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A SYMPOSIUM ON MOLECULAR STRUCTURE[1]

INTRODUCTION TO THE SYMPOSIUM

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Received November 20, 1936

The topic of molecular structure is an appropriate one for the initial symposium of this Division because of the important place held in the development of science by the molecular theory and by reasoning based on assumed molecular structures. The chemical advancements attained by the earlier applications of structural relationships are the more impressive by reason of the fact that the existence of structure was known only by chemical inference until comparatively recent years. Necessarily, this permitted only very general, and naïvely simple, conceptions. Yet some remarkably accurate representations were attained,—for instance, the tetrahedral symmetry of carbon.

For the accurate and relatively detailed representations of structure now possible for many molecules we are indebted to modern physics,—chiefly to quantum theory and the interpretation of molecular spectra. From these have come not only accurate molecular descriptions—moments of inertia, interatomic distances, bond angles, frequencies of vibration and rotation, force constants, magnetic moments, accurate energy relations—but also new approaches to problems of fundamental chemical interest. These include: the determination of highly precise values for reaction heats; the description of the primary processes in reactions initiated by

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[1] This Symposium on Molecular Structure was held, as the first annual symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society, at Princeton University, Princeton, New Jersey, on December 31, 1936 and January 1 and 2, 1937. The papers presented at the Symposium were classified for discussion into four groups: Part I, Spectra and Structure of Diatomic Molecules, and other topics—R. S. Mulliken, *Leader*; Part II, Spectra and Structure of Polyatomic Molecules—W. A. Noyes, Jr., *Leader*; Part III, Determinations of Structure by Methods Which are Non-spectroscopic—G. B. Kistiakowsky, *Leader*; Part IV, Some Chemical Applications of Knowledge of Structure—Saul Dushman, *Leader*. These papers follow the introduction in order, in this issue and in the February issue. A portion of the discussion of the papers will appear in the February issue.

The arrangements for the symposium were under the direction of a committee consisting of H. L. Johnston, *Chairman*, Farrington Daniels, Saul Dushman, W. M. Latimer, W. A. Noyes, Jr., H. S. Taylor, H. H. Willard, and H. C. Urey.

light; the elucidation of thermal activation processes and computation of reaction velocities; knowledge of mechanisms in the quenching of energy-rich molecules; explanations of valence and the correlation of molecular configurations with the quantum states of component atoms.

In combination with statistical mechanics, studies of structure through spectra are yielding important thermodynamic data of chemical value. These include heat capacities, heat contents and entropies of gases, and the equilibrium constants of gaseous reactions. The accuracy which may be obtained from the utilization of experimental studies of spectra exceeds that which may be reached with even the best care by conventional methods. In addition, the temperature range over which the thermodynamic constants may be thus evaluated greatly exceeds that open to direct methods; the time of investigation is much reduced and the cost greatly lessened.

Yet further chemical utility is exemplified in the discovery of new chemical molecules or the identification of rare intermediates. Examples of the first class are the following: the discovery of diatomic molecules in alkali metal vapors (25 per cent in sodium at its boiling point); the discovery of isotopes (notably in silicon, oxygen, carbon, and nitrogen); and the discovery of ortho and para forms of homopolar molecules (notably hydrogen). The identification of free radicals, such as OH or CH, present as accompaniments to certain reactions and frequently existent in high temperature thermal decompositions, illustrates the second class.

On the steric side, the conceptions obtained from physical evidence differ from the older ones based on chemical inference, principally in the substitution of dynamic structures for static ones. Bond stretching and bond bending vibrations characteristic of independent molecules in the gaseous state, and revealed by spectra, are found by independent lines of evidence to persist in the liquid and often in the solid state, with very little modification of frequency. Indeed there is very good reason to conclude that, where chemical bonds are preserved, vibration within these bonds persists even down to the absolute zero with energies normally little different from those at room temperature. This conception of zero-point energy is proving important sometimes in distinguishing between reaction mechanisms by reaction velocity studies, also in making predictions regarding vapor pressures of isotopic molecules or of ortho and para forms of molecules. The rotation of molecules, resolved about axes mutually perpendicular, is revealed by the spectra and is found to persist in the liquid and, infrequently, in the solid state. In addition to rotation of the molecule as a unit, rotation of its component parts—such as the methyl group in certain aliphatic structures—is a part of the modern picture and is confirmed by lines of evidence outside of spectra. The motions to which we have been referring—vibration and rotation—are of exceedingly high frequency (high powers of ten per second). Consideration of the space effects of these several motions yields effective static models, differing sometimes in significant respects from those arrived at by the older methods, and produces new conceptions of steric hindrance. For example, the presence of rotating groups or the amplitude of bending vibrations may effectively block off reactive portions of large molecules or influence physical behavior. These conceptions are of value in the consideration of anomalies in certain types of organic reactions.

Steric data obtained by methods quite independent of the spectra confirm and supplement the accurate conclusions of that method and permit the study of molecules too complex for satisfactory spectroscopic study. The x-ray diffraction method has been successfully applied to determine the grouping of carbon atoms in some organic compounds, not only in crystal lattices but even in the liquid and gaseous states. The use of electron diffraction is an analogous method and possesses the advantage that higher intensities may be obtained in refracted beams from light atoms. There is even some promise that the method can be perfected to yield the spacing of hydrogen atoms. Distances determined by these methods and internuclear distances and bond angles obtained from the spectra are, of course, secured on dynamic systems and represent average values. The amplitudes of change from the averages amount to several per cent. Furthermore, there appears to be, in some cases, resonance between structures of approximately equal energy, which makes for greater stability.

For determining reaction processes the nature and structures of what are termed excited states are apt to assume importance. Although the relative numbers of molecules present in such states is usually very small, they often constitute the paths by which reactions occur. Owing to the normally short lives of molecules in such excited states a considerable fraction of a chemical material may reach and pass through reactive states in unit time even though the equilibrium concentration is small. The spectra constitute the principal source of information on excited states, but studies by electron impact have been of importance in confirming the existence of quantum levels and in measuring their energies.

The study of dipole moments, in the gaseous state where possible; the analysis of thermochemical data; the use of molecular beams; the evaluation of gas collision areas and the measurement of magnetic susceptibility are other methods—non-spectroscopic in character—which have served, on occasion, to distinguish between alternative structures or supply other desired information.

Few of the approaches to problems of structure to which reference is made in this introduction were in use fifteen years ago. Except for diatomic molecules—and perhaps this exception should not be made—the development of these fields is only begun. Their continued development should be of considerable benefit to chemistry. The benefit will be greatest if chemists more generally realize the possibilities, and also the limitations and difficulties, in these physical methods of approach and if physicists who contribute to these fields recognize the manner in which chemists utilize this material.

In securing papers for the symposium we have attempted to obtain manuscripts which relate to various aspects both of structure determination, in the broad sense, and of chemical utilization of such material. Unfortunately, we were not able to secure representation of two or three important branches in these fields. We hope that these may be touched on in the discussion.

SOLVED AND UNSOLVED PROBLEMS IN THE SPECTRA OF DIATOMIC MOLECULES[1]

ROBERT S. MULLIKEN

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Received October 14, 1936

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[1] Presented at the Symposium on Molecular Structure, held at Princeton University, Princeton, New Jersey, December 31, 1936 to January 2, 1937, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society.

I. INTRODUCTION

In beginning the present survey of the subject of diatomic band spectra it is convenient and appropriate to quote, with slight modifications, from a recent book review[2]:

> "The subject of molecular spectra can conveniently be subdivided into the fields of diatomic spectra and polyatomic spectra. Of the former it may be said that it is in an active but mature state, of the latter that it is still in its exciting youth.
>
> "For diatomic spectra, the theory is now understood in considerable detail and is illustrated and checked by a great number of known examples; yet as compared with the degree of completeness with which the spectra and energy levels of atoms are known, our empirical knowledge of diatomic molecules is still exceedingly fragmentary. Our knowledge of the energy levels even of such important molecules as N_2 and O_2 is still very incomplete. There remains an enormous field for long-continued further work, both in the detailed investigation of known spectra and in the finding of new spectra. Here the steady improvement of experimental technique, as regards both spectrographs and light sources, will be important.
>
> "Molecular spectra are useful mainly for the information they give about the presence and condition, the energy levels, and the structure of molecules. Thus they are of interest to both physicists and chemists, especially to chemical physicists and physical chemists; also to astrophysicists. In general, it may be said that the quantum-mechanical theory, and the technique of experiment and interpretation, needed for molecular spectra, are primarily a matter of physics, while the results obtained, and their systematic comparison, are of special interest to chemists. More specifically, for diatomic spectra, it has been to a considerable extent a matter of developing and testing the theory and of arriving at various general laws and conclusions, and not just of getting information about chemically stable molecules. Most of the diatomic molecules investigated are chemically not stable, or even when they are stable, it is largely excited states about which we get information. These facts, and the relative simplicity of the diatomic case, tend to favor the classification of the latter under physics. For polyatomic spectra, however, practically all the work has been done with chemically stable molecules in their normal states. This and the complexity of the molecules dealt with tend to favor the classification of this work under chemistry.
>
> "Beyond obtaining the energy levels of a molecule from an analysis of its spectrum (*first* stage of theoretical interpretation), there are two fairly well marked further stages. The *second* is concerned with obtaining (*a*) moments of inertia, vibration frequencies and force constants and other data relating to the positions and motions of the nuclei, and (*b*) the classification and other characteristics of the electronic states involved. The *third* stage is concerned with the systematic study and interpretation of second-stage data in terms of electronic structures, involving the consideration of electron configurations and leading into questions of valence theories. In connection with this third stage, quantum-mechanical ideas and calculations, not directly based on spectra, also become important. For diatomic spectra, all the above stages of interpretation have now been fairly well developed. For polyatomic spectra, it is mainly stages I and II*a* for infra-red bands which have been developed, but active progress is being made in the other stages, and for electronic spectra, and in the connected quantum-mechanical valence theory.

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[2] Review of H. Sponer's *Molekülspektren* by R. S. Mulliken (Rev. Sci. Instruments 7, 171 (1936).

> "Of the above three stages, the first two (and the accompanying experimental work) may properly be classified under the subject of "molecular spectra," the third perhaps better under "electronic structure of molecules" or under "quantum theory of valence." Aside from these three stages, there are various other topics which may be classified under the head of *applications* of molecular spectra. These applications involve to varying extents the use of the results of one or more of the above three stages. The applications are largely of chemical, but also partly of physical and astrophysical interest."

In the present paper, a uniformly detailed survey of the history and the present status of the subject of diatomic band spectra will not be given. In particular, applications of band-spectrum results to chemistry and to other fields will be mentioned only briefly, since they belong to another session of this conference. While attempting to bring out essential points as to *modus operandi* and results obtained in nearly every important branch of diatomic band spectra, often with something also of the historical development, emphasis will be placed more especially on unusual cases and on those fields where there appear to be interesting possibilities for future work, and some suggestions will be made as to the nature of these possibilities.

II. BAND ORGANIZATION AND VIBRATIONAL ENERGY LEVELS

In the theory of diatomic molecular energy levels, the usual classification states that we have coarsely spaced electronic levels, on which are superposed vibrational levels with medium-sized spacing, and then rotational levels with small spacing. Every actual molecular energy level, of course, involves electronic, nuclear-vibrational, and nuclear-rotational properties simultaneously. "Electronic levels" and "vibrational levels" are merely convenient abstractions.

In practice, the abstractions called vibrational levels are relatively easily isolated and studied, since they are largely independent of complicated interactions which occur between electronic and nuclear rotational motions. Notable steps in the history of the analysis and theory of vibrational levels have been the empirical pre-quantum work of Deslandres, the development and application of the quantum theory of the anharmonic oscillator by Kratzer and others, the Franck-Condon explanation of vibrational intensity relations, and the Morse potential energy function.

In the practical analysis of band spectra, the first step is commonly that of grouping the bands into sets, each of which (a "band system") is associated with a single electronic transition, and of analyzing and organizing each set by a determination of the correct vibrational quantum numbers for each band. Generally this can be done without detailed examination of the structure of the bands, but not infrequently the latter or the use of other information, e.g., isotope effects, may be essential.

This process of vibrational organization has now been carried out, through the work of many investigators, for one or several band systems of each of a considerable number of molecules. The number so analyzed is, however, still extremely small compared with the 92! possible combinations of atoms in pairs (not counting isotopes), and of the infinitely many band-giving electronic transitions which are theoretically possible for each such atom-pair. Further, there is much room for improvement in the accuracy of the molecular constants already obtained from such analyses. There is thus a rich field here for future work. In this connection, it should be borne in mind that a simultaneous detailed analysis of band structure ("rotational analysis") always aids in obtaining more accurate vibrational constants and more complete information on the forms of potential energy curves.

Our knowledge of vibrational energy levels is confined at present, for most known electronic states, to a moderate number of levels of low vibrational quantum number. Only in a few cases are the levels known up to the dissociation point. It would be of great interest if we knew the higher vibrational levels of a larger number of molecules and of molecular electron states. This would give us a wider knowledge of the forms of potential energy curves and a much more complete and reliable table of dissociation energies than we now have. The obstacles to getting these higher vibrational levels are primarily experimental.

III. BAND STRUCTURES AND ROTATIONAL AND ELECTRONIC LEVELS; RAMAN EFFECT

Although the gross separations of electronic levels are obtained in connection with vibrational analyses, the greater part of our information about electronic states is obtained, together with that on nuclear rotations and moments of inertia, from detailed analyses of band structures. This is because there is a mutual "coupling" between nuclear rotations and electronic rotations and spins, such that the structures of bands, although primarily due to nuclear rotations, are greatly dependent on the natures of the electronic states involved. Spectroscopic transitions among the various types of electronic states give rise to many types of band structure and have involved a number of theoretical problems.

In the pre-quantum epoch of band spectra, a large mass of data and observations was collected by many investigators on visible and ultraviolet bands. The most important steps in the classification and analysis of bands and the representation of series of bands and band lines by empirical formulas were made by Deslandres, beginning in 1885. An important improvement in the representation of band structures was made in 1914 by Fortrat (dethronement of band-head in favor of the zero-line, with use of perturbations in establishing the latter; Fortrat parabolic representation of series). In the field of infra-red bands various workers made important progress. A. Fowler (1915) found Rydberg series in the helium bands, which were discovered by Goldstein and Curtis. R. W. Wood obtained interesting results on resonance and magnetic rotation spectra, which later yielded important tests of theory.

