{ZnSO_4}|\mathrm{Zn} \quad V = 0 + 1 + 1 + 0 + 2 = 4.$

The independent variables are the concentrations of the two solutions, the pressure and temperature. This differs from the preceding case in that the cell becomes symmetrical if the two solutions have the same concentration.

4. $\mathrm{Hg}\,|\,Hg_2Cl_2\mathrm{KCl}\,AgCl\,|\,\mathrm{Ag}$ $V = 0 + 1 + 0 + 2 = 3.$

The electromotive force is determined when the concentration, pressure and temperature are fixed.

5. $\mathrm{Hg}\,|\,Hg_2Cl_2\mathrm{KCl}\,|\,\mathrm{KCl}\,AgCl\,|\,\mathrm{Ag}$ $V = 0 + 1 + 1 + 0 + 2 = 4.$

This differs from the preceding case in that there are two solutions with independently variable compositions instead of one.

6. $\mathrm{Hg}\,|\,Hg_2Cl_2\mathrm{KCl}\,|\,\mathrm{KCl}\,Hg_2Cl_2\,|\,\mathrm{Hg}$ $V = 0 + 1 + 1 + 0 + 2 = 4.$

The independent variables are the two concentrations, the pressure and the temperature.

7. $\mathrm{Hg}\,|\,Hg_2Cl_2\mathrm{KCl}\,|\,\mathrm{NaCl}\,Hg_2Cl_2\,|\,\mathrm{Hg}$ $V = 0 + 1 + 1 + 0 + 2 = 4.$

As long as there is only potassium chlorid in one solution and only sodium chlorid in the other, the variance of the system is four. If both solutions contain both salts in independently variable proportions, the variance is six.

8. $\mathrm{ZnHg}\,|\,\mathrm{ZnSO_4}\,Hg_2SO_4\,|\,\mathrm{Hg}$ $V = 1 + 1 + 0 + 2 = 4.$

The independent variables are the compositions of the amalgam and solution phases, the pressure and the temperature, giving a variance of four.

9. $\mathrm{ZnHg}\,|\,\mathrm{ZnSO_4}\,|\,\mathrm{ZnHg}$ $V = 1 + 1 + 1 + 2 = 5.$

All three phases may vary in composition.

10. $\mathrm{AuHg}\,|\,\mathrm{Hg_2(NO_3)_2}\,|\,\mathrm{AuHg}$ $V = 1 + 1 + 1 + 2 = 5.$

This differs from the preceding case only in the relative amounts of the two components in the electrodes.

11. $\mathrm{Pt_H}\,|\,\mathrm{HCl}\,Hg_2Cl_2\,|\,\mathrm{Hg}$ $V = 1 + 1 + 0 + 2 = 4.$

The concentration of the hydrogen can change and also the concentration of the acid. Since the hydrogen dissolves to a certain extent in the water, it would be equally possible to treat this case as if it were pure platinum, water containing hydrogen, hydrochloric acid and mercurous chlorid, with mercury as the other electrode. Since the concentration of the hydrogen in the platinum is determined by the concentration of the hydrogen in the solution and vice-versa, it is not proper to treat the concentrations as though independently variable. From this point of view we should write the formula $V = 0 + 2 + 0 + 2 = 4$, which of course comes to the same thing. For the gas cells it seems more natural to treat the platinum as containing hydrogen. With reduction and oxidation cells, it is more desirable to consider the aqueous solution and not to speak of a chlorate or a sulfite electrode.

12. $Pt_{Cl} | HCl\,\mathit{Hg_2Cl_2} | Hg \quad V = 1 + 1 + 0 + 2 = 4.$

This case is essentially the same as the preceding one.

13. $Pt_H | H_2SO_4 | CuSO_4 | Cu \quad V = 1 + 1 + 1 + 0 + 2 = 5.$

The independent variables are the pressure and the temperature, and the concentrations of hydrogen, sulfuric acid and copper sulfate.

14. $Pt_H | HCl | HCl | Pt_H \quad V = 1 + 1 + 1 + 1 + 2 = 6.$

Theoretically all four phases can vary in composition. Practically the concentration of hydrogen at the two electrodes would almost always be the same. If we introduce this limiting condition explicitly the variance becomes five.

15. $ZnHg | ZnSO_4 | H_2SO_4 | Pt_H \quad V = 1 + 1 + 1 + 1 + 2 = 6.$

Here the compositions of all four phases may vary independently.

16. $Pt_H | HCl | Pt_{Cl} \quad V = 1 + 1 + 1 + 2 = 5.$

The independent variables are the three concentrations, the pressure and the temperature.

17. $Pt_H | H_2SO_4 | Pt_O \quad V = 1 + 1 + 1 + 2 = 5.$

This does not differ essentially from the preceding case.

18. $Pt | R | O | Pt \quad V = 0 + 1 + 1 + 0 + 2 = 4.$

Here R denotes a reducing agent and O an oxidizing agent.

19. $Zn | ZnSO_4\mathit{Hg_2SO_4} | Hg | \mathit{Hg_2SO_4}ZnSO_4 | Zn$

$V = 0 + 1 + 0 + 1 + 0 + 2 = 4.$

In this case of a reversed cell, the two concentrations, the pressure and the temperature are the independent variables.

20. $\mathrm{Pt_H} \mid \mathrm{HCl} \mid Hg_2Cl_2 \mid \mathrm{Hg} \mid Hg_2Cl_2\mathrm{HCl} \mid \mathrm{Pt_H}$

$$V = 1 + 1 + 0 + 1 + 1 + 2 = 6.$$

As in No. 14 the variance is decreased by one in case we add the limiting condition that the concentration of hydrogen shall be the same in the two platinum electrodes.

If we wish to introduce vapor phases we must drop the condition in regard to uniform pressure because we cannot have zinc and zinc vapor in equilibrium under the same pressure as zinc sulfate solution and water vapor. For each new pressure we have an increased variance, but each new vapor phase decreases the variance. Since we have already counted the pressure once in determining the variance for the conditions of uniform pressure and temperature with no vapor phase, the number of new pressures will be one less than the number of subdivisions or $m - 1$. As we can add one vapor phase for each subdivision, the variance of the system with uniform temperature and with a vapor phase to each subdivision will be one less than in the series with uniform pressure and temperature, but no vapor phase. The formula for this case would be written:

$$V = \Sigma(v - 2) + \Sigma p + t,$$

or more simply

$$V = \Sigma(v - 1) + t. \qquad \text{(III)}$$

Instead of having each subdivision under a different pressure, we can imagine all brought to the same pressure by introducing air or an indifferent gas into the vapor phase of each subdivision. If we ignore the dissolving of the air in the water, this new system will have the same variance as before so long as all the pressures are kept constant. In other words, on the assumption that no air dissolves in the solutions, we may calculate the variance of a voltaic cell in air by the formula $V = \Sigma(v - 1) + t$, provided the pressure be considered as fixed and the air be not counted as a component. Under these circumstances we have, for the Clark cell, $V = 0 + 0 + 0 + 1 = 1$.

Having thus shown the way in which the variance is to be determined, the question at once arises as to the change of the electromotive force with the concentration, the pressure and the temperature. We can predict these variations by means of the theorem of Le Chatelier. If we pass a current through the cell in a given direction, there will be a tendency to form the system with a higher counter electromotive force. An analysis of the solutions before and after electrolysis will answer the question as to the relation between change of electromotive force and change of concentration. In the cell $\mathrm{Zn}|\mathrm{ZnSO_4}\,\mathit{Hg_2SO_4}|\mathrm{Hg}$, passing the current through the system from left to right increases the concentration of the zinc sulfate. Therefore diluting the zinc sulfate solution increases the electromotive force of the cell, as is known to be the case experimentally. In the combination $\mathrm{Zn}|\mathrm{ZnSO_4}|\mathrm{CuSO_4}|\mathrm{Cu}$, passage of the current through the system from left to right increases the concentration of the zinc sulfate and decreases that of the copper sulfate. Therefore the electromotive force of this combination is increased by diluting the zinc sulfate solution and concentrating the copper sulfate solution, a result that has long since been obtained experimentally. Similar reasoning shows that the electromotive force of the cell $\mathrm{Zn}|\mathrm{ZnSO_4}|\mathrm{ZnSO_4}|\mathrm{Zn}$ will be raised by diluting the anode solution and concentrating the cathode solution. The combination $\mathrm{Hg}|\mathit{Hg_2Cl_2}\mathrm{KCl}\mathit{AgCl}|\mathrm{Ag}$ presents certain difficulties. At first glance one would be inclined to conclude that, since the passage of the current does not change the concentration of the potassium chlorid, the electromotive force is independent of the amount of potassium chlorid in solution. While this is approximately true for this particular combination, it is not true for all cells of this type. The experiments of Goodwin[1] have shown that this is not even true approximately for combinations with thallium as one of the electrodes. No one would claim that addition of potassium sulfate to a Clark cell would leave the electromotive force unchanged. It is, therefore, clear that the theorem of Le Chatelier has been misapplied.

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[1] Zeit. phys. Chem. 13, 673 (1894).

The error is in reasoning from a negative result. The passage of the current through the cell does not change the concentration of the potassium chlorid and the only justifiable conclusion is that, under these circumstances, we can make no prediction as to the relation between electromotive force and concentration. The theorem of Le Chatelier applies only to cases in which either of the variables may be taken as the independent variable. Another instance will show this perhaps better. In the Clark cell with a saturated zinc sulfate solution, the passage of the current does not change the concentration; but we have already seen that the electromotive force of the cell $Zn | ZnSO_4 Hg_2SO_4 | Hg$ does vary with the concentration of the zinc sulfate. It is possible, however, to state the problem a little more definitely. Increasing the concentration of the zinc sulfate decreases the potential difference between the zinc electrode and the solution. In the same way increasing the concentration of the mercurous chlorid or of the silver chlorid decreases the potential difference between the mercury or the silver electrode and the solution. If the change in the concentration of the potassium chlorid changes the solubilities of the mercurous chlorid and of the silver chlorid in the same sense and to the same extent, the electromotive force will be independent of the amount of potassium chlorid present, otherwise this will not be the case. It will be noticed that this is really only a way of rewriting Goodwin's argument[1] so as to make it a qualitative instead of a quantitative statement.

When it comes to the question of the potential difference between two solutions of the same electrolyte, the theorem of Le Chatelier enables us to predict qualitatively the effect of changing the concentration. We can get at this best by starting with a homogeneous unsaturated solution and noting the changes produced by the passage of the current. Let us suppose that the current passes through the solution from left to right. If the right-hand portion of the solution becomes more concentrated, the theorem of Le Chatelier enables us to predict

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[1] Zeit. phys. Chem. 13, 622 (1894).

that, with that particular electrolyte, there is a potential difference between two different solutions such that the current tends to pass from the more concentrated to the more dilute solution. If the left-hand portion of the solution becomes more concentrated we know that the natural potential difference is such that the current tends to pass from the more dilute to the more concentrated solution. Lastly, if no concentration change occurs we may predict that a difference of concentration involves no difference of electrical potential. Since we know from Hittorf's experiments that the change of concentration depends on the difference between the migration velocities of the cation and anion, it follows that the sign of this difference will determine the direction of the current, a result obtained years ago by Nernst.[1]

The problem is very similar when we have two different electrolytes at the same concentration. Let us start with a homogeneous solution containing potassium and sodium chlorids. If we pass the current through this solution from left to right we shall find experimentally that the ratio of sodium to potassium increases at the left-hand end of the solution. Applying the theorem of Le Chatelier we conclude that, after eliminating the question of concentration, there is a potential difference between potassium chlorid and sodium chlorid solutions such that a current tends to pass from the potassium chlorid to the sodium chlorid.[2]

If we start with a homogeneous solution containing the salts, sodium chlorid, sodium hydroxid, potassium chlorid and potassium hydroxid, we shall find experimentally on passing the current from left to right, that the solution tends to separate into two parts, the one at the left containing chiefly sodium hydroxid and the one at the right chiefly potassium chlorid. The theorem of Le Chatelier enables one to predict that in the system KCl | NaOH the current tends to pass through the solution from left to right when the concentrations of the two solutions are

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[1] Zeit. phys. Chem. 4, 137 (1889).

[2] Nernst. Ibid. 4, 165 (1889).

equivalent and that the potential difference between potassium chlorid and sodium hydroxid solutions is greater than that between sodium chlorid and potassium hydroxid solutions. If u_1 and v_1 are the migration velocities of the cation and anion for one salt, u_2 and v_2 the corresponding values for the other salt, it is clear that the direction of the current depends on the sign of the difference between $u_1 - v_1$ and $u_2 - v_2$. Equivalent to this is the statement that the direction of the current depends upon the sign of the difference between $u_1 + v_2$ and $u_2 + v_1$.[1]

Of course, this problem can also be attacked from the other end, provided we remember that the potential difference between two solutions become zero when the solutions become identical. If therefore we start with two solutions and pass the current from left to right we should conclude that the potential of the left-hand solution was higher than that of the right-hand solution in case the passage of the current made the two solutions more alike and we should draw the opposite conclusion if the passage of the current were to make the solutions less alike. If the electrolyte were hydrochloric acid and the left-hand solution were the more concentrated, we should find experimentally that, after electrolysis, the difference between the concentrations of the solutions was less than before. From this we should conclude that with hydrochloric acid the current tended to flow from the more concentrated to the more dilute solution. If we were to substitute lithium chlorid for hydrochloric acid, we should find, after electrolysis, that the difference between the concentrations of the solutions had increased and not diminished. Hence we should conclude that in lithium chlorid solutions the current tended to flow from the more dilute to the more concentrated solution. With the system KCl|NaOH we should find that the two solutions become more nearly alike as the current passes, showing that the natural potential difference causes the current to flow from left to right. The question of the sign of the potential difference between sodium chlorid and potassium hydroxid could also be determined purely by quantitative

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[1] Cf. Planck. Wied. Ann. 40, 561 (1890).

analysis without the aid of a single electrometric measurement.

The direction of the current in amalgam cells can be determined in the same way. In the cell ZnHg | $ZnSO_4$ | ZnHg the current will flow through the solution from the amalgam containing more zinc to the one containing less zinc, pure zinc and pure mercury being of course limiting cases. It should be noticed, however, that an amalgam electrode may give the value for the pure metal while there is still much mercury present while, in other cases, an amalgamated metal may never give the same value as the pure metal. It will depend entirely upon the question whether the amalgam is in equilibrium with pure metal or not. If it is, we shall have the electromotive force of the pure metal quite regardless of the concentration in the liquid amalgam. If the liquid amalgam is in equilibrium with a compound or a solid solution we shall not get the value for the pure metal. This way of considering the matter applies equally to any pair of metals; but with ordinary alloys the matter is complicated a good deal by inhomogeneity, by stresses in the solid phase or phases and by the slowness of diffusion.[1]

In the cell ZnHg | $ZnSO_4$ | ZnHg the zinc sulfate is in much the same position as the potassium chlorid in the cell Hg | Hg_2Cl_2KCl$AgCl$ | Ag. Increasing the concentration of zinc sulfate decreases the potential difference between amalgam and solution. If this change of potential difference is independent of the concentration of the amalgam, the concentration of the zinc sulfate will have no effect upon the electromotive force, otherwise it will. This is a quantitative question and cannot be answered absolutely by qualitative methods. It seems probable that if an effect due to the concentration of the salt exists, it can best be found by studying systems in which one of the liquid amalgams is in equilibrium with a compound.

The system AuHg | $Hg_2(NO_3)_2$ | AuHg is just the reverse of the cell ZnHg | $ZnSO_4$ | ZnHg. The current flows through the solution from the amalgam containing more mercury to that containing less mercury. The difference between the two cells

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[1] Cf. Ostwald. Lehrbuch II, 906.

disappears if we consider the mercury in the gold amalgam as equivalent to the zinc in the zinc amalgam. This is of course legitimate because zinc precipitates mercury from solution and mercury precipitates gold.

In the gas cell $Pt_H | HCl | Pt_{Cl}$ the passage of the current from left to right increases the concentration of the hydrochloric acid. Therefore the electromotive force of the cell increases with decreasing concentration of hydrochloric acid, a result that is in accord with the experimental data of Smale[1] and of McIntosh.[2] The cells $Pt_H | H_2SO_4 | Pt_O$ and $Pt_H | NaOH | Pt_O$ differ radically from the hydrogen-chlorin cell. The passage of the current causes formation of water, diluting the electrolytic solution. Therefore the electromotive force should rise with increasing concentration of sulfuric acid or of sodium hydroxid. On the other hand, the change of the concentration caused by the passage of 96540 coulombs is very small so that we should expect the electromotive force to vary but slightly with the concentration. Smale's experiments[3] show the approximate constancy of the electromotive force; but they do not show any signs of increasing electromotive force with increasing concentration. In a later paper[4] he has pointed out that such a change must take place, and this has recently been shown experimentally by Glaser.[5]

The cells with reducing and oxidizing agents are difficult to handle for two reasons. A change occurs in the nature of the solutions and this change is not always reversible. To take a single instance, passage of the current in one direction may cause the oxidation of pyrogallol; but reversing the current will not cause the oxidation products to be reduced back to pyrogallol. Where the reaction is readily reversible, the theorem of Le Chatelier enables us to predict that the presence of the de-

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[1] Zeit. phys. Chem. 16, 564 (1895).
[2] Jour. Phys. Chem. 2, 285 (1898).
[3] Zeit. phys. Chem. 14, 594 (1894).
[4] Ibid. 16, 563 (1895).
[5] Zeit. Elektrochemie, 4, 373 (1898).

composition products will lower the electromotive force,[1] a point on which much stress has been laid by Ochs.[2] For cases where the action is not readily reversible, it would certainly seem as though we might conclude that the electromotive force increased with increasing concentration. If so, it should be noticed that there is a fundamental difference between the cell Zn | $ZnSO_4$ | $CuSO_4$ | Cu and the cell Pt | R | O | Pt. In the former, the passage of the current from left to right causes the concentration of the zinc sulfate to increase and of the copper sulfate to decrease. In the reduction-oxidation cell the passage of the current decreases the concentration in both solutions, so that simultaneously diluting the anode solution and concentrating the cathode solution might leave the electromotive force unchanged. The facts in regard to the effect of concentration on the electromotive force of cells of this type are curiously unsatisfactory. According to the first experiments[3] the concentration had little effect and Ochs seems not to have obtained different results. On the other hand these measurements were made by comparing the swings of the galvanometer with the Clark cell and with the reduction-oxidation cell in circuit. The experiments of Ihle,[4] of McIntosh,[5] and of Carveth[6] tend to show that the concentration is a factor. These latter measurements were made with the electrometer and are therefore less open to criticism. It seems probable that the values do change with the concentration and that the theorem of Le Chatelier has been applied correctly.

If we consider the change of electromotive force with the change of pressure we see that the electromotive force must increase with increasing pressure if the volume of the cell decreases with the passage of the current. This was predicted by

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[1] Bancroft. Zeit. phys. Chem. 10, 407 (1892).

[2] Dissertation.

[3] Bancroft. Zeit. phys. Chem. 10, 401 (1892). It is stated however that, as a rule, the values for dilute solutions were lower than those for more concentrated solutions, both with oxidizing and reducing agents.

[4] Zeit. phys. Chem. 19, 577 (1896).

[5] Jour. Phys. Chem. 2, 287 (1897).

[6] Unpublished observations.

Gibbs[1] and verified by Gilbault.[2] According to the theorem of Le Chatelier rise of temperature should increase the electromotive force in case the cell works with absorption of heat, while the electromotive force must decrease with rising temperature in case the cell works with evolution of heat. Gibbs has shown that both types of cells exist,[3] and Helmholtz[4] has established the quantitative relation between the heat effect and the change of the electromotive force with the temperature. In applying the theorem of Le Chatelier to the change of solubility with the temperature, it was shown that one must consider the heat of solution in saturated solution. A similar point comes up in the case of the voltaic cell. The heat effect to be considered is the heat evolved or absorbed when the external resistance is infinite. This heat effect is usually referred to as the difference between the internal and the electrical energy, expressed in heat units; but this obscures the analogy with the saturated solutions.

The object of this paper has been twofold: to show the way in which the phase rule should be applied to reversible cells and to call attention to the usefulness of the theorem of Le Chatelier in predicting the change of the electromotive force with the change of the parameters. In both cases the result has been qualitative theory, but it has at the same time been exact theory and applies to all concentrations.

Cornell University, June 1, 1898

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[1] Trans. Conn. Acad. 3, 508 (1878).
[2] Comptes rendus, 113, 465 (1891).
[3] Gibbs. Trans. Conn. Acad. 3, 510 (1878).
[4] Ges. Abh. II, 961.

NEW BOOKS

Die Energetik, nach ihrer geschichtlichen Entwickelung. *By Georg Helm. 15 × 23 cm; pp. xii and 370. Leipzig: Veit und Comp., 1898. Price: paper 8.60 marks.* —The appearance of Helm's long-awaited work on the historical development of the energy theory having been announced in our last number (2, 386), it now remains to give some account of the contents of the book. The author's general plan is, in brief, a successive consideration of the early history of the energy law and of the entropy law; the combination of both to form the classical thermodynamics; the application of thermodynamics to chemical equilibria; an energy formulation of mechanics; and the ideas that have been advanced concerning the 'intensity and extensity factors' of energy forms.

Part I. of the book, "The Establishment of the First Law", presents early ideas of the relativity of physical phenomena; the part played by the energy law in mechanics; and the epoch-making studies of Mayer, of Joule, and of Helmholtz. Part II., "Preparation for the Second Law", considers Carnot's paper of 1824, with Clapeyron's analytical presentation of it; Holtzmann's attempt to combine the idea of Conservation with Carnot's theory; and W. Thomson's first definition of thermodynamic temperatures. Part III., "The Classical Thermodynamics", gives Clausius's combination (1850) of the energy law with Carnot's principle; W. Thomson's brilliant applications of thermodynamic theory; and C. Neumann's definitive formulation (1891) of the essential features of general thermodynamics. This line of exposition is then concluded by a Part IV., which treats Rankine's pyrotechnic theories, Clausius's ideas of disgregation and of entropy, and the discussions to which the energy and the entropy laws have given rise.

A large space, Part V., is next devoted to "The Energy Treatment of Chemistry", where we find Kirchhoff's grand researches of 1858, the thermochemical measurements of Hess, Thomsen, Berthelot, etc., the equilibrium theory of Horstmann and of Gibbs, Helmholtz's free energy equations, Duhem's recent investigations, Le Chatelier's so-called "three laws of energetics", and the work of Planck. All this is, on the whole, clear, correct, and fairly well-arranged. The account of Gibbs's energy surface should, however, have been preceded by some mention of James Thomson's p,v,t-surface; and it should have been made clear that each of Gibbs's 'fundamental equations' furnishes ,a, Gibbsian geometrical representation. The justification, too, offered for Gibbs's fundamental criteria of equilibrium is thoroughly unsatisfactory. Planck's papers, on the other hand, are well presented; and it is very properly made clear that the only *new* features of Planck's publications on the

Increase of Entropy are the mere fact of a *uniform formulation* of the thermodynamics of gases and of dilute solutions, and the introduction of a rational and useful relative molecular mass-concentration, [together with the discovery of a 'dissociation of the electrolytes'].

The next section of the book, Part VI., "The Energetic Formulation of Mechanics", has a less immediate interest for the physical chemist. Suffice it, therefore, to remark that Helm's treatment, though ostensibly historical, contains no reference to the very important Introduction of Hertz's *Mechanik*, where Hertz explains why he found the energy method unsuited to a presentation of mechanics. But topics of general interest appear again, and with a vengeance, in Part VII., "The Factors of Energy." The matters cited here are Zeuner's analogy (1866) between the absorption of heat and of gravitation work-equivalents in reversible processes; Mach's further development of this view; the ideas of Lippmann, Maxwell, and von Oettingen on antithetic relations in thermodynamics; Duhem's formulation of general thermodynamics; Helm's own 'intensities and extensities' and Ostwald's 'reduced intensities'; the unique determination of the thermodynamic temperature as an integrating divisor of the heat-differential (Budde, etc.); and Wiedeburg's new formulation of the thermodynamic equations. This is an intensely interesting subject,—even as Helm gives it,—but Helm makes nothing more out of it than his old contention that the 'intensities' are to be contrasted with the 'extensities'. He does not show how one is unequivocally to determine what these factors are in any given case, nor even that those arbitrarily assembled in the same category are all the same kind of thing,—which really they are not. The fact of the matter is that the energy differential is a sum of work terms and of work-equivalent terms; and that the former are forces multiplied into changes of spaces, while the latter are potentials multiplied into changes of quantity-coordinates. Helm confuses forces and potentials, which are *not* the same kind of thing, calling them 'intensities'; and he likewise confuses spaces and quantity-coordinates, calling them 'extensities'. This procedure, of course, leads him astray in a variety of ways, and so goes far to darken counsel throughout most parts of his book. It leads him, for example, to give the wrong definition of a quantity-coordinate (p. 271), to derive the wrong expression for the potential of the work-equivalents of motion (p. 278), to speak of adding "volume energy" for adding *work*, and so on almost indefinitely.

Quite unintentionally, the superficial character of Ostwald's employment of general energy theory is well exhibited by a quotation, on page 304, of one of Ostwald's favorite 'whirligig proofs'. In the arrangement as given,—two liquid phases and vapor in a ring-tube,—equilibrium would be reached when the lighter liquid formed a layer of the same depth on each side of the tube: which circumstance invalidates the proof.

The closing Part VIII. of the book treats chiefly the use of mechanical analogies, and of analytical methods borrowed from mechanics. In conclusion it is sturdily maintained (p. 340) that the straightforward energy method is simpler and more efficient than any of the mechanical methods can be; and that the real object of the energy theory is to establish *relations* among measurable parameters.

For the beginner the text would be easier to follow if the author had adopted Voigt's sensible notation for non-integrable differential expressions, writing, for example, $Q_{12} = \int_1^2 d'Q$, instead of $E_2 - E_1 = \int_1^2 dE$ when a differential is considered, and thus casting the simplified energy equation into the form

$$dE = d'Q + d'A.$$

This little matter is really a great help. But this is a mere item of detail. Helm's treatise is unquestionably an interesting book on an interesting subject; it gives, in most respects, a sound account of the historical development of the energy theory, and it valiantly defends the thesis that our physics and chemistry are concerned with observable relations and not with mechanical representations of phenomena. For these reasons it deserves to be widely read. The book is well printed, and its proofreading has been unusually well done.

J. E. Trevor

Lehrbuch der allgemeinen Chemie. *By. W. Ostwald. Vol. II, Part 2, Instalment 3. 16 × 24 cm; pp. 417-608. Leipzig: W. Engelmann, 1898. Price: 4.60 marks.*—The first thirty pages are given up to a discussion of the conditions of equilibrium for solid modifications, and the second thirty to a very elaborate statement of the facts in regard to sulfur. Some injustice is done to Duhem by the way the subject is developed. It was Duhem who brought comparative order out of the chaos into which the multitudinous experimental researches had plunged the matter. No one would suspect this from any statement in the *Lehrbuch*. Ostwald has used Duhem's theory as a basis for arranging and presenting the facts and then remarks casually at the end of the discussion, p. 472: "Very recently a theory of these phenomena has been developed by Duhem . . . ."

Ostwald is usually very happy in his definitions and it is therefore a surprise to find him stating, p. 477, as the criterion of a one-component system "that all the different phases, that may be formed and may exist in equilibrium, have *the same elementary composition*." A mixture of propyl acetate and ethyl propionate would satisfy this criterion and yet would most certainly be a two-component system. In one other place, p. 482, there is an extraordinary slip: "A consequence of Dalton's law is the fact that work can be obtained by the isothermal mixing of two gases." Lord Rayleigh's argument is quite independent of the gas laws or of Dalton's law. What is true is that the total amount of work obtainable can be calculated very readily in case Dalton's law does hold. These few points constitute about all that is wrong or objectionable in this instalment.

The rest of the number is devoted to two-component systems, taking up equilibrium in gases, equilibrium between solids and gases, equilibrium between solution and vapor. In the discussion of equilibrium in the vapor phase, it is a pleasure to find Friedel's experiments on methyl ether hydrochlorid referred to as not being in accord with the theory. It is now more than probable that some one will repeat these measurements and we shall then know whether the variations are due to experimental error or to defective theory. It is also very satisfactory to have Horstmann's results with ammonium carbamate recalculated and tabulated. The data of Isambert for dissociation pressures are much more useful when collected than when scattered in the original articles. One of the great advantages of the enormous size of Ostwald's *Lehrbuch* is that it becomes possible to give tables and not merely references to tables.

The chapter on Henry's law serves as an introduction to some very interesting pages on solutions supersaturated with respect to a gas, and it is but a step from the equilibrium between a gas and a solution to the equilibrium between solution and vapor when the two components are consolute liquids at the temperature of the experiment.

Taken altogether this number shows us Ostwald at his best. It illustrates his remarkable gift for presenting a tremendous array of facts and figures without a check in the easy flow of language. It brings out his wide reading and his power of arranging miscellaneous data so that they hang together after a fashion and it shows his unusual acuteness in seeing some of the more remote consequences of any particular hypothesis. Curiously enough, this same number might be cited as showing Ostwald's scorn of consistency. He begins with equilibrium in gases, trivariant systems; then he discusses the equilibrium between one solid phase and vapor, divariant systems; next comes two solids and vapor, monovariant systems; last of all solution and vapor, divariant systems. The phase rule classification is to Ostwald merely one of several ways of grouping the phenomena and he throws it overboard without a murmur.

Wilder D. Bancroft

On Laboratory Arts. *By Richard Threlfall. 13 × 18 cm; pp. xii and 338. New York: The Macmillan Co., 1898. Price: cloth $1.50.*—In the preface the author says: "Experimental work in physical science rests ultimately upon the mechanical arts. It is true that in a well-appointed laboratory, where apparatus is collected together in greater or less profusion, the appeal is often very indirect, and to a student carrying out a set experiment with apparatus provided to his hand, the temptation to ignore the mechanical basis of his work is often irresistible. It often happens that young physicists are to be found whose mathematical attainments are adequate, whose observational powers are perfectly trained, and whose general capacity is unquestioned, but who are quite unable to design or construct the simplest apparatus with due regard to the facility with which it can be constructed. That ultimate knowledge of materials and of processes which by long experience becomes intuitive in the mind of a great inventor of course cannot be acquired from books or from any set course of instruction. There are, however, many steps between absolute ignorance and consummate knowledge of the mechanical arts, and it is the object of the following pages to assist the young physicist in making his first steps towards acquiring a working knowledge of 'laboratory arts'. ... No attempt has been made at showing how work can be done without tools. Though, no doubt, a great deal can be done with inferior appliances where great economy of money and none of time is an object, the writer has long felt very strongly that English laboratory practice has gone too far in the direction of starving the workshop and he does not wish, even indirectly, to give any countenance to such a mistaken policy."

This is admirable and the body of the book is as good as the preface. The reader will find much information on glassblowing, the preparation of vacuum tubes, glassgrinding and opticians' work, coating glass with aluminum, gilding glass, soldering aluminum, the use of the diamond and the cutting wheel, grinding rock sections, cutting sections of soft substance, the production of quartz threads, soldering quartz, soldering in general, construction of insulating apparatus with remarks on sulfur, fused quartz, glass, ebonite, mica, celluloid, paper, paraffin, vaselin, wood and marble. A brief account is also given of the properties of some of the alloys used in making electrical apparatus. There is also a chapter on electroplating and allied arts, while a method of platinizing glass is described in the appendix. The book is well written and will prove indispensable in the laboratory. Practically the only criticism to be made upon it is the question whether the part on the grinding of lenses should not have been omitted as relating to processes very much more difficult than those described in the remainder of the volume. *Wilder D. Bancroft*

Notes on Observations. *By Sydney Lupton. 13 × 19 cm; pp. ix and 126. New York: The Macmillan Co., 1898. Price: cloth 75 cents.*—The book is "intended to assist a beginner in realizing the value of the quantitative results, which he himself and others have obtained in physical and chemical experiments." The headings of the chapters are: ideas; reasoning; fallacies; laws of nature; cause and effect; observation and experiment; units and dimensions; averages; differences; interpolation; mensuration; the use of tables; errors; means; the law of the frequency of errors; the weight of observations; the method of least squares; conditioned equations; general formulas; deductive method; expression of results by graphical methods; the expression of results by empirical formulae.

A book like this is bound to be useful, and this particular volume is very satisfactory in many ways. For instance, in speaking of the loose way in which people commonly use words the author says: "Before any effect can be produced several or many conditions must be present, the most marked of these conditions is picked out and spoken of as *the* cause of the effect, though in reality several of the little-noticed conditions may be as necessary for the production of the effect as the one selected as the cause." Apart from the question of style, this is a very happy way of stating the case. The same cannot be said of the following: "The study of natural sciences consists in the observation of and reflection upon, differences and changes in two manifestations which are spoken of as matter and energy." The discovery of argon and helium did not prove the fallacy of "the general statement that all elements are capable of entering into chemical combination." It proved that there are elements no compounds of which are known; but it is by no means certain that compounds of these elements cannot exist. This is an excellent instance of the importance of distinguishing between the fact and the conclusion drawn from the fact. It is instructive to find the author making this slip in the chapter on fallacies. This and one or two similar points are minor blemishes and do not detract from the value of the work except perhaps in the eyes of the hypercritical. The little volume can be recommended heartily to teacher and student alike. *Wilder D. Bancroft*

The Storage Battery. *By Augustus Treadwell. 14 × 19 cm; pp. xx and 257. New York: The Macmillan Co., 1898. Price: cloth $1.75.*—Secondary batteries are classified under five heads: lead-sulfuric acid; lead-copper; lead-zinc; alkaline zincate; miscellaneous. Over a hundred forms and modifications are enumerated; fifty-eight pages are devoted to a discussion of different installations; there is a chapter on the use of the storage battery for traction purposes and one on the precautions to be taken in setting up and running accumulators. In the appendix are some tables containing general useful information and a few pages on methods of measuring electromotive force and internal resistance. The book will prove serviceable for reference, especially since there is a very satisfactory index. In some points the volume might easily be improved. For the sake of completeness it would have been well to have referred to the sodium amalgam accumulator. Under the lead-copper type something should have been said about the difference between cuprous and cupric oxid. The reviewer is unable to agree with the author that the persulfuric acid theory of the storage battery will remain as the generally accepted one for some time to come. It would be more accurate to say that, as far as the scientific world is concerned, this theory is already a thing of the past. *Wilder D. Bancroft*

Beschreibung der Hauptmethoden welche bei der Bestimmung der Verbrennungswärme üblich sind. *By W. Louguinine. 24 × 32 cm; pp. 112. Berlin: R. Friedländer & Sohn, 1897. Price: paper 10 marks.*—In the introduction the author discusses the calorimeter, the thermometer, the calorie, the question of the room temperature, the calculation of loss of heat through radiation, the difference between combustion under constant pressure and at constant volume. He believes that the thermometer should consist simply of a reservoir with a tube attached and does not approve of thermometers with milk-glass scales. It is interesting to note that in St. Petersburg the calorimeter loses heat even when nearly one degree lower in temperature than the surrounding space—owing to the evaporation of water in the dry atmosphere. It would seem that this source of error might easily be reduced to a minimum by standing pans containing salt solution about the room. As the theoretical heat unit the author prefers the mean calorie or one-hundredth of the heat evolved by one grain of water in cooling from 100° to 0°; but he considers that this value is not yet known with sufficient accuracy, and he therefore takes the 15° calorie temporarily as the standard.

In the body of the work the author discusses the combustion in a current of oxygen under atmospheric pressure, combustion with the use of potassium chlorate, combustion under pressure using the bomb. A special chapter is devoted to the ice calorimeters of Bunsen, Schuller and Wartha, Than, Dieterici, and Boys. There are also a few pages on the determination of the heat of combustion of hydrogen in oxygen, using the ice calorimeter. The different methods are described in much detail with exhaustive critical comments. There are twenty-one illustrations in the text exclusive of three pages of plates. The work is an admirable little monograph. *Wilder D. Bancroft*

The Theory and Practice of Electrolytic Methods of Analysis. *By Bernhard Neumann, translated by John B. C. Kershaw. 13 × 19 cm; pp. x and 254. New York: The Macmillan Co. (Whittaker), 1898. Price: cloth $3.00.*—The original German edition has already been reviewed in these columns, (1,568). The translator has left out the portion of the original work dealing with primary and secondary batteries, the dynamo and the thermopile. He has added both a subject and a name index, thus increasing the usefulness of the book. The translation has been done well; but the reviewer must protest against the misspelling of cathode. *Wilder D. Bancroft*

Canada's Metals. *By W. C. Roberts-Austen. 15 × 22 cm; 46 pp. New York: The Macmillan Co., 1898. Price: cloth 75 cents.*—This is a reprint of a lecture delivered at the Toronto Meeting of the British Association for the Advancement of Science, Aug. 20, 1897. It gives a brief sketch of Canada's metals. To those who are not interested in practical mining the most important thing in the pamphlet are the three photographs showing the splashes formed by a marble striking milk, by a gold bullet striking molten gold, and by a projectile striking steel armor plate. The similarity of the three splashes is very striking and instructive. *Wilder D. Bancroft*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry

One-Component Systems

Experiments on the behavior of atmospheric air and of certain chemically prepared gases at temperatures between 350° and 500° when under atmospheric pressure. *H. Teudt. Zeit. phys. Chem.* **26**, *113* (*1898*). — Above 350° and at atmospheric pressure atmospheric air expands more rapidly than one would expect from the gas laws, the variation being about 3 percent at 450°. Removing the carbonic acid and the oxygen does not change the phenomenon. On the other hand nitrogen that has been prepared from compounds does not show this variation. Immediately after a rain atmospheric air is normal, while air that has been dissolved in water is especially abnormal, while it seems probable that filtering air at 100° through a porous cell increases the concentration of the unknown component.

W. D. B.

On the crystallization of supercooled benzophenon. *K. Schaum. Zeit. phys. Chem.* **25**, *722* (*1898*). — With benzophenon, phenol and salol it was found that the nature of the substances in contact with the melt affected the temperature at which crystals appeared spontaneously. This is not in accordance with Ostwald's views but confirms the experiments of Tammann.