The quantum theory was introduced by Schwarzschild in 1916 (and in later-published work by Bohr), following earlier suggestions of Eucken (1912). Schwarzschild's theoretical explanation of the main features of band spectra in terms of molecular energy levels reacted immediately on Heurlinger, who made tremendous progress in the analysis of existing and new band-spectrum data in the light of the new theory (1916–19). Lenz (1919–20) made further steps in this direction and, especially, added to the theory. Among other things, Lenz discussed the case of molecules having internal electronic angular momentum. Kratzer (1920–24) developed in some detail the theory of the rotating anharmonic oscillator, and applied it to the analysis both of infra-red and of simple optical bands. He also made considerable progress toward the understanding of optical bands of more complicated structure, building on and extending the work of Heurlinger. Kemble and his students made valuable contributions to our understanding of infra-red bands. At the same time and later, Hulthén, Mecke, Birge, Curtis (He_2), and their associates, and others, made important contributions to our experimental knowledge and theoretical understanding of the structures of complicated bands. Further marked progress was made by the present writer in explaining observed types of band structures in terms of transitions between various types of electronic states.

A decisive step was made by Hund (1926), who worked out the main theoretically-to-be-expected types of electronic-nuclear rotational coupling under several headings (Hund's cases *a*, *b*, *c*, *d*, etc.), and showed how transitions between molecular states of various electronic and coupling types could account for the principal known types of band structure. The development of the theory of band structures (including their Zeeman effects) has now been largely completed, thanks especially to the work of Van Vleck, Kronig, and their associates, also of Kemble, Wigner, Hill, Kramers, Dicke, perhaps the present writer, and others.

Analyses and classification according to electronic states have been worked out for many bands of various types by a large number of investigators. Among those who, with their collaborators, have been especially active since 1926 in the measurement and analysis of diatomic bands and particularly band structures, may perhaps be mentioned Hulthén (hydrides), Richardson (H_2), Dieke, Watson (hydrides), Weizel (He_2), Loomis, Jenkins, Herzberg, and the present writer. Many others also have made important and extensive contributions to this, the main central region of the field of diatomic band spectra, and excellent new workers are entering the field from time to time.

A. Normal coupling

Among the various cases distinguished by Hund with respect to the coupling between nuclear and electronic rotational motions, there are two which, it is here proposed, may well for the sake of general intelligibility be grouped together under the heading of "normal coupling" or "Λ–S coupling." This normal or Λ–S coupling forms a rather close diatomic analogue to normal or L–S coupling (usually called Russell–Saunders coupling) in atoms. Here Λ refers to the component, along the line joining the nuclei, of total electronic *orbital* angular momentum, while S refers to the resultant *spin* angular momentum of the electron system.

The designation "normal coupling" covers not only the two limiting conditions called Hund's cases *a* and *b*, but also the continuous range of intermediate cases lying between them. These intermediate cases are very common in practice, and even for a single electronic state of a molecule a gradual transition from case *a* to case *b* often occurs with increase in the rotational quantum number. This and the fact that the bands most commonly observed (especially for molecules composed of light atoms) involve electronic states with coupling closely approximating case *a* or *b* or an intermediate case, constitute strong reasons for the use of the designation "normal coupling."

The two extreme sub-cases might then be described as "tight-spin normal coupling" (Hund's case *a*) and "loose-spin normal coupling" (Hund's case *b*). There is one important sub-case of normal coupling which can be placed equally well under Hund's case *a* or case *b*, although it does not fit very comfortably under either, namely, the case where the resultant electronic spin S is zero. This might be referred to as "no-spin normal coupling," or "no-spin coupling," or "normal singlet coupling."

In the work so far carried out on diatomic band spectra, only the following types of electronic states[3] with normal coupling have been conclusively identified through the analysis of observed bands: $^1\Sigma^+$, $^1\Pi$, $^1\Delta$, $^2\Sigma^+$, $^2\Sigma^-$, $^2\Pi$, $^2\Delta$, $^3\Sigma^+$, $^3\Sigma^-$, $^3\Pi$; in short, only levels with $S = 0, \frac{1}{2}, 1$ and with $\Lambda = 0, 1, 2$. Beyond this, certain O_2^+ bands are known which are thought to involve $^4\Sigma^-$ and $^4\Pi$ levels, but the necessary proof has not yet been given by an analysis of the band structure. Further, $^3\Delta$ levels are known in He_2 and H_2, but not with pure normal coupling. In contrast to the fewness of electronic level types identified in diatomic band spectra, it is of interest to recall that in atomic spectra levels are known with S all the way from 0 to about 4 and L all the way from 0 to about 8. One good reason for

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[3] The number of known types is of course increased when we count the distinction between even and odd ($_g$, $_u$) electronic states of homopolar molecules.

this, of course, is the much greater difficulty, as compared with the atomic case, of the complicated process of band analysis which is usually necessary to establish the electronic quantum numbers for a molecular state.

Because of difficulties of analysis for molecules, there exists a corresponding richness of undeveloped possibilities and of work to be done. Particularly among molecules containing transition-group or especially rare-earth atoms should large values of S and (although less frequently) of Λ occur. Experimental difficulties, however, will doubtless be serious (e.g., among others, presence of complex line spectra, and if not, of overlapping band spectra).

B. Other types of coupling

In diatomic molecules the variety of possible rotational coupling types is greater than in atoms, because the elements between which coupling occurs include nuclear orbital motions in addition to electronic orbital motions and spins. Aside from the normal cases discussed in the preceding subsection, the three most important coupling cases so far found in practice are the following: (1) Hund's case d, which may perhaps be descriptively designated as "loose-orbit coupling," since it involves more or less complete uncoupling of the electronic orbital motion (in practice, for just one electron) from its usual precession around the line joining the nuclei; (2) the present writer's "far-nuclei form of case c," which may perhaps be called "loose-atom coupling," since it occurs when the strength of binding of two atoms in a molecule is comparable with or looser than the tightness of electronic spin–orbit coupling within one or both atoms; and (3) the present writer's "Ω–s coupling," which considerably resembles Jj coupling in atoms.

Loose-orbit coupling has been found so far only in the higher excited states of H_2 and He_2, where one electron has been excited to an orbit much larger in size than the orbits of the other electrons and of the nuclei. Through the work of several investigators, this case, and its Zeeman effect, are well known both experimentally and theoretically.

A slight *tendency* toward loose-orbit coupling, in other words *incipient* loose-orbit coupling, is found in most known molecular states, especially those with small moments of inertia; this tendency expresses itself in the well-known phenomenon of Λ-doubling. When this is interpreted in the light of the theoretical work of Van Vleck and Kronig, it gives, as was shown by Mulliken and Christy, much interesting information concerning the nature of the electronic states where it occurs, and is often also an aid to the correct analysis and interpretation of band structures.

Loose-atom coupling, or tendencies toward it, are to be expected whenever a molecule is formed from atoms at least one of which has strong internal spin-orbit coupling. This case has been studied so far mainly in the halogen spectra (Mulliken, Van Vleck) and in the spectra of the loosely bound molecules Hg_2, Cd_2, and Zn_2. It should be important also for many other spectra, especially those of molecules containing at least one heavy atom, and for other molecules in the parts of their potential energy curves near the dissociation point.

Ω–s coupling, of whose presence evidence has likewise been found by the writer in the halogen spectra, is representative of a group of possible coupling cases resembling the various Jj and similar cases in atoms. Ω–s coupling is characterized by strong electronic spin–orbit coupling (as in tight-spin normal coupling) within a *part* of the molecule, which may be called the core, containing the nuclei and all but one of the electrons. The spin of the last electron is then more or less loosely coupled in one way or another (various cases are possible) to the core. In general, the last electron will have not only spin but also a component of orbital angular momentum to complicate still further the coupling relations. It may be anticipated that, in future work on band spectra, Ω–s and similar types of coupling will be frequently encountered. Various anomalies in band structure, as compared with normal coupling, may then often be expected. Hardly anything is yet known experimentally about the band structures in such cases.

C. *Intersystem and forbidden transitions*

Each of the ordinary or normal types of band structure corresponds to a transition between two electronic states both having normal coupling and both having the same spin, the transitions being further limited to those that obey the usual (electric dipole moment) selection rules. In practice, bands involving a change in spin but obeying the other selection rules ("intersystem transitions") are not infrequent. This gives additional types of band structure (examples: CO Cameron bands, type $^3\Pi \leftarrow {}^1\Sigma^+$; N_2 Vegard–Kaplan bands, type $^3\Sigma^+{}_u \rightarrow {}^1\Sigma^+{}_g$; visible halogen bands, types $^3\Pi_0{}^+{}_{(u)} \leftarrow {}^1\Sigma^+_{(g)}$ and $^3\Pi_{1(u)} \leftarrow {}^1\Sigma^+_{(g)}$). The cause of the occurrence of such transitions is the same as that of analogous transitions in atoms, namely, a disturbance of electronic orbital motions by their interaction with electron spin; just as in the atomic case, these transitions occur more readily when heavy atoms are involved. When the spin–orbit interactions are large, it becomes difficult to draw the line between normal intersystem transitions and transitions describable in terms of special coupling cases, such as the loose-atom and Ω–s cases discussed in section III B. The halogen bands, for example, are probably more appropriately placed in the category of such special cases.

Selection rules and intensity relations have been worked out theoretically by Van Vleck, Schlapp, and Present for various types of intersystem transitions, including "forbidden" ones (see below). Detailed experimental data on such bands have been published, however, only for the halogen bands, which are of simple structure, and for certain forbidden O_2 bands. In these cases, agreement with the theory is excellent. Further work on intersystem band structures will be of interest.

Examples of "forbidden" transitions are furnished rather abundantly by the O_2 molecule. The well-known atmospheric oxygen bands in the red end of the visible region, first discovered as Fraunhofer lines in the sun's spectrum, are of special interest. It was shown by the writer that these bands belong to an intersystem transition $^1\Sigma \leftarrow {}^3\Sigma$. It was further concluded from the very low specific intensity of the bands (total absorption only moderate in the whole thickness of the earth's atmosphere) and from a consideration of the electron configuration of the O_2 molecule that the transition is not only intersystem, but is also one forbidden by the electric dipole selection rules: namely, $^1\Sigma^+{}_g \leftarrow {}^3\Sigma^-{}_g$. The same considerations led the writer to predict a second system of forbidden O_2 bands in the near infra-red, of type $^1\Delta_g \leftarrow {}^3\Sigma_g^-$, which has since been found.

As Van Vleck has shown, the weak occurrence of these "forbidden" bands must be attributed to the existence of a small *magnetic* dipole moment for the transition. This explains the observed fact that while the ${}_g \rightarrow {}_g$ prohibition for electronic states, and the $+ \rightarrow +$ prohibition for rotational levels, are violated, the limitation $\Delta J = 0, \pm 1$ is obeyed. If an electric quadrupole moment were involved, transitions $\Delta J = \pm 2$ should also occur. It is quite possible that such transitions are also present but have been overlooked, owing to extremely small intensity. Recent work of Schmid on the Zeeman effect of the atmospheric bands offers an interesting possibility of further check on the magnetic dipole theory.

The O_2 absorption spectrum offers a variety of unsolved problems connected with forbidden transitions. In the near ultra-violet there is a system of exceedingly weak bands, or apparently two different systems at almost the same wave lengths but differently affected by pressure; both, however, are evidently of forbidden type. Further investigation of these is needed. It is evident in any case that the O_2 molecule has several metastable excited states of fairly low energy. It has been difficult to get information about these levels, except for our good luck with respect to the Fraunhofer bands, because transitions to them from the normal state are forbidden, and because no emission spectra leading down to them from higher excited levels have been found. These difficulties illustrate the problems which still exist with respect to a thorough knowledge of the lower excited energy levels of even so familiar a molecule as O_2. Somewhat similar problems exist also for N_2, although there are certainly no metastable levels as low in energy as the low $^1\Delta_g$ and the low $^1\Sigma^+{}_g$ level of O_2. Several fairly low, probably metastable levels of N_2 have been predicted, but have not yet been found experimentally.

In the spectrum of oxygen under high pressure, and of liquid oxygen, additional bands appear in various places in the visible and ultra-violet, taxing our resources with respect to theoretically possible electron levels of the O_2 molecule. Certain ones of these transitions have been attributed to coördinated simultaneous forbidden jumps in two O_2 molecules temporarily loosely associated to O_4, but it is difficult to see theoretically how these could occur with so high an intensity as is observed. Much remains to be done here.

The forbidden bands we have been considering are cases where every observed line is equally forbidden. A different kind of case is that where, in addition to band lines allowed by the usual selection rules, additional forbidden series occur. Just one example of this case is known, namely, the familiar OH bands. Here, in addition to the orthodox main and satellite series, there are observed certain extra satellite series which can be explained only as violations of the $+ \leftrightarrow -$ selection rule for rotational levels. The occurrence of these, as of the totally forbidden O_2 bands, has been attributed by Van Vleck to the existence of an appreciable magnetic dipole moment for the transition. It is, however, remarkable that they have been found only in this one case, and a more complete explanation of this fact, and if possible the finding of similar series in the spectra of other molecules, would be of considerable interest. Further study of the Zeeman effect of these OH satellites might also be interesting.

D. Perturbations and predissociation

Perturbations, i.e., irregularities in position and intensities of some of the lines in a band, have been known since rather early in the history of band spectra, and have sometimes been useful in the analysis of bands, since identical perturbations occur for different lines involving a common, perturbed, rotational energy level. Predissociation, evidenced in absorption by regions of diffuseness in a set of bands, and in emission by sudden termination of vibrational or rotational series, was first found in absorption bands by Henri, and was explained by Bonhoeffer and Farkas and by Kronig. Both perturbations and predissociation in band spectra are sometimes a nuisance, especially in the higher electron levels where they occur abundantly, since they increase the difficulties of analysis by destroying regularity in, or wiping out, band structure. Remarkable examples of perturbations are found in the third positive bands of CO, where the arrangement of the band lines is almost chaotic.

The fundamental theory of perturbations and of predissociation was first developed by Kronig, using the new quantum mechanics; these phenomena could not be explained at all by the old quantum theory. In the theory, perturbations and predissociation differ in origin only in that with the former the disturbance is caused by discrete vibration-rotation levels of a stable electronic state, while with the latter it is caused by continuous unquantized levels of an electronic state which, usually, is unstable or little stable.