W. D. B.

On the variation with the temperature of the number of nuclei that form in different supercooled liquids. *G. Tammann. Zeit. phys. Chem.* **25**, *441* (*1898*). — As the temperature falls below the freezing-point the number of crystals that appear spontaneously in a given volume of liquid in a given time increases, passes through a maximum and decreases. With betol the maximum occurs at about 16° for the stable modification and a little lower for a less stable form. With piperin the maximum occurs at about 40°. Addition of small amounts of soluble substances to liquid betol lowered the temperature of the maximum formation of nuclei by amounts not exceeding 14°; but had great influence on the absolute number. Salicin and cane sugar lowered the value while succinic acid and benzamid raised it, naphthalene having little or no influence. Powdered glass, though insoluble, lowered the number of nuclei while rock crystal raised it.

The temperatures at which the maximum number of crystals appeared were determined for some eleven other substances. In many cases two or more kinds of crystals separated spontaneously from the supercooled melt. Experiments were also made with 140 substances to determine whether it was possible by rapid cooling to convert them into the state of glasses. The attempt proved successful with fifty-nine of these substances and there is no reason to suppose that this number might not be increased very largely by the use of more effective methods of cooling. The author inclines to the belief that, theoretically at any rate, all liquids may be made to pass at will either into the amorphous or the crystalline state. *W. D. B.*

Two-Component Systems

Heat of separation in solutions, lowering of the freezing-point solubility. *A. Dahms. Wied. Ann.* 64, *507* (*1898*). — The equation

$$\log c_0 = \frac{r_0}{R}\left(\frac{1}{\theta} - \frac{1}{\theta_0}\right)$$

(which for dilute solutions is identical with van't Hoff's formula for the lowering of the freezing-point) agrees well with observations on solutions *of all concentrations* of naphthalene in ethylene bromid, of diphenylamine in ethylene bromid and of diphenylamine in benzene. The author enumerates the assumptions necessary in deducing the equation in question, and characterizes the cases to which it is not applicable.

An independent section of the paper deals with the "heats of separation", i. e. the heat absorbed in evaporating, freezing, or precipitating one component from a solution. As in general the heat of separation depends on the concentration of the solution, its direct determination is attended with difficulties. If, however, in the system subjected to investigation, the number of phases exceeds by one that of the independently variable components and the pressure is kept constant, (e. g. saturated solutions boiling at constant pressure; cryohydrates at their melting-points) the individual heats of separation of the various components may be obtained from solubility measurements and one calorimetric observation. The method is illustrated by experiments with sodium chlorid solution and with the eutectic mixture of nitrobenzene and ethylene bromid. *W. L. M.*

Poly-Component Systems

Simultaneous application of the mass law and the phase rule. Effect of the solvent on the chemical reaction. *B. Kuriloff. Zeit. phys. Chem.* 25, *419* (*1898*). — By taking account of the electrolytic dissociation of acetic acid in water and of the polymerization of acetic acid in benzene and by ignoring the increased miscibility of benzene and water due to acetic acid, it is shown that Nernst's distribution law describes the equilibrium between acetic acid, benzene and water. After this encouraging start it is not surprising to learn that it can be shown theoretically and experimentally that "the solubility of β-naphthol picrate in benzene divided by the solubility of β-naphthol picrate in water is equal to the equilibrium constant for the aqueous solution divided by the equilibrium constant for the benzene solution and multiplied by the distribution coefficients of picric acid and β-naphthol. The real gist of the paper is that β-naphthol picrate is not decomposed by benzene with precipitation of either component while it is decomposed by water with precipitation of β-naphthol. This is referred very properly to the solubilities of β-naphthol and picric acid in benzene and water respectively and to the electrolytic dissociation of picric acid in water. *W. D. B.*

The equilibrium $CO + H_2O \rightleftarrows CO_2 + H_2$ and the study of explosives. *C. Hoitsema. Zeit. phys. Chem.* **25**, *686* (*1898*). — According to Naumann and Pistor the formation of carbonic acid from carbon monoxid and water can be detected at about 600° while the reverse reaction does not take place to an appreciable extent until a temperature of about 900° is reached. At higher temperatures the equilibrium should be displaced towards the carbon monoxid side. The author has taken a number of explosives and calculated the temperature reached during the moment of explosion. He finds that the ratio of carbon monoxid and water to carbonic acid and hydrogen is greater the higher the temperature. The calculated temperatures ranged from about 2100° to about 2900°. The results are only approximate, the dissociation of carbonic acid into carbon monoxid and oxygen not being considered in the calculation of the equilibrium. It would seem a question, however, whether there are not two equilibrium constants at low temperature. Though reference is made to the possibility of 'false equilibrium', this is not really taken into account at all. *W. D. B.*

Investigation of the theory of solubility effect in the case of tri-ionic salts. *A. A. Noyes and H. Woodworth. Zeit. phys. Chem.* **26**, *152*; *Jour. Am. Chem. Soc.* **20**, *194* (*1898*). — Determinations were made of the solubility of lead iodid in pure water, in presence of potassium iodid and in presence of lead nitrate. The concentrations were calculated from conductivity measurements, the migration velocity of lead as ion being taken as 68.3 at 25°. The conclusion drawn from the experiment is that the solubility of lead iodid is decreased by the addition of either lead nitrate or potassium iodid in such a way that the product of the concentration of lead as ion into the square of the concentration of iodin as ion remains constant. *W. D. B.*

Velocities

On the velocity of crystallization. *F. W. Küster. Zeit. phys. Chem.* **25**, *480* (*1898*). — A criticism of Tammann's paper (1, 749) because Tammann assumed that the temperature at the surface between solid and liquid was that of the triple point. This is disputed on the ground that the system is not in equilibrium. *W. D. B.*

On the velocity of crystallization, II. *G. Tammann. Zeit. phys. Chem.* **26**, *307* (*1898*). — Küster's claim (see preceding review) that the temperature at the surface between solid and liquid is not that of the triple point is looked upon as preposterous. The author's position is restated at length. *W. D. B.*

Electromotive Forces

On the electromotive behavior of chromium. *W. Hittorf. Zeit. phys. Chem.* **25**, *729*; *Wied. Ann.* **65**, *320*; *Zeit. Elektrochemie*, **4**, *482* (*1898*). — When chromium is made the anode in concentrated solutions of hydrochloric acid or in fused chlorids it dissolves as chromous chlorid $CrCl_2$. When anode in dilute solutions and in fused salts of oxygen acids, it dissolves as chromic acid and is hexavalent. This can be stated more definitely. When a halogen is set free at the anode the chromium is bivalent, corresponding to the oxid CrO; when oxygen is set free it is hexavalent, corresponding to the oxid CrO_3. When anode in alcoholic zinc chlorid it is trivalent, Cr_2Cl_6 being formed. When chromium dissolves as chromic acid, it stands in the voltaic series below mercury; when it dissolves as chromous chlorid it stands just below zinc. The "inactive" chromium is believed by the author not to be due to the presence of an invisible film of oxid.

W. D. B.

Studies on the electrolytic decomposition of aqueous solutions. *L. Glaser. Zeit. Elektrochemie*, 4, *355, 373, 397, 424* (*1898*).—The chief object of this paper was to clear up the discrepancy between the electromotive force of the gas cell, 1.08 volts, and the polarization value for the decomposition of water, 1.67 volts. The mean value for a series of gas cells was 1.080 volts with acids or bases. With normal caustic potash the value was about five millivolts higher. The temperature coefficient with sodium hydroxid as electrolyte was 0.00143 as against 0.001416 found by Smale. Increasing the concentration of the electrolyte raised the electromotive force, though not to the amount required by the theory. Other solvents than water were tried, but were unsatisfactory owing to decomposition at one or the other of the electrodes. Adding hydrogen peroxid to an aqueous acid solution in small quantities raised the electromotive force; added in larger quantities it reduced it to about 0.824 volt.

In the polarization experiments a small effect was noticed at about 0.5-6 volts, a marked effect at 1.06-8 volts, and yet another at 1.67 volts. The change at 0.5-6 volts was more marked in alkeline than in acid solutions. The most plausible explanation of these phenomena is that water forms two anions, hydroxyl and oxygen. In the gas cell we have an oxygen electrode and oxygen goes into solution as ion just as zinc goes into solution as ion. The value 1.08 volts represents the elimination of $2\overset{+}{H}$ and $\overset{--}{O}$. To precipitate hydroxyl requires 0.59 volt more, giving us the regular value of 1.67 volts. There being little oxygen as ion in the solution relatively to the hydroxyl as ion, the decomposition at 1.08 volts is necessarily very slow and may easily be overlooked.

By using magnesium sulfate in one case and concentrated sulfuric acid in a second, the author was able to find 1.95 volts as the value at which $2\overset{+}{H}$ and $\overset{--}{SO_4}$ separate while $\overset{+}{H}$ and $H\overset{--}{SO_4}$ require about 2.65 volts. This last value is interesting, coinciding as it does, with the "maximum polarization" of dilut sulfuric acid.

The decomposition value for hydrogen and oxygen as ions is 1.08 volts. Replacing the hydrogen by potassium gives us 1.40 volts; by sodium 1.315 volts. These figures refer to normal solutions. For more concentrated solutions they are less, though not to the extent required by the theory. With saturated calcium, strontium, and barium hydroxid solutions, the figures were 1.33, 1.20, and 1.185 volts. For a solution saturated with respect to magnesium hydroxid and magnesium sulfate, to which a few drops of caustic potash had been added, the decomposition value was 1.395 volts.

W. D. B.

Chemical equilibrium and electromotive force. *C. Knüpffer. Zeit. phys. Chem.* 26, *255; Zeit. Elektrochemie*, 4, *544* (*1898*).—The equilibrium between thallium chlorid and thallium sulfocyanate has been studied chemically and electrically with reference to van 't Hoff's equation $\pi = RT \log K/\pi$. At 39.9°, 20.0°, and 0.8° the ratio of chlorin to sulfocyanate at equilibrium was 0.85, 1.24 and 1.74 by chemical analysis, while the values calculated from the electromotive forces were 0.87, 1.27 and 1.77 for one cell, and 0.88, 1.25 and 1.82 for a second cell, the ratio of chlorin to sulfocyanate being about 0.84 in the first cell and about 1.52 in the second. The cells were made up Tl ¦ *TlCl*KCl | KSCN *TlSCN* | Tl and caustic potash was added in equal quantities to both solutions to prevent diffusion currents. It seems a pity that one set of measurements should not have been made without the caustic potash since it is quite conceivable that the error introduced thereby may be as large as the error avoided. The calculated temperature coefficient agreed well with that found experimentally. The reviewer is rejoiced to see that the van 't Hoff relation between chemical affinity and electromotive force is at last beginning to be appreciated. *W. D. B.*

On the electroanalytic precipitation of silver from nitric acid solution and the separation from copper. *F. W. Küster und H. von Steinwehr. Zeit. Elektrochemie*, 4, *451* (*1898*).—The electrolytic precipitation of silver is usually very unsatisfactory, the precipitate being crystalline only during the first period of the experiment. It has been found that satisfactory results are obtained by keeping the potential difference at the electrodes below 1.40 volts. A favorable result is obtained by heating the solution to 55°–60°, adding a little concentrated nitric acid and a little alcohol (to prevent formation of peroxid) and keeping the potential difference constant at 1.35–1.38 volts. There is no difficulty in precipitating over a gram of silver in six hours and the method has been used successfully in analyzing silver coins. *W. D. B.*

On oxidation and reduction cells and on the effect of complex ions on the electromotive force. *R. Peters. Zeit. phys. Chem.* 26, *193; Zeit. Elektrochemie*, 4, *534* (*1898*).—To bring the electrodes to the same value a current of carbon dioxid was found very effective. One object of the paper was to apply the van 't Hoff formula $\pi = \frac{RT}{ne} \log k/a$ to oxidation and reduction cells, where k is the equilibrium constant and a the ratio of the concentrations. The author considers the case of a two solution cell, one solution being a mixture of ferrous and ferric chlorid, and the other the normal calomel electrode. The reaction may be written $Hg + Fe^{\cdot\cdot} + Cl' \rightleftarrows Fe^{\cdot\cdot} + HgCl$. Considering Hg and HgCl as solid phases and Cl′ as constant by definition we shall have $\frac{C_{Fe}^{\cdot\cdot}}{C_{Fe}^{\cdot\cdot\cdot}} = a$. In the actual measurements the ratio of ferrous chlorid to ferric chlorid varied from 1 : 99 to 99.5 : 0.5. The results were given with great accuracy by the formula $\pi = A + 0.0575 \log C_{Fe}^{\cdot\cdot\cdot}/C_{Fe}^{\cdot\cdot}$. The question of dissociation appeared to be of no importance. On the other hand it was found that ferrous sulfate in solution has a very different reducing action from ferrous chlorid of the same nominal concentration.

The attempt to apply van 't Hoff's formula quantitatively to solutions of chromous and chromic salts or of manganous and manganic salts was not very successful. One interesting point was noticed. Acid solutions of chromous salts evolve hydrogen when in contact with platinum. Adding sodium fluorid to a solution of ferrous and ferric chlorid increased the reduction potential very much and this was shown to be due to the formation of a complex salt, which was obtained crystallized as $Na_3FeFl_6\frac{1}{2}H_2O$.

The author explains the catalytic action of many substances as due to the change of potential, the reaction velocity being proportional, other things being equal, to the difference of potential. In illustration of this, the fact is cited that acidified ferrous sulfate reduces silver nitrate slowly but the reaction takes place rapidly on addition of sodium fluorid.

It would seem as though there must be a misprint, p. 215, in the statement that Pt | 0.1 $FeSO_4$ differs from Pt | 0.1 $FeCl_3$ by 0.3-0.4 volt, if the difference is to be attributed to the relative dissociation in the two solutions. *W. D. B.*

On the dependence of the electromotive force and the efficiency of the lead accumulator on the concentration of the acid. *F. Dolezalek. Zeit. Elektrochemie,* 4, *349; Wied. Ann.* 65, *8,4* (*1898*).—The Helmholtz formula for concentration cells without diffusion has been applied to accumulators with different concentrations of sulfuric acid. The vapor-pressure data were taken from Dieterici's measurements. The agreement between theory and experiment is very satisfactory. Assuming that the reaction in the accumulator is represented by the equation $PbO_2 + Pb + 2H_2SO_4 \rightleftarrows 2PbSO_4 + 2H_2O$, the author has calculated the electromotive forces by means of the Helmholtz formula for the relation among electromotive force, heat effect and temperature coefficient. The heats of dilution were taken from Thomsen's measurements and Streintz's data for the temperature coefficient were used. The calculated results do not agree with the experimental data as closely as in the preceding case; but this is attributed to the inaccuracy of the figures on which the calculations were based. It may be interesting to record that the electromotive force of the accumulator varies from 1.82 to 2.29 volts as the concentration of the acid changes from four to fifty-eight per cent.

In the second part of the paper there is a discussion of the causes affecting the efficiency of the accumulator. As is well known the chief loss is due to the fact that the accumulator is charged under a higher voltage than it is discharged. The reason for this is the change of concentration at and more especially in the electrode. For a given charging current, a given excess of voltage will be necessary in order to overcome the counter electromotive force. As first approximation the author deduces the formula $\epsilon = C\frac{\gamma}{k}I^2t$ volt-coulomb where ϵ is the loss of energy, I the current strength, t the time, k the mean conductivity of the acid in the electrode, γ a factor due to the mechanical structure of the plates and C a proportionality factor. It is assumed that k is practically independent of I when the charging and discharging current are equal in strength and the equation becomes $\epsilon = KI^2t$ for constant current and $\epsilon = K\int I^2dt$ for varying currents, K being a constant characteristic of each accumulator. This formula (which is of great practical importance) was applied to some published technical measurements and gave quite satisfactory results.

W. D. B.

On the principle of the dropping electrode. *W. Palmaer. Zeit. phys. Chem.* 25, *265* (*1898*).—Nernst looks upon the dropping and the stationary mercury as forming a concentration cell. The author lets the tip of the dropping electrode dip into the solution and finds that, for several minutes after the flow of mercury has been checked, there is a potential difference between the two mercury surfaces. An important feature of the paper is the tacit admission that the dropping electrode does not permit one to measure single potential differences. At the close of the paper the author outlines a proposed method for measuring single potential difference that appears to involve reasoning in a circle. *W. D. B.*

Electrolysis and Electrolytic Dissociation

Determination of dissociation constants from increased solubility. *R. Löwenherz. Zeit. phys. Chem.* 25, *385* (*1898*).—The solubility of a weak acid in an aqueous solution of a weak base is greater than in pure water. If the dissociation constant of the acid be known as well as the dissociation of water, the dissociation constant of the base may be calculated from the increase in solubility by applying the mass law formula. The author takes 1.14×10.7 as giving the reacting weights per liter of dissociated water. To test the method the author tried different concentrations of anilin and of *p*-toluidin with saturated solutions of cinnamic acid and of *p*-nitrobenzoic acid. For anilin he obtained as mean values 5.6 and 5.8×10^{-10}; for *p*-toluidin 20.7 and 20.5×10^{-10}. By the conductivity method Bredig found 5.4×10^{-10} for anilin and 17.2×10^{-10} for *p*-toluidin. Using *p*-nitrobenzoic acid and *p*-brombenzoic acid the dissociation constant of metanitranilin was found to be 4.2×10^{-12} and 5.3×10^{-12} respectively; that of *p*-nitranilin was 1.1×10^{-12} from the experiments with the first acid and 1.3×10^{-12} for those with the second. Owing to the slight solubility of *o*-nitranilin, the solution was saturated with respect to it and varying quantities of hydrochloric acid added. The dissociation constant of *o*-nitranilin was thus found to be 1.5×10^{-14}. With *m*-nitranilin in excess and hydrochloric acid a dissociation constant of 4.5×10^{-12} was found, differing not at all from that obtained with a sparingly soluble acid. *W. D. B.*

Experimental investigation of the dissociation of substances dissolved in aqueous alcohol. *E. Cohen. Zeit. phys. Chem.* 25, *1* (*1898*).—Experiments were made with KI, KCl and CH_3CO_2Na. The alcohol had a conductivity of 1.5×10^{-11}; the water of less than 0.24×10^{-6} at $-18°$. It was found impossible to work at 25° probably because of oxidation of the alcohol in contact with the platinum black of the electrodes; at 18° this difficulty was not serious provided the measurements were not made too slowly. Special precautions were taken in diluting the solutions. The results of the investigation were quite surprising. For each mixture of aqueous alcohol the conductivity for any concentration of a given salt can be obtained by multiplying the conductivity for that concentration in pure water by a constant. This holds only for solutions containing less than sixty percent of alcohol. This statement may also be worded: "In dilute aqueous alcoholic solutions the effect of the amount of alcohol on the molecular conductivity is independent of the concentration of the solution." The author seeks the explanation of this very interesting theorem in the hypothesis that the electrolytic conductivity is not an accurate measure of the dissociation; he rejects the hypothesis that the addition of alcohol does not change the dissociation, because Kablukow and Zacconi have found that the inversion velocity of cane-sugar in dilute hydrochloric acid is lowered by the addition of alcohol. While the conclusion may be right, the reasoning seems weak. Kablukow and Zacconi obtained a constant of 21.3 in water and of 16.66 in fifty percent aqueous alcohol. If we consider that the volume concentration of the water has been increased one-half it would seem quite reasonable to say that the presence of alcohol had increased the catalytic action of the hydrochloric acid instead of reducing it. Whatever may be the explanation of the results, this paper of Cohen's is a distinct contribution to science. *W. D. B.*

Studies on the electrolytic reduction of the nitro-group. *W. Löb. Zeit. Elektrochemie,* 4, *328* (*1898*).—The author has claimed in the past that all stages were passed through in the reduction of the nitro group and this paper furnishes evidence in favor of this view. The fundamental idea is that if one introduces into the solution some substance that will react with one of the intermediate compounds, the resulting product can be isolated and identified. In formaldehyde we have a substance that reacts with hydroxylamin derivatives, with hydrazo compounds and with amins. The author has studied the products obtained when nitrobenzene or *p*-nitrotoluene is reduced electrolytically in presence of formaldehyde. It should be noticed however that the formation of a hydroxylamin derivative in the presence of formaldehyde does not prove that this same substance is formed temporarily when no formaldehyde is present. The assumption involved has often been made in organic chemistry; but it is disappointing to see it reappearing in electrochemistry.

When nitrobenzene in fuming hydrochloric acid is reduced in presence of formaldehyde under 5 volts and at 45°, there is formed a polymer or a series of polymers of *p*-anhydrohydroxylaminbenzyl alcohol, the product being the same as that found by the action of formaldehyde on phenylhydroxylamin in hydrochloric acid solution. Under 3 volts and at 30° the product is methylene-di-*p*-anhydroamidobenzyl alcohol. In other words, with high voltage a condensation product of hydroxylamin is formed, and with low voltage a condensation product of anilin. The resistance being the same in the two cases, high voltage corresponds to high current density and low voltage to low current density. From these experiments the author concludes that the voltage is of little account in determining the nature of the reaction and that the important factor is the current density. This conclusion would be of more value if the potential difference and the current density had been varied independently.

The same final products have been obtained without the current by reducing with zinc dust, the violent reaction, giving a nearly quantitative yield of the hydroxylamin derivative. Directions are also given for preparing the compounds electrolytically without using an outside source of electricity (1, 128).

It was thought that simpler results might be obtained with *p*-nitrotoluene, but this proved not to be the case. The current density seemed to be of little importance and the two chief products are *p*-dimethyltoluidin and dimethylenetoluidin. The *p*-nitrotoluene is reduced to *p*-toluidin. This reacts with formaldehyde, giving dimethylenetoluidin and dimethyltoluidin. It is worth noting that while nitrobenzene in fusing hydrochloric acid is reduced to chloranilin, no formaldehyde being present, the *p*-nitrotoluol changes to *p*-toluidin.

W. D. B.

Electrolytic reduction of aldehydes and ketones. *H. Kauffmann. Zeit. Elektrochemie*, 4, *461* (*1898*).—The two hydrobenzoins are formed when a solution of benzaldehyde in alcoholic soda is electrolyzed. If an acid solution be taken, less hydrobenzoin is formed and in its place there appears a tarry substance of unknown composition. By the electrolytic reduction of benzil in alcoholic soda there is formed tetraphenylerythrite and a substance having the formula $C_{28}H_{20}O_3$ and a melting-point at 175°. *W. D. B.*

Contribution to our knowledge of the electrolysis of calcium chlorid solutions. *H. Bischoff and F. Foerster. Zeit. Elektrochemie*, 4, *464* (*1898*).—Oettel had found that much more chlorate was formed by the electrolysis of calcium chlorid solutions than by the electrolysis of mixed caustic potash and potassium chlorid solutions. These experiments were confirmed, a mean yield of about 81 percent being obtained for the calcium salt as against about 52 percent for the potassium salt. Since barium chlorid solutions behaved much like potassium chlorid solutions, the cause of the discrepancy was not to be sought in the valency of calcium. The difference appears to be due to the insolubility of calcium hydroxid, this salt precipitating in a film on the cathode and bringing the reducing action at the cathode to a minimum. Very little free chlorin is evolved from the solution, but quite perceptible quantities of hypochlorous acid.

The percentage yield of chlorate decreases with decreasing concentration and with decreasing current density. The solution should contain not less than ten percent calcium chlorid, the current density at the anode should be about 10 amp/qdm and at least double that at the cathode. By working at 50° the voltage can be reduced without decreasing the percentage yield seriously. Much better results are obtained with nickel than with platinum cathodes.

W. D. B.

Electrolytic separation of cadmium and iron. *W. Stortenbeker. Zeit. Elektrochemie*, 4, *409* (*1898*).—To a mixture of cadmium and ferrous salts, a little potassium cyanid is added and the solution electrolyzed with a low current density, $N.D_{100} = 0.05\text{–}0.1$. Good results however may be obtained with a current density of 0.4 ampere. A little ferric salt in the ferrous salt does no harm since it is converted into flocculent ferric hydroxid and this does not cling to the electrode. When there is a good deal of ferric salt present, it is advisable to reduce it with thiosulfuric acid. *W. D. B.*

POTASSIUM CHLORID IN AQUEOUS ACETONE

BY J. F. SNELL

I. INTRODUCTION

That potassium carbonate added to mixtures of ethyl alcohol and water will cause them to divide into two layers has been known for centuries, this property of the salt having been utilized by Raymond Lully[1] in the thirteenth century for the preparation of concentrated alcohol. Brandes[2] and Schiff[3] found that manganous sulfate had the same power, Traube and Neuberg[4] showed that the property was common to a large number of salts, and Linebarger[5] found that not only could other salts be substituted for the potassium carbonate but other liquids, viz. propyl alcohol and acetone could be used in place of ethyl alcohol. Linebarger found it possible to obtain two-liquid-phase systems in the case of the following salts and bases with ethyl alcohol and water :

$$Na_2SO_4,\ (NH_4)_2SO_4,\ \mathrm{CdSO_4},\ ZnSO_4,\ \mathrm{MnSO_4},\ NaOH,\ KOH,\ Na_2CO_3,\ K_2CO_3.$$

Those printed in italics are given also by Traube and Neuberg, while they add to the list the following :

$$\mathrm{Na_2HPO_4},\ \mathrm{MgSO_4}\ \mathrm{KAl(SO_4)_2}.$$

With methyl alcohol and water, Linebarger succeeded in obtaining two layers in the case of potassium carbonate only, though he experimented with a great number of other salts. With

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[1] Lescoeur. Ann. Chim. Phys. (7) 9, 541 (1896).

[2] Pogg. Ann. 20, 586 (1830).

[3] Lieb. Ann. 118, 370 (1861).

[4] Zeit. phys. Chem. 1, 509 (1887).

[5] Am. Chem. Jour. 14, 380 (1892).

propyl alcohol and water, the following salts gave two-liquid-phase systems:

> NH_4Cl, $NaCl$, KCl, $RbCl$, $CaCl_2$, $NaNO_3$, $Sr(NO_3)_2$, Li_2SO_4, Na_2SO_4, $(NH_4)_2SO_4$, $NiSO_4$, $CoSO_4$, $CuSO_4$, $FeSO_4$, $Fe_2(SO_4)_3$, $CdSO_4$, $ZnSO_4$, $MnSO_4$, $NaOH$, KOH, Na_2CO_3, K_2CO_3, KCN, $K_4Fe(CN)_6$.

With acetone and water he obtained two liquid phases with:

> $LiCl$, $\mathit{NH_4Cl}$, NaCl, KCl, $RbCl$, $\mathit{CaCl_2}$, $SrCl_2$, $CoCl$, $CuCl_2$, $MnCl_2$, CH_3CO_2K, $(CH_3CO_2)_2Mn$, Li_2SO_4, $\mathit{Na_2SO_4}$, $\mathit{(NH_4)_2SO_4}$, $NiSO_4$, $CoSO_4$, $Fe_2(SO_4)_3$, $\mathit{CdSO_4}$ $ZnSO_4$, $MnSO_4$, NaOH, KOH, $\mathit{Na_2CO_3}$, $\mathit{K_2CO_3}$, KCN.

I have confirmed Linebarger's results with acetone in the case of the italicized substances. His negative results, however, are not to be taken as conclusive. His procedure was to take a saturated solution of the salt in a test-tube and add the organic liquid till layers formed or the salt precipitated, and then to repeat the experiment using a salt solution of one-half the concentration. He does not state that he heated the tubes, but in some cases (e. g. KCl) he must have done so in order to obtain the separation. In open tubes I have succeeded in obtaining two layers in the case of the following substances which he gives among those that do not form two layers with acetone and water: $NaNO_3$, NH_4NO_3, $(NH_4)_2CO_3$, CH_3CO_2Na, also with $BaCl_2$ in presence of solid salt. I have also observed the phenomenon in the case of the following salts, which he did not use:

> $NaBr$, KBr, NH_4Br, $MgSO_4$, Na_2HPO_4. HNH_4NaPO_4.

In some other cases, e. g. KNO_3, $Ba(NO_3)_2$ and $KClO_3$, I find, in agreement with Linebarger, that solid salt is precipitated by addition of acetone to the aqueous solutions of the salts, but it is possible that in some of these cases the formation of two layers may take place at higher temperatures. For, while it is impossible at room temperature to get two liquid phases in the system potassium nitrate, ethyl alcohol and water, I have succeeded in obtaining the division by heating a complex of the three components in a sealed tube (see below, p. 464). On the other hand I got negative results in the case of potassium nitrate with methyl alcohol, and in the case of potassium chlorid with either methyl alcohol or ethyl alcohol. The experiments were made in each case with fifty percent aqueous alcohol and a quantity of salt considerably in excess of the amount that would dissolve at room temperature. In the case of potassium nitrate and methyl alcohol, the salt dissolved completely even when it was so greatly in excess that at room temperature it was merely wetted by the liquid. Potassium chlorid neither dissolved completely nor gave two liquid layers in either solution, though the tubes were heated to 195°.

The influence of temperature on these systems has, indeed, been a matter of common observation. Thus Schiff noticed that at room temperature the mixture of alcohol and water that divided into two layers on saturation with manganous sulfate lay between 15 and 50 percent, while at higher temperatures 13,14 and 60 percent alcohol could be made to divide; Traube and Neuberg found that the concentrations and relative volumes of the two layers in unsaturated solutions of ammonium sulfate in aqueous ethyl alcohol varied with the temperature; and Linebarger observed that "a fall of a few degrees of temperature will bring about the characteristic cloudiness in a solution of potassium carbonate in a mixture of alcohol and water on the point of forming layers, and this cloudiness will disappear on warming to the previous temperature." Linebarger's deduction from this behavior of one system, that "in general, it may be stated that the lower the temperature the more water is needed to bring about the disappearance of the layers", is, however, unjustified. For with certain other systems or even with some complexes of this same system, he would have found that a *rise* of temperature would cause clouding which would disappear on recooling, and that therefore at a *higher* temperature a greater addition of water would be necessary to cause the disappearance of the layers. Indeed, with acetone and water, the latter seems to be the more common case, for of the salts with which I have experimented I have found only four (Na_2SO_4, Na_2CO_3, Na_2HPO_4, $NaNH_4PO_4$) whose solutions in mixtures of acetone and water clouded on cooling.

II. THEORY

No two of the three components of a system of this class form two liquid layers at ordinary temperatures. The organic liquids are consolute with water; they reach their critical points far below the melting-points of the salts, so a two-component system with two liquid phases cannot be obtained in the case of any of these organic liquids with any salt, and water and salt do not form two liquid layers. As, however, it is most reasonable to ascribe the cause of the appearance of the two layers to the immiscibility of the salt with the organic liquid, we may for theoretical purposes regard these two components as forming (at a high temperature) the invariant system, solid salt, two solutions and vapor. On the other hand, in view of the complete miscibility at high temperatures of potassium, sodium, and silver nitrates and of potassium chlorate with water,[1] we may regard salts in general as miscible in all proportions with water at their melting-points. These two assumptions bring the systems into Class 1 of Bancroft's classification of three-component systems in which two liquid phases appear.[2] For, A being salt, B organic liquid, and C water, we have: melting-point of A higher than that of B, A and B forming the binary invariant system solid A, two solutions and vapor, A and C and B and C not forming two liquid phases and C increasing the miscibility of A and B. One condition of the classification is not necessarily fulfilled by such systems, viz. that the components form no compounds, for in some cases hydrates of the salts may appear. Provided, however, not more than one hydrate can exist in equilibrium with the two liquid phases, we can bring the system under Class 1 so far as this particular equilibrium is concerned by taking the hydrated salt instead of the anhydrous salt

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[1] Étard. Comptes rendus, 108, 176 (1889).

[2] Jour. Phys. Chem. 1, 647 (1897).

as component A. If, now, we have the further condition fulfilled that ice and salt (or ice and hydrate) cannot coexist in equilibrium with two solutions and vapor, no "secondary" quintuple point is possible and the system falls into Sub-class 1*c*. All the above conditions are fulfilled in the case of the system that forms the special subject of this research, the solid that appears in equilibrium with the two liquid phases being in this instance the anhydrous salt. The subsequent treatment will be with special reference to this system, but it may be generalized for all systems fulfilling the same conditions. Some applications of the theory to other systems will be introduced.

The temperature-concentration diagram for a system of this nature is represented in perspective in Fig. 1 and in horizontal projection in Fig. 2, the theoretical assumptions as to the miscibility of the components at temperatures not actually attainable being therein embodied. The concentrations represented upon such a diagram are those of the liquid phases. Consequently, at temperatures above which no liquid phase can exist (critical temperatures), the system becomes incapable of representation on the diagram. Each complex of a three-component system having its own critical temperature, the actual diagram would have a surface as its upper termination. Because, however, we have no measurements of the critical phenomena of three-component systems having two liquid phases and also because the theoretical relations are hereby more clearly indicated, I have thought it better to draw the diagram as if no critical points appeared.

It may be well to point out the distinction between this diagram and that employed by Schreinemakers.[1] His diagram represents the temperature-concentration conditions of equilibrium *at constant pressure*, while this represents those conditions *at the equilibrium pressure of the system*. This diagram is, therefore, the strict analogue of the plane temperature-concentration diagram commonly used for two-component systems. It should also be mentioned that my experiments were made under condi-

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[1] Zeit. phys. Chem. 23, 429 (1897).

tions not exactly those for which the diagram calls. Some of them were conducted in corked bottles and test-tubes, the rest in sealed tubes from which no attempt was made to expel the air. In the first instance we have atmospheric pressure instead of the equilibrium pressure of the system, and in both cases air is present as a fourth (more strictly a fourth and fifth) component.