Perturbations of observable size occur when quantized levels of a (usually not yet directly known) electronic state nearly agree in energy with levels involved in observed bands, and when at the same time certain other conditions (Kronig's "selection" rules and, as pointed out by Franck and Sponer and by Herzberg, the Franck-Condon principle) are fulfilled. As a compensation for the difficulties they cause in band analysis, both perturbations and predissociation afford at least partial information about electron levels which otherwise have not proved accessible; it would seem that there is a large field for future work in this direction.

Examination of Kronig's selection rules for perturbations and predissociation discloses two allowed cases: (1) the perturbed and perturbing electronic states (whose action is of course mutual) are *exactly alike* in electronic classification type; (2) they differ in type, by one unit in the value of Λ.[3a] It should be pointed out that in the second case, the quantum-mechanical theory of the perturbations is fundamentally the same as that of rotational uncoupling and Λ-doubling (Van Vleck, Kronig: section III B). To these two cases may be added a third, forbidden according to Kronig's rules, but really just as much allowable as intersystem transitions in atoms and molecules: (3) the perturbed and perturbing electronic states differ in the value of the spin S. All these three cases are now well known in practice.

Case 3 may also appropriately be looked at, for molecules where strong spin-orbit couplings are present, from the standpoints of loose-atom, Ω–s or other coupling cases (cf. section III B). For such coupling cases, new selection rules are easily obtained to replace Kronig's, which really refer only to normal coupling. From this standpoint, case 3 breaks up into two sub-cases, analogous to the above cases (1 and 2) for normal coupling.

The writer has often found it a great inconvenience that names do not exist for the foregoing three kinds of perturbations and predissociation.[3a] He therefore proposes the following designations (1) *homogeneous* perturbations and predissociation; (2) *heterogeneous* perturbations and predissociation; (3) *intersystem* perturbations and predissociation. The suitability of these appears to be fairly obvious. Certain interesting questions connected with the nature of homogeneous perturbations and predissociation (including "vibrational perturbations") will be taken up in section V C.

Returning to the matter of applications, predissociation has often proved useful by signalizing energy values at which dissociation processes occur.

[3a] G. H. Dieke (Phys. Rev. 47, 870 (1935)) distinguishes class A and class B perturbations; the more self-explanatory respective designations "heterogeneous" and "homogeneous" are proposed in the present paper.

This method of getting at dissociation energies must, however, be used with great caution. Its reliability is greatest when the predissociation sets in sharply. By finding predissociation in various different bands and band-systems of a molecule and considering various alternatives as to the states of the products of dissociation, it has been possible in the case of N_2, with the support also of other information, to build up a consistent scheme of dissociation products and dissociation energies for several electronic states, including the normal state (Herzberg and Sponer). In this way a value which is probably accurate and reliable has at last been found for the dissociation energy of the nitrogen molecule. This study has also helped to clarify other points concerning the electronic levels of N_2.

Predissociation in H_2 has been found to yield a dissociation energy in close agreement with that found by vibrational extrapolation (Beutler and Jünger). Attempts have been made to apply the predissociation method to the molecule CO, but the results of various investigators are conflicting, and apparently none of them can yet be accepted with confidence. A reliable determination of the dissociation energy of carbon monoxide would be of great value in furnishing a key to the actual atomic dissociation energies of a great number of organic compounds, now severely in doubt.

A phenomenon similar in cause to predissociation is autoionization (Auger effect), recently observed, for the first time in band spectra, in the H_2 spectrum by Beutler and Jünger.

In the field of *induced* predissociation (magnetically induced, best-known example I_2 (Steubing, Turner, Van Vleck); collision-induced, examples I_2, Br_2, NO, etc.), interesting results have been obtained. Collision-induced predissociation is of considerable significance for photochemistry. There is room for much further work on induced predissociation.

E. Rotational instability

When a molecule rotates, it is possible for its total energy to exceed, sometimes greatly, the energy of dissociation. This was first clearly brought out in a paper by Oldenberg. When the rotation gets sufficiently great, however, there is a maximum value, varying with the vibrational quantum number, beyond which the rotational quantum number cannot go without mechanical instability. This limit is shown by a sudden termination of the band structure. The phenomenon was investigated by Oldenberg in the HgH bands (instability in lower electronic level) and found to agree with the theory.

Rotational instability is best understood (cf. Oldenberg) by plotting *effective* potential energy curves, in which the instantaneous rotational kinetic energy (expressed as a function of the internuclear distance, and increasing of course with the rotational quantum number as a parameter) is added to the ordinary potential energy. These effective potential energy curves, unlike most ordinary potential energy curves, usually have a maximum between the minimum and the dissociation asymptote.

As the rotational energy is increased, the minimum keeps getting shallower, and finally disappears. For any given rotational quantum number, mechanical instability occurs when the vibrational energy is sufficient to bring the total energy above the maximum of the effective potential energy curve for that particular rotational quantum number. If the rotation is large enough so that the effective curve has no minimum, instability exists even for zero vibration.

Besides the mechanical instability just discussed, which exists according to the old as well as the new quantum theory, there is an additional quantum-mechanical instability which occurs even before the total energy reaches the maximum of the effective potential energy curve. This phenomenon is similar in nature to radioactive decay and predissociation, and is in fact classified by Herzberg as a special type of predissociation. The band lines show the occurrence of this type of predissociation (just as of the usual type) by becoming broad and flat. In emission spectra, such band lines tend to disappear more or less completely under ordinary conditions of excitation. The best examples of the phenomenon are found in bands going to the normal states of HgH, CdH, and ZnH, and in those going to or coming from the well-known $^1\Pi$ excited state of AlH. All of these electronic states have very small dissociation energies.

The use of effective potential energy curves has been valuable not only here, but also for a clear understanding of ordinary predissociation and in other band-spectrum problems.

F. Zeeman and Stark effects

Study of the Zeeman effect in band spectra[4] has been of considerable value in checking theoretical predictions and confirming results obtained in other ways. Experimental study has disclosed an amazing variety of complicated Zeeman patterns, usually partially or wholly unresolved except for a few lines of low rotational quantum number, but all, so far as is known, in agreement with the theory.

The Zeeman effect in band lines has not, however, played a part in the analysis of band spectra comparable to that played by the Zeeman effect in line spectra. The main reason for this is that the complexity of the bands *without* magnetic field is already so great as usually to yield, on

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[4] F. H. Crawford (Rev. Modern Phys. 6, 90-117 (1934)); R. Fortrat, L'Effet Zeeman dans les Spectres des Bandes, in the series *Actualités Scientifiques et Industrielles*, Hermann et Cie., Paris, 1936, 38 pages. Crawford's review is the more thorough and detailed, and contains a critical analysis with some new interpretations.

analysis, practically all the information that one can get from the Zeeman effect. In atomic spectra, on the other hand, Zeeman patterns often have added greatly to our information about the nature of spectrum lines.

In bands whose structures have not yet been analyzed, Zeeman effects, if readily available, may give helpful hints as to the nature of the electronic states involved. This applies also to some polyatomic molecules, as shown by the work of Schmid on the CO_2^+ bands. In the case of forbidden transitions (cf. section III C) the Zeeman effect should give interesting checks on the theory.

The Zeeman effects of perturbed band lines show interesting phenomena, which may prove valuable in the study of the perturbations; this field has not yet been explored very thoroughly.

Related to the Zeeman effect in diatomic molecules are various other phenomena, such as magnetism, magnetically induced predissociation, and the Faraday effect. Of particular interest here are the "magnetic rotation spectra," which may be described as selective transmission spectra resulting from the occurrence of a strong Faraday effect in the neighborhood of magnetically sensitive absorption band lines when incident light with a continuous spectrum is used. Magnetic rotation spectra are comparatively simple in structure, and are well adapted to the location of high vibrational levels of molecules having suitable electronic states and absorption bands. They do not, however, give information about rotational levels. They have been used especially by Loomis and associates in following the vibrational energy levels of alkali metal molecules to high quantum numbers, thus making it possible by a short extrapolation to estimate dissociation energies fairly accurately.

Although the necessary theory is available, hardly any experimental data, except negative results, exist on the Stark effect in molecules, with the single exception of H_2. Linear Stark effects, i.e., effects with splittings proportional to the electric field strength, are to be expected for molecular states which have a permanent electric dipole moment and also at the same time a resultant electronic orbital angular momentum component along the line joining the nuclei (i.e., $\Lambda > 0$). Appreciable splittings may then be expected, for low quantum numbers, in the presence of strong electric fields. Unfortunately the problem of finding and observing spectra which fulfil the necessary conditions is a difficult one. The subject is, however, worth further attention because it would be of great interest from a theoretical standpoint (10), and also because possibly new dipole moment data might be obtained.

Quadratic Stark effects, which should occur even for molecules not having a permanent electric dipole, may be expected usually to be too small to observe. Large effects are possible, however, in the case of highly excited states with an electron in a large orbit, such as are well known in

H_2 and He_2 (loose-electron coupling, cf. section II B). The data of Kiuti, MacDonald, and others on H_2 (3a), where large and irregular effects occur in abundance, have as yet been analyzed only very incompletely in terms of the theory.[5] Their analysis, and further investigation, should be of considerable interest.

More or less closely related to the Stark effect in diatomic spectra are the Kerr effect, dielectric constant work, and work on molecular rays in electric fields.

G. Raman effect

The Raman effect has given some useful information concerning diatomic molecules, but on the whole has been of small importance as compared with the polyatomic case. One reason for this is that comparatively few diatomic molecules are available for the Raman technique. Another is that for diatomic molecules electronic band spectra have been the most easily available source of information, while for polyatomic molecules relatively little progress has been made with these.

As regards confirmation of the theory, diatomic Raman spectra have of course been of considerable interest. Selection rules, intensity relations, etc., are found to be in agreement with theory. Vibrational or rotational Raman effects, or both, have been observed in H_2, N_2, O_2, CO, HCl, HBr, HI, and an electronic effect in NO. These have helped out more or less in our knowledge of rotational and vibrational levels, and especially in respect to nuclear statistics as deduced from the alternating intensities in N_2. The work of McLennan and McLeod on liquid hydrogen gave valuable evidence on the failure of ordinary collisions to convert ortho-hydrogen into para-hydrogen.

IV. CONTINUOUS DIATOMIC SPECTRA AND RELATED TOPICS

In treatises on band spectra it seems to be a habit, more or less, to neglect continuous spectra, particularly those which are structureless. These spectra are often largely relegated to separate treatises[6] on continuous spectra of *atoms and* molecules. Yet in a complete survey of molecular spectra, and for an understanding of molecular energy levels and structure, a continuous spectrum appears to be just as deserving of careful attention as a spectrum full of band structure.

Continuous molecular gas spectra occur most commonly when one of the potential energy curves involved in an electronic transition is without a

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[5] The writer understands from Professor G. H. Dieke that the latter is planning an analysis of these data.

[6] A good discussion containing a wealth of material on continuous molecular as well as atomic spectra is that of W. Finkelnburg (Physik. Z. **31**, 1 (1930); **34**, 529 (1933)).

minimum or has only a shallow minimum (repulsive curves). In practice, they are most often observed in absorption spectra. In some cases a given electronic transition is represented only by a continuous spectrum; in others, a continuous region occurs at one end of a band system whose other end consists of discrete bands. In some cases continuous spectra show a wavy structure which reflects the vibrational levels of one of the two electronic states involved; this happens when the potential energy curve of the other electronic state is more or less nearly horizontal in the range of interatomic distances at which the molecule finds itself when the spectrum is produced. The theory of continuous spectra, both of the structureless and the wavy kinds, is now well understood in terms of the Franck-Condon principle, through the work of Franck and collaborators, Kuhn, Sommermeyer, Winans, and others.

In connection with the subject of continuous spectra, it should be borne in mind that no sharp line can be drawn between these and discrete spectra suffering from predissociation. When predissociation becomes sufficiently pronounced, the discrete structure is progressively blotted out and finally the spectrum may become structureless. Furthermore, wherever predissociation occurs the discrete spectrum must, according to the theory, be accompanied by an overlying continuous spectrum, possibly of considerable intensity; this has been observed in certain cases.

Continuous (and predissociation) spectra are of value in giving information about molecular electronic states whose potential energy curves are of the repulsive type. By the measurement and analysis of the intensity distribution in an absorption continuum, it is often possible to plot the approximate forms of potential energy curves of this kind. This has been done by Stueckelberg for the upper level of the Schumann-Runge bands of O_2, using measurements of Ladenburg, Van Voorhis, and Boyce; by Gibson, Rice, and Bayliss for the upper level in Cl_2; by Goodeve and Taylor for HBr and HI. More work of this kind would be desirable.

Besides its value for the plotting of potential energy curves, the quantitative measurement of (absorption) intensities in continuous spectra is of value in increasing our knowledge of the nature of the electronic states involved, through a determination and study of the integrated transition probabilities for the electronic transitions involved (cf. recent papers of the writer on the halogens and hydrogen halides). In this connection, it may be pointed out that such work furnishes perhaps the easiest way to get evidence as to the mean radiation lives of excited molecules, since intensity measurements on discrete bands with this end in view are difficult. For instance, when the spectrum of a given electronic transition contains both a continuous and a discrete part, the integrated transition probability which can be fairly well determined from the former (cf. the case of I_2 in the writer's 1934 paper) may permit an estimate of the mean radiation life of molecules excited in the latter.

Emission continua are harder to deal with than absorption continua, but much progress has been made in the measurement and interpretation of the H_2 continuum (13, 1, 6). The subject of emission continua appears to deserve continued experimental and theoretical work.

Closely related to the subject of diatomic continuous spectra is that of pressure broadening in atomic spectra (and in molecular spectra). Recently a number of papers have been published on this subject; in this country Margenau and Watson have been the chief contributors.

As a matter of fact, no sharp line can be drawn between line broadening and the subjects of continuous and wavy spectra of loosely bound molecules. In this field, extensive work has been done by Lord Rayleigh, Winans, Kuhn, Oldenberg, and others on the Hg_2, Cd_2, HgA, and similar spectra (see footnote 6).

The continuous spectra so far dealt with all belong to the category of dissociation continua, since they all involve dissociation of a diatomic molecule into atoms, or occasionally the reverse process. Another category is that of ionization continua, analogous to the corresponding category for atoms. Comparatively little is known about ionization continua of molecules, mainly because most of them must lie in the relatively unexplored vacuum spectrograph regions. The future development of this field should be of decided interest.

V. POTENTIAL ENERGY CURVES

In the preceding sections (II to IV) diatomic band spectra have been surveyed with respect to their general structure and the corresponding theory. In the following sections (V to VII) we shall deal mainly with results and applications of this analysis: forms of potential energy curves, the nature and condition of molecules responsible for observed bands, nuclear spins and statistics, isotope effects, and applications to chemistry, astrophysics, and physics. Part of these results, plus a further development of the theory, form the basis for a discussion in section VIII of the electronic structures of diatomic molecules.

A. *Forms of potential energy curves*

In the course of the development of the subject of band spectra, the problem of finding suitable reasonably simple forms of mathematical functions for approximating potential energy curves has occupied a good deal of attention. At first a form introduced by Kratzer for HCl, based on an ionic (Coulomb) attraction plus correction terms, was widely used and proved well adapted to represent actual curves not too far from their minima. Kratzer started with Coulomb attraction because he assumed that the normal state of HCl should give $H^+ + Cl^-$ on dissociation. Actually, as it happens, neither HCl nor any of the other molecules whose potential energy curves are yet known from band spectrum analysis have proved to be of really ionic character, so that the success of Kratzer's function for moderate displacements from equilibrium was somewhat accidental. For large displacements from equilibrium, it is of course not suitable for such molecules. Nevertheless Kratzer's function should be of correct form for truly ionic molecules and for the occasional ionic excited states which may be expected for other molecules. As examples of truly ionic molecules the alkali halides may be mentioned; empirical potential energy curve data for these are as yet unfortunately lacking, because of certain idiosyncracies of these molecules.

More logical than Kratzer's function, for small or moderate displacements from equilibrium, is the widely used power series function (Kemble, Birge, Fues, Dunham). Finally, Morse introduced his popular function, which has the great advantage of being able to represent the potential energy curves of molecules all the way from the equilibrium point out to dissociation, with a form adapted to the usual case of molecules which dissociate into neutral atoms.

In general, the problem of finding a type of function which by varying suitable parameters may be expected to fit all diatomic potential curves somewhat resembles that of trying to fit the outlines of all human beings in a similar way. It is hardly reasonable to hope to solve such problems exactly by the use of a single simple type of formula. The best we can expect to do is to find a fairly simple function which, after suitable choice of a few parameters that can be readily determined experimentally, may usually be relied on to approximate actual potential energy curves fairly well.

As is well known, the most generally useful function which has been found for this purpose is that of Morse. This contains three parameters, namely r_e, the equilibrium distance between the nuclei; one depending on the vibrational force constant k; and a third parameter which can best be taken as the dissociation energy D_e. Morse curves give correct representations near $r = r_e$ and at $r = \infty$, but differ more or less from the true potential energy curves at other values of r. The worst practical defect of the Morse function is that it generally gives too great an asymmetry as compared with actual cases, i.e., the curve rises too steeply for $r < r_e$ and too slowly for $r > r_e$. Also, it is entirely wrong at $r = 0$, but this is unimportant in practice. (This defect can be corrected fairly readily, but at the expense of simplicity, according to a recent paper by Newing.) Several three-parameter variations on and four-parameter refinements of the Morse type of function have been suggested and have proved more or less valuable. The four-parameter refinement permits correct representation of the asymmetry. Recently Hylleraas has developed a six-parameter function which promises to be valuable and instructive, and has applied it very successfully to two examples.

Instead of trying to fit a mathematical function of arbitrarily limited type, it is possible to build up any given potential energy curve by a semigraphical method developed by Rydberg and Klein. The degree of completeness with which the curve can be drawn in this way depends, of course, on the completeness of the experimental data. In order to follow a curve all the way out to $r = \infty$, data on high as well as low vibrational energy levels, including *rotational* energy level data for these vibrational levels, are needed. Although the method is laborious, and although it is usually difficult to secure the necessary data for higher vibrational levels, it would appear to be worth while to carry out such constructions of potential energy curves where possible. It seems likely that in this way we may often learn more about the actual forms of such curves than by trying to fit the spectroscopic data to mathematically simple types of functions.

Already the work of Birge and others on higher vibrational energy levels indicates the existence of an interesting variety in the forms of potential energy curves at large r values. Even for moderate r values, certain unusual cases are known. Thus there is the well-known case of the upper level of the familiar alkali metal hydride bands, where the potential energy curve is quite abnormal in shape. As the writer has recently shown, this can be explained as a result of a change in the nature of the electronic state with increasing r, the state being predominantly homopolar for small r, but becoming ionic for large r. Thus, if this explanation is correct,[7] the potential energy curve departs, as r increases, from the usual Morse type and goes over asymptotically into the very different ionic or Kratzer type.

Another possible kind of potential energy curve is one possessing both maxima and minima. In the past it has commonly been tacitly assumed that the potential energy curves of diatomic molecules contain at most one minimum, and no maxima. Recently, however, several investigators have been forced to the conclusion that maxima do sometimes occur. First, the investigations of Brown on the ICl and IBr absorption spectra disclosed some curious phenomena which can be interpreted in terms of a potential energy curve with a maximum, although the matter is mixed up with predissociation (cf. section V C). Next, Hulthén and Rydberg (5) concluded that the potential energy curve of the well-known $^1\Pi$ state of AlH, which is remarkable in having a high vibration frequency in spite of a very small dissociation energy, possesses a slight maximum (about 0.05

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[7] Dr. E. J. Rosenbaum of the Department of Chemistry has been applying the Rydberg-Klein method to the graphical construction of the curve for LiH, using the accurate and extensive data of Crawford and Jorgensen. This should give an interesting test of the theoretical explanation.

e.v. (electron-volt) above the dissociation asymptote) at rather large r values. Finally, as the writer shows in a current paper, it seems necessary to conclude that for the upper electronic level of the well-known vapor absorption bands of each of the silver halides, the potential energy curve rises, as r is decreased from ∞, to a maximum above 1 e.v. above the asymptote, then dips 0.1–0.3 e.v. to a shallow minimum before resuming a steady rise; incidentally, there are reasons to believe that there may be a second shallow minimum in these curves at large r values. Here a theoretical calculation by Pauling on He_2^{++} should also be mentioned, in which he found that the potential energy curve should have a pronounced maximum, the curve being somewhat like those of the silver halides just discussed.

In view of these several examples where recognition of the existence of maxima has been practically *forced* on us, it seems likely that such cases may prove relatively frequent if we try to *seek* them. After all, maxima in potential energy curves are obvious necessities for polyatomic molecules, in view of the existence of activation energies, so that their occurrence also for diatomic molecules is not at all shocking.

All in all, it will be seen that the subject of potential energy curves of diatomic molecules is far from a closed one.

B. Dissociation product correlations

When two atoms unite to form a molecule, or a molecule in a given electronic state dissociates into two atoms, there are certain theoretical restrictions which limit the types of molecular electronic states that correspond to a given pair of atomic electron-state types or, conversely, the possible types of atomic states which can appear when a molecule in a given type of molecular state is dissociated. (In either case, it is assumed that no spectroscopic quantum jump takes place during the process.) These restrictions are given by the well-known rules of Wigner and Witmer, applicable for normal rotational coupling, supplemented by some rules given by the writer (based on the work of Wigner and Witmer) and applicable especially for loose-atom coupling. According to the theory, these rules are absolutely rigorous in so far as the existing molecular electronic-rotational and atomic orbit–spin couplings correspond to those assumed.

With this last-mentioned condition in mind, the rules can be and are used as an important supplement to experimental data in determining the asymptotic behavior ($r = \infty$), and therefore in part also the course at smaller r values, of potential energy curves. In this way they are also an important aid, and often an essential element, in correctly determining the dissociation energies of molecules from band-spectrum data, as was shown for instance by Herzberg in the case of O_2. According to what was said above, there is little point in trying to test the rules experimentally.

As a matter of fact, existing data in most cases do not suffice for such tests, but at any rate no contradictions have been found.

The non-crossing rule, its violation, and its relation to potential energy curve forms and to homogeneous predissociation

In connection with the Wigner–Witmer rules there is one further companion rule, based on general quantum-mechanical considerations, and introduced by Hund. This may be stated as follows: Potential energy curves of the *same electronic species* never cross. An "electronic species", for *normal coupling* and a given molecule, includes all electronic states which are identical in Λ and S, and in certain possible further properties as follows. Among Σ states, Σ^+ and Σ^- belong to different species. Similarly, $_g$ and $_u$ types (which occur in homopolar molecules) belong to different species. [In other than normal coupling, electronic species must be differently defined. In certain coupling cases, Λ and S become ill-defined, and Ω takes their place in the definition of electronic species ($\Omega h/2\pi$ = component, along the line joining the nuclei, of total, i.e., orbital plus spin, electronic angular momentum). Even in tight-spin normal coupling, *sub-species* defined by Ω values exist, and in this case the non-crossing rule runs as follows: Potential energy curves of the same species and sub-species never cross.]

For instance, the curves of the two well-known $^2\Sigma^+$ states of the CN molecule should not cross. This condition, combined with the Wigner–Witmer rules, is found to require that the lower $^2\Sigma^+$ curve (which is that of the normal state) shall give two unexcited atoms—N(^4S) + C(^3P)—on dissociation, but that the upper $^2\Sigma^+$ shall give one excited atom,—N(^2D) + C(^3P). Nevertheless, on the basis of experimental evidence from vibrational energy levels, Heitler and Herzberg concluded that this correlation is not correct, but that the *upper* $^2\Sigma^+$ dissociates to give unexcited atoms, and the lower to give one excited atom. It now appears, however, that their evidence was insufficient, so that there is now no real reason to doubt that the correlation is that predicted using the non-crossing rule.

Nevertheless, the same kind of question has arisen in other cases, e.g., in that of the $^3\Sigma^+$ level of N_2 which has been identified as the upper level of the Vegard–Kaplan bands and the lower level of the first positive nitrogen bands. Apparently at moderate r values this is the lowest $^3\Sigma^+_u$ level of N_2 and, if so, it ought to dissociate into two unexcited (^4S) nitrogen atoms according to the non-crossing rule, i.e., it ought to remain the lowest $^3\Sigma^+_u$ level all the way out to $r = \infty$.

However, the known vibrational levels of this state extend to an energy considerably above that of two unexcited atoms, thus indicating that on dissociation one atom is excited (^4S + ^2D). If this is correct, the potential energy curve of the as yet unknown $^3\Sigma^+_u$ state which *does* dissociate into two unexcited atoms must cross that of the known $^3\Sigma^+_u$ state somewhere, most probably at moderately large r values, violating the non-crossing rule. Another example of a similar situation is found in the lowest known $^2\Sigma^+$ state of NO, which according to the non-crossing rule should give unexcited atoms on dissociation.

As an explanation of such failures (or probable failures, see below) of the non-crossing rule, it has been pointed out by Herzberg and others that two electronic states, even if of the same formal species, may still differ so much in electronic constitution, in one way or another, as to be in effect of different species for the purposes of the non-crossing rule. In that event the curves of two such states, at least for all practical purposes, might cross, although there would necessarily be more or less mutual disturbance of their quantized energy levels near the crossing point. Unless negligibly small, this disturbance would give rise to a set of homogeneous perturbations or to homogeneous predissociation (cf. section III D). Perturbations would occur if the crossing took place below, predissociation if it took place above, the asymptote of the curve giving the lower-energy dissociation products. If the mutual disturbance were strong, the two curves would be replaced by two new curves which did not cross, i.e., the non-crossing rule would be obeyed. Intermediate cases, forming a sort of no man's land, are also possible.

This leads us to the necessity of recognizing the fact that, fundamentally, the concept of potential energy curves of molecules has no precise meaning according to the quantum mechanics (3, 8, 12). For stable molecular states we do not need to worry about this, but can think freely in terms of potential energy curves. When we come to perturbations and predissociation, the limitations of the concept begin to appear. If, however, we are content with a somewhat superficial treatment, we can still for most purposes think and talk in terms of potential energy curves if the perturbations or predissociation are not too violent. Violent effects are not to be expected for heterogeneous nor (usually) for intersystem, but only for *homogeneous*, perturbations and predissociation, and not by any means always in the homogeneous case.

Homogeneous perturbations and predissociation involve a mutual disturbance between states belonging to the *same electronic species* (cf. section III D). They usually involve a violation of the non-crossing rule, since perturbations and predissociation occur most readily near the intersection of two potential energy curves, and since the two curves here are alike in electronic type. They *can*, however, also occur when two potential energy curves merely come near each other without tending to cross.

It is helpful to approach the phenomena now under consideration from a somewhat different viewpoint. Let us define our field of interest, for this purpose, to include all cases where two potential energy curves of the same electronic species *either cross or tend to cross*. For brevity, we may refer to all such cases by the expression "tendential crossing". More accurately, we ought to say "tendential homogeneous crossing", but in the following discussion this is to be tacitly understood.

There are various reasons why tendential crossing is of common occurrence. They all have to do with details of electronic structure, which may usually be expressed in terms of electron configurations. Generally tendential crossing arises because a particular electron configuration or electronic structure which has relatively low energy in the molecule is closely related to, or tends to go over into, a configuration which has relatively high energy when the molecule is separated into atoms, *or vice versa*. When two electronic states of the same species, but different detailed structure or electron configuration, have energies not far apart, and if one is of a type whose energy increases when the molecule is formed, while in the other it decreases, tendential homogeneous crossing occurs if the ascending-energy state lies below the descending-energy state when the atoms are separated.

Various cases may now occur, depending on the strength of interaction between the two potential energy curves near the tendential crossing-point. If the interaction is vigorous, two new potential energy curves of more or less normal character take the place of the original tendentially intersecting curves (case of *avoided crossing*). If the interaction is weak, one can most conveniently describe the observed phenomena by saying that crossing takes place, accompanied by perturbations or (more often) predissociation (*effective crossing* case). If the interaction is of intermediate intensity, a confused picture is to be expected, in which the usual classification in terms of electronic and vibrational energy levels and based on potential energy curves can be used only with difficulty (*intermediate* or no-man's-land case).

It is of interest to give probable examples of the three cases. In molecules like LiH it is likely that we have tendential crossing of two $^1\Sigma^+$ potential energy curves, one derived from neutral atoms Li + H, the other from ions $Li^+ + H^-$. The ionic curve is the higher in energy for large distances, but (very likely) tends to be the lower in energy for small distances. Strong interaction occurs, however, and crossing is avoided. The two actual potential energy curves then change from predominantly ionic to predominantly atomic character, or *vice versa*, as the distance increases. The effects of the tendential crossing, however, are apparent in the unusual shape of the upper of the two actual curves (cf. section VA).