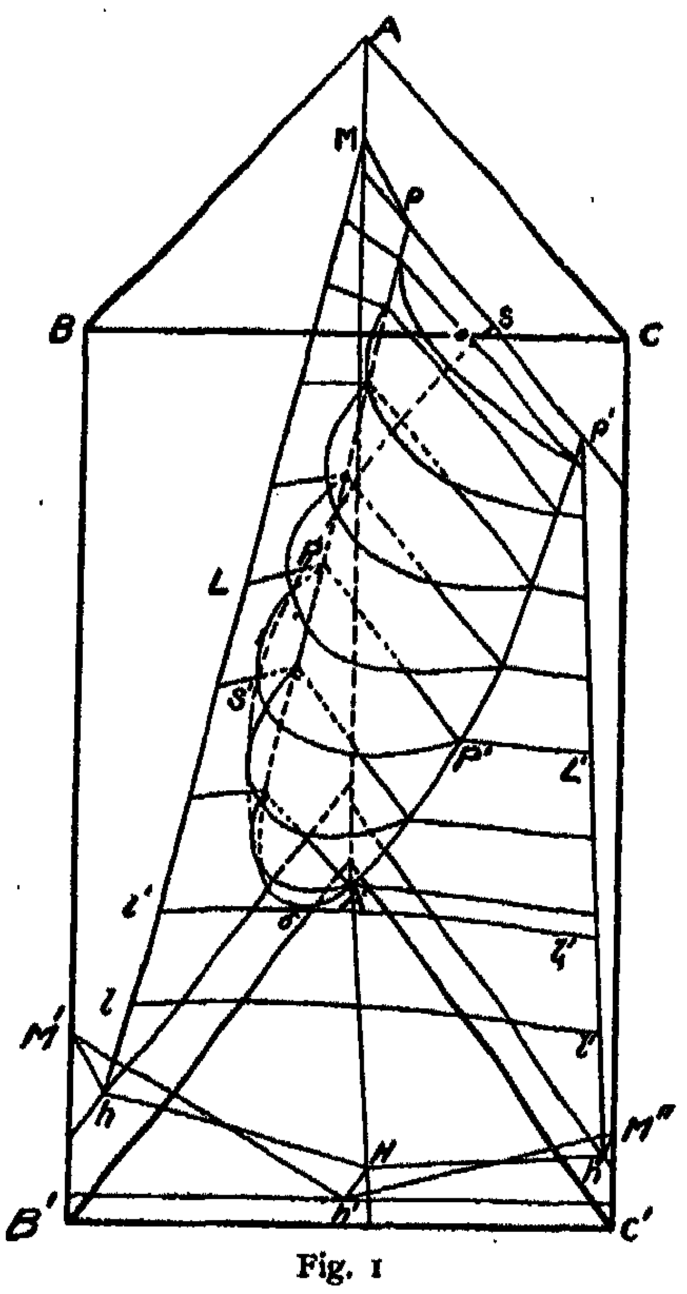

Fig. 1

In Figs. 1 and 2, H represents the cryohydric point for the three components, *h*, *h'* and *h''* are the cryohydric points of the three binary systems and *pσp'* is the boundary curve for salt, two solutions and vapor. In the solid figure, M, M' and M'' being the melting-point of the pure components, *h*M is the

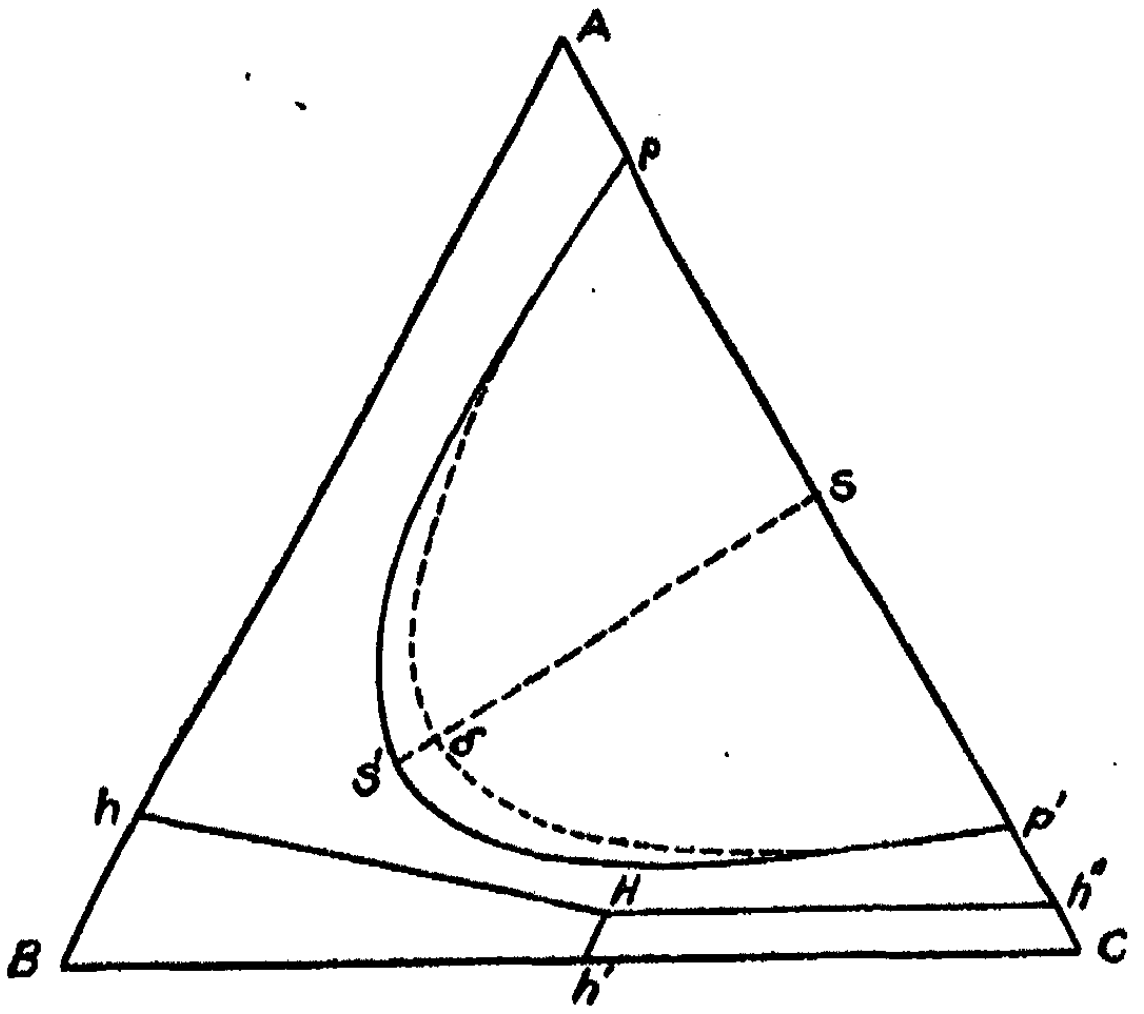

Fig. 2

solubility curve of potassium chlorid in water, $h''p'$ the solubility curve of the salt in acetone. These two curves are connected by a surface, $ll_1l''_1l''$, representing the temperature-composition condition of the equilibrium, salt-solution-vapor — the solubility surface of potassium chlorid in mixtures of acetone and water. This surface separates the region of supersaturated complexes from that of unsaturated solutions. At the point σ it divides into two — one connecting $h''p'$ with the curve $p'P'\sigma$ (one branch of the boundary curve $p\sigma p'$), the other connecting h M with the curve $pP\sigma$ (the other branch of the same boundary curve). The divided surface continues to represent the equilibrium salt-solution-vapor, while from the curve $p'\sigma p$ rises a convex surface PS′P′, representing the equilibrium two-solutions-vapor. This convex surface, I propose to call the *dineric surface.*[1] Every point upon the boundary curve $p'\sigma p$ has a con-

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[1] From δι and νηρός. This word was suggested by Prof. E. B. Titchener of this University, to whom my thanks are due.

jugate point of equal temperature upon the same curve, the two representing the two solutions which at that temperature can coexist in equilibrium with solid salt and vapor. By drawing the tie-lines joining these successive pairs of conjugate points, we obtain a ruled surface $p'Sp\sigma$. In other words, the ruled surface is developed by a horizontal line whose motion is guided by the curves $pP\sigma$ and $p'P'\sigma$. Between the ruled surface and the dineric surface is enclosed the region of temperature-composition conditions for the formation of two liquid phases and vapor. That is to say, any complex whose composition at a given temperature falls within this enclosed space is instable as a homogeneous system and will divide into two liquid layers and vapor. The enclosed space may therefore be appropriately termed the *dineric space*. Beyond the dineric surface is the region of unsaturated solutions, and beyond the ruled surface lies another enclosed space representing instable complexes dividing into solid salt, two liquid phases and vapor. This we may call the *stereo-dineric space*. Its boundaries are the ruled surface of the boundary curve and another ruled surface developed by the motion of a horizontal line guided along the straight line AA′ and the curve $p\sigma p'$ as directrices. The latter ruled surface separates the stereo-dineric space from the two divisions of the region of supersaturated complexes that divide into solid, one liquid phase and vapor.

The results of an experiment with a complex of potassium nitrate, ethyl alcohol and water may serve to illustrate the changes that take place along a temperature ordinate that passes through all the spaces into which the triangular prism is divided by the surfaces. At room temperature, the complex consisted of a saturated solution of potassium nitrate in 50 percent alcohol and a quantity of solid salt in excess. When this complex was heated in a sealed tube, the following states were realized:

(1) The complex consisted of three phases — solid salt, one solution and vapor.

(2) The liquid divided into two layers, making the total number of phases four.

(3) The salt dissolved completely, leaving the three phases — two solutions and vapor.

(4) The two liquid phases coalesced, leaving only one — liquid and vapor.

Thus the temperature ordinate for the complex traverses:

(1) The region behind the surface $l_1l'_1l''l_1$ (the region of supersaturated solutions).

(2) The stereo-dineric space.

(3) The dineric space.

(4) The region of unsaturated solutions.

Every point of the dineric surface has a conjugate point at the same temperature, the two representing the compositions of the coexistent liquid phases. But along a limiting curve $\sigma S'S$, which we may call the *crest-curve*, the two conjugate points for any given temperature coincide, that is, the composition of the coexistent phases are identical and therefore equal also to that of the whole liquid. The point σ is the *plait-point* of the surface. Its temperature is the minimum temperature at which two liquid phases can coexist in stable equilibrium with vapor, and as the point lies also on the curve $p\sigma p'$, solid salt can exist in equilibrium with the two solutions and vapor at this minimum temperature.

A peculiarity common to many, if not to all, of these systems of salt, water and organic liquid is that the dineric surface extends out so far as to overhang the boundary curve $p\sigma p'$. This is indicated in Fig. 2 where $p\sigma p'$ is the horizontal projection of the boundary curve, while $pS'p'$ is the projected limit of the dineric surface. (I have assumed that the two curves meet in p and p'. It is possible, however, that they may meet in some other conjugate points of σp and $\sigma p'$. No experiments have been made to settle the question.) The physical fact expressed by this property of the surface is that certain solutions unsaturated with respect to the salt can be made to divide into two layers by heating. For example, a complex of the composition, water 51 g, acetone 39 g, potassium chlorid 10 g, forms a homogeneous solution at 30° and at 40°, but is divided into two liquid layers at 50°. The temperature ordinate for this composition must therefore pass through the dineric surface at a point between 40° and 50°. The same behavior may be observed in the case of many other salts with acetone and water. This peculiarity in the form of the dineric surface distinguishes the systems possessing it from some others belonging to Bancroft's Sub-Class 1*c*. For example, with naphthalene, acetone and water Cady[1] found no unsaturated solution that formed two layers on heating. In such a system the limit of the dineric surface does not overhang the boundary curve. The difference between the two varieties of systems is expressed in the projected diagram (Fig. 2) by the presence or absence of the curve $pS'p'$.

From Fig. 1 it would appear that by following up the temperature ordinate for water 51 g, acetone 39 g, potassium chlorid 10 g, we should eventually pass through the dineric surface a second time and come back into the region of unsaturated solutions. In other words, the complex that divided into two liquid layers below 50° would become homogeneous again at some higher temperature. This I have not been able to realize with the system acetone, water and potassium chlorid. On account of the steepness of the dineric surface, the temperature at which the liquid becomes homogeneous lies so high (at any rate in the case of the complexes used in the few experiments made) as to be irrealizable by my method of experimentation (see p. 479). But by taking 11.6 cc water, 3.7 cc absolute alcohol and 2.93 g potassium carbonate (= 66.40 g water, 16.8 g alcohol and 16.8 g salt to 100 g solution), I obtained a complex which is an unsaturated solution below 40° and above 70° and a two-liquid-phase system between these two temperatures. With such a system it is possible to realize in an open test-tube the formation of two layers on heating and their disappearance on further heating.

It will be observed that in systems of this class the plait-

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[1] Jour. Phys. Chem. 2, 168 (1898).

point is the point of minimum temperature for the coexistence of solid and two liquid phases (and also for that of two liquid phases), while in the system water, sodium chlorid and ethylene cyanid studied by Schreinemakers[1] it is the point of maximum temperature for this equilibrium.[2] The latter system belongs to a different class, for here the appearance of the two layers is due to the incomplete miscibility of water and ethylene cyanid and the third component is such as to *decrease* the miscibility of the other two. If we neglect the possibility of the recurrence of two liquid layers at a higher temperature (due this time to the incomplete miscibility of sodium chlorid with ethylene cyanid), this system comes under Sub-class 3*a* of Bancroft's paper, A being ethylene cyanid, B water and C sodium chlorid. The experimental data of Schreinemaker's paper fulfil the predictions of Bancroft that in the projected temperature concentration diagram for systems of this Sub-class, (1) the two branches of the boundary curve for solid A, two solutions and vapor will diverge as they leave the side AB of the triangle; (2) the temperature will rise along this curve as we pass away from the side of the triangle; and (3) the temperature will rise from the quintuple point along the two branches of the boundary curve for solid C, two solutions and vapor, the curve having therefore a point of maximum temperature.[3] For while the concentrations of the ethylene cyanid in the two liquid phases at the binary quadruple point (on the side of the triangle) are:

Upper layer 72 g-mols to 100 g-mols in all
Lower " 2.5 " " " " " "

at the ternary quintuple point they have diverged to

Upper layer 82.79 g-mols to 100 g-mols in all
Lower " 1.99 " " " " " "

The temperature of the quadruple point is 18.5° and that of the quintuple point 29°, a rise as we pass from the side of the triangle. And, finally, the temperature rises as we pass from the

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[1] Zeit. phys. Chem. 23, 417 (1897).
[2] See diagram in Schreinemaker's paper, p. 429.
[3] Bancroft. Jour. Phys. Chem. 1, 655 (1897).

quintuple point along the boundary curve for solid sodium chlorid, two solutions and vapor, and reaches a maximum at 145.5°. In assigning this system to Sub-class 3*a*, we have assumed that sodium chlorid and ethylene cyanid do not form two liquid phases. It would be more consistent, however, to make the same assumption in this case as in that of the acetone and potassium chlorid, i. e. to regard the two components as forming two layers at a temperature not actually realizable. This assumption would require that there should proceed from the AC side of the triangle a second dineric surface, which would be analogous to that of Fig. 1, for here, as there, the effect of the third component, water, is to render the other two more miscible. Though it seems probable that not far above 145.5° chemical action between water and ethylene cyanid will occur to such an extent as materially to alter the nature of the system, still it is just possible that a portion of the second dineric surface may be realizable; in other words, mixtures of ethylene cyanid, water, and sodium chlorid that clear at or below 145.5° may cloud again at higher temperature. But Schreinemaker's work shows that at least this second dineric surface does not cut the first. The lower dineric surface will therefore not differ in any respect from that of systems of Sub-class 3*a* and this application of Bancroft's predictions is legitimate.

The Isotherms and Isothermal Planes

An isothermal plane is, of course, a horizontal section of the triangular prism and the *isotherm* is made up of the curves of intersection of this plane with the dineric and solubility surfaces. For temperatures, at which only one solid and one liquid phase exist, the isotherm is a single curve (an element of the surface, $ll_1l_1'l$) representing the solubility of the salt in varying mixtures of acetone and water. For temperatures at which one solid and two liquid phases can appear, the isothermal plane has the form of Fig. 3, the isotherm consisting of the three curves LP, PSP′ and P′L′. The solubility of the salt A in water at the given temperature is represented by the point L and the

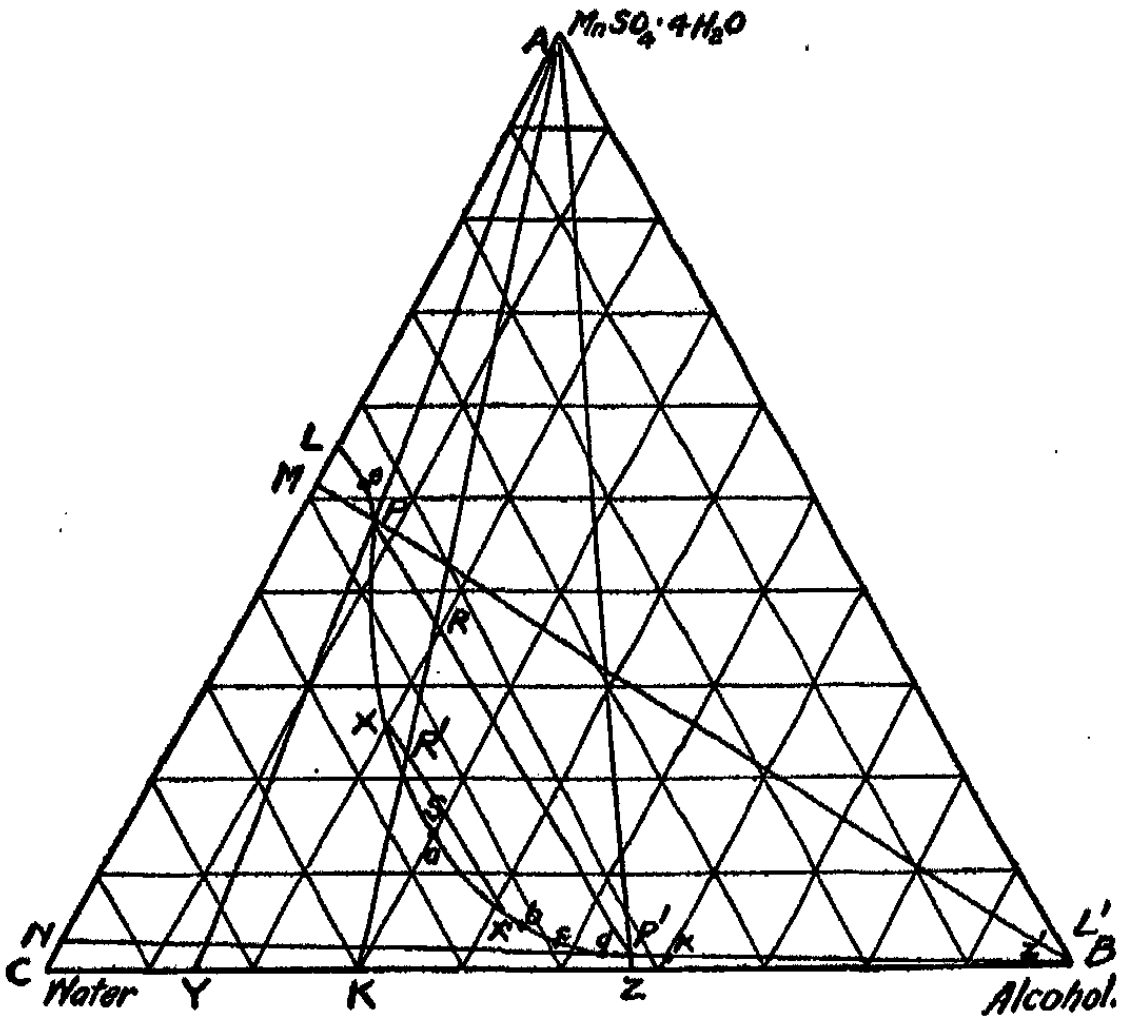

Fig. 3

solubility of the salt in the organic liquid by L′. (As the diagram is drawn to represent the system alcohol, water and manganese sulphate, the point L′ is practically coincident with B. The same is true in the system acetone, water and potassium chlorid). The field CLPSP′L′BC is a section of the region of unsaturated solutions, PSP′P, a section of the dineric space, and the triangle APP′ a section of the stereo-dineric space. Therefore at the temperature of the isotherm, complexes whose compositions are represented by points within the field CLPSP′L′BC are stable as homogeneous liquid (and vapor); complexes within the fields, ALP, AL′P′ are instable as homogeneous liquid and break down into solid salt and solution represented by points of the curves LP, L′P′ respectively; complexes within the triangle APP′ break down into solid salt and two solutions having the composition P, P′, and complexes within the dineric field PSP′P break into two solutions represented by conjugate points of the dineric curve PSP′. S being the *crest-point* — the point of the crest-curve for this temperature — the composition of the lower layer in a system of two liquid phases and vapor will be denoted by a point X between S and P, that of the upper layer by the conjugate point X′ between S and P′, while the composition of the whole complex will be denoted by that point of the tie-line XX′, which would be the center of gravity of the whole mass if the mass of the lower layer were situated at X and that of the upper layer at X′.

If, to a mixture of organic liquid and water, whose composition is represented by a point K between Y and Z, we continuously add salt, the composition of the mixture will vary along the line KA until it reaches the dineric curve PSP′, where the solution will divide into two liquid phases of compositions represented by conjugate points of the dineric curve. As the composition of the whole complex proceeds along the line KA, the two layers will differ more and more in composition, the conjugate points separating farther and farther. At the same time, the relative *masses* of the two layers will vary continuously, because they must always be such that their center of gravity will lie at the intersection of the tie-line with the line KA. When the composition of the whole has reached the value R, the compositions of the two layers will be P, P′, and their masses as P′R : PR. Further addition of salt will have no effect on either the composition or the relative masses of the two phases. It is evident also that mixtures of the organic liquid and water having compositions between C and Y or between Z and B cannot be made to divide into two layers by addition of salt. In both cases we should get first a homogeneous solution, then a solid salt in equilibrium with a homogeneous solution of a composition represented by a point of the curve LP in the one case or of the curve L′P′ in the other. In like manner, N and M being the points of intersection of BP′ and BP with the side AC, it is evident that we get different results by continuous additions of organic liquid to aqueous salt solutions of different concentrations. In the case of the most dilute solutions, C to N, we get first homogeneous solutions, then solid salt and a solution of the curve P′B. More concentrated solutions, M to N, give first homogeneous liquid, then two liquid phases of changing composition and relative masses, then solid salt and two liquid phases of constant composition but varying relative masses, and finally solid and solution of the curve BP′, the mass of the lower layer having now become zero. Solutions of concentrations between M and L (the latter being the composition of the saturated aqueous solution) give first homogeneous liquid, then solid salt and solution of the curve LP, then solid salt and two solutions, the mass of the lower layer continuously decreasing, and finally solid and solutions of the curve BP′, the lower layer having disappeared.

Very few quantitative experiments have been made with systems of this class. Of measurements at constant temperature there are a few by Schiff,[1] Traube and Neuberg,[2] Bodländer,[3] and Linebarger.[4]

Schiff observed that at room temperature aqueous alcohol of from 15 to 50 percent strength separated into two layers on saturation with manganous sulfate. Table I gives his measurements of the percentage weight of crystallized salt ($MnSO_4.4H_2O$) in the saturated solutions. The data for this system are represented in Fig. 3, where the hydrated salt is taken as one of the components. As Schiff's measurements were of saturated solutions in all cases, they give the points P, P′ and points of the curves LP and P′B. They can be immediately plotted on the diagram from the figures of Table I by marking off the given percentage of salt on the straight line joining the point A with the point for the strength of alcohol. If more accurately made, Schiff's measurements of the compositions of the two layers would undoubtedly have been exactly the same in the 20, 30, and 40 percent alcohol. A few points of the dineric curve are obtained from the measurements of Linebarger. As he worked

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[1] Lieb. Ann. 118, 370 (1861).

[2] Zeit. phys. Chem. 1, 509 (1887).

[3] Zeit. phys. Chem. 7, 318 (1891).

[4] Am. Chem. Jour. 14, 380 (1892).

at 20° his results may fairly be plotted on the same isotherm as Schiff's. Table II gives Linebarger's results, recalculated on the basis of grams water, alcohol and hydrated manganous sulfate respectively to one hundred grams solution. The letters in Table I and II, refer to Fig. 3. The position of the point P′ is uncertain. I have plotted Linebarger's last determination as probably the nearest approach to that point, though he does not mention that salt was precipitated in the experiment. As already intimated, Schiff's analyses of the upper layers in the 20, 30 and 40 percent alcohol do not accord with the theory. The same is true of his analysis of the 50 percent alcohol solution. But the discrepancies may easily be due to experimental error.

It appears from the diagram (points N and M) that the range of manganous sulfate solutions that can be made to divide into two layers at room temperature by addition of alcohol is very wide, running from solutions containing about 3 to solutions containing over 51 percent of the tetrahydrate, i. e. 2 to 34 percent solutions of manganous sulfate. Schiff's observation that in presence of the crystals the volume of the upper layer is the greater the stronger the alcohol is evidently in accord with the theory. For the nearer the point K approaches Z, the greater is the ratio PR : PR′.

Traube and Neuberg determined a number of conjugate points of the dineric curve of the 33° isotherm of the system alcohol, water and ammonium sulfate and Bodländer determined the position of the intersections of the dineric with the salt solution curves (i. e. points P, P′, Fig. 3) on the 15° isotherm of the same system. The methods of the phase rule having been already applied to these measurements by Schreinemakers,[1] it is unnecessary to discuss them here.

Linebarger conceived of the layer formation as taking place in systems of salt, an organic liquid and water only within certain limits of composition and defined the "upper" limit as "the limit attained when the formation of a layer is rendered impossible by the presence of too much organic liquid", and the

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[1] Zeit. phys. Chem. 23, 657 (1897).

"lower" limit as "the point where a layer ceases to form on account of the presence of an excess of water." His method of determination of the lower layer was as follows: "Varying quantities of organic liquid and water were added from burettes to a titrated solution of a salt until a drop of water would clear up the milkiness caused by a drop of alcohol." It is evident that this procedure gives a point of the dineric curve. For he begins with a point on the side AC of the triangle and proceeds in a straight line toward B (by adding alcohol) till he has overstepped the dineric curve, then he proceeds in a straight line towards C (adding water) until he has again overstepped the curve and so moves in an ever-narrowing zigzag until he has approached so close to the dineric curve that a drop of one liquid causes a change in one direction and a drop of the other causes a change in the other direction. The tables given in Linebarger's paper are therefore data of the dineric curve of the 20° isotherms of the various systems. His measurements are limited to a small portion of the curve and no conjugate points are determined.

In attempting to determine the "upper" limit, Linebarger took a certain volume of salt solution and added the organic liquid in small quantities until the volume of the lower layer became zero. A glance at the diagram will show that this result cannot be attained without precipitation of salt unless a line joining some point on AC with the point B has two intersections with the dineric curve and none with the line PP′, which can occur only in case the dineric curve which has been tending downward toward the side CB begins to tend upward when we get near the side AB. In general this is not the case and Linebarger found that precipitation of salt prevented his attaining the "upper" limit of layer-formation in all systems but one — potassium carbonate, ethyl alcohol and water. In the case of this system, either the dineric curve has the peculiar form just referred to or, what seems more probable in view of the fact that "crystals appeared as soon as the layer disappeared", Linebarger was really determining points on a metastable extension of the dineric curve.

An interesting confirmation of the theory of the tie-lines is afforded by some measurements by Traube and Neuberg of the variations of the conjugate solutions of a complex of ammonium sulfate, alcohol and water with the temperature. They added 250 cc of 99.6 percent alcohol to 750 cc of a solution of ammonium sulfate, containing 340 g to the liter and analyzed the two layers into which the mixture divided at four different temperatures. Their results recalculated into mass-percentages are given in Table III. According to our theory the tie-lines joining each pair of conjugate points must pass through the temperature ordinate of the composition of the whole complex. In other words, the horizontal projections of the four tie-lines must intersect in the point that gives the composition of the whole complex. If the tie-lines be actually drawn on a triangular diagram they are found to intersect, as nearly as one can tell, in the point

Water 58.7 Alcohol 18.1 Salt 23.2

Taking the specific gravity of the ammonium sulfate solution used as 1.168 and that of the alcohol as 0.795, I calculate for the composition of the complex as made up by Traube and Neuberg:

Water 57.86 Alcohol 18.42 Salt 23.72

The diagram shows also that with rising temperature there is an increase in the relative mass of the lower layer, i. e. the ratio R′X′ : R′X (Fig. 3) increases as the temperature rises, and Traube and Neuberg found that with increasing temperature the lower layer increased in volume, while the upper layer decreased.

TABLE I

Manganous Sulfate, Alcohol and Water — Schiff

Strength of alcohol	Pct $MnSO_4.4H_2O$		Point on Fig. 3
0	56.25		L
10	51.4		*l*
	Upper layer	Lower layer	
20	2.2	47	
30	1.66	48	P
40	1.37	48.6	
50	2.0		
60	0.66		*k*

TABLE II

Manganous Sulfate, Alcohol and Water — Linebarger, 20° C

g water	g alcohol	g salt ($MnSO_4.4H_2O$)	Point on Fig. 3
55.86	30.03	14.11	*a*
52.25	43.59	4.16	*b*
49.41	47.66	2.94	*c*
45.34	53.00	1.66	*d*
42.56	56.24	1.20	P'

TABLE III

Ammonium Sulfate, Ethyl Alcohol and Water — Traube and Neuberg

Composition of 100 g solution

	Upper layer			Lower layer		
Temp	g water	g alcohol	g salt	g water	g alcohol	g salt
16.6°	52.80	40.21	6.99	60.33	10.19	29.48
33.0°	47.99	46.75	5.26	61.02	9.80	29.18
41.8°	47.34	47.67	4.99	61.16	9.74	29.10
55.7°	45.90	49.47	4.63	61.59	9.46	28.95

III. EXPERIMENTS

In order to gain a more accurate knowledge of the shape of the dineric surface for the system acetone-water-potassium chlorid, I have made the following experiments:

I. A series of measurements of the temperatures at which different unsaturated solutions of the system divide into two layers, i. e. a determination of the points at which given temperature-ordinates cut the dineric surfaces and so pass from the region of unsaturated solutions into the dineric space.

II. A few experiments to discover whether divided solutions become homogeneous again at higher temperatures, i. e. whether the temperature-ordinate passes a second time through the dineric surface — this time from the dineric space to the region of unsaturated solutions.

III. Measurements of the temperatures of division of saturated solutions, i. e. determination of points of the boundary curve.

IV. Measurements on the 30° and 40° isotherms.

The Materials

The potassium chlorid used in all the experiments described in this paper was carefully purified by three recrystallizations, then fused in a platinum dish. It gave no reactions for sulfate and none for magnesium and an analysis by precipitation with silver nitrate gave:

KCl taken	AgCl found	Calc. for pure KCl
0.5359 g	1.0313 g	1.032 g

One portion used in some of the experiments of Series III was made from acid potassium carbonate. Analysis of this portion gave:

KCl taken	AgCl found	Calc. for pure KCl
0.7360 g	1.4125 g	1.418 g

The acetone was dried over calcium chlorid and fractionated. The portions used distilled within half a degree.

(a) Temperature of Division of Unsaturated Solutions

The salt was weighed out from weighing tubes and the water and acetone added from burettes. The complex was then heated and the temperature at which the clouding took place noted. Where the temperature of division was low, the measurements were made in a wide test-tube provided with a cork through which the thermometer passed. For higher temperatures, pressure flasks were tried at first, but, these proving leaky, sealed tubes were used, the tubes being heated in a water- or oil-bath.[1] Here, of course, the temperature measurement was not as accurate as for the lower temperature, the thermometer being immersed in the bath instead of in the inner liquid. In all cases a number of observations of the temperature of division were made. For the lower temperature, these observations did not in general differ from one another by more than a few tenths of a degree, but in the case of the solutions in 30 percent acetone the clouding was indistinct and the temperature of division, therefore, much harder to distinguish. The error in all the

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[1] For the temperatures above 150° an air-bath was used.

temperature readings for this strength of acetone and in the higher reading for other mixtures may amount to more than one degree. The results are given in Tables IV–IX. They show that with rising temperature the dineric surface approaches the acetone-water plane of the triangular prism. Table X shows the nearest approaches to that plane that were realized and so gives an approximation to the position of the limit-curve of the projected diagram — the curve $pS'p'$ of Fig. 2. The limit-curve as thus approximately determined is shown together with the boundary curve in Fig. 4.

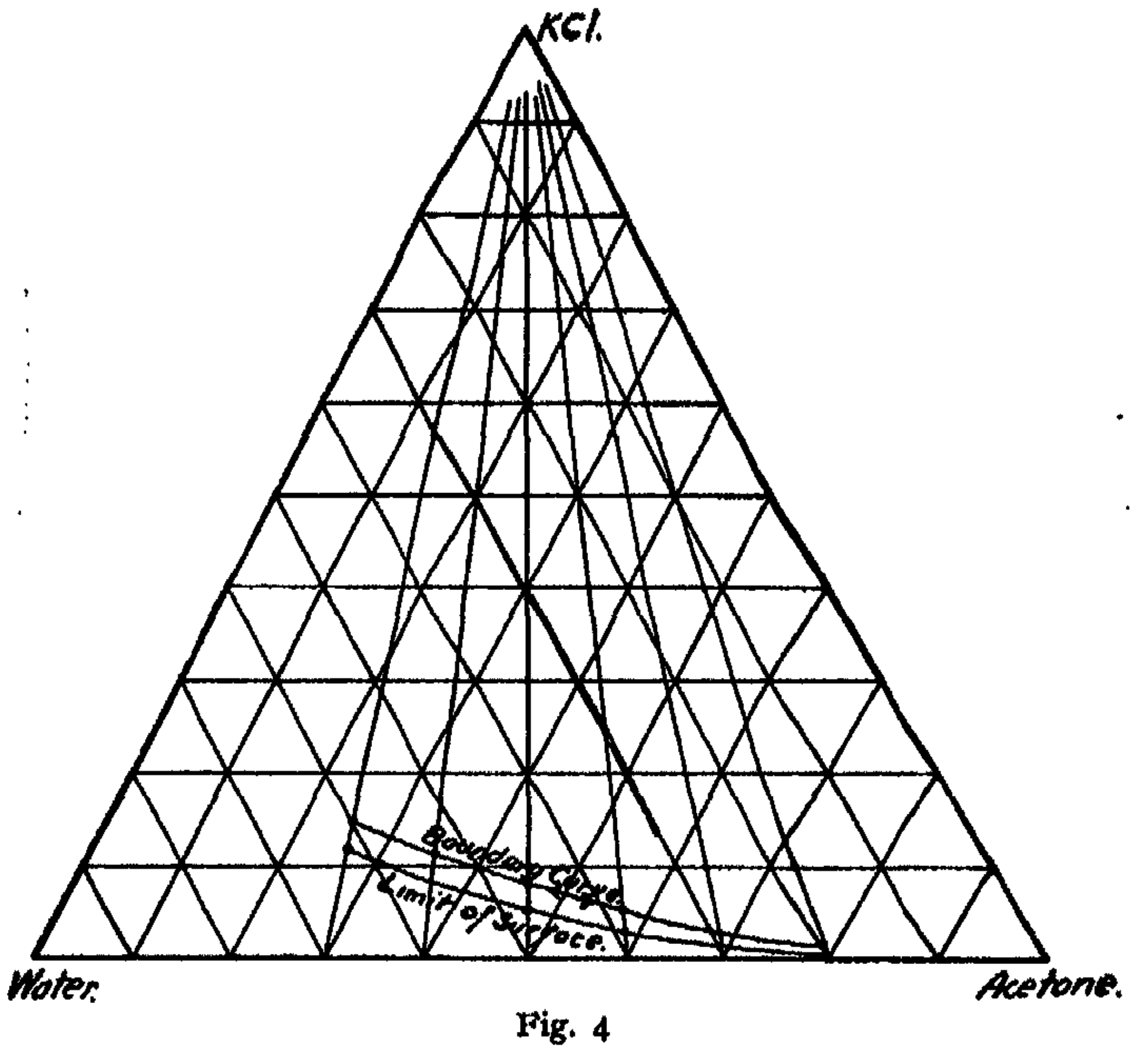

Fig. 4

TABLE IV

Temperatures of Division

30 pct acetone

Composition of 100 g solution			Temperature of division
g water	g acetone	g salt	
63.46	27.20	9.36	No division up to 290°
62.00	26.57	11.43	" " " 150°
61.75	26.47	11.79	" " " 290°
61.68	26.43	11.92	103°
61.73	26.46	11.85	100°
61.19	26.22	12.62	81°
60.50	25.93	13.60	67°
60.40	25.88	13.71	62°
59.86	25.64	14.50	48.5
59.98	25.72	14.30	48
59.02	25.31	15.68	36 (?) Metastable
	Saturated solution		40°

TABLE V

Temperature of Division

40 pct acetone

Composition of 100 g solution			Temperature of division
g water	g acetone	g salt	
54.42	36.28	9.28	About 65° (in pres. flask)
54.00	36.00	10.00	49.3
53.84	35.90	10.28	45.6
53.48	35.65	10.87	39.0
53.27	35.51	11.22	35.1
	Saturated solution		34.2

TABLE VI

Temperature of Division

50 pct acetone

Composition of 100 g solution			Temperature of division
g water	g acetone	g salt	
47.48	47.48	5.04	No division up to 150°
47.12	47.12	5.79	97.5°
46.96	46.96	6.09	76
46.66	46.66	6.69	57.2
46.61	46.61	6.80	56
46.54	46.54	6.94	52.6
46.38	46.38	7.23	47.4
46.06	46.06	7.90	35.4
45.75	45.75	8.50	27.4 (?) Metastable
	Saturated solution		32.6

TABLE VII

Temperature of Division
60 pct acetone

Composition of 100 g solution			Temperature of division
g water	g acetone	g salt	
38.80	58.20	2.97	149°
38.42	57.64	3.95	71.5
38.20	57.49	4.32	51.9
38.05	57.24	4.70	45.1
38.04	57.25	4.69	44.4
38.00	57.19	4.79	41.0
37.95	57.11	4.94	39.0
37.78	56.96	5.27	34.0
	Saturated solution		33.3

TABLE VIII

Temperature of Division
70.12 pct acetone

Composition of 100 g solution			Temperature of division
g water	g acetone	g salt	
29.24	68.61	2.13	54.1
29.19	68.50	2.30	47.2
29.16	68.44	2.41	42.6
29.14	68.37	2.48	40.4
29.14	68.33	2.53	39.0
	Saturated solution		35.4
	70 pct acetone		
	Saturated solution		35.6
	75 pct acetone		
	Saturated solution		39.0

TABLE IX

Temperature of Division
80 pct acetone

Composition of 100 g solution			Temperature of division
g water	g acetone	g salt	
19.90	79.60	0.55	110.5
19.88	79.52	0.65	95
19.84	79.36	0.80	67
19.82	79.29	0.93	55.5
19.80	79.21	0.99	45.8
	Saturated solution		45.6

TABLE X

Minimum quantity of salt that will cause division

pct acetone	g salt to 100 g solution
30	11.8
50	Between 5.0 and 5.8
60	2.9
80	0.5

(b) Attempts to Realize Clearing

A number of divided unsaturated solutions were heated to higher temperatures to determine whether the two liquid phases become one again. A beaker was used as an air-bath and the sealed tubes were shaken by means of wires wrapped about them and projecting through the asbestos cover of the beaker. With carefully made tubes, it was found possible to reach a temperature of 250° in this way, but when heated to 300°, the tubes invariably burst. It is not known to what extent decomposition of acetone at high temperatures may alter the equilibrium between the phases. That decomposition does take place to an appreciable extent is shown by the coloration of the liquid in the tubes. The following complexes remained divided at about 300°:

(1) Water 60.77 g Acetone 26.04 g Salt 13.19 g (30 pct acetone)
(2) " 46.30 g " 46.30 g " 7.40 g (50 pct acetone)

When the approximate position of the limit-curve (Fig. 4) had been determined, a few complexes in the neighborhood of the curve were chosen in the hope that they would become homogeneous at realizable temperatures:

(3) Water 47.0 g Acetone 47.0 g Salt 6.0 g (50 pct acetone)
and
(4) " 47.1 g " 47.1 g " 5.8 g (50 pct acetone)
remained divided at 220°–230°.

(5) Water 61.68 g Acetone 26.43 g Salt 11.92 g (30 pct acetone) which did not divide till it had reached a temperature of nearly 100° appeared to be homogeneous above 180°, no second layer being visible and no clouding being caused by shaking. But

the volume of the upper layer was so very small as to make it difficult to decide whether the two had really coalesced, and the evidences of decomposition were specially marked in this tube. It is therefore not claimed that reclearing has been certainly realized in any complex of the system potassium chlorid, acetone and water. That it can be realized in the analogous systems, potassium nitrate, ethyl alcohol and water and potassium carbonate, ethyl alcohol and water is shown by the experiments described above (pp. 464–466).

(c) Temperature of Division of Saturated Solutions—The Boundary Curve

In determining the temperature of division of saturated solutions, a difficulty is met with. Here one cannot make one's readings by heating the tube containing solution and salt and observing the temperature at which the liquid clouds, for the solubility of the salt increases with the temperature and the chances are that the solution will not be saturated when the clouding occurs. Consequently it is necessary to heat the tube to a temperature above the temperature of division of the saturated solution and then, shaking it as it cools, observe the temperature at which the clouding disappears. If the tube be cooled rapidly, a temperature below that of the boundary curve is reached, a metastable extension of the dineric surface into the region of the supersaturated solutions being realized. Such a state is realizable even in the presence of an excess of solid salt, for the crystals form slowly and a temperature below that of the stable equilibrium is easily reached before clearing takes place.