Other possible examples of avoided crossing are the normal states of HgH, CdH, ZnH, etc. Here are observed potential energy curves with small r_e and large ω_e, such as are typical for highly stable molecular states, yet the curves are very shallow, going asymptotically into unexcited atoms on dissociation. A reasonable explanation is that the observed curve is the lower of two curves which have resulted from the avoidance of a tendential crossing (cf. G. Herzberg (3)). Taking the case of HgH, one would expect from Heitler–London theory that two unexcited atoms Hg($6s^2$, ^1S) + H(^2S), should repel each other, giving a rising potential energy curve of the $^2\Sigma^+$ species. If, however, we take Hg($6s6p$, ^3P) + H(^2S), there should result, among others, a descending curve of the $^2\Sigma^+$ species, with a deep, stable minimum. Tendential crossing seems possible for these two curves. If this is avoided by suitable strong interaction, the lower of the two resulting curves would be of the observed type.

A similar possible example of avoided crossing is the $^1\Pi$ upper level of the well-known AlH bands. Here the observed potential energy curve resembles that just described for HgH, but is even more extreme in having a very small dissociation energy (giving unexcited Al + H), combined with small r_e and large ω_e like a stable state. This again may be explained by avoided crossing of two tendentially intersecting $^1\Pi$ curves, one starting up from unexcited Al(s^2p, ^2P) + H, the other coming down from excited Al(sp^2) + H. Of particular interest here is the fact that, according to Hulthén and Rydberg (5), the observed curve rises to a small maximum before going down to its minimum. This is readily understood if the upper of the two tendential curves does not interact with the lower quite as strongly as in the otherwise similar case of HgH, or if the lower curve rises relatively faster at fairly large r values than in HgH. From this example we reach the interesting conclusion that tendential crossing furnishes an explanation of the occurrence of maxima in potential energy curves. It should, however, be remarked that maxima could occur also for other reasons. In the case of the silver halide curves with maxima (section V A), tendential crossing *may* be the cause, but certain features of these examples are better explained if we suppose that the observed *minimum* is produced, in a curve which otherwise would ascend steadily with decreasing r, by the *tendential close approach* from above of a second curve having a pronounced minimum. The mutual perturbation of the two curves could then produce the observed dent in the lower one, the maximum being an incidental result.

[*Added in proof.* Subsequent consideration makes it probable that the silver halides after all are examples of tendential crossing, but that, on the other hand, AlH, HgH, CdH, ZnH are examples only of tendential close approach. However, in BeH, which is analogous to HgH but is more stable, we have almost certainly tendential crossing. In any event, it seems clear that tendential crossing and tendential close approach can both give rise to similar phenomena, including maxima and other unusual features in potential energy curves.—In connection with the whole foregoing discussion, it should perhaps be explicitly pointed out that the difference between "tendential" and actual behavor of potential energy curves corresponds merely to that between certain simple (usually Heitler-London type) wave function approximations and the actual exact wave functions.]

The no-man's-land case of tendential homogeneous crossing with predissociation tendencies is probably represented by the phenomena in ICl and IBr discovered by Brown (cf. section V A). In these electronic states the coupling is of the loose-atom type.

The case where tendential crossing results in actual effective crossing, giving homogeneous perturbations or predissociation, is a fairly common one. A well-known example where this case is believed to exist, although no band-spectrum data exist for the crossing point, is that of the diatomic alkali halides (London, Hund, Pauling). Here the normal state is a $^1\Sigma^+$ level which is believed to give ions on dissociation. Its potential energy curve must then (except in CsF) cross at large r values the $^1\Sigma^+$ curve derived from neutral atoms.

In general, it may be said that effective crossing is sure to occur if tendential crossing takes place at sufficiently large r values, but that the probability of avoidance is greatly increased or perhaps even made certain if the tendential intersection takes place at small r values.

Of common occurrence is the phenomenon of "vibrational perturbations", i.e., perturbations involving more or less equally all the rotational levels associated with a given vibrational level. Vibrational perturbations are attributable to rather strong interaction of two tendentially crossing potential energy curves of the same electronic species (cf. Weizel (12)), but not so strong as to reach the no-man's-land case. The phenomenon is possible only for homogeneous perturbations, since heterogeneous perturbations do not occur appreciably for low rotational energies. An example of vibrational perturbations approximating the no-man's-land case in intensity has recently been discussed by Dieke (1a).

In the future, a considerable development in our empirical knowledge and theoretical understanding of tendential crossing and its results is to be anticipated. In particular, more examples and a better understanding of the no-man's-land case are to be expected. This case, and even worse cases where no classification at all can be made into electronic, vibrational, and rotational levels, appear likely to be found frequently as research progresses into the upper reaches of diatomic energy level diagrams, where many electronic levels with their attached vibrational levels must be crowded and mixed up together. (A similar situation, but greatly aggravated by the existence of several vibrational degrees of freedom, is also expected in polyatomic molecules.)

Returning now to the cases of the N_2 and NO potential energy curves discussed early in this section, it is evident that the failure (or probable failure) of the non-crossing rule there must be due to tendential crossing. In these and other similar cases, it is likely that we have examples of effective crossing with predissociation, but until or unless the presence and nature of such predissociation have been established, it would be wise to keep in mind the possibility of avoided crossing with fulfillment of the non-crossing rule and accompanied by maxima in the potential energy curves of the states under consideration. It is likely that maxima, small or large, will prove to be more common than has been supposed.

If so, some of the existing conclusions as to dissociation energies based on predissociation phenomena or on convergence of vibrational series to a limit may need revision. When convergence to a limit is observed for vibrational levels associated with a potential energy curve having a maximum, it is the energy of this maximum, not of the desired dissociation asymptote, which is given by the convergence. In such a case the bands near the limit should be diffuse, but this would be difficult to detect. Good examples of this case are found in the silver halides, according to the writer's interpretation.

D. Dissociation energies

The accurate determination of the dissociation energies of a number of chemically important molecules not previously obtained by the usual physicochemical methods has been, as is well known, one of the more important services of band spectra to chemistry. The principal method used has been that of determining the convergence limits of vibrational levels, either by direct observation (Franck) or with the help of extrapolations (Birge–Sponer, etc.); this method has been supplemented by the use of predissociation evidence (section III D) and sometimes of chemical and other data; in order to be reliable, it has required a knowledge of the theoretically allowable dissociation product correlations (section V B).

Dissociation energies have been determined not only for chemically stable molecules (H_2, O_2, N_2, NO, halogens, etc.) but also for many molecular fragments and free radicals. This information has been of much value for chemical problems, including the promotion of our understanding of valence forces. One interesting example in this connection has been the finding from band spectra that alkali metal molecules are tolerably stable, contrary to earlier beliefs.

Much still remains to be done; in a great many cases the data have been insufficient to permit reliable extrapolations and accurate determinations of dissociation energies (examples, CO, CN, C_2, CH, NH, BO, and many others). In such cases, extension of vibrational data to higher quantum numbers, and further study of predissociation, should be of great value. Particularly for the carbon compounds, accurate determinations would yield important contributions to our knowledge and understanding of valence forces. Even in cases such as O_2, N_2, and NO there remains a shadow of doubt as to the reliability or at least the accuracy of the accepted values. For instance, the existence of hitherto unsuspected maxima in potential energy curves might affect some of these values; also, the use of predissociation data appears to be somewhat risky unless great caution has been used.

The danger of long extrapolations of vibrational level series is now generally realized among those acquainted with the field. Such extrapolated values are, however, in the absence of anything better, given in existing tables, usually without special danger signals, and are often accepted with undue faith by the uninitiated. This is not to say that all extrapolated values are worthless; nearly all are better than nothing, and where the extrapolations are short the results are very probably nearly correct, having in several cases been checked by other methods.

E. Systematics of molecular constants

A considerable amount of attention has been devoted to the formulation and refinement of approximate empirical rules giving relations between the two molecular constants r_e and ω_e, and expressing these constants as a function of the positions of the two atoms in the periodic table (Mecke, Birge, Morse, Clark, Badger, Huggins, and others). The original Mecke rule was more limited in scope, stating an approximate relation, $\omega_e r_e^2 = \text{constant}$, only between any two states of a given molecule.

The chief value of such rules appears to be that of enabling one to predict approximately the values of unknown constants in cases where band spectra have as yet been only partially analyzed, or not analyzed. The rules likewise constitute an aid and check in any new analysis. Besides the r_e, ω_e relations, some attention has been given to the mode of variation of r_e itself, especially for hydrides, with position in the periodic system.

From a theoretical standpoint, it would seem more logical to seek relations involving the force constant k, rather than the vibration frequency ω_e, since ω_e depends on the reduced mass μ as well as on k. Further, the problem of possible systematic relations between r_e and k is of course merely a part of the general problem of the forms of potential energy curves (section V A), since r_e and k are just the two most important parameters for the part of a potential energy curve near its minimum. So far, the relations found between r_e and ω_e, or r_e and k, are purely empirical. Relatively little attention seems to have been given to search for a possible theoretical basis for the observed approximate relations. It seems likely that such a search would help toward a better understanding of valence forces. In this connection, Slater's paper (9) on "The Virial and Molecular Structure" should not be lost sight of.

Even an explanation of the important and *almost universally valid* qualitative Birge–Mecke rule which states that, for different states of a given molecule, ω_e always increases when r_e decreases, would be very welcome. While the usual validity of this rule seems plausible in a general way, no one has ever given theoretical reasons to explain why it is rarely, if ever, seriously violated in practice.

In connection with the question of molecular constants, the importance of critical surveys of existing data is obvious. Here we owe much to the careful work of Birge for *International Critical Tables,* followed by that of Weizel, Jevons, and finally Sponer in their respective books on band spectra.

F. Collisions of the second kind

Although no extensive discussion will be given, the subject of "collisions of the second kind" between atoms should be at least mentioned, since the theory of diatomic molecular electronic states and potential energy curves, and the dissociation product correlation rules, are directly applicable here. A successful "collision of the second kind" involves really a jump (possibly with radiation, but generally of the nature of predissociation) from one molecular potential energy curve to another, and is subject to the usual selection rules and other restrictions valid for such transitions.

G. Ionization potentials and Rydberg series

The accurate determination of molecular ionization potentials is valuable in that it aids in the location of potential energy curves of a molecule and molecule-ion on a single diagram. If the dissociation energy is known for the molecule but not for the molecule-ion, or *vice versa,* determination of the ionization potential permits the one to be deduced from the other, provided certain atomic ionization potentials are accurately known, as is true in many but not all important cases.

Two categories of ionization (and excitation) potentials have been proposed by the writer; the *vertical* and the *adiabatic.* An adiabatic or ordinary ionization potential corresponds to passage from the zero-vibration state of the normal electronic state of the neutral molecule to the zero-vibration state of the molecule-ion in its normal or a suitable excited electronic state. A vertical ionization potential corresponds to a transition, on a potential energy curve diagram, from the minimum of the potential energy curve of the normal state of the neutral molecule, vertically up to a potential energy curve of the molecule-ion. That is, it corresponds to ionization without change of internuclear distance. Vertical ionization potentials are particularly useful in characterizing the binding energies of electrons in a study of electronic structures (section VIII).

Ionization potentials can be obtained either directly from electron-impact studies, or by computing the limits of Rydberg or Rydberg–Ritz series observed in band spectra (cf. Weizel's book for a discussion of Rydberg series and certain other possibilities). The latter method is still much the more reliable, even when the best latest technique is used in the former method. It seems likely that, in accordance with the Franck-Condon principle, the former method has a tendency to give a vertical rather than an adiabatic ionization potential; but if so, the result varies with the sensitivity with which the onset of ionization can be detected. In H_2, the results of the two methods now check well, and in N_2 fairly well. In H_2 a third method, that of autoionization (cf. section III D) has been used, giving apparently an even more accurate result than the other two methods. Clear-cut Rydberg series have not yet been reported in other diatomic molecules than H_2 and N_2, except in He_2, but in the latter the instability of the ground state makes the series useless for ionization-potential determination. Series have been found in O_2, but their reliability is not yet absolutely certain. Further accurate ionization-potential determinations may be expected from the future discovery of new Rydberg series, and perhaps of autoionization, in vacuum ultra-violet absorption spectra especially.

VI. CARRIERS OF BAND SPECTRA; APPLICATIONS OF BAND SPECTRA

The usefulness of diatomic band spectra in giving information about the presence and condition of various molecules, and especially of molecular fragments or free radicals, in various light sources or light-absorbing regions is generally appreciated. At the present time there are comparatively few known diatomic band spectra whose carriers are not known, but some work remains to be done in this direction, and of course the spectra of immense numbers of molecules remain to be discovered. In the growth of our present knowledge of band spectra, the identification of the carriers of a given spectrum has been based partly on chemical evidence and partly on internal evidence from structural details of the spectrum itself, including isotope effects.

Once the identity of the carrier of a given spectrum has been established, the presence or intensity of the spectrum in various light sources or absorbers can be used as an indication or measure of the presence of this carrier there. In this way the presence of various atoms and molecules in astronomical and chemical sources (flames, discharge tubes, electric arcs, active nitrogen, luminescent chemical reactions, the sun, stars, comets, the earth's atmosphere, aurora, etc.) has been established, and further deductions have then been made therefrom.

Further, much can often be learned from a study of the intensity distribution among different band lines or bands. Thus, information has been obtained about temperatures (Birge and others), and about the mean radiative lives of excited molecules (cf. section V). Much has been and much more probably can be learned about the transfer of vibrational and rotational energy in collisions between molecules, or between atoms and molecules (e.g., from "resonance" spectra in the presence of foreign gases, active nitrogen spectra, etc., etc.). In these and other ways (e.g., by affording data on molecular energy levels and dimensions), information from band spectra has been an important factor in bringing the kinetic theory of gases up to date.

Band-spectrum data, by providing exact values for the energy levels of gas molecules, have been of great value, as is well known, in specific heat and entropy calculations, and so for problems of chemical equilibrium. Band spectra have been of value in photochemistry by giving information about photochemical primary processes of dissociation and predissociation, and about the energy levels of free radicals.

In the recently emphasized field of quantitative chemical analysis by means of spectra, there seem to be possibilities, which so far as the writer is aware have been little availed of, for using band spectra. For instance, the CN or N_2 bands might conceivably be adapted to the determination of nitrogen, the CN, CH, or C_2 bands to that of carbon, the CuCl bands to that of chlorine. These are all bands which are very easily excited in emission spectra.

A great deal more could be said about applications and possible applications of the study of diatomic band spectra to chemistry, astronomy, and physics, but since this subject belongs largely to section IV of the present conference, it will not be further dealt with here.

VII. NUCLEAR MANIFESTATIONS

A. Isotope effects

In several ways properties of nuclei make themselves felt in the structure of band spectra. First may be mentioned the isotope effect. The masses of nuclei are of course essential factors in determining the moments of inertia and vibration frequencies of molecules and, through these, the energy levels and band-spectrum structures. The variation in the spectrum produced by a change in nuclear masses alone, for a given chemical species, is called the isotope effect. The magnitudes of the differences in frequency between corresponding bands or band lines of two isotopes A_1B and A_2B of a molecule AB are ordinarily approximately proportional to $(\mu_1 - \mu_2)/\mu_1$, where μ_1 and μ_2 are the reduced masses of A_1B and A_2B, respectively ($\mu_{AB} = M_A M_B/(M_A + M_B)$).

The existence of the isotope effect in band spectra was first pointed out by Loomis and by Kratzer in data of Imes on an infra-red HCl band. The isotope effect in electronic bands was first found by Grebe and Konen for PbO; it was then found and analyzed in a number of instances and its importance for various questions brought out by the present writer. A great deal of work in this field has subsequently been carried out by many investigators.

This has proved of interest in a variety of ways: (1) in the discovery of new isotopes, notably those of oxygen, nitrogen, and carbon; (2) in the determination of relative masses of isotopic atoms; (3) in the determination of relative abundance of isotopes; (4) determination of the nature of the carriers of certain band spectra; (5) as an aid in the verification of details of quantum-mechanical theory of band spectra, giving in part (half-integral vibrational quantum numbers) an anticipation of the results of the latter; (6) as an aid in the technical analysis of band spectra, e.g., in the correct determination of vibrational quantum numbers; (7) as an aid to band-spectrum analysis in the study or revelation of details concerning electronic structures in various molecules (under this heading the discovery of "electronic isotope effects" may be included). In all these ways the isotope effect has proved useful, either in new discovery or in confirmation of results found in other ways.

More work still remains to be done with the isotope effect, although perhaps relatively not so much as in the past. Under item 1 above, it may be remarked that the supply of discoverable new isotopes is limited; on the other hand, band spectra have certain advantages over the mass spectrograph in respect to positiveness of identification. At the beginning, the potentialities of the isotope effect for the discovery of new isotopes were greatly limited by the thorough prior work which had already been done in finding isotopes with the mass spectrograph. These potentialities nevertheless finally blossomed forth with the finding by Giauque and Johnston of the oxygen isotopes O^{17} and O^{18} in data of Babcock and Dieke on the O_2 atmospheric bands, following the writer's analysis of the structure of these bands. This work stimulated search for and discovery of C^{13} and N^{15} in band spectra (Birge and King, Naudé), and indirectly stimulated the discovery of H^2.

Under items 2 and 3, it may be remarked that the band-spectrum method is relatively laborious for these purposes, and often involves the careful introduction of corrections, also that good mass comparisons are hardly feasible except for light molecules, so that it appears likely that positive-ray methods will usually furnish an easier path to accuracy. Nevertheless the band-spectrum method has yielded valuable results here. In connection with items 1 to 3, it should always be kept in mind that isotopes become much more difficult to investigate when the reduced mass of the molecule becomes large, since the isotope shifts then become small. Item 6 will be important as long as band spectra are analyzed. Items 5 and 7 show considerable possibilities of further development.

Of considerable interest recently has been the "electronic isotope effect." This may be defined, roughly at least, as that residual part of the total isotope effect which cannot be explained as a direct effect of nuclear mass on moments of inertia, vibration frequencies, and other such molecular constants. In molecules, as in atoms, the electronic isotope effect may be divided into two parts: (1) effects due to the direct or indirect reaction of nuclear mass on electronic motions, and appreciable only for isotopy in the lightest atoms such as H and Li, and (2) effects ascribed by Bohr to slight differences in the fields of force of isotopic nuclei, affecting the planetary electrons. In atoms, effects of the second kind are often called "electrical hyperfine structure", since they are manifested by the appearance of closely spaced components in spectral lines, one for each isotope. [In addition, lines or components belonging to isotopes possessing a nuclear spin may be split up (magnetic or ordinary hyperfine structure).]

The occurrence of electrical hyperfine structure is more difficult to establish in molecules than in atoms because of the relatively large non-electronic isotope effects which must first be subtracted. In HgH, however, where the ordinary isotope effect is extremely small, the presence of a true electrical hyperfine structure similar to that found in Hg atom lines seems to have been definitely established by Mrozowski (6a). Mrozowski finds (after subtracting the nuclear mass effect) four components in each band line, corresponding to the hydrides of the four even mercury isotopes $Hg^{198}H$, $Hg^{200}H$, $Hg^{202}H$, $Hg^{204}H$. (The odd mercury isotopes are apparently affected by a magnetic hyperfine structure (see section VII C).) The results are very interesting in that the magnitude of the effect is found to decrease as the mercury and hydrogen atoms get closer together; this fact is deduced from a study of the size of the effect in different vibrational levels of the relatively unstable normal state of HgH. The result has a bearing on the electronic structure of HgH.

Evidence of electronic isotope effects has been obtained also in various other molecules (H_2, various hydrides and deuterides, BO, etc.). For some states of H_2, large effects have been reported. In cases where hydrogen-deuterium isotopy is involved, the effects are presumably due to reaction of nuclear mass on electronic motion, not to isotopic variations in nuclear force fields. It is difficult in molecules to make a clear-cut distinction between *this* kind of "electronic isotope effect" and the usual non-electronic isotope effects. Certain fine details of the latter are inherently more or less mixed up with the former. This problem has been discussed theoretically by Van Vleck (10a) and others, in connection with the results of a number of recent papers comparing band spectra of hydrogen and deuterium compounds.

B. Nuclear spins and statistics

In respect to the determination of nuclear *"spins"* and *statistics*, especially for the lighter elements, the study of the phenomenon of alternating intensities in band spectra has been important. Most notable was the discovery that the nitrogen nucleus has an angular momentum of $1h/2\pi$, and that it obeys the Bose-Einstein statistics. Both of these results emerged, together, from a study of the alternating intensities in N_2 and N_2^+ bands combined with simple theoretical considerations as to the electronic structure of the nitrogen molecule. The decisive information was obtained in quantitative intensity measurements of Ornstein and Van Wyck on the N_2^+ emission bands, and in investigation of the rotational Raman band of N_2 by Rasetti. These two results, on spin and statistics of the nitrogen nucleus, were difficult to reconcile with a theory of nuclear structure using protons and electrons as building stones, and both pointed toward the now popular theory using protons and neutrons.

The band-spectrum method has also been especially valuable in establishing the existence of nuclei having zero spin (He^4, C^{12}, O^{16}, S^{32}, Se^{80}). These could not be distinguished by line-spectrum hyperfine structure and other methods from possible cases with zero or practically zero *magnetic moment* but spin not zero. In band spectra, zero spin causes alternate band lines to be completely missing, so that, with the help of the general theory of structure types in band spectra, zero spin can often be established almost by inspection.

For other nuclear spin values, quantitative or semiquantitative estimates of the "alternation ratio" of the intensity of adjacent band lines are needed, with increasing accuracy required for increasing spin, since the alternation ratio then rapidly approaches unity. The spins of hydrogen, deuterium, and many other nuclei (especially of the lighter ones, which are the least accessible to the atomic hyperfine structure method) have been determined in this way. Most but not all of these have now also been checked by atomic hyperfine structure or by other methods; no disagreements between the results of different methods are now known.

The band-spectrum method (including some use of the theory of molecular electron configurations) is still our chief source of information about nuclear statistics.

Historically, alternating intensities were first noticed by Deslandres in N_2^+ and N_2 bands; alternate missing lines were first assumed by Heurlinger in C_2 and later by Mecke in He_2; Mecke first suggested that these phenomena are characteristic of molecules with two equal nuclei.

The theory relating alternating intensities in band spectra to nuclear spins and statistics started from Heisenberg's extension of the quantum-mechanical form of the Pauli exclusion principle to nuclear motions, and was developed by Hund. The same theory gave an explanation of the anomalies in the specific heat of H_2 (Dennison) and from this led on to the discovery of ortho- and para-hydrogen. The insensitivity of nuclear-spin orientation to collisions, shown experimentally by the mere fact that pure para-hydrogen can be prepared, was further verified by the interesting band-spectrum observations of Wood and Loomis on the effect of collisions on the rotational structure of the I_2 resonance spectrum.

Further services from the band-spectrum method in the determination of nuclear spins and statistics may be expected in the future. Especially will this be true when the less abundant isotopes of lithium, carbon, nitrogen, and oxygen can be produced in sufficient quantities. Considerable quantities are needed since, in order to get alternating intensities, it is necessary to have spectra of molecules in which both atoms belong to the same isotope. Mixed molecules, e.g., $O^{16}O^{18}$, do not show the phenomenon, and so give no information about nuclear spins or statistics.

C. Hyperfine structure in band lines

Aside from alternating intensities, nuclear structure could also manifest itself in band spectra through hyperfine structure in band lines due, just as in atomic spectra, to the magnetic moments of nuclei. For various reasons, however, this effect should in general be much less prominent than the corresponding phenomenon in line spectra. The greater initial complexity of the edifice of angular momentum vectors, and the more frequent occurrence of closed electron shells, in diatomic molecules as compared with atoms, are the principal unfavorable factors. It can be shown that as a result of the operation of these, the coupling of the nuclear spin vector to the J vector should give rise to measurable hyperfine structures much less frequently in the molecular than in the atomic case. Still, it does not appear out of the question that favorable cases could be found, and a study of these would be interesting in itself, even if it contributed nothing new to our knowledge of nuclear spins and magnetic moments.

The most favorable kind of case for the appearance of magnetic hyperfine structure in a molecule would be one simultaneously fulfilling two conditions: (1) the electronic state should be one having ideal or very nearly ideal loose-spin coupling (Hund's case *b*); this is most likely to be found in $^2\Sigma$ or $^3\Sigma$ states; (2) the resultant spin, or a part of it, should belong to an *s* electron which penetrates close to the nucleus. Condition 2 is one which in atoms gives the largest hyperfine structures. Condition 1 is important because if it is fulfilled, the desired coupling between nuclear spin and electronic spin is not appreciably disturbed by the molecular rotation (6a), whereas with tight-spin coupling (Hund's case *a*) the coupling between nuclear spin and electron spin would be appreciable only for the lowest rotational quantum numbers, being rendered more and more ineffective at larger quantum numbers by the molecular rotation (4). Small hyperfine structures, usually diminishing in width with increasing molecular rotation, are, however, possible for all types of molecular states. A more complete theory is easily developed.

So far as the writer is aware, the only reported indications of (magnetic) hyperfine structure in band lines are for HgH and perhaps CdH ($^2\Pi \rightarrow {}^2\Sigma^+$ transition (6a)), and for BiH ($^1\Sigma \rightarrow {}^1\Pi$ transition, for lines of low quantum number only (2, 3). In each case, the indications consist only in broadening of certain lines or line-components. In HgH, as described above in section VII A, each band line contains four components attributable to isotope shifts and corresponding to four even isotopes (198, 200, 202, 204) of mercury. The even mercury isotopes have zero nuclear spin, and so should give no hyperfine structure. The odd isotopes Hg^{199} and Hg^{201}, however, have nuclear spins. The apparent absence of distinct $Hg^{199}H$ and $Hg^{201}H$ components in the HgH band lines has been explained by Mrozowski (6a) as due to a splitting of these components into hyperfine structure. An apparent absence of odd isotope components in the CdH band lines has also been tentatively explained in the same way (6a).

VIII. ELECTRONIC STRUCTURES OF MOLECULES

A. General considerations

As was noted in the introduction, the problem of the electronic structures of molecules constitutes really a subject outside the scope of "band spectra". Although the subject is a large one, it will therefore be dealt with relatively very briefly in the present survey. It may be pointed out, however, that in the present stage of development of experiment and theory, band-spectrum data on molecular electronic states, combined with some general rules and theorems from quantum mechanics, furnish in the case of diatomic molecules a large part of the foundation for our knowledge of this subject.

The most convenient way to describe the electronic structure of an atom or molecule is by means of an electron configuration, plus a symbol for the total or over-all electronic state. The description of electronic structures is a more complicated and less accurate procedure for molecules than for atoms (7). For an atom there is usually only one important point of view from which an electron configuration can be assigned. For a molecule, on the other hand, there are usually two or more points of view which have more or less equal validity, but no one of which is capable of indicating the true structure as accurately as is possible for an atom.

The most important points of view for describing molecular electronic structures may be listed as the united-atom, the molecular orbital, and the atomic orbital or separate-atom viewpoints. There are also mixtures and variations of these. Still other viewpoints, some of them more accurate, are possible if one does not insist on the idea of electron configurations. In connection with the use of band-spectrum data and the consideration of excited as well as the normal states of molecules, the molecular orbital viewpoint is the most natural one to use. For molecules containing a hydrogen atom, and certain other cases, the united-atom viewpoint is also valuable. In an approach to the subject of molecular electronic structures from the ordinary chemical viewpoint in which a molecule is thought of as *composed* of atoms or ions, and in which emphasis is placed almost entirely on the normal state of a molecule, the separated-atom atomic orbital viewpoint is the natural one.

At the present time it can be said that the electronic structures of the normal states of many of the more important diatomic molecules and radicals are fairly well understood. In respect to excited electronic states, our experimental knowledge and even more our theoretical understanding in terms of electron configurations are for most molecules still very incomplete, especially for the more polar molecules.

The greatest mass of data, and the greatest degree of understanding of electronic structures in the normal and excited states, exist for the H_2 and He_2 molecules, but even here very much remains to be done. Fairly extensive data exist on the electronic levels of CO and N_2 (including their positive ions), and less extensive data on many other molecules.[8] Serious questions still exist concerning the electron configurations of many of the excited states[8] even of CO and N_2. It appears likely that vast amounts of work on known and on as yet undiscovered band spectra will be needed before the electronic energy level diagrams of diatomic molecules can be said to be well understood, and it may be anticipated that the results will be interesting.