The compositions and temperatures of divisions of the saturated solutions are given in Table XI. The compositions were derived from the data of Tables IV–IX by plotting the variation of the temperature of division with the salt-content of the unsaturated solutions and extrapolating for the observed temperature of division of the saturated solution. The relative proportions of acetone and water in the solutions were, of course, already known. On the projected triangular diagram the boundary curve, so far as I have determined it, has the position shown in Fig. 4. The data of Table XI plotted with temperature and strength of acetone as coordinates gives the curves of Fig. 5, which may also be regarded as traced upon the water-acetone face of the triangular prism by the horizontal line which moves upon the salt-temperature axis and the boundary curve as directrices. Such a curve might be used in the estimation of the strength of aqueous acetone. The error due to the difficulty of determining accurately the temperature of division of saturated solutions could be eliminated by making the readings always under the same conditions, but at best the method would be applicable only to mixtures of say between 20 percent and 85 percent acetone not containing any third substance and would not be very accurate for mixing between 50 percent and 60 percent acetone because of the flatness of this portion of the curve.

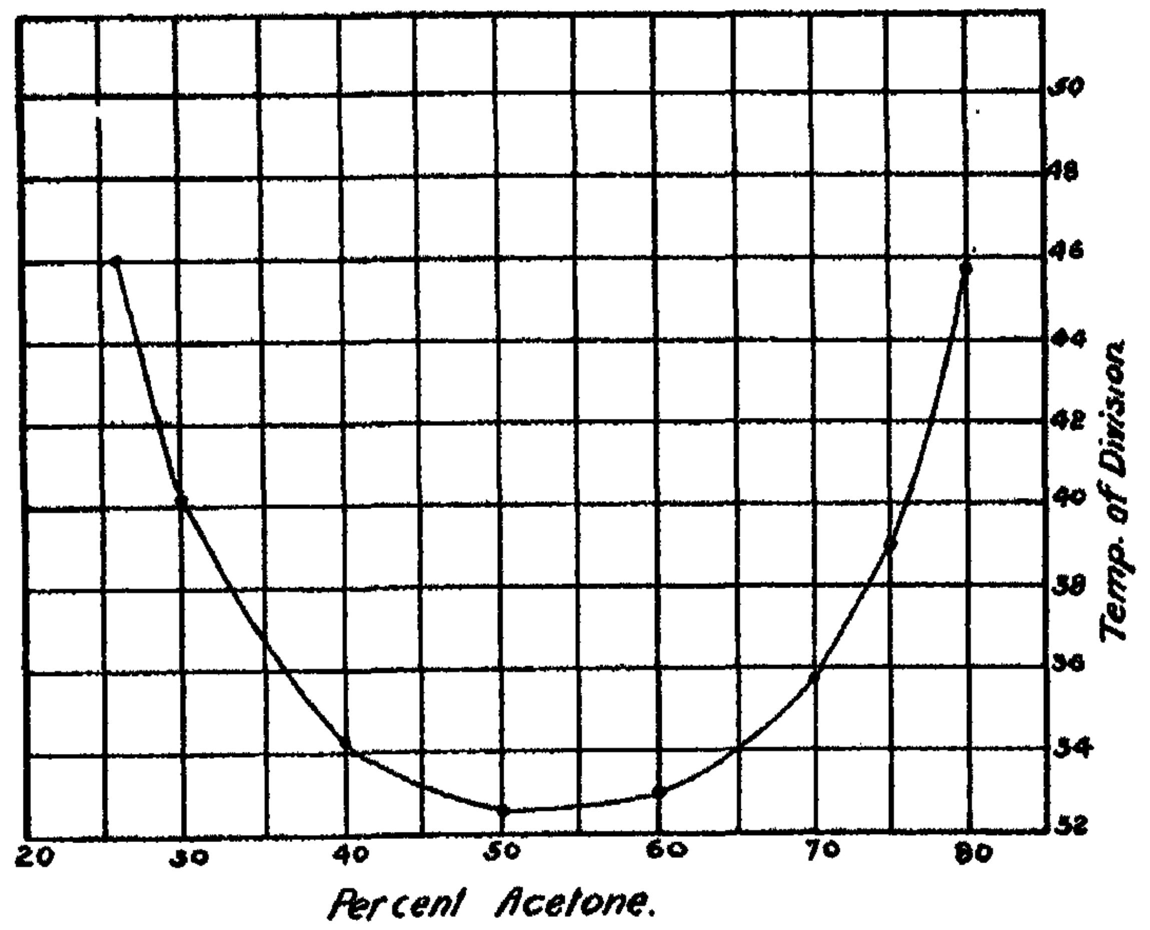

Fig. 5

TABLE XI

Temperature of Division of Saturated Solutions

pct acetone	Temp of division	Composition of 100 g solution g water	 g acetone	 g salt
26	46.5	....	....	....
30	40.0	59.36	25.44	15.20
40	34.2	53.21	35.47	11.32
50	32.6	45.97	45.97	8.06
60	33.3	37.86	56.80	5.34
70	35.5	29.09	68.25	2.66
75	39	....	....	...
80	45.6	19.80	79.20	1.00

An experiment to determine the effect of a further increase of temperature on a divided saturated solution may be here described. A portion of 75 percent acetone was heated in a sealed tube with a quantity of salt more than sufficient to saturate it at any temperature realized. About 230°, the upper liquid phase became identical with the vapor, the lower liquid phase remaining. On cooling, the upper phase divided into liquid and vapor with the turbulent clouding characteristic of a critical point.

(d) The Isotherms

THE 30° ISOTHERM

At 30°, two liquid phases do not appear. This isotherm, therefore, consists of a single curve representing the solubility of potassium chlorid[1] in varying mixtures of acetone and water.

In the solubility determinations I used small bottles that had been steamed out. The acetone solutions were made up by weight and with the finely-powdered salt were heated to 40° for seven hours with frequent shaking. The bottles were then transferred to an Ostwald thermostat set at 30°. After they had stood over night, salt had crystallized out from all these solutions, showing that they were saturated. The 40, 50 and 60 percent acetone solutions were still divided into two layers but became homogeneous on shaking. The bottles were left standing in the thermostat two days longer before the analyses were

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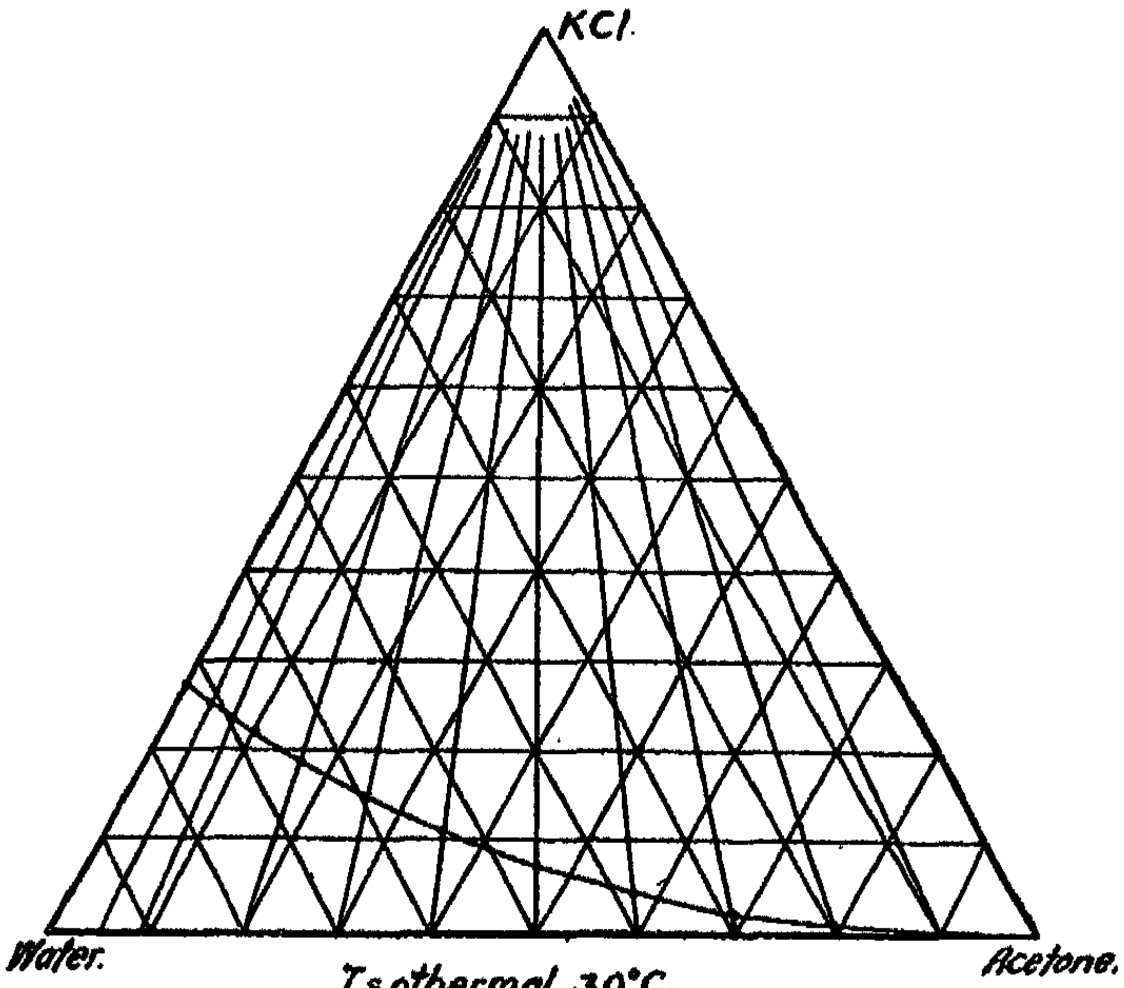
[1] The solubility of potassium chlorid in water at 30° appears from my measurements as 37.495 parts in 100 parts water. Mulder, Scheik. Verh. 1864, 39, found 37.4, and Andreä, Jour. prakt. Chem. 137, 470 (1884), got by interpolation of his results 37.275.

made. After two days more a second analysis of each was made and the mean of the two determinations is given in Table XII. The analyses were made by evaporation according to the method described by Trevor[1]. The isotherm is represented in Fig. 6.



Isothermal. 30°C.
Fig. 6

TABLE XII

Isotherm 30° C

pct acetone	Composition of 100 g solution g water	g acetone	g salt
0	72.73	0.00	27.27
5	71.15	3.74	25.11
9.09	69.62	6.96	23.42
20	64.88	16.22	18.90
30	59.49	25.45	15.06
40	53.17	35.52	11.31
50	45.98	45.98	8.04
60	37.97	56.91	5.12
70	29.22	68.18	2.60
80	19.82	79.43	0.76
90	9.98	89.88	0.13
100	0.00	100.00	0.00

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[1] Zeit. phys. Chem. 7, 468 (1891).

THE 40° ISOTHERM.

The isotherm for 40° is represented by Fig. 7 and Tables XIII–XV. The points upon the curve KP and P′B, the solubility curves, were determined according to the same method used for the 30° isotherm. The results are given in Table XIII.[1] For the points of the dineric curve I proceeded as follows:

Portions of an aqueous solution of potassium chlorid of known strength were measured out by carefully calibrated pipettes (5 cc in most cases, but in some cases 1 cc) varying quantities of water were added from a calibrated burette and just sufficient acetone run in from another burette to cause permanent separation at 40°. Of course, a number of such experiments were necessary for the determination of each point. A glance at Fig. 7 will show that this method gives points upon

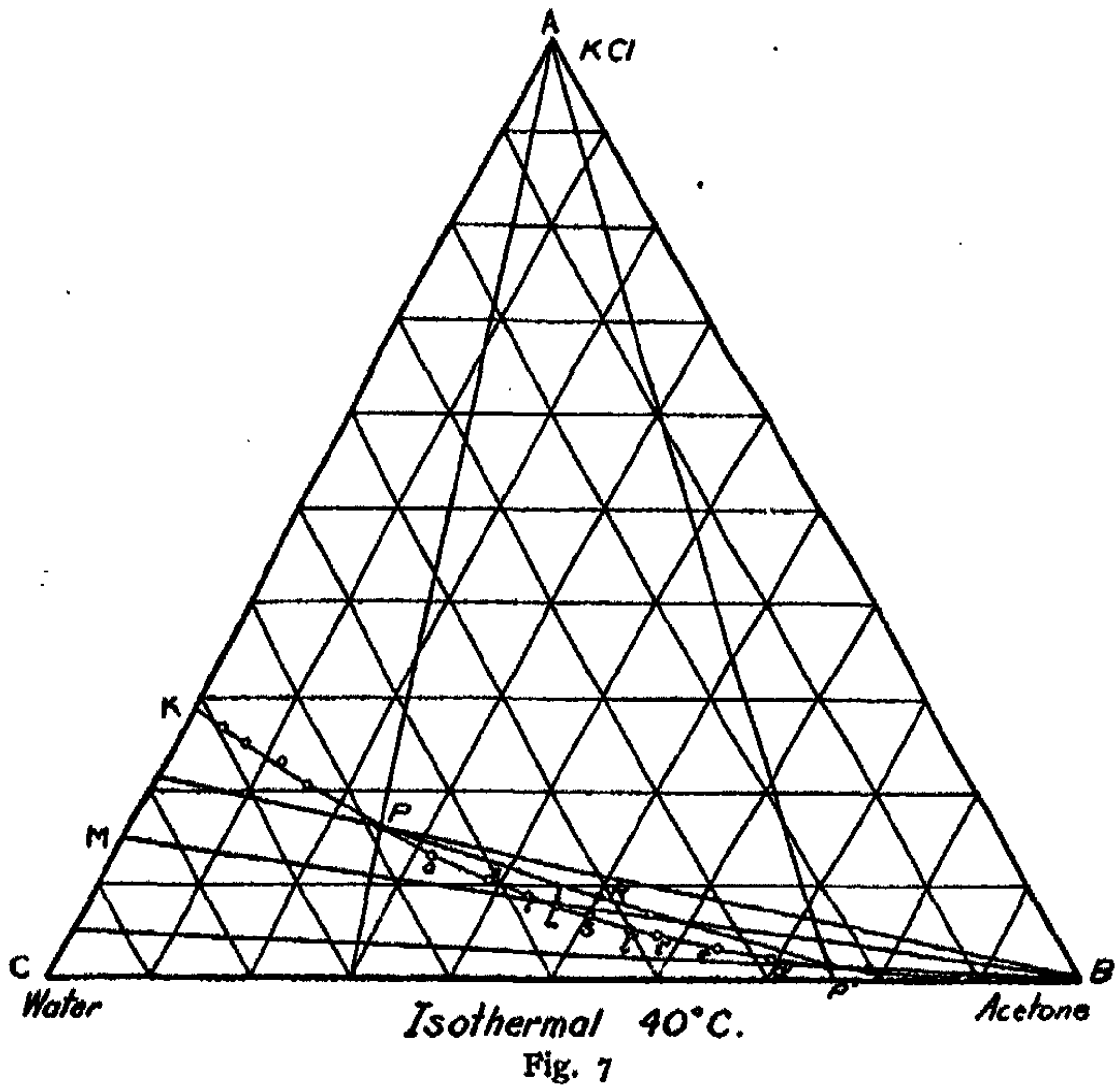

Fig. 7

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[1] The solubility of potassium chlorid in water amounts to 40.18. Mulder found 40.1, Andreä 40.12.

the dineric curve PSP′. For, if to an aqueous solution of potassium chlorid represented by the point M, we continuously add acetone, the composition of the complex will vary along the line MB and the solution will remain homogeneous until the point L is reached, when it will divide into two layers. If, then, we know the composition of the original aqueous solution (M) and the quantity of acetone added, the point L is determined.

The points of the dineric curve so obtained are given in Table XIV. The compositions of the solutions that just divide at 40° are there expressed in two ways: (1) For plotting on rectangular coordinates, as grams water and acetone respectively per gram salt; (2) For triangular coordinates, as grams of each component per hundred grams solution. In calculating these results, the specific gravity of water at room temperature was taken as equal to unity and that of acetone as 0.792, the value given in Landolt and Börnstein's Tables for acetone at 19.8° as compared with water at the same temperature.

A number of pairs of *conjugate* points of the dineric curve were determined. This was done by the following method: The data of Table XIV were used to plot a curve with acetone per gram salt (x) and water per gram salt (y) as coordinates. A two-liquid-phase system having been allowed to come to equilibrium at 40° C, portions of each layer were pipetted off and weighed. Their salt content was then determined by evaporation and the difference gave the number of grams of acetone and water together. Reduced to one gram salt, this gave the value of $x + y$ and reference to the curve enabled one to determine what values of x and y gave the found value of $x + y$. The composition of the conjugate phases is given in Table XV.

An approximation to the position of the point P can be obtained by producing the salt-solution curve, KP, and the dineric curve to their intersection, and in the same way the point P′ can be found by producing BP′ and the dineric curve. On either the rectangular or the triangular diagram, however, these approximations are very rough. I obtained a more accurate determination of the points by evaporating a portion of each of the two liquid phases that existed in equilibrium with solid salt, so determining what percentage of the solution consisted of water and acetone together, and then finding from Table XI (Fig. 5) what were the *relative* quantities of acetone and water in the solutions that coexist with solid and a second liquid phase at 40°. A direct observation there tabulated gives 30 percent acetone as one of these and interpolation shows that 76 percent acetone is the other. The former will, of course, be the lower layer. Evaporation-analyses of the lower layer were made in the case of the 40, 50 and 60 percent acetone solutions and gave as an average 84.23 as the percentage of acetone and water in this layer. For the upper layer, an average from the 50, 60 and 70 percent solutions gave 98.57 percent. Hence the figures given in Table XV for the composition of these coexistent phases.

The following deductions can be drawn from the diagram of the 40° isotherm:

1. At 40° aqueous solutions of potassium chlorid of from 5 to 21.5 percent strength can be made to divide into two liquid layers by addition of a sufficient quantity of acetone. From weaker or stronger solutions, salt will be precipitated. We have already seen that the acetone-water mixtures that can be made to divide by addition of potassium chlorid lie between 30 and 76 percent acetone.

2. The crest-point S lies between l and l'. Thus there is a solution of a composition of about 50 percent acetone, 43 percent water, and 7 percent salt that an infinitesimal addition of salt or of acetone will cause to divide into two layers of almost exactly equal composition.

3. The point R being the middle point of the line PP′, the line BR produced cuts the side AC of the triangle at about 17 percent salt, and the line AR produced cuts CB at 55 percent acetone. Therefore, if we begin with a 17 percent solution of potassium chlorid and add acetone till salt just begins to precipitate, we shall have two liquid layers of equal mass, and we

get the same two layers by saturating 55 percent acetone with potassium chlorid. The compositions of the complexes that divide into layers of equal mass without precipitation of salt is given by the middle points of the tie-lines connecting the different pairs of conjugate points.

Table XIII

Solubility Curves 40° C

pct acetone	Composition of 100 g solution		
	g water	g acetone	g salt
	Curve KP		
0	71.31	0.00	28.69
5	69.62	3.67	26.72
9.09	67.88	6.79	25.33
15	65.15	11.51	23.34
20	62.97	15.75	21.28
	Curve P'A		
80	19.81	79.34	0.58
85	14.94	84.66	0.40
90	10.00	89.84	0.16
95	4.97	94.96	0.07
100	0.00	100.00	0.00

Table XIV

Dineric Curve 40° C

Per gram salt		Composition of 100 g solution		
g water	g acetone	g water	g acetone	g salt
3.86	1.95	56.68	28.63	14.68
4.70	3.16	53.05	35.67	11.29
5.12	4.05	50.34	39.82	9.83
5.55	5.11	47.60	43.83	8.58
6.08	6.63	44.35	48.36	7.29
6.50	7.73	42.68	50.75	6.57
7.39	10.79	38.53	56.26	5.21
8.01	12.88	36.59	58.84	4.57
9.39	18.62	32.37	64.18	3.45
10.38	22.52	30.62	66.43	2.95
11.53	28.47	28.12	69.45	2.44

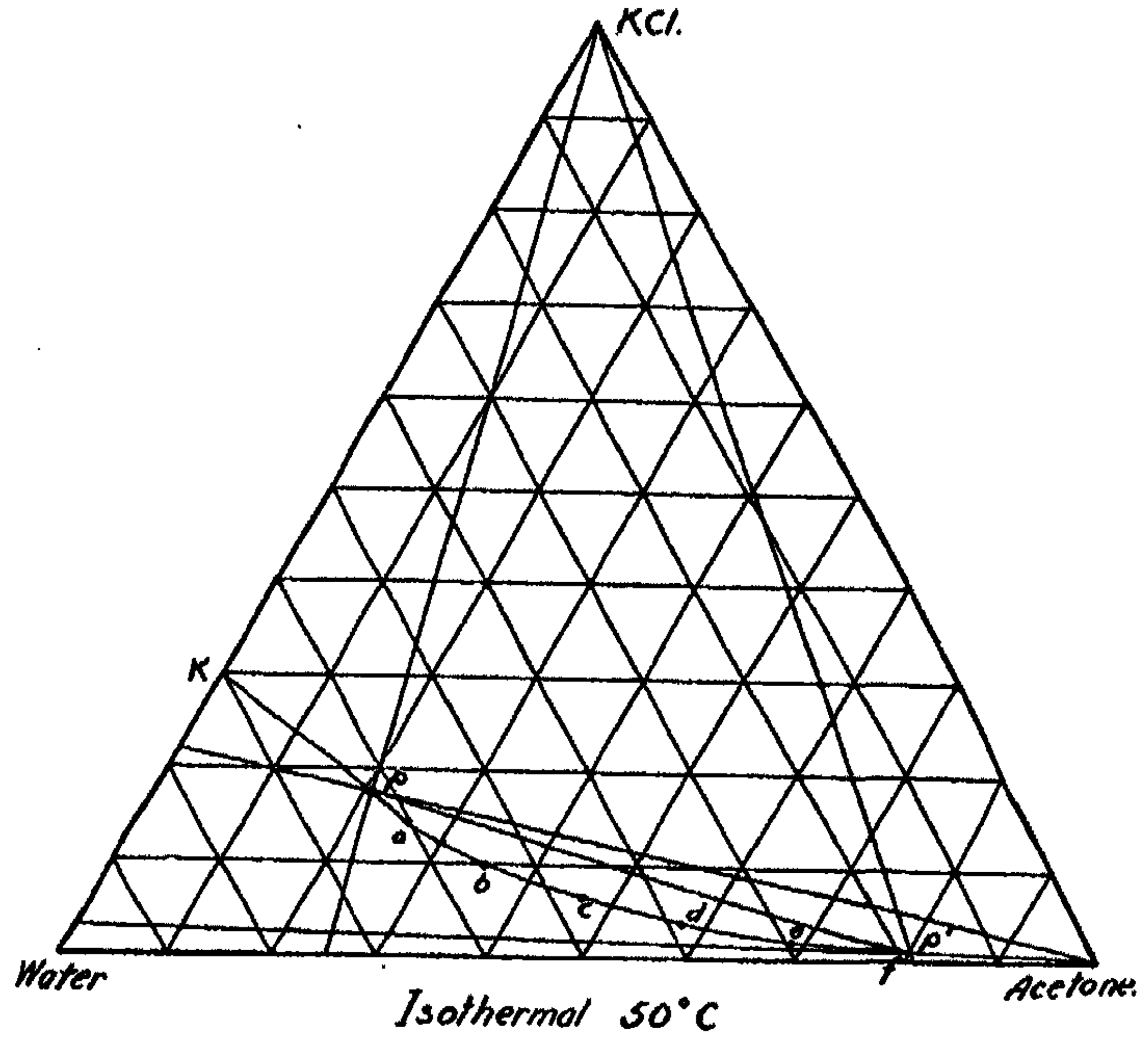
TABLE XV

Conjugate Points of the Dineric Curve 40°C

Point on curve	Upper layer To 100 g solution g water	g acetone	g salt	Point on curve	Lower layer To 100 g solution g water	g acetone	g salt
a	55.20	31.82	12.99	*a*′	28.14	69.42	2.44
	54.27	36.69	12.03		29.45	67.83	2.72
	53.27	35.44	11.29		30.96	65.97	3.07
	51.69	37.76	10.55		31.83	64.83	3.33
e	51.23	48.50	10.27	*e*′	32.64	63.79	3.56
	50.34	39.88	9.77		34.07	62.01	3.92
	49.08	41.67	9.26		35.27	60.49	4.24
i	48.02	43.18	8.79	*i*′	37.44	57.67	4.89
	47.62	43.73	8.64		38.00	56.96	5.04
	46.49	45.34	8.17		38.68	56.17	5.25
l	45.65	46.52	7.83	*l*′	39.98	54.36	5.66
	45.64	46.57	7.79		40.41	53.78	5.81
P	58.99	25.24	15.77	P′	23.66	74.91	1.43

THE 50° ISOTHERM

This isotherm for 50° is represented in Table XVI and Fig. 8. The data for this isotherm are deduced entirely from



Isothermal 50°C

Fig. 8

the experimental results of Series I and III, with the exception of the point K which is taken from Andreä's measurements of the solubility of potassium chlorid in water. The sources of the figures are indicated in the table. Points *a–f* are obtained by interpolation on curves for each acetone water-mixture, the co-ordinates being temperature and g salt per 100 g solution. Points P and P′ I have located by producing the dineric curve to its intersection with the lines joining the point ror pure potassium chlorid to the point for 25 percent and 81 percent aqueous acetone. It will be observed that both the range of acetone-water mixtures that can be caused to divide by addition of salt and the range of aqueous salt solution that can be caused to divide by addition of acetone are greater at 50° than at 40°.

TABLE XVI

Isotherm 50° C

pct acetone	Point on curve	Composition of 100 g solution			Source of figures
		g water	g acetone	g salt	
		Dineric Curve			
30	*a*	59.91	25.67	14.42	Table IV
40	*b*	54.04	36.03	9.93	" V
50	*c*	46.46	46.46	7.07	" VI
60	*d*	38.25	57.37	4.38	" VII
70.12	*e*	29.22	68.56	2.22	" VIII
80	*f*	19.81	79.25	0.94	" IX
81 ±	*p′*	Saturated solution			" XI
25-26	*p*	"			" XI
		Solubility curve K*p*			
0	*k*	70.0	....	30.0	Andreä

SUMMARY

The knowledge thus gained of the form of the dineric surface for the system potassium chlorid, acetone, and water, may be summed up as follows:

The plait-point of the surface lies at a temperature of about 32.5° and a composition somewhere near water 43, acetone 50, salt 7 (saturated solution of the salt in 54 percent acetone at 32.5°). From this point the boundary curve extends in the direction indicated in Fig. 4, the temperature rising from the plait-point in both directions. From the boundary curve, the dineric surface extends upward and outward toward the acetone-water plane at least as far as the position of the outer curve of Fig. 4 and to temperatures as high as 149° (See Table VII). That at some higher temperature it reaches its actual limit and begins to slope back in the other direction is indicated by the fact that solutions differing very little in composition from others that divide at about 100° can be heated to very high temperatures without dividing and would also seem probable from the fact that in the analogous systems, potassium carbonate, ethyl alcohol and water and potassium nitrate, ethyl alcohol and water, solutions that divide into two layers on heating become homogeneous again at still higher temperatures.

In conclusion, I desire to express my hearty thanks to Prof. Bancroft upon whose suggestion this work was undertaken and whose valuable advice has been ever at my service.

Cornell University, May, 1898

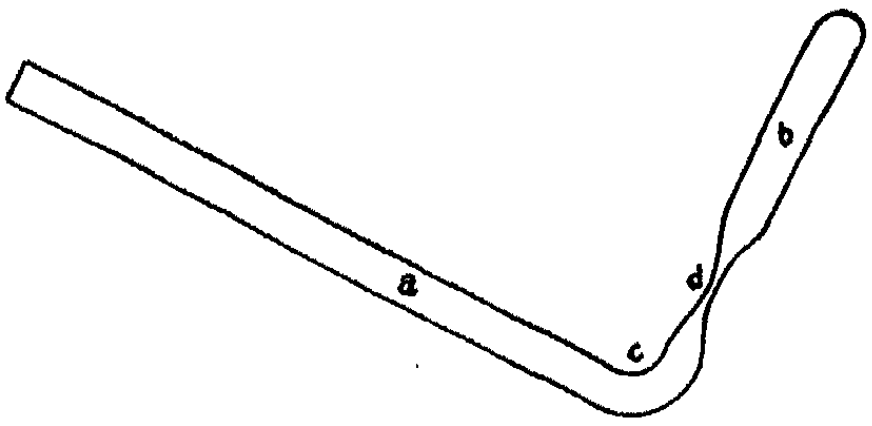
ON THE HEAT OF SOLUTION OF LIQUID HYDRIODIC ACID

BY F. G. COTTRELL

Some two years ago while investigating some chemical properties of liquid hydriodic acid[1] the question arose as to the thermochemical relations of the acid in this state; and it was mainly with the intention of throwing some light upon this, that the present work was undertaken.

The plan adopted was to break a glass tube of the liquid under water in the cup of a calorimeter and thus observe directly the heat of solution of the liquid acid.

The acid was prepared by the action of water on iodin and red phosphorus, and dried by passing over phosphorus pentoxid. In order to prevent the formation of free iodin while sealing the tubes, the following device was resorted to. A very thin glass tube (walls not over 0.5 mm thick) was sealed at one end, as shown in the cut; then drawn out to a capillary at *d* and finally bent at right angles as at *c*. The compartment *a* was then packed in solid carbon dioxid, and the gaseous acid conducted into it by a narrow delivery tube. When sufficient liquid had been collected, the delivery tube was with-



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[1] Norris and Cottrell. Am. Chem. Jour. 18, 96 (1896).

drawn and the whole allowed to freeze. A spiral of fine copper wire was now dropped in and the tube sealed up with the blast lamp. When the tube was completely cooled, it was inverted and the acid allowed to melt and run down into the end just sealed. The free iodin which had separated at this point dissolved in the acid, but was quickly removed by the copper, leaving a perfectly colorless liquid, which was then distilled into the limb *b* by simply surrounding the latter with solid carbon dioxid. It may be noted here that distillation alone will almost completely free the liquid from iodin. Finally when the whole of the acid had passed over and solidified, a very fine pointed flame was applied to the capillary *d*, which instantly sealed up with the appearance of only the slightest trace of free iodin; scarcely enough, in fact, to give a perceptible color to the liquid when dissolved in it.

This tube was placed at the bottom of a calorimeter cup containing 500 g of water. The thermometer, stirrer, etc., were placed in position and the whole allowed to stand over night in a room in the basement; the determinations being made the first thing in the morning.

The contents of the calorimeter cup were kept stirred by a three-bladed platinum stirrer operated by an electric motor. The temperature was read by telescope on a Beckmann boiling-point thermometer divided to 0.01° C, which had been compared with a standard thermometer from the Yale Observatory. A clockwork tapper was kept running on this throughout each determination. The contents of the tubes were discharged into the water by snipping off the capillary tip by means of a loop in the end of a platinum wire. The liquid was projected into the water and passed into solution without the loss of a single bubble. The total thermal capacity of the calorimeter cup and content was equal to 507 g of water.

The dilution (1 mol of HI to over 700 mols water) was sufficient to be taken as infinite. The initial temperature was in each case within a few tenths of 12°. The following is the data for three determinations. W = weight of acid taken. Δt = rise in temperature corrected for errors of thermometer and for radiation. Q = heat liberated by solution of 1 g-mol HI (126.89 g) expressed in K (1K = heat necessary to raise 100 g water 1° C at temperature of experiment).

No	W	Δt	Q
1	3.7299 g	0.860°	148.3 K
2	4.7086	1.080	148.0
3	4.6961	1.085	148.7
		Mean	148.3

The value for the solution of the gaseous acid is given by Thomsen[1] as 192.1 K; by Favre and Silbermann[2] as 189.1 K; by Favre[3] as 189.0 K, and by Berthelot and Louguinine[4] as 195.7 K. Accepting Thomsen's value, as appearing on the whole the most trustworthy, we find his titration of the acid depending upon the assumption of the molecular weight of NaCl = 58.5 and $AgNO_3$ = 170, while according to Clarke's report of March, 1896,[5] these are to be taken as 58.06 and 168.69. Applying this correction to Thomsen's value for the heat of solution we have 190.6 K.

In the present determinations the weight of acid was determined by weighing the tube full of acid before the experiment and the fragments of the tube afterward. They therefore depend only upon the assumption of the molecular weight of HI (126.89). Accepting this corrected value, and neglecting the small difference in the initial temperatures of Thomsen's determinations (which were made at about 17° C), and those at present under discussion, we have for the latent heat of the gas per gram molecule 42.3 K.

One necessary correction to the above measurements arises from the tubes of acid being only about two-thirds full of the liquid. At the temperature of the experiment the liquid has a specific gravity of 2.27 and the saturated vapor is under a pres-

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[1] Pogg. Ann. 148, 199 (1873).

[2] Ann. Chim. Phys. (3) 37, 412 (1853).

[3] Comptes rendus, 73, 974 (1871).

[4] Ibid. 69, 630 (1869).

[5] Jour. Am. Chem. Soc. 18, 197 (1896).

sure of 7.5 atmospheres.[1] Assuming the vapor to obey the ordinary gas law, the liquid will be 54 times as dense as the vapor, and the latent heat being about one-third the heat of solution we have a correction of some 0.3 percent to subtract from our value for the heat of solution; which brings it to 147.8 K and for the latent heat 42.8 K; or dropping the decimal as somewhat uncertain:

$$\text{HI (liquid)} + \text{Aq} = \text{HIAq} + 148\ \text{K}.$$
$$\text{HI (gas)} = \text{HI (liquid)} + 43\ \text{K}.$$

Thomsen gives us

$$\text{H (gas)} + \text{I (solid)} = \text{HI (gas)} - 60\ \text{K}$$

which upon recalculation with the atomic weights here adopted becomes 59.9, practically identical with the former value. From these we obtain

$$\text{H (gas)} + \text{I (solid)} = \text{HI (liquid)} - 17\ \text{K};$$

that is to say, liquid hydriodic acid at 12° C is still an endothermic compound with respect to solid iodin and hydrogen under atmospheric pressure; but its heat of decomposition is only a little over a quarter of that of the gaseous acid under atmospheric pressure.

University of California, May, 1898

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[1] Dammer. Handbuch der anorganischen Chemie, 1, 553.

NOTE ON THE TRANSFERENCE NUMBER OF HYDROGEN

BY WILDER D. BANCROFT

In the paper by Mr. McIntosh[1] reference should have been made to the work of Hopfgartner.[2] Hopfgartner determined the transference number of chlorin in hydrochloric acid by Hittorf's method. The mean of his values is $n_{Cl} = 0.163$, while McIntosh found $n_{Cl} = 0.159$ by the electrometric method. These two numbers agree so well that one would be inclined to take the mean as the true value, were it not that some recently published work does not confirm this result. Bein[3] has determined the transference number for chlorin in hydrochloric acid by Hittorf's method. He finds that the value varies enormously with the temperature. From his experiments the most probable value at 18° is $n_{Cl} = 0.167$, a trifle higher than that of Hopfgartner and quite a bit higher than that of McIntosh. Even this highest value does not agree well with the results of Kohlrausch.[4] The latter considers 353 as the most probable value for the molecular conductivity of 18° of hydrochloric acid at infinite dilution. The migration velocity of chlorin as ion being taken as 63, the corresponding value for hydrogen as ion becomes 290. According to these data the transference number of chlorin in hydrochloric acid should be $\frac{63}{290 + 63} = 0.178$, a value that is much higher than that of Bein, differing from it by more than Bein's value differs from that of McIntosh. Under these circumstances it would seem best to waive for a time the conclusion that "the

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[1] Jour. Phys. Chem. **2**, 273 (1898).

[2] Zeit. phys. Chem. **25**, 115 (1898).

[3] Ibid. **27**, 1 (1898).

[4] Wied. Ann. **50**, 406 (1893).

Helmholtz method of determining transference numbers is not applicable to gas cells."

If we take 63 as the migration velocity of chlorin as ion, the migration velocity of hydrogen as ion becomes 314 (Bein), 324 (Hopfgartner), or 333 (McIntosh). Professor Jahn has called my attention to the fact that by throwing part of the error into the value for chlorin as ion, we can calculate the values of hydrogen as ion as 294, 295 and 297 respectively by means of the formula $n_H = \frac{u}{353}$. These values may be considered as identical with the 290 of Kohlrausch. These values, however, give us for the migration velocity of chlorin the numbers 59 (Bein), 58 (Hopfgartner), and 56 (McIntosh) instead of 63 (Kohlrausch). The percentage discrepancy is as serious as ever and there seems to be quite as much difficulty in assuming an error of four to seven units in the value for chlorin as there is in assuming an error of twenty-five to thirty-five units for the value of hydrogen. The sum total of our knowledge is then that the values for the transference numbers as determined by the two methods agree better than they do with the values calculated from the conductivity. It is interesting to note that Bein, Hopfgartner and McIntosh are agreed that the transference number does not vary with the dilution and also to note that McIntosh's value for the anion in sulfuric acid (0.174) is identical with that obtained by Bein. The paper by Kümmell,[1] in which Helmholtz's method is used, was not received in this country until after Mr. McIntosh's paper had been sent to the printer or reference would have been made to it.

Cornell University

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[1] Wied. Ann. 64, 655 (1898).

ALCOHOL, WATER AND POTASSIUM NITRATE

BY NORMAN DODGE AND L. C. GRATON

In the investigation here recorded we have determined the concentration-temperature curve for two liquid layers in mixtures of alcohol and water, in the presence of an excess of potassium nitrate. A serious experimental difficulty was encountered. If to a mixture of two consolute liquids a constituent soluble in one of them be added, then at some temperature there will be a separation of the two liquids into distinct layers. And usually the point at which this separation takes place can be detected with considerable accuracy by the clear solution clouding suddenly. In the case we are describing this "clouding" did not take place readily, and the temperature would frequently be carried far beyond the proper point, when two liquid layers would be found to exist without its being possible to say at what precise temperature the separation took place. It was necessary to make many determinations and with great caution; to use a large bath, to heat up the mixture very slowly, and to keep them at each temperature for a considerable time. In each case the lowest temperature noted, at which clouding took place, was selected as the true value. The determinations for one set of concentrations were made by one of us, and for the remaining set by the other. They were subsequently verified by us conjointly. Owing to the great difficulty of determining the point at which clouding took place, we do not feel justified in claiming great accuracy for our results, but do not believe that in any case the possible error amounts to 0.5°.