To the chemist it may appear that an understanding of the electronic structures of diatomic molecules in their excited electronic states is not very important, since he nearly always deals with molecules in their normal states. There are, to be sure, various ways in which excited states are chemically important, e.g., in photochemistry, and (especially in the case of free radicals) in the formation and dissociation of more complex molecules. In the writer's opinion the study of excited electronic states of diatomic molecules is sufficiently justified in any case by the usual arguments used to justify "pure science." Further than this, however, the writer has the feeling that a thorough understanding of excited as well as of normal states will contribute very considerably toward a better insight into the true nature of the structure of molecules.

What has just been said in regard to diatomic molecules and their spectra applies emphatically also, although with some variations, to the much more extensive but less explored field of polyatomic spectra. The theory of the electronic states of diatomic and polyatomic molecules is closely related to—or may more accurately be said to include—the quantum theory[9] of valence.

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[8] See R. S. Mulliken (Rev. Modern Phys. 4, 1 (1932)) for a fuller discussion. Some but not very great, progress has been made since the date of this publication.

[9] See reference 11 and references there given.

B. Band-spectrum bases for understanding the nature of molecular electronic states

In the process of reaching conclusions as to the nature of molecular electronic states and their electronic configurations, many and varied items of information from band-spectrum analysis are used. A survey of these here appears to be of interest, both in itself and in pointing directions of investigation which should be pursued if more is to be learned from band spectra about electronic structures.

In the first place, the gross energies of electron states are needed. Every band system involves two electronic levels. If the bands can be observed in absorption at moderate temperatures, the lower of the two levels is the normal state of the molecule, and the energy of the excited electronic level relative to this is also located. Other excited levels of the same molecule can be located from additional absorption band systems, or from emission band systems which may be directly or indirectly connected with the absorption systems through the possession of common levels (examples, CO, N_2). In a number of cases the normal level has not been located by the absorption method, but the lowest level found in emission bands has been identified as the normal level through systematic comparison of spectra of different molecules in the light of theoretical considerations, and with the possible help of other evidence (examples, BO, CN, AlO, SiN). In the case of molecule-ions, ionization-potential data (either electron-impact data or, more reliably, Rydberg series limits; cf. section V G) are needed in order to locate the energy levels of the ion relative to those of the neutral molecule. Electron-impact excitation potentials of bands sometimes furnish contributory evidence as to electronic levels of molecules and their ions, but have often proved not very reliable.

In investigating absorption spectra, diffuse and continuous as well as discrete absorption regions, with their shapes and their intensities, are carefully noted, since these are our chief source of empirical information about electron levels having repulsive potential energy curves (cf. section V). Emission continua, although less common, give further information.

The approximate locations of electronic levels not yet found directly from band spectra can often be inferred from data on perturbations and predissociation (cf. section III D).

Next, the detailed analysis of the structure of a band ordinarily gives readily the important angular momentum quantum numbers (Λ and S, for normal coupling) of each of the two electronic states involved. The type of electronic-nuclear rotational coupling in each of the states can ordinarily also be determined at the same time. Intensity relations, missing lines near the center, fine structure in lines, etc., are important. In special cases difficulties may arise because one type of transition simulates another. Difficulties in interpretation are often encountered unless the band structure is practically completely resolved, and unless the usually relatively weak lines of low quantum number are detected; such lack of complete resolution or complete data can, however, often be overcome more or less convincingly by various ingenious procedures. Diamagnetism or paramagnetism of a molecular gas also gives information limiting the possibilities as to Λ and S of its molecules in their normal state.

There are certain further details as to the types of electronic states ($_g$ or $_u$ character in the case of a molecule composed of two like atoms, $^+$ or $^-$ character in the case of a Σ state) which cannot be ascertained directly from analysis of the bands of a single system. Generally, however, these can be determined with more or less certainty by intercomparison of different band systems of a single molecule, combined with the introduction of a certain amount of electron configuration theory. For example, if the lower state of a set of bands is a $^1\Sigma$ state, and if this is the normal state of a molecule, then in most cases configuration theory will leave no reasonable doubt as to what kind of a $^1\Sigma$ state it is. Nearly always in practice it is $^1\Sigma^+$, as, for example, in CuH, or $^1\Sigma^+_g$ if the molecule is homopolar, as, for example, in N_2. If one of the levels involved in a band is $_g$, then, according to the usual selection rules (forbidden transitions excepted), the other is $_u$, and *vice versa*. In homonuclear molecules, with their alternating intensities in band-line series, observation of whether the even- or the odd-numbered lines are the more intense helps, if the statistics obeyed by the nuclei can be assumed known, in limiting the choices between $_g$ and $_u$, and between Σ^+ and Σ^-, states. A study of perturbations, or sometimes still other considerations, may also help here.

If the coupling is normal, and if Λ and S are greater than zero for at least one of the two electronic levels, the bands have a multiplet structure. It is then important to find for each electronic level the value of the coefficient A, which measures the strength of coupling between Λ and S and which determines the multiplet width if the coupling is of the tight-spin normal type. It is also important to know whether the multiplet is regular or inverted, i.e., whether the sign of A is positive or negative. The latter point can be decided by a careful examination of fine details of the band structure (missing lines, or else mode of variation of Λ-doubling with rotational quantum number). The value of A can best be found by fitting the energy levels determined from the band-structure analysis to a theoretical formula of the Hill-Van Vleck type.

Given the values of Λ and S, the $_g$ or $_u$ character, and the value and especially the sign of A if the level is multiple, the possibilities for the electron configuration are usually greatly restricted. By systematic comparison of these items of information for different levels of a molecule, and for analogous and other levels of different molecules, and by sifting the restricted numbers of possibilities which are within reason according to theory, the correct electron configuration can often be determined uniquely or at least pinned down to one of a very few remaining possibilities. The values of certain fine-structure constants which result from band-structure analysis (p, q, γ) give further information which is often valuable in showing relations between the electron configurations of different states of a given molecule. Other fine details detectable through the isotope effect may also prove useful.

The possibilities are further sifted by taking additional information into consideration. Comparisons of potential energy curve constants (r_e, ω_e, and D_e), for different states of a molecule and if possible for its positive ion, throw light on the nature of the several electron configurations. For instance, if an excited, or an ionic, state of a molecule shows a decided increase in r_e and decrease in ω_e as compared with the normal state, we conclude that the process of excitation or ionization has involved removal of an electron from a "bonding" molecular orbital. If, on the other hand, r_e shows a decided decrease and ω_e a corresponding increase, we conclude that the electron removed was "anti-bonding". Or the electron removed may turn out to have been nearly "non-bonding". Comparison with the theory of molecular orbitals now often suffices to decide just what type of orbital was occupied by the removed or excited electron; if not, systematic comparison of data on many states and many molecules may bring success.

IX. EXPERIMENTAL ASPECTS

In general it may be said that, for the investigation of band spectra, concave diffraction gratings are particularly useful. For such gratings, the greatest possible resolving power and dispersion (combined of course so far as possible with high intensity) should be sought. Fine structures of many band spectra, particularly those of heavier molecules, have been opened to successful investigation by large grating spectrographs recently constructed. Better spectrographs will render still further spectra amenable to analysis. There is, however, an abundance of known spectra already awaiting analysis and within the powers of existing spectrographs. Besides good gratings, the best possible photographic plates are important. Fine grain in photographic plates furnishes an alternative to increased dispersion and increased size of spectrographs.

Other things being equal, increased sensitivity of photographic plates, like high intensity of gratings, is important because very many spectra have not yet been obtained with high intensity. In such cases lack of intensity is often a limiting factor that removes the possibility of fine-structure analysis.

Intensive study of existing spectroscopic sources and possible development of new ones deserves great emphasis as a means of finding new spectra and of increasing the intensity of many known spectra up to a point permitting fine-structure analysis.

Among the important experimental advances in recent years has been the development of photographic plates sensitive out to λ 12,000 and beyond, permitting the use of large gratings for the analysis of spectra in those regions. Mecke, Herzberg, and collaborators have been especially active in band-spectrum work in this region.

The richest field for work, experimentally, is that in the vacuum ultra-violet, which is full of band spectra. There is still room here, in emission as well as in absorption spectra, for a great deal of exploration with instruments of moderate power. There is also a great field for fine-structure work with spectrographs which should be made as large as possible in resolution and dispersion. The recent production of large crystals of pure LiF should be a considerable help in connection with the study of absorption and emission spectra down to λ 1050.

Among matters of importance in the far ultra-violet is the study of absorption Rydberg series and thereby the determination of ionization potentials of inner electrons of molecules, already begun in the work of Hopfield, Price, and others. Relative intensity relations of absorption transitions in the near and the far ultra-violet also offer problems of interest. Absorption, emission, and fluorescence bands involving highly excited electronic levels should furnish interesting and often more or less novel results.

Extension of these studies into the region of soft x-rays should have possibilities of giving further information in regard to tightly bound electrons. Here, however, we cannot expect to find structural details, both because the very short life of x-ray states would largely blot these out, and because available experimental methods would not permit resolution of fine structures even if present.

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SPECTRA OF DIATOMIC MOLECULES OF ELEMENTS OF THE FIFTH GROUP[1]

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Molecules formed by the union of two atoms in the same group of the periodic table should, to a first approximation, exhibit similar spectra. In each atom of the group the outermost shell of electrons is the same, except for the total quantum number, and the type of molecular binding and kind of molecular states depend largely upon these electrons. But, just as in the atomic spectra, the relative positions of the energy levels and the type of electronic coupling in the molecular spectra depend also upon the inner shells of electrons; therefore more or less gradual changes should occur in the spectra of a series of homologous molecules. The only thorough study of such a series is the one made by Mulliken (12) on the halogen molecules, in which he made use of the very extensive data on the rotational and vibrational structure of their spectra.

Sufficient information concerning the spectra of the symmetrical diatomic molecules of the elements of the fifth group (nitrogen, phosphorus, arsenic, antimony, bismuth) has been accumulated to begin a correlation of the energy states and certain molecular constants of this group. It is the purpose of this paper to attempt such a correlation. In the case of the ground states the continuity is clear. Even for the excited states the analogies run in most cases through all or a part of the group. In the case of the latter, however, many conclusions are tentative. Some states have no observed counterparts in other molecules. Except for N_2 and P_2, conclusions are based upon vibrational analysis alone. The rotational structure of the heavier molecules is exceedingly fine, though probably not beyond the range of the best grating spectrographs. The uncertainties in the correlations, as well as the question of the nature of the electronic coupling, could be largely settled by a rotational analysis of the various spectra.

In table 1 are listed all of the known states of P_2, As_2, Sb_2, Bi_2, and the more important states of N_2. For each state is given the electronic energy,

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TABLE 1

States and transitions of diatomic molecules of the elements of the fifth group

		N_2	P_2	As_2	Sb_2	Bi_2	PRODUCTS OF DISSOCIATION	PROBABLE MOLECULAR STATE
X	$T_e =$ $\omega_e =$ $k \times 10^4 =$ $D_0 =$	0 2359.6 57.1 59500	0 780.4 13.84 40593	0 429.4 10.13 31500	0 269.9 6.51 22700	0 172.7 4.57 13750	$^4S + {}^4S$	$^1\Sigma_g^+$
A	$T_e =$ $\omega_e =$ $D_0 =$				14968 217.2 7700 or 16200		$^4S + {}^4S$ or $S + {}^2D$	$^3\Sigma_u^+$
B	$T_e =$ $\omega_e =$ $D_0 =$	49715 1460.4 28700		24598 337 17800	19043 216.8 13500	17722 132.2 11500	$^4S + {}^2D$	$^3\Sigma_u^+$
C	T_e D_0		Hypothetical state at 47000 Small	42003 700	32000 Repulsive	32000 Repulsive	$^4S + {}^2D$	$^3\Pi_u$
D	$T_e =$ $\omega_e =$ $D_0 =$	68957 ($^1\Pi$) 1692.3 38600	46790 475.2 23900	40261 280 20500	32027 215 16000	36455 157 10000 ?	$^2D + {}^2P$	$^1\Sigma_u^+$
E	$^3\Pi_g$ $D_0 =$ $^3\Pi_u$ $D_0 =$	59235 38700 88887 9000		$T_e = 40833$ $\omega_e = 295$ $D_0 = 12300$		42200 129 ?	$^2D + {}^2D$	?
F	$T_e =$				44000	46000		
Transitions....	$B \leftrightarrow X$ $D \leftrightarrow X$ ($^3\Pi_g \rightarrow B$) ($^3\Pi_u \rightarrow {}^3\Pi_g$)		$D \leftrightarrow X$	$B \rightarrow X$ $C \rightarrow X$ $D \leftrightarrow X$ $E \leftrightarrow X$	$A \leftrightarrow X$ $B \leftrightarrow X$ $C \leftarrow X$? $D \leftarrow X$ $F \leftarrow X$	$B \leftarrow X$ $C \leftarrow X$ $D \leftarrow X$ $F \leftarrow X$ $E \leftarrow B$?		

* All quantities are expressed in cm.^{-1}, except k.