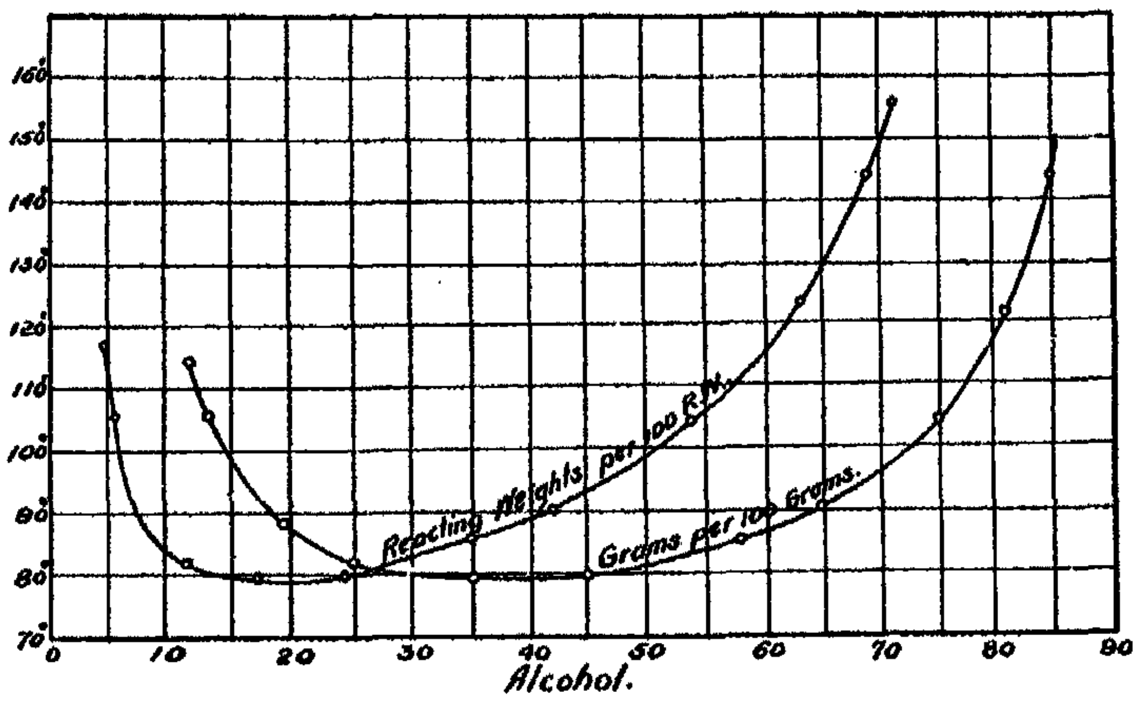
The alcohol was distilled from lime, and then kept in contact with dehydrated copper sulfate for several weeks, decanted and distilled with a Hempel column. It all distilled constantly, but the first and last portions were discarded. The water used was prepared by taking about three liters of the distilled water of the laboratory, adding about 2 g potassium permanganate, and distilling. The first 500 cc was discarded; the next 500 cc was used to rinse out the receiver, a 2-liter glass-stoppered bottle which had previously been washed out with ether and alcohol. About a liter of the water was then distilled, and carefully kept until used. The potassium nitrate was recrystallized repeatedly until no traces of other salts or impurities could be detected. It was then dried, pulverized in an agate mortar and kept in a glass-stoppered reagent bottle until used.

The determinations were all made in sealed tubes, about 1.5 cm in diameter and about 20 cm in length, and terminated by a long capillary tube. These tubes were never more than one-third filled by the mixture used for the investigation. The upper part of the tube was always relatively cool, and the danger of the tube bursting reduced to a minimum. The desired temperature was obtained by immersion in a beaker containing about 2 liters of water. The thermometer was rigidly supported in the water which was constantly agitated by using the sealed tube as a stirrer. Temperatures above 100° were obtained by adding calcium chlorid to the water, until a solution with the right boiling-point was obtained. We found this a most convenient and satisfactory method for controlling the temperature. Some care must be exercised in its use, however, and if it be desired to raise the boiling-point, the salt should be carefully added, in small quantities at a time. It seems scarcely necessary to say that under no circumstances should water be added to the solution while hot.

Our tabulated results follow. The first column contains the percentage by weight of alcohol in the aqueous alcohol, the second the number of reacting weights of alcohol per hundred reacting weights of aqueous alcohol, and the third column the temperature at which the solution clouded.

pct Alc	pct R. W. Alc	Temp	pct Alc	pct R. W. Alc	Temp
13.1	5.57	106.0°	57.8	34.89	86.0°
24.9	11.48	82.5°	64.7	41.76	91.0°
35 1	17.24	80.0°	74.9	53.86	105.0°
44.8	24.10	80.5°	84.9	68.75	144.0°

On the accompanying chart the curve to the left is plotted



for molecules per 100 molecules in solution, the curve to the right for percentages by weights. From the curves it would appear that the minimum temperature at which a separation into two liquid layers would occur is 79.5°–80°, and the composition of the solution which would cloud at this point is about 39 percent by weight or 20 reacting weights of alcohol per 100 reacting weights of aqueous alcohol, the amount of potassium nitrate in solution being of course unknown.

It has seemed desirable to study the effect of an excess of two substances on a solution of two consolute liquids. We have not been able to complete our investigation in this respect for lack of time, but the following preliminary experiment indicates the desirability of further study. At what temperature a solution containing 35 percent alcohol will cloud in the presence of an excess of potassium chlorid we do not know. Certainly it will not below 140° C as we have found by experiment.[1] But this same solution with an excess of both potassium nitrate and potassium chlorid (carefully purified) clouded at 65.5°. This point will be further investigated. Thus the addition of potassium chlorid to a mixture of aqueous alcohol saturated with respect to potassium nitrate lowers the temperature, at which this solution clouds, some 15° in spite of the fact that potassium chlorid by itself has very little effect in causing aqueous alcohol to form two liquid layers. The experimental work described in this paper has been carried on under the supervision of Dr. Frank K. Cameron.

Cornell University

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[1] Cf. also Snell. Jour. Phys. Chem. 2, 457 (1898).

NEW BOOKS

Praktikum der wissenschaftlichen Photographie. *By Carl Kaiserling. 16 × 24 cm; pp. xii and 404. Berlin: Gustav Schmidt, 1898. Price: paper 8 marks.*—The chapters are: light and its action; the camera; the exposure; the preparation of the negative; the preparation of the positive; enlargements and microphotography; stereoscopy; the use of the Röntgen rays; photography in natural colors. The book is very complete and should prove very useful. In one or two points the German practice does not seem to be up to the American standard. No mention is made of the ball and socket tripod head and the merits of celluloid as a substitute for the ordinary focusing glass are not considered. One or two of the illustrations might have been omitted without harm either to the scientific or artistic merits of the book. The general public will probably be most interested in the chapter on photography in color in spite of the shockingly bad colored plate that purports to be a fair sample of what can be done in this line. The amateur photographer will find much in the book by which he can profit and it will become a necessity to him if he is also a student of medicine. *Wilder D. Bancroft*

Reform of Chemical and Physical Calculations. *By C. J. T. Hanssen. 21 × 26 cm; pp. xvi and 72. New York: Spon and Chamberlain, 1897. Price: $2.60.*—The author proposes to refer all specific gravities to the gravity at sea-level under atmospheric pressure at 0° and at the latitude of 41°. This latitude is chosen as the "circle of international gravity" because the weight of a cubic meter of oxygen then becomes ten-sevenths of a kilogram. The author then proceeds to calculate a mass of data with what he calls "absolute accuracy." As he takes whole numbers for the combining weights and assumes that the gas laws hold absolutely, it would seem as though a great deal of time and ingenuity had been wasted. *Wilder D. Bancroft*

Canalisations électriques, Lignes aériennes industrielles. *By R. V. Picou. 12 × 19 cm; 172 pp. Paris: Gauthier-Villars et Fils, 1898. Price: paper 2.50 francs, boards 3 francs.*—This little volume is intended for the engineer as might be gathered from the title. The first part treats of the material of the lines, conductors, insulators and supports. The second part is devoted to a discussion of the methods of setting up posts and stringing wires, together with a chapter on the protection and care of the system. The third part contains tables likely to be useful to the engineer. *Wilder D. Bancroft*

Angewandte Elektrochemie. *By Franz Peters.* **Vol. III, Organische Elektrochemie.** *13 × 18½ cm; pp. xii and 206. Wien, Pest, Leipzig: A. Hartleben, 1898. Price: paper 3 marks, bound 4 marks.*—The first two volumes have already been reviewed (1, 501; 2, 197). This volume, dealing with organic chemistry, is the last of the series. The three main divisions of the book are: aliphatic series; aromatic series; different applications of organic electrochemistry. Under the first head the subjects are taken up in the following order: hydrocarbons; halid derivatives of the hydrocarbons; alcohols; ethers; esters; sulfur derivatives of the hydrocarbons and alcohols; acids; sulfur derivatives of the acids; aldehydes and ketones; sugars and carbohydrates; acid amids; acid nitriles. Under the second head the order is hydrocarbons; nitro, sulfur and ammonia derivatives of the hydrocarbons; phenols; sulfur derivatives of the phenols; alcohols; phenol alcohols; acids; aldehydes and ketones; quinones; camphors and glucosids; dye-stuffs of unknown composition; thiophen substances; bases with one and with two atoms of nitrogen. Under the third head we find a discussion of the application of electrolysis to dyeing, printing and tanning. Other subheads in this section relate to the use of electricity for preserving milk and meat as well as for making plants grow.

There is an excellent index and the literature has been reviewed down to the beginning of the present year. The book is a success and makes a fitting close to a very satisfactory series. Occasionally the condensation has been carried too far. For instance, we are told that diphenyl can be obtained by the action of zinc on dissolved brombenzene; but there is no clue as to the nature of the solvent. This and other similar points are, however, unessential because the reference to the original paper is given. *Wilder D. Bancroft*

REVIEWS

The object of this department of the Journal is to issue, as promptly as possible, critical digests of all Journal articles that bear upon any phase of Physical Chemistry

General

A table of atomic weights. *T. W. Richards. Am. Chem. Jour.* 20, *543* (*1898*).—A recalculation of the atomic weights based on the author's judgment as to the value of the different processes. Only with antimony, cadmium, calcium, magnesium, platinum, tungsten and uranium do the values differ much from those of Clarke. The author proposes to revise this table every year.
W. D. B.

Recent experiments on certain of the chemical elements in relation to heat. *W. A. Tilden. Nature*, 58, *160* (*1898*). — A lecture delivered at the Royal Institution in which are described experiments made to test the question whether Dulong and Petit's law becomes absolutely accurate when applied to highly purified metals. For cobalt and nickel, the specific heats are 0.10348 and 0.10931 respectively. This would make the atomic heat of cobalt about 6.1 and that of nickel about 6.4. For gold the value 5.94 was obtained and 6.05 for platinum. Iron containing 0.01 percent of carbon gave 6.13, while pure copper gave 5.83. It is thus clear that the law of Dulong and Petit is only a first approximation. *W. D. B.*

On the molecular velocity of liquids and its variation with the pressure. *G. Guglielmo. Nuovo Cimento*, (*4*) 7, *177* (*1898*).—Reviewed (2, 395) from Rend. Accad. Lincei, (5) 6, II, 254 (1897).

A comparison of Rowland's mercury thermometers with a Griffiths platinum thermometer. *C. W. Waidner and F. Mallory. Phil. Mag.* [*5*] 44, *165* (*1897*).—The comparison showed that the difference (1 in 400) between Rowland's determination of the mechanical equivalent of heat and that made by Griffiths cannot be due to an error in thermometry. *W. D. B.*

A recalculation of Rowland's value for the mechanical equivalent of heat in terms of the Paris hydrogen thermometer. *W. S. Day. Phil. Mag.* [*5*] 44, *169* (*1897*); 46, *1* (*1898*).—At 20° the old value was 417.9 × 10^4; the corrected value is 418.1 × 10^4, while Griffiths found 419.32 × 10^4. The discrepancy may be due "to some error in the electrical standards of resistance, or of electromotive force." *W. D. B.*

Notes on thermometry. *C. Chree. Phil. Mag.* [*5*] 45, *205*, *299* (*1898*).—This is intended to be an exposition for English-reading people of the present state of scientific knowledge with regard to expansion thermometry. The different subheads are: natural scale of ideal thermometer; properties of real glass, fixed and movable zero scales; depression of zero; experimental relation of different scales; lag; freezing-point of water; boiling-point of water; calibration; external and internal pressure corrections, standard position for thermometers; emergent column; Welsh's method of graduation, and its modern developments; method of finding mean coefficient of expansion of mercury in glass; comparison of thermometric methods. *W. D. B.*

An instrument for the comparison of thermometers. *W. Watson. Phil. Mag.* [5] 44, *116* (*1897*). — "If the bulbs of two different thermometers are placed close together in a water-bath, a considerable length of one of the mercury columns must be out of the bath involving an uncertain correction for cool column. Again, the difference in size of the bulbs renders the lag of the thermometer different, so that unless the temperature of the bath is kept absolutely constant for some time, we cannot be sure that *both* thermometers have reached a steady temperature." To obviate these difficulties the author suggests the use of a vapor-jacket, the temperature being varied by changing the pressure under which the liquid boils. [The use of a Reichert regulator in a water-bath would seem to involve less trouble.] *W. D. B.*

Nomenclature and notation in calorimetry. *J. Y. Buchanan. Nature*, 58, *30*, (*1898*). — It is proposed to use names and notations to show what heat unit is meant, thus g°. C denotes a gram-degree Celsius, the small calorie; while k° C denotes a kilogram-degree Celsius, the large calorie. Ostwald's calorie could then be written 100 g° C, g 100° C, 0.1 k° C or h° C, this last being hectogram-degree Celsius. For oceanographical work where the heat exchanges between one layer of water and another, or between the water and the air, are under discussion, the author finds the most convenient heat unit to be the fathom-degree Fahrenheit, f° F, or the metre-degree Celsius, M° C. These last two units are interchangeable practically, because the fathom is about 1.8 meter and the Celsius degree is 1.8° F. *W. D. B.*

One-Component Systems

Note on the liquefaction of hydrogen and helium. *J. Dewar. Jour. Chem. Soc.* 73, *528* (*1898*). — "Starting with hydrogen cooled to —205°, and under a pressure of 180 atmospheres, escaping continuously from the nozzle of a coil of pipe at the rate of about 10 to 15 cubic feet per minute, in a vacuum vessel doubly silvered and of special construction, all surrounded with a space kept below —200°, liquid hydrogen commenced to drop from this vacuum vessel into another doubly isolated by being surrounded with a third vacuum vessel." Liquid hydrogen is clear and colorless with a meniscus as well-defined as that of liquid air. The density is 0.08 and the boiling-point is estimated at — 238°. On standing a tube containing helium in liquid hydrogen, the helium was seen to condense.

"Hydrogen in the liquid state is 100 times denser than the vapor it is giving off at its boiling-point, whereas liquid oxygen is 255 times denser than its vapor. It appears, therefore, that the atomic volume of liquid hydrogen at its

boiling-point is 14.3 as compared with 13.7 for oxygen under similar circumstances." The critical pressure probably does not exceed fifteen atmospheres.
W. D. B.

Latent heats of evaporation of zinc and cadmium. *W. Sutherland. Phil. Mag.* [5] 46, *345* (*1898*).—Attention is called to the fact that, by means of the thermodynamic relation between pressure and temperature for liquid and vapor, the heats of vaporization of zinc and cadmium may be calculated from the observations of Barus on the change of the boiling-points of these metals with the external pressure. Under atmospheric pressure the calculated values for zinc and cadmium are 283 K and 296 K respectively. *W. D. B.*

Density measurements with two areometers. *C. Marangoni. Nuovo Cimento*, (*4*) 6, *407* (*1897*).—When two areometers are used the density may be calculated by the formula $d = \frac{c}{c + (a - b)}$, where a and b are the readings on the two areometers and c is the difference of volumes when the scales are immersed to the zero. In this way the effect of capillarity is eliminated because we are dealing with the difference of the readings for the same material in the same liquid. By making the ratio of the volumes of the two instruments about two to one, an accuracy of ±2 in the fourth place of decimals can be obtained. The method is thus simpler and more accurate than that of Sandrucci (2, 61). The apparatus was suggested by the author as far back as 1886. *W. D. B.*

The isothermals of isopentane. *J. Rose-Innes. Phil. Mag.* [5] 44, *76* (*1897*).—The author has developed a formula containing four unknown constants that represents Young's data (1, 585) with a fair approach to accuracy.
W. D. B.

On the isothermals of ether. *J. Rose-Innes. Phil. Mag.* [5] 45, *102* (*1898*).—It was found that the temperature for which the pressure is accurately given by the laws of a perfect gas at a given volume, remains practically constant for all large volumes until the neighborhood of the critical volume was reached. It was possible to represent the data of Ramsay and Young for ether by means of a formula containing four constants characteristic of the gas, the error not exceeding two percent. See preceding review. *W. D. B.*

Two-Component Systems

The freezing-points of pure stearic and palmitic acids and of their mixtures. *L. E. O. de Visser. Recueil Trav. Pays-Bas,* (*2*) 17, *182* (*1898*).—Palmitic and stearic acids form two sets of solid solutions, the temperature of the quadruple point being 54.82° and the liquid solution containing 29.8 percent of stearic acid. The solution containing 47.5 percent stearic acid freezes at 56.4° without change of temperature. This is the first instance on record of the curve for the solid solution meeting the curve for the liquid solution in a system in which two solid solutions are possible. It is much to be regretted that the concentrations of the two limiting solid solutions at the quadruple point were not determined. *W. D. B.*

On the solid solutions of benzene in phenol. *G. Bruni. Gazz. chim. Ital.*

28, *I*, *249* (*1898*).—The distribution of benzene between liquid and solid phenol was determined by van Bijlert's method, using benzil as the third substance. The distribution ratio is fairly constant, the concentration in the solid phase being about three-tenths of that in the liquid phase. *W. D. B.*

On the solid solutions of pyridin and piperidin in benzene. *G. Bruni. Gazz. chim. Ital.* 27, *I*, *259* (*1898*).—Pyridin and piperidin dissolve in solid benzene. The distribution ratio for piperidin varies with the concentration from 0.13 to 0.09 and then 0.16. Owing to the difficulties of analysis, no satisfactory quantitative results were obtained with pyridin. *W. D. B.*

Solid solutions among compounds with open chains. *G. Bruni. Rend. Accad. Lincei,* (*5*) *7*, *I*, *166; Gazz. chim. Ital.* 27, *I*, *277* (*1898*).—Chloroform gives slightly abnormal values in bromoform, iodoform very abnormal values, both substances forming solid solutions with bromoform. The ratio of the concentrations of iodoform in solid and liquid bromoform is about 0.36, diphenyl being taken as the third substance. Ethylene chlorid and ethylene iodid are abnormal in ethylene bromid, owing to formation of solid solutions. *W. D. B.*

On real and apparent freezing-points and the freezing-point methods. *M. Wildermann. Phil. Mag.* [*5*] 44, *459* (*1897*).—Reprinted from Zeit. phys. Chem. 19, 63 (1896).

On the properties of liquid mixtures. *R. A. Lehfeldt. Phil. Mag.* [*5*] 46, *42* (*1898*).—The author has determined the partial pressures at 50° corresponding to all mixtures of alcohol and benzene, alcohol and toluene, carbon tetrachlorid and benzene, carbon tetrachlorid and toluene. With the first two systems the vapor pressure passes through a maximum. With the last two systems straight lines are not obtained when the partial pressures are plotted against composition, nor does the curve for carbon tetrachlorid in benzene correspond with that for carbon tetrachlorid in toluene. Calculating the association of alcohol in benzene and toluene on the assumption that the partial pressure-concentration curves should be straight lines led to discordant results, the two series not agreeing at all. *W. D. B.*

Experiments on the condensation and critical phenomena of some substances and mixtures. *J. P. Kuenen. Phil. Mag* [*5*] 44, *174* (*1897*).—Reviewed (2, 400) from Proc. Phys. Soc. Lond. 15, 235 (1897).

Molecular weights of some carbon compounds; a few words more. *C. L. Speyers. Jour. Am. Chem. Soc.* 20, *546* (*1898*).—In reply to a criticism in a review by A. A. Noyes, the author states that he does not consider that there is any appreciable error in his results (1, 766) due to the effect of variations of pressure on the bulb of the thermometer. *W. D. B.*

Poly-Component Systems

Determination of molecular weights—modification of Landsberger's boiling-point method. *J. Walker and J. S. Lumsden. Jour. Chem. Soc.* 73, *502* (*1898*).—The Landsberger method (2, 400) is modified by "reading the volume of the solution after equilibrium has been attained instead of ascertain-ing its weight." To do this the boiling-tube is graduated. If the solution consists originally of only 5-7 cc and 2-3 cc of solvent condenses each time, a succession of readings gives a series of readings at different solutions, the only weighing being that of the original pellet. The method is not intended for exact work, but for "obtaining values easily and rapidly in the course of ordinary organic or inorganic research work." *W. D. B.*

On the reciprocal transformation of tartaric, racemic and mesotartaric acids. *A. F. Holleman. Recueil. Trav. Pays-Bas*, (*2*) *17*, *66* (*1898*).—At 110° there is practically no change when tartaric acid (dextrorotary) is heated with normal hydrochloric acid. At 120° some eight percent of mesotartaric acid is formed and this amount increases with rising temperature. Racemic acid is not formed in perceptible quantities until the temperature is above 140°. Some decomposition with evolution of carbon dioxid takes place. This is unimportant at 120° but becomes serious at 155°.

Racemic acid begins to change into mesotartaric acid above 130°; the reverse change takes place but much less rapidly. No tartaric acid is formed and the evolution of carbon dioxid is much more marked than when tartaric acid is heated.

When tartaric acid is heated with caustic soda at 118°, the tartaric acid disappears completely in the course of a few hours while the ratio of racemic to mesotartaric acid increases with the time. *W. D. B.*

Action of dilute and concentrated caustic alkali solutions on tartaric acid. *J. Boeseken. Recueil Trav. Pays-Bas*, (*2*) *17*, *224* (*1898*).—Dilute alkalies cause the change of dextro-tartaric acid into mesotartaric and racemic acids, the reaction velocity decreasing with increasing dilution of the alkali. Although the racemic and mesotartaric acids are mutually convertible and the mesotartaric acid is formed in larger quantities from the dextro-tartaric acid, the author believes that the racemic acid is not formed entirely from the mesotartaric acid as a secondary reaction, but that the tartaric acid can change directly into racemic acid. These experiments are in accord with the results of Holleman (preceding review). *W. D. B.*

Some double salts containing selenium. *J. P. Norris. Am. Chem. Jour.* *20*, *490* (*1898*).—A number of double salts of selenium bromid and oxychlorid with trimethylamin and dimethylamin have been isolated and analyzed. The work, which was finished before June of 1895, has not been carried out according to the modern methods of investigation and will have to be repeated. On p. 506 it is stated that a third bromid, crystallizing in green needles, could be obtained when a given solution was allowed to stand at 60°-70°. At lower temperatures a red salt was formed. "Analysis of samples of the [green] salt prepared in this way gave results which agreed with another, but not with any possible formula." The analyses are not given. *W. D. B.*

On the peroxynitrate and peroxid of silver. *E. Mulder. Recueil Trav. Pays-Bas*, (*2*) *17*, *129* (*189.*).—A further study of the black compound, $AgNO_3 3Ag_2O_2$ (1, 323; 2, 142). In a current of air the substance loses 2O, silver nitrate and silver peroxid, Ag_2O_2, being left behind. Water dissolves and decomposes $AgNO_3$, the final products being solid Ag_2O_2 and dissolved silver nitrate. The author recommends this as a method of preparing the peroxid. After a discussion of the experiments of others, the author expresses the opinion that *the compound* Ag_2O_2 is the *only* peroxid of silver and that the substances with other formulas were either mixtures of this compound with Ag_2O or contained nitrogen. *W. D. B.*

On the coloring matters due to iron in sedimentary rocks and on the probable origin of the red rocks. *W. Spring. Recueil Trav. Pays-Bas,* (*2*) *17, 202* (*1898*).—The red rocks of the Devonian period contain ferric oxid mixed through the mass and also a ferrous salt dissolved in the mass. When the rock is treated with hydrochloric acid, the ferric salt dissolves and the green color of the ferrous salt appears. The color of the yellow brown rocks of the same period is due to a ferric silicate. When this is dissolved in hydrochloric acid, a white sand is left.

Ferric hydroxid does not lose water under pressure but does when compressed in contact with magnesium oxid. By oxidizing ferrous carbonate with hydrogen peroxid, a hydrated oxid was formed having approximately the composition of limonite. On these facts the author bases a theory as to the formation of colored sedimentary rocks. Where there is much oxidation or a low concentration of iron salts, the prevailing color will be red. Increase in the concentration of ferrous salts or of silicic acid will change the color to green while cracks and consequent diffusion may give a particolored rock, red and green. The yellow rocks are due to the precipitation of mixed magnesium, calcium and ferric salts, no ferrous salts being present and the whole settling rapidly. The yellow rocks come chiefly from turbid water while the green and red rocks were precipitated from a clearer water. *W. D. B.*

Osmotic Pressure and Diffusion

Studies on the nature of semipermeable walls. *J. Mijers. Recueil Trav. Pays-Bas,* (*2*) *17, 177* (*1898.*).—Ostwald found that, when a current passed through a solution of copper sulfate bounded at one end by a copper ferrocyanid diaphragm, metallic copper was precipitated on the diaphragm. He drew the conclusion that semipermeable walls were 'atom-sieves' acting like metallic conductors. The experiments of the author show that this view is not tenable because copper as ion does pass through the membrane to a certain extent.

W. D. B.

The causes of osmotic pressure and of the simplicity of the laws of dilute solutions. *W. Sutherland. Phil. Mag.* [*5*] 44, *493* (*1897*).—"While the new school of physical chemists has been busy pushing on the theory of dilute solutions to all its available conclusions, physicists have been more concerned about the secure establishment of the premises on which all these conclusions are based." A semipermeable membrane is then assumed to have a mesh structure such that water molecules pass through and sugar molecules do not. Disregarding the point that this hypothesis does not represent the experimental facts, the laws for dilute solutions are then "deduced". The following paragraph is delightfully characteristic. "Van't Hoff has shown how, given semipermeability, it is possible by thermodynamics to deduce the laws of dilute solutions in a simple manner; the difficulty has been to get a conception on molecular grounds of the rationale of osmotic pressure and the simple laws of dilute solutions. But with a direct molecular explanation for osmotic pressure we can then adopt van 't Hoff's thermodynamical extensions and treat the whole matter as placed on a molecular basis." *W. D. B.*

Osmotic pressure. *C. L. Speyers. Jour. Am. Chem. Soc.* 20, *579* (*1898*). —The author objects to the arrangement of Noyes and Abbott (1, 745) in which the semipermeable diaphragm and the solution are imagined as being at the top of a tube filled with pure water on the ground that, for osmotic pressures exceeding one atmosphere, the column would break. He also insists that the density of the solvent and not the density of the solution is to enter into the calculations. In the text it seems to be implied that Noyes and Abbott used the density of the solutions in making their calculations. This was not the case and the author cannot have intended to give this impression. *W. D. B.*

Comment on the paper "The diffusion constants of several metals in mercury." *G. Meyer. Wied. Ann.* 64, *752* (*1898*).—Ostwald's suggestion that the products of the diffusion constants into the square roots of the combining weights is a constant is not justified by the facts, the case of gold having been overlooked. It is more probable that the product of the diffusion constant into the specific gravity of the diffusing metal is a constant; but as yet the data are not sufficient to warrant putting this hypothesis forward in more than a tentative manner. *W. D. B.*

Velocities

Reduction of bromic acid and the law of mass action. *W. Judson and J. W. Walker. Jour. Chem. Soc.* 73, *410* (*1898*).—The authors first studied the reduction of bromic acid by hydrobromic acid in presence of a large known excess of sulfuric acid. An adaptation of the Harcourt and Esson method was tried, adding thiosulfate solution continuously so that there should be no free bromin. The results obtained in this way gave a good constant for a reaction of the second order for each particular series; but the constant varied with the initial concentrations. This was found to be due to the direct action of the thiosulfate on the bromic acid. To avoid this error the authors fell back upon the ordinary method and obtained very satisfactory data for a reaction of the second order. They next studied the same reaction when no sulfuric acid was present. Calculating the order of the reaction by the van 't Hoff method, they obtained 3.97 which is as close to four as could be expected. The reaction is therefore quadrimolecular and the velocity constant, as calculated by the formula for this case, is satisfactory.

Adopting the hypothesis of Noyes that only one stage of the reduction takes place with a measurable velocity, the authors write the reaction $2\overset{+}{H} + \overset{-}{Br} + \overset{-}{BrO_3} = HBrO + HBrO_2$, the hypobromous and bromous acids being considered as practically undissociated. This makes the reaction quadrimolecular. In presence of a large excess of sulfuric acid the concentration of hydrogen as ion remains practically constant and the reaction becomes a bimolecular one, as found experimentally. *W. D. B.*

On the speed of coagulation of colloid substances. *C. E. Linebarger. Jour. Am. Chem. Soc.* 20, *375* (*1898*). —It was found that colloid solutions did not coagulate throughout the whole mass even after coagulation had been started in one portion. With colloid iron solutions, the amount of coagulation appeared to be related to the amount of acid added. The author concludes that "it is extremely improbable that colloid solutions are comparable with supersaturated solutions." It would have been well to have added that the analogy to be overthrown is not generally accepted. The author's statement that he knows of no quantitative measurements on the rate of crystallization is a very surprising one.
W. D. B.

Baker's research on the non-combination of dry hydrogen chlorid and ammonia, vapor density of dry ammonium chlorid. *S. Gutmann. Liebig's Annalen*, 99, *267* (*1898*). —The author finds that dry hydrogen chlorid and dry ammonia are absorbed by phosphorus pentoxid; that dried hydrogen chlorid and dry ammonia combine to form ammonium chlorid though not so rapidly as when moist; and that the vapor-density of dry ammonium chlorid corresponds to complete dissociation. This is in flat contradiction with Baker's results, Jour. Chem. Soc. 65, *611* (1894). [See next review.] *W. D. B.*

The drying of ammonia and hydrogen chloride. *H. B. Baker. Jour. Chem. Soc.* 73, *422* (*1898*). —Gutmann (preceding review) having disputed the previous data of the author in regard to ammonium chlorid, the latter has repeated the experiments obtaining the same result as before. The discrepancy between the work of the two men is probably due to the presence of a little metaphosphoric acid in Gutmann's phosphorus pentoxid, Baker having shown that Gutmann's results can be obtained if this condition is fulfilled. In the past the author had obtained data for the vapor-density of ammonium chlorid by Victor Meyer's method, showing that this compound did not dissociate when thoroughly dry. He has since obtained the same result by the Dumas method.
W. D. B.

Electromotive Forces

The electromotive behavior of different cadmium amalgams. *W. Jaeger. Wied. Ann.* 65, *106* (*1898*)—As the composition of cadmium amalgam varies from one to five percent of cadmium, the electromotive force varies some 0.02 volt. As the composition varies from five to fifteen percent, the electromotive force remains absolutely constant. From fifteen percent up to amalgamated cadmium there is a change of about 0.044 volt, while pure cadmium gives a value about 0.01 volt higher than that of amalgamated cadmium. It is a pity that the author did not determine the composition of the solid phase existing between five and fifteen percent cadmium since it is evident that it was a solid solution. Some experiments are also given to show the diffusion of mercury into cadmium. *W. D. B.*

Variations in the electromotive force of the H-form of Clark cells with temperature. *F. S. Spiers, F. Twyman and W. L. Waters. Phil. Mag.* [*5*] 45, *285* (*1898*). —The cells were passed through a temperature cycle, the temperature being raised at a constant rate per minute and then lowered at the same rate. When the temperature changed at a rate of one degree in seven minutes the lag of the electromotive force was about four ten-thousandths of a volt; at a rate of change of one degree in fifteen minutes the lag was about 0.00025 volt; at a rate of one degree in thirty minutes it was about 0.00005 volt. "About half of the lag of electromotive force observed in the H-form of cell is due to the lag of the temperature of the cell behind that of the bath and the rest is diffusion lag". In the H-form of cell the lag is only about one-fourth that of the B. T. cell. *W. D. B.*

On apparatus for self-acting temperature compensation of standard cells. *A. Campbell. Phil. Mag.* [*5*] 45, *274* (*1898.*).—To eliminate the temperature coefficient a Wheatstone's bridge with a Leclanché cell instead of galvanometer is placed in series with the standard cell. Two opposite arms of the bridge are of a metal such as copper or iron with a large temperature-coefficient, while the other pair of resistances is made of manganin. It is also possible to make only one of the resistances of copper when the cell to be regulated does not have a higher temperature-coefficient than that of the Clark cell. *W. D. B.*

On electrolytic thermopiles. *W. Duane. Wied. Ann.* 65, *374* (*1898*).—Two types of cells were studied. The first was arranged schematically

$$\text{electrode} \mid \text{solution I} \underset{T_1}{\mid} \text{solution II} \underset{T_2}{\mid} \text{solution I} \mid \text{electrode.}$$

As electrodes were used mercury and calomel while the solutions were potassium chlorid, sodium chlorid, hydrochloric acid and nitric acid. In the last case an extra pair of solutions was added so that the nitric acid should not come in contact with the calomel. The potential difference between any solutions I and II at any temperature T is $\frac{u-v}{u+v}$ RT log c_1/c_2 according to Nernst's theory. To extend this expression to the case in which there is a temperature difference at the point of contact, it is necessary to know the temperature coefficient for the transference number. As a first approximation the author assumed that it was a constant. Considering the experimental difficulties and that the values measured are the relatively small differences between much larger numbers, the results are satisfactory. With hydrochloric acid the formula used required that the electromotive force should be a maximum when one of the contacts was kept at 51° C and this was found to be the case experimentally.

In cells of the second type the concentration of solution II was the same as that of solution I, but the electrolyte was different. The results with these cells differed essentially from the calculated values even after allowing for the Thomson effect. It is then assumed that beside the osmotic pressure and the electrical forces, there are other forces acting on the ions, directly proportional to the temperature difference. Granting that these forces exist, it is easy to show that, in the Soret phenomenon, the ratio of the equilibrium concentrations will not be exactly equal to the ratio of the absolute temperatures. Since the data of Arrhenius do not show strict proportionality between concentrations and temperatures, the author considers the hypothesis of the other forces as well established. Conclusions of this sort are very depressing. Apart from this blemish, the paper is very interesting. *W. D. B.*

The Thomson effect in a binary electrolyte. *F. G. Donnan. Phil. Mag.* [*5*] 45, *529* (*1898*).—For the Thomson effect in a completely dissociated binary electrolyte the author deduces the equation $E = \frac{R}{\omega\epsilon}\int_{T_1}^{T_2}(1 - 2n)dT$, where E is the potential difference, R the gas constant, ω the valency of the cation, ϵ the quantity of electricity associated with a monovalent gram-ion, n the transference number for the cation, and T the absolute temperature. For lithium hydroxid as electrolyte and a temperature difference of 100° the potential difference would be about six millivolts. With other electrolytes it would be much less.

W. D. B.

On some improvements in the Roberts-Austen recording pyrometer with notes on thermoelectric pyrometry. *A. Stansfield. Phil. Mag.* [*5*] 46, *59* (*1898*).—A description is given of the methods employed in registering the galvanometer readings automatically on a photographic plate. In this way the cooling curve for an alloy can be recorded. A discussion follows of the thermodynamical relation between electromotive force and the Thomson and Peltier effects. From a comparison of the relations between temperature and electromotive force the author concludes that there are probably two classes of metals, the ordinary metals for which $\frac{dE}{dt} = const.$ and the platinum metals together with nickel and cobalt for which $T\frac{dE}{dt} = const.$ An alloy of platinum containing five percent of iridium and five percent of rhodium does not give as high a thermoelectric force when balanced against pure platinum as does an alloy containing ten percent of iridium and no rhodium or ten percent of rhodium and no iridium.

W. D. B.

The thermo-electric properties of some liquid metals. *W. B. Burnie. Phil. Mag.* [*5*] 43, *397* (*1897*).—Reviewed (2, 205) from Proc. Phys. Soc. Lond. 15, 76 (1897).

On the decomposition of silver salts by pressure. *J. E. Myers and F. Braun. Phil. Mag.* [*5*] 44, *172* (*1897*).—Reviewed (2, 404) from Proc. Phys. Soc. Lond. 15, 200 (1897).

Influence of proximity of substances upon volta-electricity. *G. Gore. Phil. Mag* [*5*] 43, *441* (*1897*).—Bars of lead and of other substances were arranged so that they could be placed near either end of a horizontal tube containing zinc electrodes and a solution of zinc sulfate to which a little chlorin gas had been added. When the circuit was closed through a galvanometer it was found that there was always a current. Bringing the mass of lead near the cathode increased the deflection of the galvanometer needle; bringing it near the anode decreased the deflection and sometimes even reversed the current. It is believed that these effects are due to the attraction of the mass of lead. No quantitative measurements of the electromotive force were made nor is there any reference to the work of Des Coudres.

W. D. B.

On the reality of Hall's phenomenon in liquids. *H. Bagard. Nuovo Cimento,* (*4*) 7, *187* (*1898*).—A reply to Florio (2, 73) and to Chiavassa (2, 404). The original experiments (1, 268) were repeated with a liquid layer 1 cm thick, 7 cm wide and 40 cm long, the electrolyte being zinc sulfate in one case and ferric chlorid in another. The same results were obtained as before so that the author believes that there can no longer be any doubt as to the actual occurrence of Hall's phenomenon in liquids. *W. D. B.*

Susceptibility of water and of aqueous solutions. *H. du Bois. Wied. Ann.* 65, *38* (*1898*). — Commenting on a paper by Jäger and Meyer (2, 268) the author points out that he had recognized the variation of the magnetic susceptibility with the temperature years ago, Wied. Ann. 35, 167 (1888). He also believes that the value obtained by Jäger and Meyer for pure water is twenty percent too high and that their conclusions in regard to the susceptibility of Ni, Co, Fe and Mn as ion call for further study. The author recommends the method of inactive solutions, — described in his first paper — as the most convenient and "most accurate for the determination of the molecular susceptibility of solutions of paramagnetic compounds". *W. D. B.*

Electrical properties of newly prepared gases. *J. S. Townsend. Phil. Mag.* [*5*] 45, *125* (*1898*). — The oxygen and hydrogen given off by electrolysis of dilute sulfuric acid are charged positively and retain this charge even after passing through potassium iodid solution and pure water. In this charged state they have the power of condensing moisture to a cloud (at any rate above 20°) and the weight of the cloud is proportional to the charge on the gas. The oxygen evolved during the electrolysis of a caustic potash solution carries enough caustic potash with it, even after passing through sulfuric acid, to give an alkaline reaction. From the fact that this takes place both above and below 20° while the formation of cloud occurs only above 20°, the author concludes that the caustic potash carried over has nothing to do with the cloud formation. The oxygen from the sulfuric acid solution is charged positively, that from the caustic potash solution negatively. When charged hydrogen diffuses through porous earthenware the charge is left behind and this means may be employed to increase the electrification per unit volume.

When a twenty percent hydrochloric acid solution is electrolyzed between carbon electrodes the chlorin has a small negative charge while the hydrogen at first has a positive charge, but after a few minutes has a negative charge. This is probably due to the presence of chlorin gas in the electrodes since the hydrogen has a large positive charge when platinum electrodes are used and this charge does not change its sign as the electrolysis is carried farther. With sulfuric acid as electrolyte the hydrogen has a positive charge whether carbon or platinum electrodes are used. *W. D. B.*

On the influence of dissolved substances and of electrification on the re-formation of clouds. *H. A. Wilson. Phil. Mag.* [*5*] 45, *454* (*1898*). — The object of the experiments was to see whether clouds consisting of dilute solutions of various substances after being destroyed by bubbling through sulfuric acid would reappear on passing into air saturated with moisture, and also to see whether electrifying the cloud had any effect on its reappearing. The chief results were:

1. A cloud of pure water when evaporated by bubbling through H_2SO_4 does not reappear over water.

2. A cloud of a dilute solution of a non-volatile substance when evaporated reappears over water.

3. Electrification of the original cloud in either of the above cases does not affect the reappearance of it over water after evaporation, although the electrification is not stopped by the acid.

These experiments are explicable on the hypothesis that solid particles are carried off by the spray. Saturated water vapor would, of course, condense on these and it is interesting to notice that the concentration of the original solution has an effect on the density of the cloud. As far as these experiments are concerned, there is no reason to assume that the phenomenon is electrical in nature; but Townsend's experiments (preceding review) would seem to show the contrary. In any case the tenacity with which the gas holds on to the solid particles is in itself a very surprising phenomenon. *W. D. B.*

Application of diffusion to conducting gases. *J. S. Townsend. Phil. Mag.* [*5*] 45, *469* (*1898*).—The first section contains the mathematical treatment of the problem: "If there are two gases A and B, contained inside a vessel the walls of which absorb A, what quantity of A will remain unabsorbed and be left distributed throughout B inside the vessel after a given time has elapsed?" In the second section the results obtained in the first section are applied to the case of charged gases, the charged carriers or ions constituting the gas A and the indifferent molecules the gas B. "The loss of conductivity of a gas is due partly to the recombination of some of the positively charged carriers with the negatively charged ones and partly to the carriers coming into contact with it. ... When a carrier comes into contact with a conductor it either gives up its charge, or remains in contact with the surface. ... When there is an excess of carriers charged with electricity of one kind, the gas not only conducts but exhibits the properties of a charged body. ... The properties of these gases vary in many ways in regard to their power of retaining conductivity; thus some of them can be passed along tubing, bubbled through liquids, or sent through gauze or wool without losing more than from 20 to 50 percent of their conductivity, whereas others are made perfect non-conductors when so treated."

"When newly prepared gases are evolved from a solution it is probable that the electrification is acquired immediately as the gas is generated, so that each little bubble of the gas as it rises in the liquid contains carriers which are charged. Since these bubbles are small it would only require a very short time for carriers which diffused rapidly to be completely discharged by striking the liquid round the bubble, so that in order that an appreciable number of charged carriers should escape with the gas from the liquid it is necessary to assume that they diffuse slowly, or what amounts to the same thing, that they should be large compared with the molecules." *W. D. B*

On a new form of capillary electrometer. *G. Vanni. Rend. Acrad. Lincei*, (*5*) *7*, *I*, *309* (*1898*).—The solution is contained in a covered glass vessel having plane, rectangular sides. The vertical tube is supported by the cover to the vessel. It is not easy to see any striking novelty or merit in the proposed apparatus. *W. D. B.*

Electrolysis and Electrolytic Dissociation

The transference numbers for zinc and cadmium salts in very dilute solutions. *G. Kümmell. Wied. Ann.* **64**, *655* (*1898*). — With dilute solutions of zinc and cadmium salts, hydroxid is often precipitated at the cathode even when large potential differences are employed. It was proved that this was due to the dissolving of alkali from the glass. Experiments showed that the total of zinc or of cadmium precipitated as metal and salt agreed well enough with the values calculated from Faraday's law. With the halid salts the precipitated salt is exclusively hydroxid; with zinc sulfate the precipitate contains basic sulfate.

The salts studied were the chlorids, bromids, iodids, and sulfates of zinc and cadmium; the concentrations were 0.01–0.0025 normal, referred to equivalents. No variation of the transference number with the concentration could be established, though there were signs of this with zinc iodid and cadmium bromid. The mean values, referred to the anion, were $ZnCl_2$ 0.603, $ZnBr_2$ 0.600, ZnI_2 0.589, $CaCl_2$ 0.576, $CdBr_2$ 0.584, CdI_2 0.552, $ZnSO_4$ 0.664, $CdSO_4$ 0.619. The values for zinc and cadmium chlorids and cadmium sulfate were also determined by the Helmholtz electrometric method. The results were $ZnCl_2$ 0.585, $CdCl_2$ 0.572, $CdSO_4$ 0.627 The values for the molecular conductivity at infinite dilution as calculated from these values on the assumption of 63, 64, 64 as the migration velocities of chlorin, bromin, and iodin respectively, do not agree very closely with the values obtained by Wershofen for the cadmium salts. The value for zinc chlorid agrees well with that determined by Kohlrausch. The most probable value for the migration velocity of zinc as ion is 43 and of cadmium as ion 46. The general conclusion is reached that at a dilution of two thousand liters complex salts still exist with solutions of cadmium iodid, cadmium sulfate, and zinc sulfate while this is no longer the case for the other salt studied. *W. D. B.*

Dissolving of platinum and gold in electrolytes. *M. Margules. Wied. Ann.* **65**, *629* (*1898*). — When a cell consisting of platinum or gold electrodes in an acid or alkaline solution is placed in shunt with an induction coil, the metal dissolves. A certain electromotive force is necessary, platinum not dissolving perceptibly in dilute sulfuric acid during fourteen days that the induction coil was run by one Daniell, while the platinum began to dissolve at once when two Daniells were used. The conditions and details are to be worked out later, this article being purely preliminary. *W. D. B.*

On the electrolytic precipitation of gold. *E. Wohlwill. Zeit. Elektrochemie*, **4**, *379, 402, 421* (*1898*). — When a solution of $HAuCl_4$ is electrolyzed between gold electrodes, chlorin is given off at the anode and practically no gold goes into solution. An excess of hydrochloric acid stops the evolution of chlorin at once. Since the gold goes into solution as a complex ion, $AuCl_4$, it is suggested that gold dissolves only when there is enough free acid present to permit the formation of $HAuCl_4$. The author himself points out that this cannot be a complete statement of the facts because chlorin is evolved when hydrochloric acid is electrolyzed between platinum electrodes. Another difference between gold and platinum is shown by the behavior of the solutions toward silver nitrate. With platinum we get precipitation of the stable silver chlorplatinate. With gold the corresponding chloraurate can be obtained temporarily but it soon passes into a mixture of silver chlorid and gold trioxid.

With increasing current density it is necessary to increase the amount of free acid that must be added to prevent evolution of chlorin. With rising temperature a smaller excess of acid is sufficient. For this reason a temperature of 60°–70° is found the most satisfactory. In the preparation of pure gold, very high current densities are permissible, satisfactory results having been obtained with thirty amperes per square decimeter. It is essential, however, that the electrolytic solution should not contain less than thirty grams of gold per liter.

By electrolytic separation there is no difficulty in obtaining gold that is 999.8 fine. The silver is converted at the anode into silver chlorid and drops down. While platinum by itself does not dissolve in hot dilute hydrochloric acid, it does when alloyed with gold. Luckily it is not precipitated at the cathode when the solution contains a good deal of platinum. It is therefore an easy matter to convert the platinum into solid ammonium chlorplatinate while palladium and the other metals of that group remain undissolved at the anode.

Experiments have shown that gold does not dissolve at the anode nor precipitate at the cathode in the amounts required by Faraday's law, on the assumption that the electrolyte is $HAuCl_4$. The author has found that the gold dissolves not only as auric chlorid but as aurous chlorid. If some of the solution be pipetted off while the electrolysis is in progress, metallic gold will precipitate from it in the course of time, due to the change of the aurous chlorid into auric chlorid and metallic gold. This accounts also for the fact that the gold anode disintegrates with unusual rapidity. This simultaneous formation of two salts of gold with different electrochemical equivalents explains the apparently anomalous relations between the amount of current and the weight of gold precipitated. This is analogous to the behavior of mercury, Ibid, 2, 73, 93, 183 (1895) and of copper (1, 525). The ratio of univalent to trivalent gold is about one to nine under ordinary conditions of electrolysis. With rising temperature the ratio decreases. It was found also that even without the current gold dissolves in an acidified chloraurate solution—presumably as aurous chlorid. *W. D. B.*

On electrolytically precipitated iron. *F. Haber. Zeit. Elektrochemie*, 4, *410* (*1898*).—The Austrian government prints its bank notes from electrotype plates having an iron face and copper back. This iron face is precipitated electrolytically, is about 0.3 mm thick, is very hard and does not rust. These last two properties are said to be due to the presence of hydrogen. An analysis showed that the ratio of hydrogen to iron by volume was about twelve. An important condition for obtaining a good film of iron is a very low current density. The author made some experiments on the amount of hydrogen in iron when using a high current density. The solution contained iron and magnesium sulfates in equivalent quantities. With 2.25 amperes a very brittle iron film was obtained that contained one hundred and twelve volumes of hydrogen to one of iron (2, 342). *W. D. B.*

On electrostenolysis. *A. Coehn. Zeit. phys. Chem.* 25, *651* (*1898*).—The very plausible hypothesis is put forward that a perceptible precipitation of metal in capillary channels can take place only in case the metal does not dissolve when made the anode in that particular solution. As a matter of fact stenolysis is obtained with platinum salts and with gold chlorid. With lead acetate, lead nitrate and silver nitrate there is formation of peroxide and therefore stenolysis. With potassium silver cyanid there is no precipitation of metallic silver and no copper is precipitated from copper sulfate solution. On the other hand there is stenolysis with cuprous chlorid because the chlorin set free oxidizes some of the salt to cupric chlorid. There is stenolysis with cobalt salts and none with nickel salts; this is in harmony with the requirements of the theory because cobalt peroxid is formed by electrolysis and nickel peroxid is not (2, 69). *W. D. B.*

The electric current in organic chemistry. *E. F. Smith. Science*, **8**, *413* (*1898*).—This is the address of the vice-president before the chemical section of the last meeting of the American Association for the Advancement of Science. It gives a brief account of the development of electrochemistry, special stress being laid on the applications of electrochemistry to organic chemistry.
W. D. B.

The industrial applications of electrochemistry. *T. Ewan. Nature*, **58**, *112* (*1898*).—A brief sketch of some electrochemical processes. *W. D. B.*

The formation of mercury films by an electrical process. *R. Appleyard. Phil. Mag.* [*5*] **44**, *74* (*1897*).—Reviewed (**2**, 142) from Proc. Phys. Soc. Lond. **15**, 119 (1897).

On the taste and affinity of acids. *J. H. Kastle. Am. Chem. Jour.* **20**, *466* (*1898*).—Qualitative measurements on the relative sourness of 0.02 normal solutions of different acids, made in 1893. In about 76 percent of the cases the sourer tasting acid was the more dissociated (see **2**, 260). Picric acid and benzoic sulphinid do not taste sour in solution, the former being intensely bitter and the latter intensely sweet. Since the solutions of the salts of these substances have the same taste as the substances themselves, it is reasonable to suppose that the taste in each case is due to the anion and that the characteristic taste of hydrogen as ion is masked by it. *W. D. .B*

On evolution of light at some electrodes in electrolytic solutions. *F. Braun. Wied. Ann.* **65**, *361* (*1898*).—When an alternating current is passed through an aluminum electrode into sulfuric acid, the surface of the metal sends out a phosphorescent white light that becomes intense at times. On examining the light with a rotating mirror, it was found that when a narrow strip of aluminum was used, the chief part of the light was intermittent, the flash coming when the density of hydrogen exceeded an (undetermined) limit. With a continuous current the cathode becomes illuminated for a moment but the light then dies away. When aluminum has not previously been polarized with oxygen, it does not send out light on being made cathode. The effect is due therefore to the action of hydrogen on passive aluminum. In sodium chlorid solution an alternating current is not changed to a direct one by an aluminum electrode and no luminescence can be detected. Magnesium gives a light effect in some solutions as does zinc when made anode in sodium sulfid solutions. The subject is being studied further. *W. D. B.*

On platinum temperatures. *J. D. Hamilton Dickson. Phil. Mag.* [5] 44, *445* (*1897*).—The experiments of Griffiths, Callendar and Griffiths, Dewar and Fleming, Heycock and Neville, Holborn and Wien are discussed at length, the final conclusion being that for a platinum thermometer the best formula is $(R+a)^2=p(t+b)$, where R is the resistance of the wire and a, p and b are constants that must be determined for each sample of wire. *W. D. B.*

The reduction to normal air temperatures of the platinum temperatures in the low temperature researches of Professors Dewar and Fleming. *J. D. Hamilton Dickson. Phil. Mag.* [5] 45, *525* (*1898*).—The author has used his formula for the relation between resistance and temperature (see preceding review) to reduce to normal air temperatures the platinum temperatures in which the results of Dewar and Fleming were expressed. The temperatures as calculated are tabulated for reference. *W. D. B.*

On the constancy of normal resistances of manganin. *W. Jaeger and St. Lindeck. Wied. Ann.* 65, *572* (*1898*).—Standards made from manganin are better than the mercury copies with which they used to be compared. They show a tendency to increase at the rate of a few millionths per year, while the mercury ones fall off rather more than that. The institute at Charlottenburg is now prepared to give certificates showing the true values for decade resistance boxes from 0.001 up to 10,000 ohms with an error not exceeding 0.02 percent. *W. D. B.*

On the calculation of the conductivity of aqueous solutions containing two electrolytes with no common ion. *J. G. MacGregor and E. H. Archibald. Phil. Mag.* [5] 45, *151* (*1898*).—The authors have deduced the formula for the conductivity of mixtures of two electrolytes having no common ion and have tested the formula by means of experiments on mixtures of potassium chlorid and sodium chlorid and of sodium sulfate and potassium chlorid. The differences between the observed and calculated values do not exceed 0.7 percent. *W. D. B.*

On the determination of the conductivity of liquids in thin layers. *C. B. Bryan. Phil. Mag.* [5] 45, *253* (*1898*).—Koller, Sitzungsber. Akad. Wiss. Wien. 98, IIa, 201 (1889), found that, with certain liquids, the specific conductivity decreased as the thickness of the layer was decreased. On repeating the work, taking especial pains to eliminate polarization and to keep the plates true and clean, it was found that "for dilute solutions, alcohol and aniline, the conductivity is the same for all thicknesses within the limits of the experiments." *W. D. B.*

A method for determining the resistance of electrolytes. *P. C. McIlhiney. Jour. Am. Chem. Soc.* 20, *206* (*1898*).—The method consists in determining with a D'Arsonval galvanometer "the potential difference between the ends of a known resistance placed in series with the resistance to be determined. The current is supplied by a gravity battery and, before passing through the electrolyte, it is transformed into an alternating current by means of a rotary pole changer, but the current passing through the known resistance is direct." It is not claimed that this method is more accurate than the usual one. It is a quick method, however, and has proved serviceable in studying rapidly cooling silicates. *W. D. B.*

The conductivity of aqueous solutions of praseodidymium and of neodidymium sulphates. *H. C. Jones and H. M. Reese. Am. Chem. Jour.* 20, *606* (*1898*). — Measurements at dilutions varying from fifteen to five thousand liters. *W. D. B.*

Aluminum used as an electrode. *G. J. Hough. Jour. Am. Chem. Soc.* 20, *302* (*1898*). — Aluminum can be used in place of platinum as cathode in nitric acid, oxalate and cyanid solutions. *W. D. B.*

A new electrolytic stand. *G. J. Hough. Jour. Am. Chem. Soc.* 20, *268* (*1898*). — To a horizontal board or stand is fastened an upright board in which the binding-posts are screwed. Copper disks are let into the horizontal board offering a large surface for contact in case platinum dishes are used. The apparatus is easily made, is inexpensive and effective. *W. D. B.*

Electrode-holder. *R. Lorenz. Zeit. Elektrochemie*, 4, *359* (*1898*). — The apparatus consists of two half cylinders held together by an isolating cement. One electrode goes in one side and the other in the other. The electrodes are exactly one centimeter apart. The apparatus is cheap, costing only 2.80 M. It can be obtained from A. Jöge, Zürich. *W. D. B.*

Dielectricity and Optics

On a law governing the generation of electricity. *A. Coehn. Wied. Ann.* 64, *217* (*1898*). — A distinction is made between the electricity of the voltaic cell and that generated by the friction of two insulators, the paper dealing with the second class of phenomena. The law as formulated is: "Substances with a higher dielectric constant become charged positively when brought in contact with substances having a lower dielectric constant." As proof of this the author cites the experiments of Ritter, Riess, Riecke, Faraday and Hoorweg as well as some of his own. The same phenomenon occurs, in a modified form, in the transport of liquids through capillary tubes as shown in the experiments of G. Wiedemann and of Quincke. The theory was also applied to the case of two non-miscible liquids. Although the data relied upon are not phenomenally accurate, they serve to establish the extreme probability of the hypothesis. Only in a few cases, chloroform being one, were positive disagreements found and, even here, the source of error is probably to be sought in impurities in the liquids. The paper is a very interesting one, and it is to be hoped that it will be followed by another in which may be taken up the problems, expressly excluded from this article. As far as the generation of electricity by friction is concerned, there is no obvious reason why the phenomenon should not be observed with metals as with other substances. The question of conductivity is relative, and therefore metals must show these phenomena, though possibly to a much less extent. *W. D. B.*

The ionizing power of solvents. *W. C. D. Whetham. Phil. Mag.* [5] 44, *1* (*1897*). — The author has made conductivity determinations on mixtures of acetic acid and water, trichloracetic acid and water, formic acid and water. The first two curves have the same general form, the first addition of water producing a very slight increase of conductivity. With further addition of water the conductivity increases rapidly to a maximum and then falls off even more rapidly. With formic acid the first additions of water produce an increase of conductivity that is practically proportional to the change of concentration. The dielectric constants of water, formic acid, acetic acid and trichloracetic acid are 75.5, 62.0, 10.3 and < 10 respectively. The difference in the curves is attributed by the author to the dielectric constants of water and formic acid being nearly equal while the values of the other two acids are much lower. It is a pity that mixtures of acetic and trichloracetic acids were not examined. Water dissolved in formic acid gives normal lowerings of the freezing-point.

W. D. B.

Specific electric conductivities and freezing-points of solutions of water in formic acid. *V. Novak. Phil. Mag.* [5] 44, *9* (*1897*). — A careful study of the conductivity and freezing-points of mixtures of formic acid and water. The experiments confirm the results obtained by Whetham (preceding review).

W. D. B.

On the dielectric behavior of ice. *R. Abegg. Wied. Ann.* 65, *229, 923* (*1898*). — With Nernst's method it is difficult to get a sharp minimum when measuring the dielectric constant of ice. This is attributed by the author to dissolved gases in the water so that even at −80° the ice is not entirely solid but is filled with pores containing liquid. It is to some such cause that the abnormally high values obtained by Dewar and Fleming (1, 706) are due and not to electrolytic polarization (2, 74). Using the Nernst method of very rapid oscillations (1, 630) the value of 3.2 ± 0.2 was obtained for ice between 0° and −24° while the cryohydrate of salt and ice gave 3.8 at −80° as against 156 found by Dewar and Fleming at 100°. The most probable value for ice at 0° is 3.1 and for water at 0° about 87.

W. D. B.

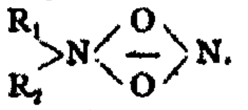
On the relation between fluorescence and actino-electricity. *G. C. Schmidt. Wied. Ann.* 64, *708* (*1898*). — The author sums up the results of this investigation as follows:

1. From the measurements with liquid solutions, it appears that fluorescence and electrolytic dissociation do not stand in any definite relation to actino-electric sensitiveness.
2. The same thing is true for pure solids and for solid solutions.
3. With the exception of uranium and thorium and of the compounds of these elements, all substances, in so far as they absorb ultra-violet light, show actino-electric sensitiveness at high potentials.
4. Uranium and thorium, as well as their compounds, dissipate positive electricity as readily as negative electricity.
5. Solids, showing actino-electric sensitiveness, retain this property in solid solutions.

6. Solid solutions containing uranium salts show no actino-electric sensitiveness. Even in the dark they dissipate positive and negative electricity with equal readiness.

7. Those substances, which show the most intense thermo-luminescence on being exposed to the cathode rays and then heated, dissipate negative electricity the most under the influence of light. *W. D. B.*

Optics.

Spectrochemistry of nitrogen, VI. *J. W. Brühl. Zeit. phys. Chem.* 25, *577* (*1898*). — From a study of the optical properties the author concludes that nitrogen has no structure formula; that azoxybenzene is a diazo compound as are also the nitrosacylamins; that nitrates should be represented by the formula RO—O—N = O; that the metallic and alkyl nitrites should be represented by R — N = O while the formula for the alkyl nitramins would be 

W. D. B.

Spectrochemistry of nitrogen, VII. *J. W. Brühl. Zeit. phys. Chem.* 26, *47* (*1898*). — This paper deals with the oxygen compounds of nitrogen in solution and leads to conclusions in regard to the structure formulas for nitroso hydrocarbons, phenylhydroxylamin, nitrourethane, diazobenzene acids, derivatives of benzylnitramins. The reviewer feels certain that he is not the only person who regrets that these papers were not published in Liebig's Annalen. *W. D. B.*

On light action, I. *M. Roloff. Zeit. phys. Chem.* 26, *337* (*1898*). — The author distinguishes sharply between polymeric transformations and those which are not. When the less stable form is the more soluble, the more fusible and the more volatile, the two modifications have the same reacting weight and the change from the less to the more stable is accompanied by evolution of heat. As criterion of a polymeric substance is the fact that it changes into the corresponding monomer when the temperature is raised sufficiently. The polymeric form is therefore less soluble, less fusible and less volatile than the monomeric form. It is to be noticed that neither of these definitions is sufficient, nor are they mutually exclusive. Benzaldoxime furnishes an instance of a substance occurring in two modifications having the same reacting weight, the more stable form having the lower melting-point. The only difference between the two definitions appears to be that in the case of polymeric transformations, each form is stable at some temperature and that this is not the case where no change in reacting weight occurs. Benzilorthocarboxylic acid is an instance to the contrary.

The author states that amorphous selenium is precipitated from solution and therefore exists as such in the solution. Five lines farther down the page the statement is made that yellow mercuric iodid is precipitated from solution and the implied inference is that it exists as such in the solution. Since the red form always separates on sudden cooling it would be just as reasonable to say that the red modification existed in the solution and not the yellow.

After an interesting discussion of many cases the general conclusion is reached that the action of light is favorable to polymerization and that the change is always exothermal. As an explanation of the action of light the author assumes that the ions (atoms?) in the molecule possess a certain electrical polarity that is changed by the light.

The remainder of the paper is devoted to evolution of light in chemical transformations, phosphorescence and the coloring of crystals, the influence of other substances. This part is a recapitulation of what is known in regard to these subjects and contains no conclusions of importance. *W. D. B.*

Effect of the mono-, di- and tri-chloracetyl groups on the rotatory power of methylic and ethylic glycerates and tartrates. *P. Frankland and T. S. Patterson. Jour. Chem. Soc.* 73, *181* (*1898*).—Introduction of two monochloracetyl groups increases the laevo-rotation of methyl and ethyl glycerate, the effect being very similar to, but slightly greater than, that produced by the introduction of two acetyl groups. Introduction of two monochloracetyl groups considerably reduces the dextro-rotation of methyl tartrate and barely increases that of ethyl tartrate; the effect on the latter is, in fact, barely appreciable. The effect of the two monochloracetyl groups resembles, but is much less than, that produced by the introduction of two acetyl groups. Introduction of two dichloracetyl groups increases the laevo-rotation of both methyl and ethyl glycerate and increases very greatly the dextro-rotation of both methyl and ethyl tartrate. The introduction of two trichloracetyl groups increases the laevo-rotation both of methyl and ethyl glycerate. The introduction of a single trichloracetyl group into methyl and ethyl tartrates increases the dextro-rotation. The authors have also studied and tabulated the effect of changing temperature. *W. D. B.*

Influence of pressure on the index of refraction of gases. *P. Carnazzi. Nuovo Cimento,* (*4*) 6, *385* (*1897*).—Experiments on air and hydrogen show that Gladstone's expression $(n-1)/d$ increases with increasing pressure while the reverse is the case with carbon dioxid. With hydrogen and with air the range of pressures was from one to forty or fifty atmospheres; with carbon dioxid the highest pressure was about thirty atmospheres. *W. D. B.*

On the catalytic action of different gases and vapors on the oxidation of phosphorus. *M. Centnerszwer. Zeit. phys. Chem.* 26, *1* (*1898*).—The partial pressure of the oxygen necessary to cause phosphorus to phosphoresce varies with the nature and concentration of the admixed gas. The author has determined the change of the partial pressure with the concentration for some thirty substances, each of which lowered the pressure at which phosphorescence takes place. It was not possible to establish any well-defined relation between the percentage change and any other properties of the added vapor. Ozone raises the pressure, and since ozone is produced during the oxidation of phosphorus, it is now clear why phosphorus does not cease phosphorescing at temperatures at which it will not begin to phosphoresce. *W. D. B.*

Crystallography, Capillarity and Viscosity

The surface-tensions of aqueous solutions of oxalic, tartaric and citric acids. *C. E. Linebarger. Jour. Am. Chem. Soc.* 20, *128* (*1898*).—The surface-tension of solutions of tartaric acid increases with increasing concentration while the reverse is the case for solutions of oxalic and of citric acid. The most concentrated solutions contained 9.13, 53.52 and 65.08 percent of oxalic, tartaric and citric acids respectively. *W. D. B.*

On the determination of capillary constants by the bubble method. *A. Heydweiller. Wied. Ann.* 65, *310* (*1898*).—An empirical formula of Lohnstein's for the relation between the surface-tension, diameters and radius of curvature of drops, Wied. Ann. 54, 713 (1895), was checked by comparison with the more accurate but less convenient formula used by Siedentopf (1, 532, 751). The author has then calculated and tabulated for reference the corresponding values of a/h and h/r, where r is the largest radius, h the height of the drop and a^2 is the specific cohesion. Starting from this table the author recalculates some data of Quincke's for air bubbles in water at 18°. The average value is $a = 3.855$ and the single values do not vary one percent from this. From Volkmann's observations on the height to which liquids rise in wide capillaries, we have $a = 3.851$ at 20°. From Lord Rayleigh's method of ripples we have $a = 3.884$ at 18°, while Lenard found $a = 3.815$ at 16° by yet another method. For mercury the most probable value from all the methods is $a = 2.615$ at 20°.

A series of measurements by Quincke on solidified silver drops does not give constant results and this is attributed to the deformation of the drops due to the evolution of gas bubbles at the moment of solidification. *W. D. B.*

The surface-tension of certain dilute aqueous solutions, determined by the method of ripples. *N. E. Dorsey. Phil. Mag.* [*5*] 44, *369* (*1897*).—Reviewed (2, 272) from Phys. Rev. 5, 170, 213 (1897).

A criterion whether a conducting surface layer is coherent and on the vapor-pressure of such films. *F. Braun. Wied. Ann.* 65, *365* (*1898*).—In contradistinction to the experiments with gypsum (1, 321) the films on surfaces of rock salt show scarcely any traces of electrical residue. The following conclusions are then drawn. "Really homogeneous, coherent, conducting surface-films furnish no electrical residue." "The lack of formation of an electrical residue is a criterion whether a coherent film is or is not present." The statement is made that the thickness of the layer varies with the partial pressure of water vapor in the atmosphere. [This is a case of a system in which the solution has not the properties of 'matter in mass' and therefore the usual formulation of the phase rule does not apply.] *W. D. B.*

THE CONVERSION OF AMMONIUM THIOCYANATE INTO THIOUREA AND OF THIOUREA INTO THIOCYANATE

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BY JOHN WADDELL

The course of a monomolecular reaction running to an end, in one direction, is at any instant represented by the formula

$$\frac{dx}{dt} = k\,(\mathrm{A} - x)$$

where k is the velocity coefficient, A is the amount of substance at the start, and x the amount that has been changed at the time t. If $x = 0$ when $t = 0$ we arrive, by integrating between the limits zero and t, at the formula

$$\log \frac{\mathrm{A}}{\mathrm{A} - x} = kt;\ \text{or}\ \log_{10} \frac{\mathrm{A}}{\mathrm{A} - x} = 0.4343\,kt.$$

When the reaction is reversible the form of the differential equation (and therefore of the integral equation) will be the same, the difference being in the constants.

If the substance A changes only partially into the substance B, we have at any moment (except at the very start if the action begins with A only present) two reactions going on which finally reach a state of equilibrium; and at any instant

$$\frac{dx}{dt} = k_1\,(\mathrm{A} - x) - k_2 x \qquad (1)$$

where k_1 and k_2 are the velocity coefficients.

Since after equilibrium is reached, no change takes place we have at that point

$$\frac{dx}{dt} = k_1(\mathrm{A} - \xi) - k_2\xi = 0 \ \text{or}\ k_2 = k_1\,\frac{\mathrm{A} - \xi}{\xi}$$

ξ being the value of x at equilibrium. Substituting the value of k_2 in equation (1)

$$\frac{dx}{dt} = k_1(\mathrm{A} - x) - k_1\frac{\mathrm{A} - \xi}{\xi}x$$

$$= k_1\mathrm{A} - k_1x - k_1\frac{\mathrm{A}}{\xi}x + k_1x$$

$$= k_1\mathrm{A} - k_1\frac{\mathrm{A}}{\xi}x$$

$$= k_1\frac{\mathrm{A}}{\xi}(\xi - x).$$

This equation is of the same form as for the non-reversible action, and becomes identical with it when $\xi = \mathrm{A}$. The equation is integrable in the same way as before, giving a constant which is however not the velocity coefficient, but the velocity coefficient of the reaction in one direction multiplied by a factor obtained by dividing the original quantity of the substance taken, by the quantity of substance which is changed at the state of equilibrium. Since the point of equilibrium will depend upon the relative velocity coefficients, the constant obtained should be the same whether we start from one end or the other.

If instead of starting with substance A, we start with substance B, the equation becomes

$$\frac{dx}{dt} = k_2\frac{\mathrm{A}}{\mathrm{A} - \xi}\Big((\mathrm{A} - \xi) - x\Big).$$

But our equation of equilibrium has already given us that

$$\frac{k_2}{\mathrm{A} - \xi} = \frac{k_1}{\xi};$$

therefore

$$\frac{dx}{dt} = \frac{k_1\mathrm{A}}{\xi}\Big((\mathrm{A} - \xi) - x\Big),$$

so that the constant obtained on integration is the same as before. In a reversible reaction we should therefore get the same constant, no matter from which end the reaction proceeds. Küster[1] thought of experimenting on the change of ammonium

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[1] Zeit. phys. Chem. 18, 161 (1895).

thiocyanate into thiourea but was deterred from doing so, because he considered that side-reactions would interfere too seriously with the course of the main reaction; and he decided to work on the change of hexa-chlor-α-keto-β-R-pentene into hexa-chlor-α-keto-γ-R-pentene and vice-versa.

His constant is not calculated in so simple a manner as the above, and does not show the similarity between the reversible and non-reversible reaction. Küster's constant is however identical with the one so calculated, and he saw that it should be the same, no matter from which end he started. He was not fortunate enough to arrive at this result; a slight impurity in the γ-R-pentene appearing to produce hydrochloric acid which hastened the reaction when starting from that end. Walker and Hambly[1] showed that the change of ammonium cyanate into urea is not a monomolecular reaction, and they concluded from the constant they calculated that it is bimolecular. It became all the more interesting to study the behavior of ammonium thiocyanate, and in spite of the risk of side-reactions I decided to investigate the matter.

Solid ammonium thiocyanate heated at 93° for a couple of months on the average eight hours a day, was somewhat changed, the color becoming a deep yellow, but this change though apparently great was almost inappreciable on titration and no thiourea could be detected. Similarly a solution of thiocyanate heated at the same temperature for about fifty hours gave no indication of change.

An approximately decinormal solution in which there was about 5 cc sulphuric acid to 250 cc solution kept boiling for eighty hours gave very little color to ferric alum and contained a large quantity of thiourea. As some evaporation had taken place, although I used a reflux condenser, I did not determine whether the thiourea corresponded in quantity to the original thiocyanate. An aqueous solution in which there was about 50 grams thiocyanate in 100 cc solution was kept at its boiling temperature, 109° C, for fifty hours and after that period showed the

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[1] Jour. Chem. Soc. 67, 746 (1895).

presence of thiourea, but at most there could not have been more than 0.25 percent.

The main experiments were conducted at the temperatures 152°–153° and 160°–161°. At these temperatures the substance was liquid, and it was hoped that the by-products formed would not be very considerable. Test-tubes containing in some series about one gram, in other series two grams of the solid were placed in an oil-bath kept stirred by a small motor. As the substance had to melt the time was not taken from the minute when the tubes were put into the bath, but from the minute when the first tube was withdrawn. It was for this reason that the quantity of substance in each of the tubes was approximately the same, otherwise the reaction in one tube might be more or less advanced than in another, at the same time. As each tube was taken out it was rapidly cooled, and the analysis of its contents made later on.

I had not anticipated any difficulty in using the ordinary method of titration for the thiocyanate, by means of silver nitrate acidified with nitric acid, but concordant results were not obtained. This was doubtless due to the formation of a certain amount of the compound of silver nitrate and thiourea described by Reynolds[1] and by Kurnakow,[2] which though partially decomposable, is somewhat stable in the presence of nitric acid. Before I had seen the papers of Reynolds and Kurnakow I had decided to use sulphuric acid as less unsatisfactory than nitric acid, but unfortunately, even in that case there is much to be desired.

The contents of the test-tubes were dissolved in water to the volume 100 cc, portions of this solution pipetted off, and diluted till 0.2 gram of the substance was contained in about 200 cc in some cases; while in other cases about five times as much water was added. 5 cc or 10 cc of a fairly concentrated solution of ferric ammonium alum was added as indicator and about 10 cc of dilute sulphuric acid.

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[1] Jour. Chem. Soc. 61, 250 (1892).

[2] Ber. chem. Ges. Berlin, 24, 3956 (1891).

Usually in the analysis of any given sample the first approximation was made by using the less dilute solution and afterwards, with the more dilute solution, a little more than the proper quantity of silver nitrate was run in and then a back titration made with ammonium thiocyanate solution. Since the results obtained were not so good as one would wish I attempted on the other hand to estimate the thiourea. Volhard[1] says that thiourea can be determined by means of ammoniacal silver nitrate solution which gives silver sulphide and cyanamid.[2] The reaction is represented by the equation

$$CS(NH_2)_2 = H_2S + CN.NH_2.$$

Cyanamid, when treated with silver nitrate, forms silver cyanamid, a yellow compound, but not till all the thiourea is decomposed. The precipitate formed by adding silver nitrate, changes from black to yellow when the thiourea is exhausted, and in order to determine the exact point at which this occurs a piece of filter-paper is, from time to time, moistened with a test-drop of the solution, and then a drop of silver nitrate added which gives to the paper a dark stain of silver sulphide, or a bright yellow one of silver cyanamid.

Volhard says that the method is slow in the presence of considerable thiocyanate but that it can be used with sufficient accuracy. He did not however anticipate its use in a series of estimations, and it is not very satisfactory as a method of titration. In the first place silver thiocyanate is not very readily soluble in ammonia and when silver sulphide is precipitated it is liable to enclose some of the thiocyanate, which would probably be all extracted by sufficiently long digestion in the ammoniacal solution, but which tends to vitiate results in an ordinary titration.

Moreover, I found that it was difficult to determine with exactness the point at which the stain on the filter-paper, changed

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[1] Jour. prakt. Chem. [2] 9, 28 (1874).

[2] Watts' Dictionary, IV, 709 (1894) states, without giving the authority, that ammoniacal silver nitrate produces silver sulphide and urea.

from being dark to being pure yellow, the limit of accuracy being one or two or in some cases even three-tenths of a cubic centimeter of decinormal silver nitrate solution. Finally when I had reached the point at which I decided that the stain was certainly yellow I found that on filtering and adding silver nitrate to the filtrate, a dark cloudiness and in some cases a slight black precipitate made its appearance. As however I do not know any perfectly reliable method of titration I was forced to content myself with these two, using the first method when the substance heated was ammonium thiocyanate, and the second when the substance heated was thiourea. The result as a whole then fell far short of perfection, but there seems to be no doubt regarding the character of the reaction. The constants obtained by heating ammonium thiocyanate on the one hand, and thiourea on the other, are the same, and are as near that required for a monomolecular reaction as the conditions of the experiment permit. It was found that when heated at 152°–153° the amount of thiocyanate changed into thiourea was 21.1 percent and at 160°, 20.9 percent. Volhard gives the amount of thiourea obtained by heating thiocyanate at temperature 160°–170° as 17.7 percent. It may be that at the higher temperature some of the thiourea was decomposed into cyanamid, or it may be that in using large quantities some disturbing element entered into the reaction.

Thiourea heated at 152°–153° for the same time as the thiocyanate contained 21.4 percent of thiourea so that practically the same end-point was reached, no matter which substance was heated. In calculating the constant for the change of thiocyanate into thiourea I have used $\xi = 21.2$; and for the reverse reaction $\xi = 78.8$. The time in all cases was measured in minutes. Tables I and II show two separate series heated at 152°–153°.

TABLE I

Thiocyanate

Temp. 152°–153°. $\xi = 21.2$

No.	t min	x	$\xi - x$	$\frac{\log(\xi - x_1) - \log(\xi - x)}{t - t_1}$
1	0	2.0	19.2	....
2	5	3.8	17.4	0.00885
3	12	6.2	15.0	0.0089
4	19	6.9	14.3	0.00684
5	28	8.2	13.0	0.00605
6	38	10.4	10.8	0.00658
7	48	12.3	8.9	0.00700
8	60	13.5	7.7	0.00661
9	78	14.5	6.7	0.00587
10	480	21.2	0.0	....
		Average, omitting the first two		0.00649

TABLE II

Thiocyanate

Temp. 152°–153°. $\xi = 21.2$

No.	t min	x	$\xi - x$	$\frac{\log(\xi - x_1) - \log(\xi - x)}{t - t_1}$
1	0	2.0	19.2	....
2	5	3.6	17.6	0.00755
3	10	4.5	16.7	0.00606
4	15	5.4	15.8	0.00564
5	20	7.1	14.1	0.00670
6	27	7.9	13.3	0.00590
7	34	10.0	11.2	0.00688
8	46	11.9	9.3	0.00684
9	57	13.3	7.9	0.00676
10	71	13.7	7.5	0.00575
			Average	0.00645

In Table I the value of x was obtained, by taking as correct the titration in the more dilute solution, a preliminary approximation having been made in a less dilute solution. The second titration was made in a large Erlenmeyer flask with about a liter of water, and 10 cc of the ferric alum indicator. After a slight excess of silver nitrate had been run in, the flask was gently shaken so that the silver thiocyanate should be as flocculent as possible, then 10 cc of dilute sulphuric acid added, and decinormal ammonium thiocyanate till the color of the ferric thiocyanate appeared.

In Table II the value is that obtained by taking the average of the titrations that were considered the best. Sometimes four or five titrations were made of the same sample.

Table III shows how far the values of x given in Table II differ from what would have been required for a perfect constant, the x in the third column being calculated on the basis of the constant 0.0063.

TABLE III

Thiocyanate

Temp. 152°–153°

No.	t	x calc	x found	Diff.
1	0	...	2.0	....
2	5	3.34	3.6	+0.26
3	10	4.59	4.5	—0.09
4	15	5.75	5.4	—0.35
5	20	6.83	7.1	+0.27
6	27	8.22	7.9	—0.32
7	34	9.47	10.0	+0.53
8	46	11.35	11.9	+0.55
9	57	12.80	13.3	+0.50
10	71	14.34	13.7	—0.64

TABLE IV

Thiourea

Temp. 152°–153°. $\xi = 78.8$

No.	t min	x	$\xi - x$	$\frac{\log(\xi - x_1) - \log(\xi - x)}{t - t_1}$
1	0	31.1	47.7	....
2	15	41.4	37.4	0.00704
3	27	45.2	33.6	0.00564
4	38	51.5	27.3	0.00638
5	53	54.4	24.4	0.00550
6	68	56.3	22.5	0.00637
7	90	65.0	13.8	0.00588
			Average	0.00622

Table IV gives the results obtained by heating thiourea at the temperature 152°–153°. Thiourea is said by Prätorius-Seidler[1] to fuse at 170°, but if the mass is cooled the melting-point is lowered to 149°. It would seem natural to suppose that some of the thiourea is changed into ammonium thiocyanate, thus lowering the melting-point, but one would expect that melting-points intermediate between 149° and 170° might be obtained, and though I did not make a special investigation of the matter my experience seems to confirm that expectation. The thiourea that I used was not entirely freed from thiocyanate. The tubes were placed in the bath at the temperature 154°, but as the substance did not fuse the temperature of the bath was raised to 166° when the contents of the tubes were entirely liquefied. The bath was then cooled down to 152° and the first tube taken out forty minutes after the beginning of the experiment. By this time, as will be seen in the table, more than thirty percent of the thiourea had been changed.

The thiourea which was heated at 160° was a portion of another lot, and was not so pure as the first, and melted more easily.

TABLE V

Thiocyanate

Temp. 160°–161°. $\xi = 20.9$

No.	t	x	$\xi - x$	$\frac{\log(\xi - x_1) - \log(\xi - x)}{t - t_1}$
1	0	2.7	18.2	....
2	6	5.4	15.5	0.0115
3	17	11.1	9.8	0.0158
4	22	12.9	8.0	0.0162
5	29	13.1	7.8	0.0127
6	36	16.2	4.7	0.0163
7	43	14.6	6.3	0.0107
8	50	18 7	2.2	0.0183
			Average	0.0145

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[1] Jour. prakt. Chem. (2) 21, 141 (1880).

TABLE VI

Thiourea

Temp. 160°–161°. $\xi = 79.1$

No.	t	x	$\xi - x$	$\frac{\log(\xi - x_1) - \log(\xi - x)}{t - t_1}$
1	0	40.3	38.8	....
2	6	44.9	34.2	0.0091
3	14	53.3	25.8	0.0127
4	21	58.1	20.9	0.0128
5	26	60.7	18.4	0.0125
6	31	60.0	19.1	0.0100
7	37	66.8	12.3	0.0135
		Average, omitting the first		0.0123

Tables V and VI represent the change of thiocyanate into thiourea and of thiourea into thiocyanate at temperature 160°–161°.

The constant varies still more than at the lower temperature. The velocity of the reaction is about double and any inequalities of temperature in different parts of the bath would have more effect. At the same time the deviations from the constant are irregular and the constant is practically the same whether starting from the thiocyanate or thiourea end.

The conclusions arrived at in the course of the investigation are mainly these:

I. Ammonium thiocyanate is very slowly if at all changed at temperatures below 110° whether heated alone or in aqueous solution.

II. The addition of sulphuric acid to the aqueous solution causes the disappearance of the thiocyanate, thiourea being formed at the same time.

III. Heated at temperatures above 150° the velocity of the reaction increases rapidly, doubling in the eight degrees between 152° and 160°.

IV. At these temperatures the point of equilibrium reached by heating ammonium thiocyanate and by heating thiourea is the same; the product containing a little more than 20 percent of thiourea.

V. The constant obtained in each reaction is the same.

VI. The change of ammonium thiocyanate into thiourea is a monomolecular one as is also the converse reaction.

I desire to express my thanks to Professor Bancroft, for suggesting this investigation and for the interest taken in its progress.

Cornell University

SOLUTION DENSITIES

BY H. T. BARNES AND A. P. SCOTT

It has been shown[1] that with the first quantities of zinc sulphate added to a solution there is produced no change in the volume of the water solvent until a density of about 1.150 is reached, so that the density may be calculated by adding to the weight of one cc of water the weight of zinc sulphate contained in one cc, without making an error of more than two or three parts in one thousand. For densities higher than 1.150 one molecule of zinc sulphate displaces one molecule of water, giving rise to the linear expression—

$$\text{density} = \text{wt. water} + \text{wt. salt} - \frac{18}{161}(\text{wt. salt} - 0.150).$$

The break in the curve which appears to be so marked seems to have been entirely overlooked in the work of previous observers. For this reason we have considered it of interest to investigate the point further, with a view to seeing how far it is a characteristic feature of density curves. The one molecule relation is also a very simple and obvious one, suggesting similar expressions for other salts.

Of the immense amount of data available on solution densities, we have found as a rule that either they extended over too short a range or the observations had been plotted, the curves smoothed out and the densities given at equal intervals. This made them of little value for reduction by the difference method used by us. It was necessary therefore for us to repeat a great deal of work that had already been done.

Our work has included a study of $MgSO_4$, $CdSO_4$, K_2SO_4, Na_2SO_4, $Mg(NO_3)_2$, $Zn(NO_3)_2$, KNO_3, $NaNO_3$, $NaCl$, KCl, HCl,

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[1] Callendar and Barnes. Proc. Roy. Soc. 62, 117 (1897), afterwards given as loc. cit.

H_2SO_4, and a verification of the $ZnSO_4$ results already obtained. We have not found that any of these curves show the flat part so strikingly as $ZnSO_4$. We have found, however, distinct breaks in what are otherwise straight lines in our difference curves, which we cannot consistently smooth out. Without wishing to bring forward any "Hydrate theory", we are inclined to think that these peculiar "breaks" are probably caused by a change in the hydration of the salt, but in just what way we are not at present prepared to say. It is apparent that all the salts do not displace one molecule of water; some seem to displace two or three molecules, but not one less than one molecule. The relation can hardly be said to hold, however, in some cases.

Method and Accuracy of Work

Our method of measuring the densities is the most common and generally accepted one of filling a weighed "Ostwald" pyknometer. The capacity of our pyknometers we have restricted to 10 cc, as this enabled us to obtain an accuracy of one in ten thousand quite easily. Our weights were taken, however, to a tenth milligram, and it was found that no unusual care was required to enable the "fillings" to be made to two or three-tenths milligram. The capacity of the pyknometers was measured by weighing a number of times with air-free distilled water, and we found that after immersing in a constant temperature water-bath for fifteen or twenty minutes and drying so as to leave a maximum coating of water vapor on the glass we could obtain water equivalents to one or two-tenths milligram. The capacity was calculated assuming one cc of water to weigh one gram at 4° C.

The constant temperature water-baths already described[1] were of great assistance in the present work. Always before filling the pyknometers they were immersed in the bath for a short time so that when they were taken out and wiped dry they were in the same condition for weighing as when filled with solution. After obtaining their weights they were quickly filled with solution nearly to the mark and again immersed in the water-bath.

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[1] Loc. cit. p. 119.

Only a very small quantity of solution was then required to fill them to the mark after which they were wiped dry and weighed. For refilling they were washed out with water and alcohol and dried in a current of hot air.

The chemical analysis of the saturated solutions was by far the most uncertain of our determinations. We thought for this reason that the great refinement obtained in density determinations, which seems to be limited only by the capacity and working convenience of the pyknometer, was quite unnecessary. Of course the relative values of our densities are not affected by a slight error in the determination of the concentration, but until the chemical methods are more refined and we are more certain of the atomic weights, there can be little value in measuring densities to six or seven decimal places.

Nearly all our salts used were Merck's standard and those that were not were purchased chemically pure. Saturated solutions were made by shaking an excess of salt with pure distilled water at room temperature, and filtering. After the strength of the saturated solution was determined the dilutions were made by weighing out amounts of the main solution in a corked test-tube, and then weighing the quantity of added water. As soon as this complete weight was obtained the mixture was carefully stirred by means of a flattened glass rod, without outward agitation, and then sucked up into the pyknometer. The dilutions ranged from ½ to 100 volumes of water.

All the distilled water used was rendered air-free through exhaustion by a water pump under a layer of heavy paraffin oil. We found it very necessary to do this as otherwise there was quite a serious accumulation of air bubbles on the inside surface of the pyknometers. By using from eight to ten pyknometers and weighing out a number of dilutions one after the other, it was possible to proceed with considerable rapidity, the only limit being the time taken with the chemical analysis.

The method of reducing the observations is the same as that already described.[1] The percent strength of the

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[1] Loc. cit. p. 142.

solution p, obtained by a chemical analysis, was multiplied by the observed density d and the product divided by 100, giving the volume concentration w in grams per cc. By adding to the weight of one cc of water, at the temperature of the observed density, the weight of the salt w, the density of the solution was obtained assuming there was no change in volume. By subtracting the observed density from this a series of differences was obtained which we have plotted against the volume concentration.

We have, besides obtaining the observations about to be described, reduced the observations of a number of other observers on the same plan and have found with a few marked exceptions a very good agreement with our own. We find however that the expression of density is rather an arbitrary matter and that some have give nnot the true density which is defined as

$$\frac{\text{Mass}}{\text{volume}}$$

but a density in terms of water at the temperature of the experiment. In most cases of course the observer has stated that the density is in terms of water, but it appears to us that a stricter adherence to the true meaning of density would be desirable.

Observations

We have arranged our results in tabular form and have plotted the values of w and (wt. of water $+ w) - d$. The position of the dotted points, which represent the observations on the plot, will give quickly the divergence from a one, two or three molecule relation, represented by a straight line, either from the origin or a point along the w axis. The abscissae represent values of w, while the ordinates, values of the difference. In the tables we have put in the first column the values of p the percentage strength of solution. In column two are the observed values of the density d, made at a temperature $t°$. Column three contains the values of $\frac{pd}{100}$ or w. The calculated density is placed in column four, obtained by adding to the weight of

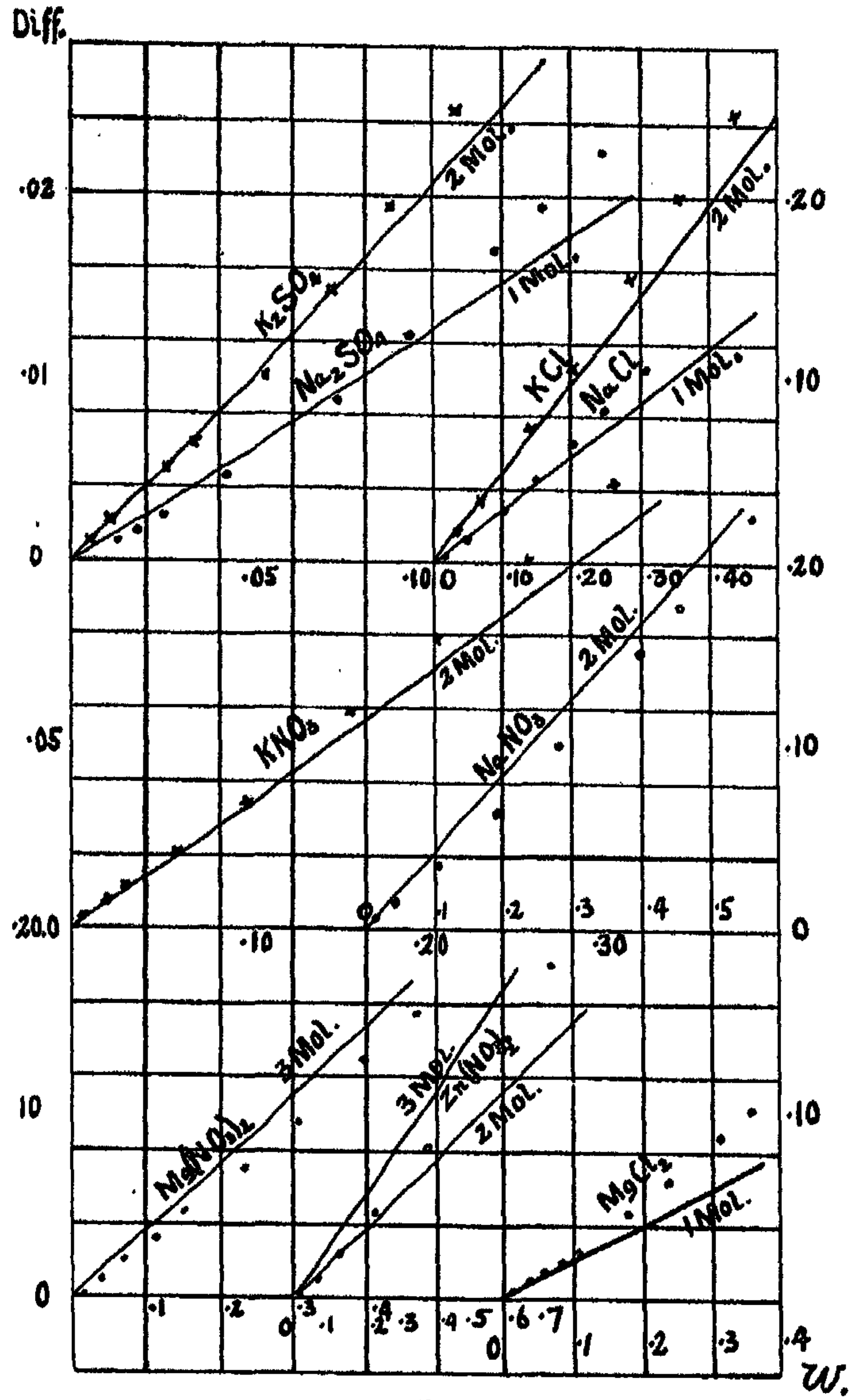
Diff.
·02
·01
0
·05
·20.0
10
0
·20
·10
·20
·10
0
·10
·4
W.
K₂SO₄
2 Mol.
Na₂SO₄
1 Mol.
KCl
NaCl
2 Mol.
1 Mol.
KNO₃
2 Mol.
NaNO₃
2 Mol.
Mg(NO₃)₂
3 Mol.
3 Mol.
Zn(NO₃)₂
2 Mol.
MgCl₂
1 Mol.
·05
·10
0
·10
·20
·30
·40
·10
·20
·30
·1
·2
·3
·4
·5
·1
·2
0
·3
·1
·2
·3
·4
·5
0
·6
·7
·1
·2
·3

Fig. 1

one cc of water at $t°$, the weight of salt w. In five the difference between the calculated and observed density; and in six a calculated difference is put representing either a one, two or three molecule relation. In plotting it has been necessary to cramp the curves somewhat, but the general relations may be very clearly seen. It will be noticed at once that the molecule relation is by no means an accurate one for all the salts, although it holds for a few with surprising closeness. The peculiar break in the curves is unmistakable. In some cases the density curve appears to start out to follow a one molecule relation and then bends to a two molecule, or starting with a two molecule bends to a three. We cannot conscientiously draw curves, other than straight lines, through the observations plotted in Fig. 1, but in Fig. 2 it appears that the sulphates of magnesium, cadmium and zinc would be best represented by a parabolic curve.

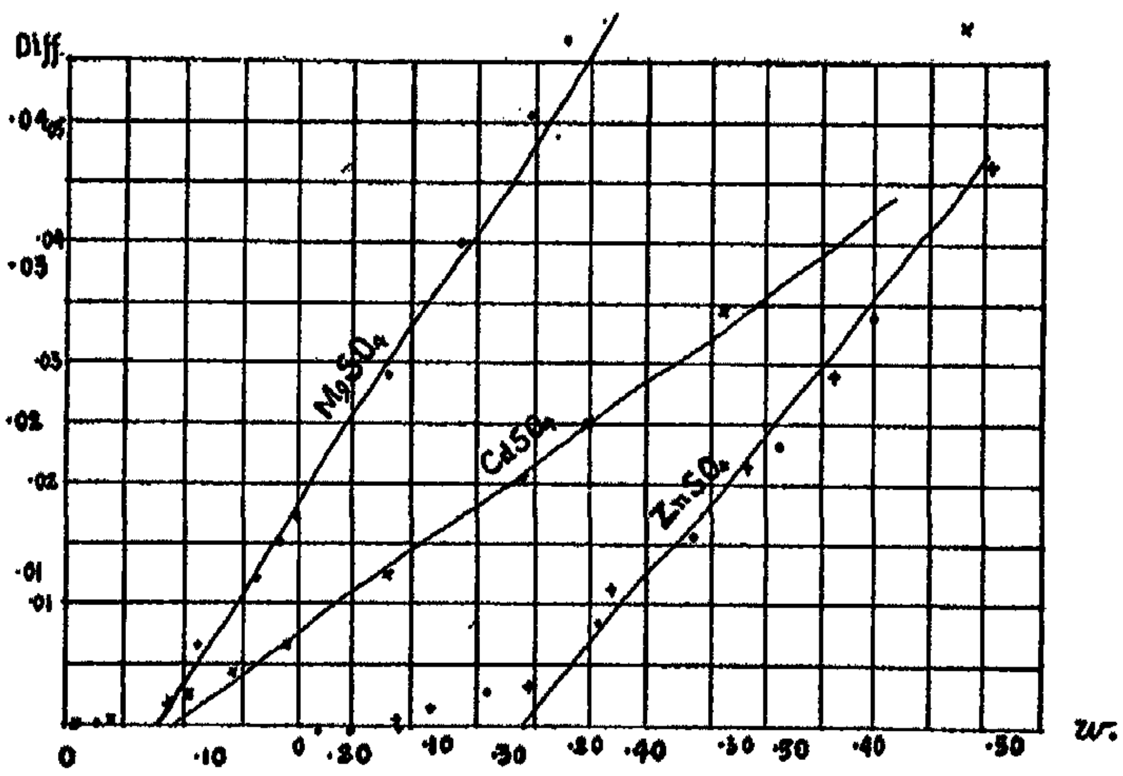

Fig. 2

Objections have been raised repeatedly to the idea of breaks occurring in density curves on the ground that if they were due to hydration the change would take place gradually and not suddenly.[1] Of course we do not suppose that any transition occurs

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[1] Nernst. Theor. Chemie, 420.

with abruptness, but that there is a rounding off of the meeting-point of the otherwise straight lines. There is no doubt whatever that the change of hydration with temperature occurs with great abruptness[1] and there seems hence very little reason not to suppose that a similar change with concentration might occur. As we have already said, however, we do not wish to bring forward any hydrate theory but merely to give our experimental results.

TABLE I

$ZnSO_4$ $t^\circ = 18.5^\circ$ M = 161

p	d	w	$0.9986 + w$	$(0.9986 + w) - d$	$\frac{18}{161}(w - 0.150)$
29.22	1.3718	0.40057	1.3992	0.0274	0.0280
25.14	1.3091	0.32910	1.3277	0.0186	0.0200
21.28	1.2528	0.26659	1.2652	0.0124	0.0130
17.08	1.1957	0.20422	1.2028	0.0071	0.0061
11.20	1.1220	0.12567	1.1243	0.0023	0.0000
8.44	1.0894	0.09195	1.0906	0.0012	0.0000
6.65	1.0696	0.07112	1.0697	0 0001	0.0000
3.82	1.0387	0.03968	1.0383	−0.0004	0.0000
3.18	1.0318	0.03281	1.0314	−0.0004	0.0000
1.46	1.0138	0.01480	1.0134	−0.0004	0.0000
0.577	1.0045	0.00580	1.0044	−0.0001	0.0000

TABLE II

$MgSO_4$ $t = 18.2^\circ$ M = 120

p	d	w	$0.9987 + w$	$(0.9987 + w) - d$	$\frac{18}{120}(w - 0.060)$
26.25	1.2903	0.3387	1.3374	0.0471	0.0419
25.91	1.2860	0.3332	1.3319	0.0459	0.0410
24.53	1.2693	0.3114	1.3101	0.0408	0.0377
21.60	1.2330	0.2663	1.2650	0.0320	0.0312
18.41	1.1950	0.2200	1.2187	0.0237	0.0240
13.79	1.1423	0.1575	1.1562	0.0139	0.0146
12.63	1.1292	0.1426	1.1413	0.0121	0.0124
11.29	1.1147	0.1259	1.1246	0.0099	0.0099
8.08	1.0803	0.0872	1.0859	0.0056	0.0041
2.01	1.0187	0.0204	1.0191	0.0004	0.0000

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[1] Ernst Cohen. Zeit. phys. Chem. 14, 53 (1894); loc. cit. p. 150.

TABLE III

$CdSO_4$ $t = 18.2°$ $M = 208$

p	d	w	$0.9987 + w$	$(0.9987 + w) - d$	$\frac{18}{208}(w - 0.070)$
39.86	1.5639	0.6231	1.6218	0.0579	0.0477
31.53	1.4080	0.4439	1.4426	0.0346	0.0324
26.85	1.3310	0.3574	1.3561	0.0251	0.0248
24.17	1 2901	0.3118	1.3105	0.0204	0.0209
18.35	1.2084	0.2217	1.2204	0.0120	0.0132
13.27	1.1437	0.1518	1.1505	0.0068	0.0071
9.97	1.1045	0.1102	1.1089	0.0044	0.0035
7.46	1.0764	0.0803	1.0790	0.0026	0.0009
6.12	1.0619	0.0650	1.0637	0.0018	0.0000
2.52	1.0242	0.0259	1.0246	0.0004	0.0000
1.45	1.0132	0.0147	1.0134	0.0002	0.0000
0.464	1.0033	0.0046	1.0033	0.0000	0.0000

TABLE IV

K_2SO_4 $t = 20.1°$ $M = 174$

p	d	w	$0.9983 - w$	$(0.9983 + w) - d$	$\frac{36}{174} w$
9.83	1.0800	0.10615	1.1045	0.0245	0.0219
8.172	1.0657	0.08708	1.0854	0.0197	0.0180
6.779	1.0539	0.07144	1.0697	0.0158	0.0148
5.021	1.0394	0.05218	1.0505	0.0111	0.0108
3.127	1.0238	0.03202	1.0303	0.0065	0.0066
2.508	1.0186	0.02554	1.0238	0.0052	0.0053
1 448	1.0100	0.01463	1.0129	0.0029	0.0030
1.079	1.0070	0.01087	1.0092	0.0022	0.0022
1.047	1.0066	0.01053	1.0088	0.0022	0.0022
0.455	1.0018	0.00456	1.0029	0.0011	0.0009

TABLE V

Na_2SO_4 $t = 17.5°$ $M = 142$

p	d	w	$0.9989 + w$	$(0.9989 + w) - d$	$\frac{18}{142} w$
13.06	1.1226	0.14662	1.1453	0.0227	0.0185
11.75	1.1094	0.13043	1.1291	0.0197	0.0165
10.68	1.0990	0.11737	1.1161	0.0171	0.0148
8.544	1.0784	0.09214	1.0908	0.0124	0.0117
6.762	1.0615	0.07178	1.0705	0.0090	0.0091
4.015	1.0358	0.04159	1.0403	0.0045	0.0053
2.599	1.0225	0.02658	1.0253	0.0028	0.0034
2.375	1.0204	0.02423	1.0229	0.0025	0.0030
1.818	1.0154	0.01846	1.0172	0.0018	0.0023
1.349	1.0109	0.01364	1.0123	0.0014	0.0017
0.5204	1.0037	0.00522	1.0039	0.0002	0.0006
0.2921	1.0014	0.00293	1.0016	0.0002	0.0004

TABLE VI

KCl $t = 20.1°$ $M = 74.6$

p	d	w	$0.9983 + w$	$(0.9983 + w) - d$	$\frac{36}{74.6}w$
36.43	1.1853	0.43171	1.4300	0.2447	0.2083
31.12	1.1554	0.35954	1.3578	0.2024	0.1735
24.79	1.1215	0.27887	1.2772	0.1557	0.1345
18.06	1.0866	0.19610	1.1944	0.1078	0.0945
13.17	1.0617	0.13980	1.1381	0.0764	0.0675
8.412	1.0386	0.08736	1.0857	0.0471	0.0421
6.610	1.0297	0.06806	1.0664	0.0367	0.0328
4.419	1.0193	0.04505	1.0433	0.0240	0.0218
3.456	1.0148	0.03507	1.0334	0.0186	0.0169
1.197	1.0040	0.01202	1.0103	0.0063	0.0058

TABLE VII

$NaCl$ $t = 18.0°$ $M = 58.5$

p	d	w	$0.9987 + w$	$(0.9987 + w) - d$	$\frac{18}{58.5}w$
25.37	1.1928	0.30263	1.3013	0.1085	0.0930
21.25	1.1592	0.24637	1.2451	0.0859	0.0756
17.35	1.1277	0.19563	1.1943	0.0666	0.0602
13.25	1.0958	0.14518	1.1439	0.0481	0.0446
9.34	1.0665	0.09960	1.0983	0.0318	0.0306
4.810	1.0332	0.04969	1.0484	0.0152	0.0153
2.991	1.0202	0.03052	1.0292	0.0090	0.0094
2.593	1.0173	0.02638	1.0251	0.0078	0.0081
1.746	1.0111	0.01765	1.0164	0.0053	0.0054

TABLE VIII

KNO_3 $t = 20.1°$ $M = 101.1$

p	d	w	$0.9983 + w$	$(0.9983 + w) - d$	$\frac{36}{101.1}w$
25.54	1.1783	0.30095	1.2993	0.1210	0.1072
21.95	1.1510	0.25270	1.2510	0.1000	0.0900
17.88	1.1200	0.20033	1.1986	0.0786	0.0713
13.93	1.0913	0.15203	1.1503	0.0590	0.0541
8.706	1.0553	0.09186	1.0902	0.0349	0.0327
5.393	1.0331	0.05571	1.0540	0.0209	0.0198
4.389	1.0264	0.04506	1.0434	0.0170	0.0160
2.848	1.0165	0.02895	1.0273	0.0108	0.0103
2.030	1.0113	0.02053	1.0188	0.0075	0.0073
0.741	1.0030	0.00743	1.0057	0.0027	0.0027

Table IX

$NaNO_3$ $t = 20.1°$ $M = 85$

p	d	w	$0.9983+w$	$(0.9983+w)-d$	$\frac{36}{85}w$
42.05	1.3380	0.56267	1.5609	0.2229	0.2383
35.65	1.2765	0.45510	1.4534	0.1769	0.1927
31.72	1.2407	0.39365	1.3919	0.1512	0.1667
23.24	1.1696	0.27180	1.2701	0.1005	0.1151
17.370	1.1228	0.19505	1.1933	0.0705	0.0826
11.915	1.0819	0.12888	1.1272	0.0453	0.0545
9.665	1.0656	0.10300	1.1013	0.0357	0.0436
7.039	1.0468	0.07369	1.0730	0.0262	0.0312
4.241	1.0273	0.04357	1.0418	0.0145	0.0184
1.589	1.0096	0.01604	1.0143	0.0047	0.0068

Table X

$Mg(NO_3)_2$ $t = 20.1°$ $M = 148$

p	d	w	$0.9983+w$	$(0.9983+w)-d$	$\frac{54}{148}(w-0.030)$
35.62	1.3110	0.46695	1.4653	0.1543	0.1594
31.15	1.2655	0.39420	1.3925	0.1270	0.1329
25.03	1.2057	0.30172	1.3000	0.0943	0.0990
19.55	1.1551	0.22585	1.2242	0.0691	0.0713
13.43	1.1028	0.14815	1.1465	0.0437	0.0432
10.09	1.0753	0.10850	1.1068	0.0315	0.0287
6.650	1.0480	0.06968	1.0680	0.0200	0.0145
4.672	1.0330	0.04826	1.0466	0.0136	0.0066
4.001	1.0276	0.04112	1.0394	0.0118	0.0041
1.372	1.0085	0.01383	1.0121	0.0036	0.0000

Table XI

$Zn(NO_3)_2$ $t = 17.3°$ $M = 189$

p	d	w	$0.9988+w$	$(0.9988+w)-d$	$\frac{36}{189}w$
47.28	1.5504	0.73310	1.7319	0.1815	....
41.32	1.4579	0.60240	1.6012	0.1433	....
30.86	1.3136	0.40535	1.4042	0.0906	....
29.21	1.2933	0.37780	1.3766	0.0833	....
19.65	1.1830	0.23246	1.2313	0.0483	....
14.39	1.1284	0.16232	1.1611	0.0327	....
11.36	1.0988	0.12478	1.1236	0.0248	0.0238
7.091	1.0597	0.07515	1.0740	0.0143	0.0143
5.923	1.0491	0.06213	1.0609	0.0118	0.0118
1.574	1.0118	0.01593	1.0147	0.0029	0.0030
1.210	1.0087	0.01221	1.0110	0.0023	0.0023

TABLE XII

$MgCl_2$ $t = 20.1°$ M = 95.0

p	d	w	$0.9983 + w$	$(0.9983 + w) - d$	$\frac{18}{95} w$
28.83	1.2569	0.36237	1.3607	0.1038	....
25.59	1.2241	0.31327	1.3116	0.0875	....
20.31	1.1735	0.23842	1.2367	0.0632	....
15.79	1.1324	0.17877	1.1771	0.0447	....
10.185	1.0833	0.11033	1.1086	0.0253	....
8.058	1.0650	0.08583	1.0841	0.0191	0.0163
5.919	1.0473	0.06198	1.0603	0.0130	0.0117
3.913	1.0304	0.04022	1.0385	0.0081	0.0076
3.903	1.0240	0.03210	1.0304	0.0064	0.0061
1.743	1.0126	0.01765	1.0160	0.0034	0.0033

TABLE XIII

HCl $t = 19.5°$ M = 36.5

p	d	w	$0.9983 + w$	$(0.9983 + w) - d$
36.00	1.1818	0.4255	1.4238	0.2420
29.97	1.1511	0.3450	1.3433	0.1922
24.35	1.1207	0.2729	1.2712	0.1505
18.55	1.0910	0.2024	1.2007	0.1097
12.22	1.0587	0.1294	1.1277	0.0690
9.148	1.0433	0.0954	1.0937	0.0504
6.559	1.0305	0.0676	1.0659	0.0354
3.540	1.0159	0.0360	1.0343	0 0184
5.345	1.0246	0.0548	1.0531	0.0285
1.356	1.0051	0.0136	1.0119	0.0068

TABLE XIV

H_2SO_4 $t = 19.4°$ M = 98.0

p	d	w	$0.9983 + w$	$(0.9983 + w) - d$
94.10[1]	1.8380	1.7295	2.7278	0.8898
84.59	1.7998	1.5223	2.5206	0.7208
73.08	1.6743	1.2235	2.2218	0.5475
61.35	1.5341	0.9412	1.9395	0.4054
40.72	1.3220	0.5383	1.5366	0.2146
31.94	1.2430	0.3970	1.3953	0.1523
23.77	1.1747	0.2792	1.2775	0.1028
14.72	1.1023	0.1623	1.1606	0.0583
9.802	1.0670	0.1046	1.1029	0.0359
4.826	1.0320	0.0498	1.0481	0.0161

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[1] A rough approximation taken from density tables, which will be quite sufficient to give a general idea of the way in which the difference curve follows the rate of dilution.

Zinc Sulphate

In Table I will be found the observed densities and the differences assuming a one molecule relation starting from a density of 1.150. The plot in Fig. 2 will perhaps show this more clearly. The rounded points show the observations from Table I, while the crosses show the original observations already described.[1] The peculiar feature is the sharp bend towards the origin, causing the curve to pass in along the axis of *w*. There is certainly no abrupt change here, but just what the explanation is we are not yet able to say. We hope, however, soon to be able to do so. We have made density determinations at 0° and find that the effect is to lower all the points and cause the flat part to be much more exaggerated, that is to make the curve run into the axis of *w* much sooner. Determinations at 35° show the curve higher and passing into the origin apparently without any flat part. The scale commences four divisions from the extreme left and for the horizontal axis is two and one-half divisions to $w = 0.100$. The vertical scale is two and one-half divisions to diff. $= 0.0100$.

Magnesium Sulphate

Table II and Fig. 2 give the observations and plot of this salt. The flat part is not nearly so marked as for zinc. The one molecule relation holds very closely until the more concentrated or more nearly saturated solutions when the divergence is quite marked. We have drawn the one molecule line from a density of 1.060. The density of solutions of $MgSO_4$ may be quite accurately estimated from the following linear expression

$$d_{18^\circ} = 0.9987 + w - \frac{18}{120}(w - 0.060).$$

The scale for the plot commences at the extreme left, but otherwise is the same as for $ZnSO_4$.

Cadmium Sulphate

Table III, Fig. 2. The divergence from the one molecule

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[1] Loc. cit. p. 142.

relation is more marked in the case of strong solutions of $CdSO_4$, but holds with remarkable closeness for dilute solutions. The flat part is quite clearly shown in the plot. The scale commences at the extreme left as for $MgSO_4$, but differs from that salt and $ZnSO_4$ on the vertical axis by having only two divisions to the diff. = 0.010. The horizontal scale is the same as for $MgSO_4$. The expression for the density is in every way similar to the ones for Mg and Zn, substituting, of course

$$\frac{18}{208}(w - 0.070).$$

Potassium and Sodium Sulphates

Tables IV and V, Fig. 1. These sulphates are plotted to the same scale and show a close similarity except that the potassium salt follows more nearly a two molecule relation while sodium follows a one. One decided break occurs in each density line, and this is brought out clearly in the plot. The calculated difference column shows this break by diverging from the observed difference column at a density of 1.0539 in the case of K_2SO_4 and for $NaSO_4$ at 1.0990. Similar density expressions may be given for these two salts, as have already been cited.

Potassium and Sodium Chlorides

Tables VI and VIII, Fig. 1. These salts are also plotted to the same scale, commencing five divisions to the right of the sulphate curves. Like K_2SO_4, KCl follows the two molecule line, but shows no definite break. It is practically a straight line running in towards the origin. NaCl shows a bend and, like the sulphate, follows the one molecule line.

Potassium and Sodium Nitrates

Tables VIII and IX, Fig. 1. KNO_3 like KCl is almost a perfect straight line approximating to a two molecule slope. $NaNO_3$, however, follows the two molecule line and in this respect differs from NaCl or Na_2SO_4. A break occurs in the $NaNO_3$ curve at about $w = 0.20$.

Magnesium and Zinc Nitrates

Tables X and XI, Fig. 1. Both these salts approximate to a three molecule relation, but in the case of $Zn(NO_3)_2$ we have not considered it necessary to put in the three molecule differences in the table, merely wishing to show the remarkable agreement of the two molecule differences for the more dilute solutions and the position of the well defined break. The vertical scale is the same in the plot for both salts. The horizontal scale begins for $Zn(NO_3)_2$ three divisions to the right and is represented by one division $= 0.20$.

Magnesium Chloride

Table XII, Fig. 1. $MgCl_2$ follows for dilute solutions the one molecule relation shown by the difference column in the table. At a value of $w = 0.10$, however, a decided bend occurs, causing the differences to approximate more nearly to a two molecule line. The vertical scale is numbered to the right and is represented by two and one-half divisions to 0.10. The horizontal scale commences six divisions to the right and is one division to 0.10.

We have, besides studying the salts already mentioned, determined the densities of pure HCl and H_2SO_4 to see if any relationship existed between the pure acids and the salts. Tables XIII and XIV give the results of these observations, but we have not considered it necessary to plot them. The difference curve for HCl follows approximately a one molecule relation and apparently is a straight line passing into the origin without a break. The difference curve for H_2SO_4 shows a certain similarity to the sulphates of cadmium, magnesium and zinc. Whether the observations should be smoothed out into a parabolic curve or whether they would be more nearly represented by a number of straight lines, as was pointed out by Mendelejew,[1] we are not at present prepared to say. Plotting the observations on a large scale and feeling assured as we do that the densities are accurate

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[1] Zeit. phys. Chem. 1, 273 (1887).

to one in ten thousand, we are inclined to doubt whether we could conscientiously smooth out the points. There is a slight indication also of a flat part similar to that shown in the sulphates of Cd, Mg and Zn.

It is not altogether clear whether the similarity in density changes should be looked for in salts with a common acid or with a common base. From the study of the K and Na salts, with the exception of $NaNO_3$, it looks as though similar relations might be expected from a common base. On the contrary, from the results of H_2SO_4 and the sulphates of Mg, Cd and Zn, it looks like a similarity in a common acid radical. It is exceedingly unlikely, however, that we can find any simple expression for the change of density with strength of solution that will hold for all salts. The secondary reactions of the salt on the water solvent and the anomalous changes possibly produced by the different degrees of dissociation make the question a difficult one. We would have wished to give more extended work here for some of the organic salts and with different solvents, but unfortunately the stress of other and more important work, as well as the lack of time allotted for the present work have prevented.

McDonald Physical Laboratory, McGill University, Oct. 12, 1898

ELECTROMOTIVE FORCE BETWEEN AMALGAMS

BY HAMILTON P. CADY

The theory of the electromotive force between amalgams of different concentrations was developed almost simultaneously by V. von Türin[1] and G. Meyer.[2]

If two amalgams containing the same metal but differing in concentration be connected by a solution of a salt of the dissolved metal there will be a tendency to a transfer of the metal from the more concentrated to the dilute amalgam. This can take place only when accompanied by a transfer of electricity: for the metal must dissolve from the concentrated amalgam as ion and be precipitated on the more dilute from the ionic condition.

Let p_1 and p_2 be the osmotic pressures of the metal in the amalgams. Then for the transfer of one gram molecular weight of the dissolved metal from the concentrated to the dilute amalgam the reversible work done will be

$$-\int_{p_1}^{p_2} v dp.$$

Substituting for v its value in terms of p from

$$pv = \mathrm{RT}$$

and integrating we get

$$\mathrm{RT} \log \frac{p_1}{p_2}.$$

The equivalent electrical energy is

$$\pi \nu \epsilon,$$

where π is the electromotive force, ϵ the number of coulombs

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[1] Zeit. phys. Chem. 5, 340 (1890).

[2] Ibid. 7, 477 (1891).

required to transfer one gram molecular weight of the metal, and ν its valence in the electrolyte. From this

$$\pi\nu\epsilon = \mathrm{RT}\log\frac{p_1}{p_2}$$

or

$$\pi = \frac{\mathrm{RT}}{\nu\epsilon}\log\frac{p_1}{p_2}$$

$$= 0.0002\frac{\mathrm{T}}{\nu}\log_{10}\frac{p_1}{p_2}.$$

Since the osmotic pressures are proportional to the concentrations the latter can be substituted for the former and the equation becomes

$$\pi = 0.0002\frac{\mathrm{T}}{\nu}\log_{10}\frac{c_1}{c_2}.$$

The equation contains no terms for either the solvent or the solute and hence the electromotive force should be independent of the nature of the solvent and the nature and concentration of the solute provided the latter is a salt of the metal in the amalgam. G. Meyer modified the equation so that he could use the measurement of electromotive forces between amalgams of known concentrations as a means of determining the molecular weights of the metal when dissolved in mercury. He did not show what effect, if any, the concentration of the electrolytes or the nature of the solvent had upon the electromotive force. This research was primarily undertaken to determine these two points.

Zinc was chosen as the metal with which to test the theory. The amalgams were made up either by adding a known weight of very pure zinc to a known weight of mercury or by electrolysis, using mercury as the cathode. In either case the dilute amalgams were made by diluting a known weight of the stronger amalgam with a known weight of mercury. Later in the work a determination with calcium amalgams in two solvents was also made.

The solvents used were water, alcohol,[1] and pyridin with

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[1] The alcohol was 95 percent alcohol and the pyridin was that supplied by Bender and Hobein.

the zinc amalgams, and pyridin or alcohol with calcium. The electrolytes were zinc chlorid with zinc amalgams in all cases and calcium iodid in pyridin and calcium chlorid in alcohol with the calcium amalgams.

For the measurement of the electromotive force Poggendorff's method was adopted. A very sensitive galvanometer[1] was used as a zero instrument. It was a double astatic four coil instrument and as it was set up would give a double deflection of one scale division for 1×10^{-9} amperes. A Clark cell was used as the standard and was compared with a Reichsanstalt cell.

The results are given in the following table. The concentrations of the electrolyte are expressed in grams per 1000 cc of solvent and the concentrations of the amalgams in grams per hundred grams of amalgam.

Metal	Solvent	Conc. of solute	Conc. of amalgams c_1	c_2	$\log_{10}\frac{c_1}{c_2}$	t	π calc	π obs
Zn	water	100	1.138	0.0977	1.066	17	0.0308	0.0290
Zn	water	10	1.138	0.0977	1.066	17	0.0308	0.0290
Zn	alcohol	10	1.138	0.0977	1.066	17	0.0308	0.0290
Zn	alcohol	120	1.138	0.0977	1.066	17	0.0308	0.0290
Zn	pyridin	*ca.* 50	1.138	0.0977	1.066	18	0.0310	0.0291
Ca	pyridin	CaI_2[2]	0.11	0.0546	0.303	20	0.0088	0.0188
Ca	pyridin	CaI_2[2]	0.11	0.0546	0.303	20	0.0087	0.182
Ca	alcohol	$CaCl_2$	0.11	0.0546	0.303	20	0.0088	0.0191

It will be seen from this that the electromotive force is independent of the nature of the solvent, and, within certain limits, of the concentration of the solute. If the concentration of the solute is small, errors of the most erratic nature come in on the measurement of the electromotive force. It will also be noticed that for calcium the electromotive force observed is very much greater than that calculated. More will be said about this later.

Reference has already been made to the fact that G. Meyer

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[1] I take this opportunity to thank Prof. Nichols of the Physics Department of this University for the use of this galvanometer and much of the other apparatus used in this work.

[2] Saturated solution.

used the electromotive force between amalgams as a means of determining the molecular weight of the metal. In order to do this he modified the equation as follows. The equation

$$\pi = 0.002 \frac{T}{v} \log_{10} \frac{c_1}{c_2}$$

was changed to

$$\pi = 0.0002 \text{ atomic wt.} \frac{T}{v \text{ mol. wt.}} \log_{10} \frac{c_1}{c_2} .$$

In words this means that if the calculated electromotive force equals that observed, the molecule is monatomic. This does not follow at all, because the electromotive force depends upon the ratio between the number of molecules dissolved in one amalgam and the number in the other, and this ratio will be the same whether the molecule is monatomic, diatomic or even more complex. It, however, apparently means that whatever the complexity of the molecule may be in one amalgam it is the same in the other, since if these changes of association are due to changes of concentration, the ratio would no longer be the same whether the molecule were monatomic or polyatomic. So it would seem at first sight as though we could say that the molecule was becoming more or less complex with the change in the concentration by determining the relation of the observed electromotive force to the calculated. We shall see later however that one cannot do even this, and that the electromotive force between amalgams is no indication whatever of the molecular complexity of the dissolved metal.

Before it was fully realized that this was not a method of molecular weight determinations, a number of measurements were made on the amalgams of the alkali and alkaline earth metals. The results will be given below. Meyer had measured amalgams of zinc, lead, tin, copper, cadmium and sodium. His results agreed well with those obtained by Prof. Ramsay[1] by the vapor-pressure method, with the exception of sodium. Ramsay found for sodium molecular weights approaching one-half the atomic weight, while Meyer found the molecular and atomic

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[1] Jour. Chem. Soc. 56, 521 (1889).

weights to be the same. He, however, did find that potassium gave too high an electromotive force, indicating a molecular weight of less than the atomic weight. This he ascribed to impurities in the potassium used. It would seem that the action of sodium amalgam on an aqueous solution would introduce such errors as to make Meyer's results of but little value, especially since sodium amalgam in pyridin gives values agreeing with Ramsay's.

The fact that Ramsay found molecular weights for the alkali and alkaline earth metals that approached more or less closely one-half their atomic weight is certainly very surprising, and it is important that it should be either confirmed or refuted in some other way. It was in the endeavor to do this that the determinations tabulated below were made. The results are expressed in molecular weights to show their agreement with those obtained by Ramsay, and to bring out the fact that the same thing is the cause of the abnormality in each case, as will be shown later. Amalgam of sodium, potassium, lithium, barium, and calcium were used, with zinc as a check.

The sodium amalgams used were made by successive dilution of a concentrated solid amalgam prepared from the metal. The potassium amalgams were prepared in the same way as the sodium.

Lithium amalgam was made by electrolysis of a solution of lithium chlorid, using mercury as the cathode. The same process served for the preparation of barium amalgam.

Calcium amalgam was more difficult to prepare owing, apparently, to the slight solubility of the metal in mercury. By electrolyzing a boiling concentrated solution of calcium chlorid, an amalgam was obtained containing a moderate quantity of calcium but hardly enough for the purpose. The metal was therefore prepared by electrolysis of the fused chlorid and from this an amalgam was made by heating with mercury to the boiling-point of the latter, under paraffin. Even then but little calcium was dissolved.

The zinc amalgams were made either by dissolving the metal in mercury or by electrolysis.

The concentrated amalgams were analyzed by dissolving out the metal from the mercury with dilute hydrochloric acid and weighing the mercury remaining from a weighed quantity of the amalgam. The dilute amalgams were in all cases made by adding a known weight of pure mercury to a known weight of the concentrated amalgam. Hence their concentrations could be easily calculated.

Sodium at. wt. 23, electrolyte NaI in pyridin

C_1		C_2						
pct	At. per 100 Hg	pct	At. per 100 Hg	$\log_{10}\frac{c_1}{c_2}$	t	π obs	π calc	Mol. wt
0.59	5.15	0.137	1.19	0.633	19.5°	0 0753	0.0371	11.35
0.59	5.15	0.137	1.19	0.633	19.5	0.0755	0.0371	11.30
0.46	4.02	0.041	0.357	1.050	20.5	0.0910	0.0617	15.6
0.46	4.02	0.041	0.357	1.050	20.5	0.0910	0.0617	15.6
0.46	4.02	0.0321	0.282	1.153	19.0	0.0950	0.0674	16.3
0.46	4.02	0.0321	0.282	1.153	19.0	0.0949	0 0674	16.3
Potassium at. wt. 39.1, electrolyte KI in pyridin								
....	....	....	....	1.002	20.5°	0.0947	0.0588	24.3
0.193	1.68	0.045	0.353	0.677	19.0	0.0547	0.0394	28.2
0.193	1.68	0.045	0.353	0.677	19.0	0.0553	0.0394	28.0
Lithium at. wt. 7, electrolyte LiCl pyridin								
1.80	0.51	0.623	17.65	0.459	20.0°	0.0351	0.0269	5.36
1.80	0.51	0.419	11.85	0.632	20.0	0.0525	0.0370	4.95
1.80	0.51	0.419	11.85	0.632	20.0	0.0517	0.0370	5.02
Barium at. wt. 137, electrolyte BaI_2 in pyridin								
0.356	0.518	0.0753	0.1097	0.674	19.0°	0.0343	0.0197	78.6
0.356	0.518	0.0856	0.1248	0.618	19.0	0.0311	0.0180	79.8
Calcium at. wt. 40, electrolyte CaI_2 in pyridin								
0.11	0.55	0.0546	0.2765	0.303	20.0°	0.0182	0.0088	19.57
0.11	0.55	0.0546	0.2765	0.303	20.0	0.0188	0.0088	18.9
Calcium at. wt. 40, electrolyte $CaCl_2$ in alcohol								
0.11	0.55	0.0546	0.2765	0.303	20.0°	0.0191	0.0088	18.7
Zinc at. wt. 64.9, electrolyte $ZnCl_2$ in water								
2.05	6.3	0.273	0.837	0.875	20.0°	0.0246	0.0256	67.5
1.138	3.56	0.0997	0.306	1.066	17.0	0.0290	0.0308	69.0
1.138	3.56	0.0997	0.306	1.066	17.0	0.0290	0.0308	69.0
1.12	3.45	0.551	1.695	0.306	18.0	0.0086	0.0089	67.3
Zinc at. wt. 64.9, electrolyte $ZnCl_2$ in alcohol								
1.138	3.56	0.0977	0.306	1.066	17.0°	0.0290	0.0308	69.0
Zinc at. wt. 64.9, electrolyte $ZnCl_2$NaI in pyridin								
1.138	3.56	0.0977	0.306	1.066	18.0°	0.0291	0.0360	69.0

The agreement between the values for the molecular weights obtained in this way, and Ramsay's values from vapor pressure measurements, is striking, and indicates, as said above, that the same cause is at the root of the abnormality in each case. For comparison, the molecular weights obtained by the two methods are given below.

Metal	Molecular weight calculated Vapor pressure	 E. M. F.	Atomic weight
Na	22.6–15.1	16.3–11.3	23.0
K	30.2–29.0	28.0–24.3	39.1
Li	7.1	5.36–5.0	7.0
Ca	19.1	19.7–18.7	40.1
Ba	75.7	79.8–78.6	137.0
Zn	70.1–65.4	69.0–67.3	65.4

In order to find the cause of the abnormal behavior of some of the metals it may be well to examine the formula again and see where it is incorrect.

Consider the equation

$$\pi \nu \epsilon = \mathrm{RT} \log \frac{p_1}{p_2}.$$

The variation of π observed from π calculated must be due to ν or to some false assumption made in the deduction. From the derivation of the equation, ν is the valence of the metal in the particular salt forming the electrolyte connecting the two amalgams. This can be tested by choosing a metal that can form two series of salts in which it has different valences. Tin is a convenient metal, since it easily forms stable amalgams and is bivalent in stannous chlorid and quadrivalent in potassium stannate.

Meyer has measured the E. M. F. of tin amalgams, using stannous chlorid as electrolyte, and obtained values agreeing well with

$$\pi = 0.0002 \frac{\mathrm{T}}{\nu} \log_{10} \frac{c_1}{c_2}$$

where $\nu = 2$.

It remained only to measure a tin amalgam cell, using potassium stannate as electrolyte. This was done with the following results.

c_1	c_2	$\log_{10}\frac{c_1}{c_2}$	π obs	π calc if $\nu = 4$
1.73 %	0.24 %	0.856	0.0129	0.0126

Hence for any given salt ν is known and fixed since it is the valence of the metal in that salt. Therefore the cause of the variation of π lies in the quantity RT $\log\frac{p_1}{p_2}$, or in some other term that has been neglected.

We can look upon an amalgam cell as a concentration cell in which the two concentrations can be made equal either by transferring the dissolved metal from one side to the other or by distilling mercury from the more dilute to the more concentrated amalgam. The reversible work will be the same in each case.

Letting h be the number of gram-molecules of the solvent in which one gram-molecule of the solute is dissolved, and $h_1 > h_2$, we get[1]

$$\pi\nu\epsilon = \int_{h_2}^{h_1} hv \frac{\partial p}{\partial h}\, dh.$$

Substituting for v its value in terms of p from

$$pv = \mathrm{RT}$$

$$\pi\nu\epsilon = \mathrm{RT} \int_{h_2}^{h_1} \frac{h}{p}\ \frac{\partial p}{\partial h}\, dh.$$

Assuming the van 't Hoff–Raoult relation $n/\mathrm{N} = \log (p/p_1)$ and noting that $\frac{n}{\mathrm{N}} = \frac{1}{h}$, we have $\frac{dp}{p} = -\frac{dh}{h^2}$ and $\frac{1}{p}\cdot\frac{\partial p}{\partial h} = -\frac{1}{h^2}$.

Substituting $-\frac{1}{h^2}$ for $\frac{1}{p}\cdot\frac{\partial p}{\partial h}$

$$\pi\nu\epsilon = \mathrm{RT} \int_{h_1}^{h_2} \frac{dh}{h} \qquad [A]$$

Since equation [A] does not describe the facts, it follows that $\frac{n}{\mathrm{N}} \neq \log\frac{p}{p_1}$. The experiments show that the apparent

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[1] Helmholtz. Ges. Abh. II, 979. Cf. McIntosh. Jour. phys. Chem. 2, 273 (1898).

osmotic pressure decreases less fast than the concentration. This phenomenon cannot be due to a dissociation because this would produce the contrary effect. One way of representing this state of affairs is to cast the van't Hoff–Raoult expression for the relation between concentration and vapor-pressure into the form $a\frac{n}{N} = \log\frac{p}{p_a}$ in which a may or may not be a function of n. In case it is not, the equation [A] becomes

$$\pi\nu\epsilon = RTa\int_{h_1}^{h_2}\frac{dh}{h} \qquad [B]$$

From this equation we see that the calculated electromotive force will exceed the observed value in case $a < 1$; will be equal to it in case $a = 1$; and will be less than it of $a > 1$. These general relations will still hold, even when, as in the case of the amalgam cells, a is an unknown function of the concentration. In the abnormal amalgam cells the observed electromotive force is higher than the calculated, and therefore $a > 1$.

For abnormal cases like those under discussion the van't Hoff formula[1]

$$PV = RT\frac{N}{n}\log\frac{p}{p_1} \qquad (1)$$

will have to be replaced by the very similar one:

$$aPV = RT\frac{N}{n}\log\frac{p}{p_1}. \qquad (2)$$

This second formula can be deduced in the same way as the van't Hoff formula, merely letting $P'V$ denote the total amount of work necessary to squeeze out, by means of a semipermeable piston, the mass of solvent in which one gram-molecular-weight of the solute is dissolved. Postulating that $P'V = aPV$, where P is the osmotic pressure, equation (2) follows at once. Equation (2) can be put in a more general form by writing $P'V = PV + RTf(n)$, whence follows:

$$PV + RTf(n) = RT\frac{N}{n}\log\frac{p}{p_1}. \qquad (3)$$

---

[1] Zeit. phys. Chem. 1, 493 (1887).

At infinite dilution equation (3) becomes identical with equation (1), in case $f(n)$ becomes zero when $n = 0$.

$RTf(n)$ is a measure of the disturbing influences,[1] such as the affinity between solvent and solute, polymerization, dissociation, etc. In the particular cases studied in this paper, it appears to be a measure of the difference of the affinity between the metal and the mercury in the two amalgams. This term can be evaluated with a very close degree of accuracy, by means of the Helmholtz relation between electromotive force and heat effect.

Helmholtz[2] has deduced the following equation, which applies to any voltaic system whatever:

$$\pi = q + T\frac{\partial \pi}{\partial T}$$

where q = heat of reaction. In the Daniell and most other primary cells the term $T\frac{\partial \pi}{\partial T}$ is small in comparison with q, and the electromotive force is measured fairly accurately by the heat of reaction. In the case of concentration cells q is generally assumed to be zero, and the electromotive force is therefore assumed to be equal to the temperature coefficient multiplied by the absolute temperature. Take the formula for concentration cells $\pi = 0.0002\frac{T}{v}\log_{10}\frac{c_1}{c_2}$; differentiate with respect to T, and multiply by T. We get

$$T\frac{\partial \pi}{\partial T} = 0.0002\,\frac{T}{v}\log_{10}\frac{c_1}{c_2} = \pi.$$

From this it follows that the formula can be correct only in case the heat of dilution is zero. Most metals dissolve in mercury with little or no heat effect and the heat of dilution is practically zero. The electromotive force of such amalgams would therefore agree with that calculated from the usual formula. The alkali metals, however, form amalgams with evolution of considerable quantities of heat and the heats of dilution differ

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[1] Cf. Ewan. Zeit. phys. Chem. 14, 409 (1894).

[2] Ges. Abh. II, 961.

markedly from zero, so that the electromotive forces of such systems must be represented by the formula $\pi = q + \mathrm{T}\frac{\partial \pi}{\partial \mathrm{T}}$, where q is no longer negligible. The term $\mathrm{T}\frac{\partial \pi}{\partial \mathrm{T}}$ cannot be evaluated unless q is known in terms of the concentration and the temperature, which is not the case. We shall however introduce but a slight error by writing[1]

$$\mathrm{T}\frac{d\pi}{d\mathrm{T}} = 0.0002\,\frac{\mathrm{T}}{\nu}\,\log_{10}\frac{c_1}{c_2} = \pi \text{ calc.}$$

Substituting in the Helmholtz equation we shall have

$$\pi = q + \pi \text{ calc}$$

or

$$\pi - \pi \text{ calc} = q$$

Expressed in words: the heat of dilution should be a measure of the discrepancy between the observed and the calculated electromotive force.

To test this, a direct determination of the heat of dilution of a sodium amalgam was made by the method suggested by Waterman,[2] using a Nernst calorimeter. To avoid the determination of the specific heat of the amalgam, the water in the calorimeter was kept at as nearly constant temperature as possible during the experiment and the two end temperatures were the same. The variation was never more than 0.03° from the mean. This was accomplished by adding cold water as soon as the temperature showed a tendency to rise. The temperature of the water in the calorimeter was adjusted until it was the same as that of the air, which remained practically constant during the experiment, the latter requiring only a few minutes. Working in this way no correction is necessary for the water equivalent of the calorimeter, the radiation constant or the specific heat of the amalgam. Beckmann thermometers were used in the experiment.

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[1] No error is introduced in case the heat of dilution is not a function of the temperature.

[2] Phys. Rev. 4, 161 (1896).

621.6 g of an amalgam containing 1 g-mol wt of Na in 20.2 g-mol of Hg was diluted with 2038.9 g of Hg, making an amalgam of one mol Na to 86.7 mols of Hg. 135 g-cal were given off. Calculating from this the correction to be applied to the amalgam No. 1 in Table II, an amalgam which differs but slightly from the one given above, we get

π calc from $\pi = 0.0002 \frac{T}{n} \log \frac{c_1}{c_2} = 0.0371$ volt
π calc from q $= 0.0372$ "

Sum 0.0743 "
π observed 0.0753 "

Difference 0.0010 "

Therefore

$$\pi \text{ observed} = \pi_q + \pi \text{ calc}$$

or

$$\pi - \pi \text{ calc} = q.$$

A cell containing another set of sodium amalgams was made up and its electromotive force measured over a range of temperature from 22° to 4° with the following results.

t	π obs	π calc	π obs$-\pi$calc
22°	0.0673	0.0373	0.0300
19	0.0668	0.0369	0.0300
9	0.0656	0.0656	0.0300
4	0.0648	0.0649	0.0299
7	0.0654	0.0654	0.0300

π obs$-\pi$ calc being constant shows that for this amalgam q, the heat of dilution, does not change through a range of temperature from 22°–4°.

If the amalgam shows a negative heat of dilution, and consequently gives too large an electromotive force, it will also give an abnormally large vapor-pressure diminution, and this to an equivalent degree. Hence the agreement between the results obtained by the electrometric method and by Ramsay's vapor-pressure method. If the heat of dilution be positive the amalgam should show too small an electromotive force and an abnormally small vapor-pressure diminution and therefore a rising molecular weight. Ramsay has found this to be true for tin, lead, antimony and bismuth, all of which dissolve in mercury with the absorption of heat and probably have positive heats of dilution.

These conclusions are not confined to amalgams alone, but apply to all solutions, as can be shown by Tamman's measurements of the vapor-pressures of H_2SO_4 at 100°; n = number of g-mols of H_2SO_4 in 1000 g of H_2O; Δp = diminution of vapor-pressure.

n	Δp	Mol. wt	n	Δp	Mol. wt
0.5	12.9	55.5	4.0	148.0	32.8
1.0	26.5	50.0	5.0	198.4	29.2
2.0	62.8	41.0	6.0	247.0	27.0
3.0	104.0	35.8	8.0	343.0	23.3

Here again we have negative heat of dilution, and the molecular weight apparently decreases as the concentration increases.

The results of this investigation are:

1. The electromotive force of amalgam cells has been shown to be independent of the nature of the solvent and the concentration of the solute.

2. The electromotive force varies inversely as the valence of the metal in the electrolyte.

3. With amalgams of the metals of the alkalies and alkaline earths abnormal results are obtained.

4. These abnormal results are in harmony with Ramsay's observations on the vapor-pressure of these amalgams.

5. In the case of sodium amalgam it has been shown experimentally that the results become normal when the heat of dilution is taken into account.

6. The heat of dilution for one pair of sodium amalgams is independent of the temperature between 4° and 22°.

7. The formula $n/N = RT \log (p/p_1)$ holds theoretically only when the heat of dilution is zero.

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[1] Mém. Acad. Petersb. 35, No. 9 (1887).

8. The equation for concentration cells should be written $\pi = q + 0.0002 \frac{T}{v} \log_{10} \frac{c_1}{c_2}$, when the heat of dilution is not a temperature function.

This work was done under the direction of Professor Bancroft and I wish to thank him for his many valuable suggestions.

Cornell University

NEW BOOKS

Leçons de Chimie physique. *By J. H. van 't Hoff; translated by M. Corvisy. Part I, Chemical Dynamics; 16 × 25 cm; 263 pp. Paris: A. Hermann, 1898. Price: paper 10 francs.*—The German edition of this work has already been reviewed (2, 256) so that it is only necessary to call attention to the existence of a French translation, to the promptness with which it has been issued, and to the excellency of the press-work. The type is a little small for the size of the page; but, barring this, the general effect is excellent. To an American eye a page of French necessarily presents a better appearance than a page of German, the latter looking spotty owing to the superabundance of capital letters. *Wilder D. Bancroft*

A Manual of Chemical Analysis. *By G. S. Newth. 13 × 19 cm; pp. xii and 462. New York: Longmans, Green & Co., 1898. Price: cloth $1.75.*—So many mediocre treatises upon analytical chemistry are already in print that a new treatise must present a plausible excuse for its existence. In this case everyone will agree with Mr. Newth's ardent desire to stem the mechanical tide always waiting to swamp and suffocate the unwary beginner in laboratory work, and one is glad to see that in some instances at least he has undoubtedly accomplished his object. The treatment of the perplexing reactions of the phosphates of the alkaline earths in particular is praiseworthy as directing the student's attention to the rationale of the matter, although the language is far from modern. Indeed, after a careful perusal of the book one is unconsciously inclined to seek the title page in order to see if it was really published in 1898. Very few paragraphs in it could not have been written fifteen years ago. A book on quantitative analysis containing no mention of the Gooch crucible, the Schellbach burette, or the Ostwald calibrator for burettes, is indeed an anachronism. Nothing could demonstrate the old-fashioned nature of the book more conclusively than a sentence descriptive of electrolysis:—"The action of the current is to separate the salt into its ions." After seeing that remark one is not surprised to meet with no further mention of ions from beginning to end. On the whole the qualitative part of the book is better than the quantitative, for the crudity of the methods employed is there of less serious import. In keeping with the rest of the quantitative part is the table of atomic weights, which is based upon the ancient and obsolete standard $O = 15.96$ and is inaccurate even upon that basis. In short, however useful this book may be as an initiator of neophytes, it will never be sought by the chemist who desires light upon the most recent intelligence concerning any point discussed in it.

Theo. W. Richards

Physico-Chemical Methods. *By J. Traube. Authorized translation by W. L. Hardin. 16 × 22 cm; pp. vii and 236. Philadelphia: P. Blakiston's Son & Co., 1898. Price: cloth $1.50.*—The book contains chapters on the balance; density; capillarity; constant of viscosity; solubility; electric conductivity of liquids; expansion of liquids; melting-point and solidifying-point; depression of the freezing-points of solutions; boiling-point and vapor-pressure; elevation of the boiling-points of solutions; specific heats; heat of fusion; heat of vaporization; thermochemical constants; measurement of crystals; index of refraction; spectrum analysis; rotation of the plane of polarization; general contrivances for measurements. In the appendix are a series of tables including the very useful one for the Pulfrich refractometer. The general descriptions are good, the most serious criticism being that in discussing boiling-point (p. 91) the thermometer should have been placed in the liquid and not in the condensing vapor. The method of Ramsay and Young for determining vapor pressures of univariant systems is not referred to and it is very difficult to see why references to the literature on reaction velocity should have been given in the chapter on solubility. The translation is thoroughly satisfactory though it is better to speak of the rotation of the plane of polarized light than to say "plane of polarization". *Wilder D. Bancroft*

Commercial Organic Analysis. *By Alfred H. Allen. Second Edition, Revised and Enlarged; Vol. IV. 16 × 23 cm; pp. xi and 584. Philadelphia: P. Blakiston's Son & Co., 1898. Price: cloth $4.50.*—With the publication of this volume the work of the revision of the book, which has extended over fourteen years, is completed. Those who have used the book and who know its almost inestimable value will be glad to welcome the concluding volume of a work to the writing of which Mr. Allen has devoted the best years of his life.

This volume like the others which have preceded it is a model in its thoroughness and completeness. The methods given have been examined by Mr. Allen or his assistants and the results of their experience are stated. This of course adds very materially to the value of the book. The subjects considered are among the most important with which the chemist has to deal and it may be added those about which the average chemist knows least.

Among the subjects considered are first the general character of the proteids and their analytical reactions, then the proteids of the egg, blood plasma, urines, plants and milks are treated. Milk and milk products, meat and meat products are then dealt with and the volume ends with chapters on the proteids of digestion, haemogloblin and the albuminoids. The book is clearly and concisely written, well printed and neatly bound. It is a book which should be in every chemical library, and in the possession of every working chemist.

W. R. Orndorff

Lectures on Explosives. *By Willoughby Walke. Second Edition, Revised and Enlarged. 15 × 23 cm; pp. xvi and 435. New York: John Wiley & Sons. Price: cloth $4.00.*—From the preface we learn that this book "is intended to serve as a manual and guide in the practical laboratory-work in the course of explosives at the U. S. Artillery School". Berthelot classifies explosives under eight heads: explosive gases; detonating gaseous mixtures; explosive inorganic compounds; explosive organic compounds; mixtures of definite explosive compounds with inert substances; mixtures of an explosive oxidizable compound with a non-explosive oxidizing substance; mixtures with an explosive oxidizing base; mixtures of oxidizable and oxidizing substances, neither of which is explosive separately. This classification, while excellent for a study of all possible explosives, is rather too far-reaching for the purposes of military instruction and, in the book under consideration, explosives are classified under the two main heads of mixtures and compounds. The former class is subdivided into nitrate mixtures and chlorate mixtures; the latter class into nitro-substitution products, nitric ethers or esters, smokeless powder, explosives of the Sprengel class, fulminates and amids.

The nitrate class of mixtures includes all the ordinary powders. The regulation black gunpowder is very nearly the same all the world over and consists of KNO_3 75 parts, C 15 parts, and sulfur 10 parts. Persia and Spain are the only two countries in which variation from these figures is more than one part in a hundred. In Spain and Persia the official black powder contains KNO_3 75 parts, C 12.5 parts and S 12.5 parts. The brown "Cocoa Powder" introduced into Germany in 1882 consisted of KNO_3 80.44, C 15.9, S 2.24, and water 1.08 parts. The color is due presumably to the charcoal having been made by carbonizing rye straw. This powder burns very slowly in the air. The advantages claimed for it are that it imparts "a high initial velocity to the projectile while exerting a relatively low pressure on the walls of the gun." The DuPont brown powder, invented in 1887, owes its peculiar properties to the charcoal being prepared in such a way as to retain the cellular state of the wood, and also to the addition of carbohydrates. Saxifragine is a slow burning powder containing $Ba(NO_3)_2$ 77, C 21, and S 2 parts. In the "Amid Powder" the sulfur is done away with entirely, the ingredients being potassium nitrate, ammonium nitrate, and charcoal. Blasting powders, especially when intended for use in hot climates, often contain sodium nitrate instead of potassium nitrate. In addition to a discussion of the different styles of gunpowder in use, the author gives an exhaustive description of the methods for preparing and testing powders.

The so-called white powders come under the head of chlorate mixtures, and contain potassium chlorate instead of nitrate. These powders are apt to explode unexpectedly; and the position of the author in regard to them is summed up in the following words: "Those mixtures intended for use as fuse compositions are the only ones that have become of any practical value". Two fuse mixtures used at the U. S. Naval Torpedo Station consist of potassium chlorate 44.44, manganic oxid 44.45, amorphous phosphorus 11.11 parts, and potassium chlorate 45.00; antimonious sulfid 20.75, amorphous phosphorus 5.75, carbon 28.50 parts respectively.

Under the heading of explosive compounds consisting of nitro-substitution products, picric acid, and potassium picrate take first place. The French mélinite as first invented consisted of guncotton 30 parts and fused picric acid 70 parts. This is thought to be the composition of the English "Lyddite" of which so much was heard during the recent campaign in the Soudan. The composition of the mélinite now used in France is not known; but the explosive is "believed to contain picric acid mixed with some oxidizing substance." Crésilite is trinitrocresol. In France it is mixed with mélinite and used for charging shells. Bellite is a mixture of potassium nitrate, ammonium nitrate and metadinitrobenzene. Roburite is a mixture of ammonium nitrate and monochlordinitrobenzene, to which nitronaphthalene is sometimes added. It is claimed for these last two explosives that they cannot be exploded by friction, shock pressure, fire, lightning, or electricity, and that they can be made to explode only by means of a detonating cap. For this reason they are sometimes known as "safety explosives".

The nitric ether or ester class of explosives consist of guncotton and its derivatives, nitroglycerin, and its derivatives, either pure or mixed with other substances. Dynamite is a technical term for mixtures of nitroglycerin with a "dope" or substance which absorbs and retains it under conditions of temperature and pressure. In the ordinary dynamite the dope is an inert substance known as kieselguhr, tripoli or rottenstone. Carbodynamite consists of 90 parts of nitroglycerin and 10 parts of very absorbent charcoal obtained by carbonizing cork. Other dynamites consist of nitroglycerin absorbed by some one of the explosives already considered. Nobel's blasting gelatine is nitroglycerin and guncotton. In the military explosive gelatines, camphor is added to reduce the sensitiveness to shock.

To obtain a smokeless powder it is essential that the ingredients shall be such and in such proportion that practically no solid matter shall be formed. This condition is satisfied by guncotton, but this explosive is too powerful to be used by itself. Modern smokeless powders consist essentially of insoluble guncotton, or soluble nitrocotton, or mixtures of the two, with addition of other substances. They are subdivided into two classes depending on whether nitroglycerin is or is not one of the substances added. Vieille's powder consists of insoluble nitrocellulose 68.21, soluble nitrocellulose 29.79, and paraffin 2.00 parts. The Swedish smokeless powder contains insoluble nitrocellulose 96.21, soluble nitrocellulose 1.80, resin 1.99 parts. Cordite, the English smokeless powder, contains nitroglycerin 58, guncotton 37, and vaselin 5 parts. It is a very stable powder but tends to erode the gun too much. The latest form of Maxim powder consists of guncotton 90, nitroglycerin 9, and urea 1 part. None of the sporting powders are smokeless in the strict sense of the term, being composed of nitrocellulose and metallic nitrates in varying proportions; but the cloud formed settles so quickly that they may be considered as practically smokeless. Under this head come the Schultze powder, the E. C. powder No. 1, the S. K. powder, the S. R. powder, and the American wood powder grade C, analyses of which are given in the book. Under the same head come the U. S. Naval Smokeless Powder (nitrocellulose 80, barium nitrate 15, potassium nitrate 4, calcium carbonate 1 part), and the Troisdorf or German military powder.

"The essential principle of all explosives of the Sprengel class is the admixture of an oxidizing with a combustible mixture at the time of, or just before, being required for use, the constituents of the mixture being themselves separately non-explosive". Rack-a-rock is the best known explosive of this class owing to its having been used in large quantities in the work at Hell Gate. The ingredients are potassium chlorate 79 and nitrobenzene 21 parts. The components are transported and stored separately until required for use. Other explosives of this class are hellhoffite, metadinitrobenzene, and nitric acid;

oxonite, picric acid, and nitric acid; panclastite, liquid nitrogen tetroxid and carbon bisulfid. The great drawback to the Sprengel class of explosives is that the proper mixing of the ingredients requires more skill than the average miner possesses. The author considers that these explosives are admirably adapted for military purposes.

None of the fulminates, amids, or similar compounds are used practically as explosives. The only substance of this class that is of real importance is mercury fulminate, used as one of the ingredients in percussion caps and detonators. The ordinary blasting cap contains mercury fulminate 75 parts and potassium chlorate 25 parts. For ordinary gunpowder priming a very good composition consists of mercury fulminate 37.5, potassium chlorate 37.5 and antimony sulfid 25.0 parts. A small percentage of ground glass is sometimes added and the mixture is often made more coherent by means of a solution of gum.

In addition to the chapters on explosives proper the author has added chapters on manipulation, storage and transport of high explosives; on the application of high explosives for military purposes; on the use of high explosives in shell; and a very interesting chapter on sympathetic explosion. A portion of the theoretical treatment is very weak, the author accepting Berthelot's principle of maximum work as a statement of fact. He appears also not to be familiar with Dixon's work on explosion waves. On the other hand a perusal of this book brings out a number of points of great interest to the theoretical chemist for which answers cannot yet be found. Chief among these is the fact that fulminating mercury will explode guncotton while the more powerful explosive nitroglycerin will not. The statement, on page 51, that naphthalene does not belong to the aromatic series of hydrocarbons will hardly be accepted, even though supported by the definition given two pages back.

Wilder D. Bancroft

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