T_e (measured from $v = 0$ in the ground state to $v' = 0$), the equilibrium vibration frequency, ω_e, and the heat of dissociation, D_0, all expressed in cm.$^{-1}$ For the ground states a force constant, k, is also given, which is

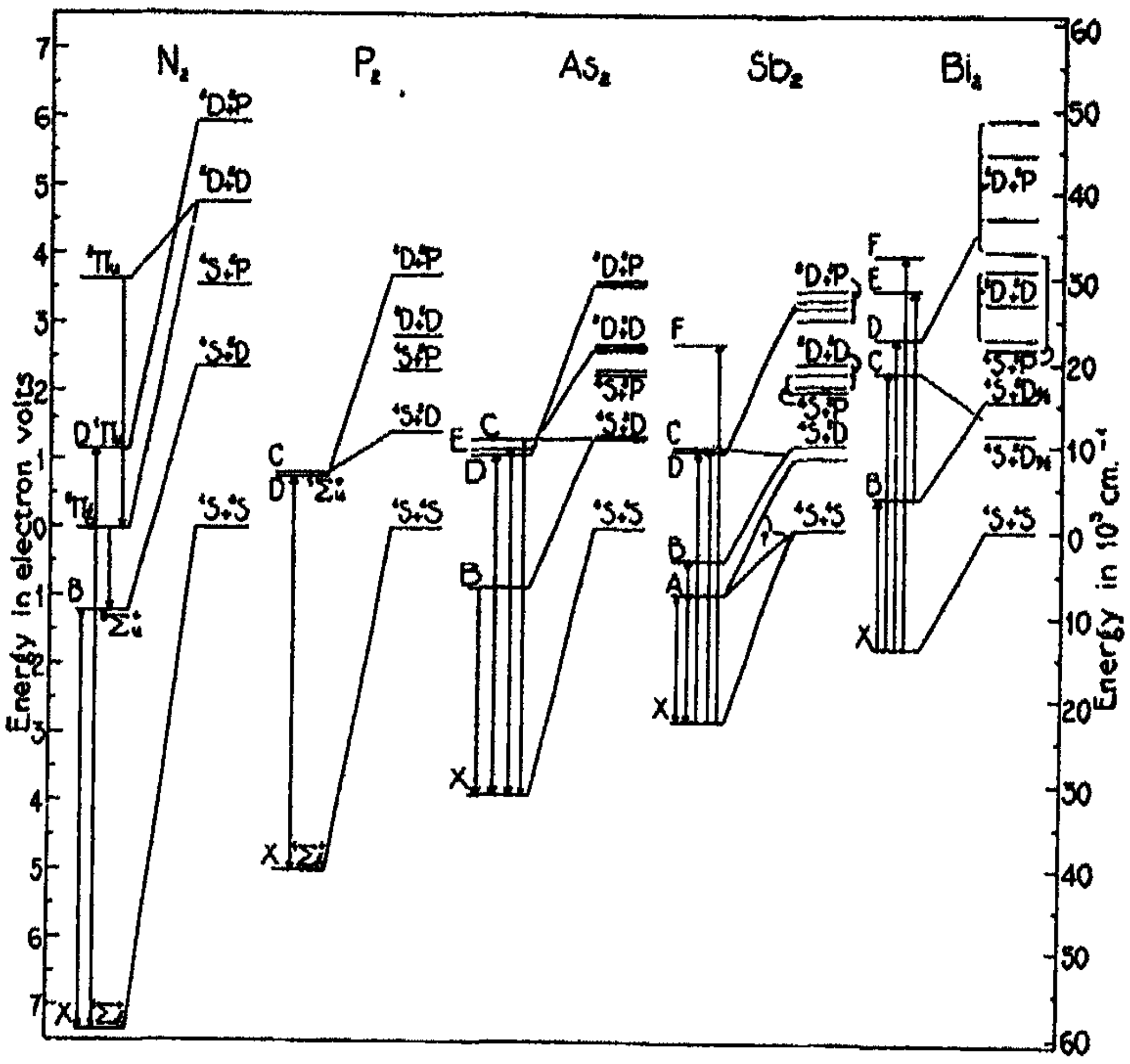

FIG. 1. Term schemes of the symmetrical diatomic molecules of the fifth group

twice the constant appearing in the approximate expression for the potential energy near equilibrium

$$U(r) = T_e + \frac{k}{2}(r-r_e)^2$$

where r_e = the equilibrium distance between atoms and

$$k = 2\pi^2 c^2 \omega_e^2 \mu$$

where c = the velocity of light and μ = the reduced mass of the molecule. D_0 is the depth of the potential energy curve with respect to the energy of the dissociated atoms, and k tells one something about its width. A relatively narrow, steeply rising curve has a large k.

Corresponding states of the various molecules, as nearly as can be determined at present, are arranged in rows. At the left the states are given a letter (which seldom corresponds to previous designations of the same states) and at the right appear the most likely (certain in N_2 and P_2) molecular states and the best choice as to the atomic states of the products of dissociation. At the bottom of the table are given the observed transitions in the various molecules. The energy relations and the more prominent transitions are also represented in figure 1. In this diagram the energy of two normal ^4S atoms is taken as the common zero for all the molecules. In figure 2 are plotted the values of $D_0(X)$ (heat of dissociation of ground state), $k(X)$, and $r_e(X)$.

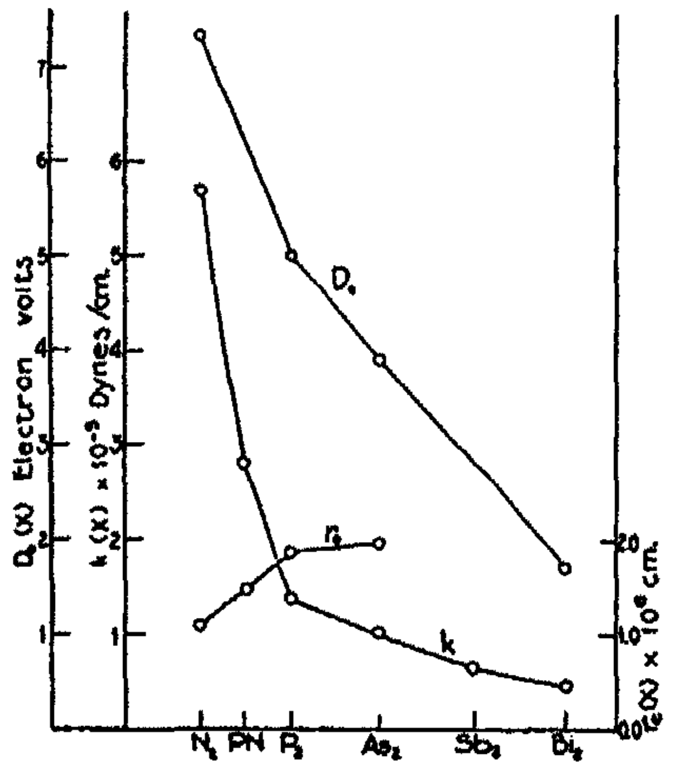

FIG. 2. Constants of the ground states (X). D_0 is the heat of dissociation; k is the force constant for small displacements about the equilibrium internuclear distance r_e. The value of r_e (1.95) for As_2 is estimated from a partial rotational analysis.

In the discussion of the reasons for the arrangement and assignments in table 1 and figure 1 each molecule will be taken up in order. The sources of the data and a brief description of the spectra will be given. Some recent unpublished work on As_2 and Sb_2 is included. Assignments of the states will be made as definite as possible, considering each molecule as an independent problem. In several cases further limitations will be imposed by making use of the fact that a considerable continuity should run through the series of molecules.

NITROGEN

The molecular spectrum of nitrogen has been the subject of numerous investigations (5). The well-established relations among the various states are shown in table 1 and figure 1. The heat of dissociation, long in doubt, has recently been fairly definitely fixed. Diverse evidence, including the position of recently discovered $^3\Sigma \rightarrow {}^1\Sigma$ (Vegard–Kaplan) bands (15, 6), predissociation in the upper $^3\Pi$ state, Lozier's electron-impact data (8), and the interpretation by Mulliken (11) of Hopfield's Rydberg series of N_2 absorption bands, points consistently to $D_0(X) = 7.3$ volts. The ground state of N_2 certainly dissociates into two normal ^4S atoms. Although it has been assumed that a similar situation exists in the heavier molecules of this group, N_2 does not fit in smoothly, as to $D_0(X)$, $r_e(X)$, or $k(X)$ (figure 2) with the succeeding molecules. But, as Herzberg (4) and Mulliken (10) have pointed out, N_2 approaches the "united atom," Si, much more closely than P_2 or the heavier molecules approach the corresponding united atoms. This discontinuity between N_2 and P_2 in the behavior of the group appears also in the nature of the excited states.

PHOSPHORUS

The spectrum of P_2 consists of a single system extending at the least from 2000 A.U. to 3300 A.U. It has been thoroughly studied in emission by Herzberg (4), who gives references to other work, including investigations of the absorption spectrum. Through a rotational analysis, including a consideration of the alternating intensities, he concludes that the transition is $^1\Sigma_u^+ \leftrightarrow {}^1\Sigma_g^+$. $^1\Sigma_g^+$ can come reasonably only from two ^4S atoms. The excited state comes almost certainly from $^2D + {}^2P$, as indicated by its D_0 obtained by extrapolation and by a consideration of possible states from available atomic pairs.

Predissociation in the upper state enables Herzberg to fix $D_0(X)$ quite precisely, the most probable value being 40,593 cm.$^{-1}$ To account for the predissociation and also for perturbations occurring in the upper state he assumes the existence of a shallow state arising from $^4S + {}^2D$ which, to satisfy the rigid selection rules for perturbations, must be $^3\Sigma_u^+$ or $^3\Pi_u$. Either of these states violates the rule $\Delta S = 0$, which is not rigid.

This transition corresponds approximately to the strong $^1\Pi \rightarrow {}^1\Sigma$ system in N_2. The unobserved, perturbing triplet state may correspond to the upper state of the Vegard–Kaplan N_2 bands ($^3\Sigma_u^+$).

Besides this strong system Herzberg observed a few weak bands near 4200 A.U. which may be due to another electronic transition.

PN AND AsN

The emission spectra of PN (2) and AsN (14) consist of single $^1\Pi \rightarrow {}^1\Sigma$ systems, corresponding presumably to the similar transitions in N_2. The constants of the ground state of PN have been interpolated between those of P_2 and N_2 in figure 2.

ARSENIC

The absorption spectrum of As_2 has been found by Gibson and MacFarlane (3) to extend from 2200 A.U. to 2750 A.U. and to consist largely of a single system ($D \leftarrow X$). Some bands of another transition ($E \leftarrow X$) were observed. The lower state was not extended beyond $v'' = 9$. This work established the identity of the ground state.

The emission spectrum (1) consists of five systems. Two prominent systems, $D \rightarrow X$ and $E \rightarrow X$, extend from 2200 A.U. to 5800 A.U., overlapping one another almost completely. In the published analysis the $D \rightarrow X$ system was extended to $v'' = 44$, but the extrapolation to dissociation was so great that even with the use of predissociation in state D we could not choose conclusively among the various possible values of $D_0(X)$ corresponding to the assumptions made as to the atomic states near the predissociation level. Recent work by Kinzer (7), using an improved quartz discharge tube operating in a furnace at about 500°C., has extended the system to bands with $v'' = 72$. $D_0(X)$ obtained by extrapolation of the vibrational levels to convergence is approximately 31,000 cm.$^{-1}$. Since the vibrational energy $G_0(X)$ is now observed to 24,574 cm.$^{-1}$, only one value of $D_0(X)$ obtained from predissociation of state D can now be admitted, namely $D_0(X) = 31{,}900$ cm.$^{-1}$. This is obtained by assuming that predissociation, observed at a total energy $(T_e(D) + G_0(D))$ of 42,700 cm.$^{-1}$, occurs into a state from $^4S + {}^2D$, 10,800 cm.$^{-1}$ above $^4S + {}^4S$. Other assumptions as to the atomic states at predissociation give $D_0(X)$ equal to 42,700 cm.$^{-1}$ (predissociation at $^4S + {}^4S$), or 24,200 cm.$^{-1}$ ($^4S + {}^2P$), or smaller values, all of which are definitely excluded. Since the details (rotational structure) of predissociation have not been studied, $D_0(X)$ obtained by this method (31,900 cm.$^{-1}$) is to be regarded as an upper limit. We will take 31,500 cm.$^{-1}$ as the most probable value of $D_0(X)$. It is probably correct within 3 per cent.

The vibrational intervals of D and E are violently perturbed at low v', owing, it appears, to an interaction of the two. State D smooths out above the perturbations and is observed in absorption to $v' = 17$ (predissociation occurs at $v' = 9$). $D_0(D)$ obtained by extrapolation is roughly 19,000 cm.$^{-1}$, which makes $^2D + {}^2P$ the most likely products of dissociation for, assuming this, $D_0(D)$ is 20,500 cm.$^{-1}$

Since $D \rightarrow X$ is the strongest system, D is probably $^1\Sigma_u^+$ and $D \rightarrow X$ corresponds to the only known P_2 system. State E does not extend beyond the region of perturbation, but appears to be converging more rapidly than state D. It is assumed to dissociate into the next lower pair[2], $^2D + {}^2D$, in

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[2] Since this system has not been extended beyond $v' = 8$ it is probable that predissociation occurs in E as well as in D. The break-off is not as definite. Our previous suggestion that dissociation by rotation occurs is probably incorrect, for the vibrational interval has dropped from 295 cm.$^{-1}$ only to 210 cm.$^{-1}$ at the level of $^4S + {}^2D$, where this dissociation would occur.

which case it is $^1\Pi_u$, or violating $\Delta S = 0$, $^3\Pi_u$ or $^3\Sigma_u^+$. Photographs with large dispersion do not give sufficient resolution near the origin to permit rotational analysis, but the more isolated bands appear to be of a simple two-branch type. This observation points to $^3\Sigma_u^+$ which should give, with $^1\Sigma_g^+$, only two strong branches, but this conclusion is not definitely established.

System $C \rightarrow X$ consists of a single progression extending from $v'' = 21$ to $v'' = 32$, as determined by the best fit of the vibrational intervals. Assuming that it is the $v' = 0$ progression of a distinct system, it arises from a state at $T_e = 42{,}003$ cm.$^{-1}$, with r_e considerably greater than r_e of state X, probably shallow and dissociating into $^4S + {}^2D$ at an energy of 42,700 cm.$^{-1}$ Thus it could account nicely for the predissociation of states D and E at this level. Exactly such a state was assumed to exist, though not observed, by Herzberg in the case of P_2. It must be either $^3\Sigma_u^+$ or $^3\Pi_u$ to satisfy the Kronig selection rules (except $\Delta S = 0$).

Finally, two new systems, weaker than the three described, were obtained in the recent work on As_2. The details will be published elsewhere. One system $(B \rightarrow X)$ fits the equation,

$$\nu = 24643 + \{337.0\,(v' + \tfrac{1}{2}) - 0.83\,(v' + \tfrac{1}{2})^2\} \\ - \{430.0\,(v' + \tfrac{1}{2}) - 1.20\,(v'' + \tfrac{1}{2})^2\}$$

It consists of about thirty bands, distributed in a wide parabola, extending from $v' = 5$ to $v'' = 12$. The upper state converges slowly; $D_0(B) = \dfrac{\omega_e^2}{4x_e\omega_e} \sim 30{,}000$ cm.$^{-1}$ (very rough and probably much too high). Assuming the upper state to be from $^4S + {}^2D$ we find $D_0(B) = 17{,}800$ cm.$^{-1}$ On this assumption B must be $^3\Pi_u$ and C must be $^3\Sigma_u^+$, or *vice versa.*

The second new system, probably due to As_2, extends from 5600 A.U. to 7000 A.U. The bands are degraded sharply to the violet (all other bands are degraded to the red). Upon analysis the bands are found to occur in pairs, matched in intensity, with a constant interval of 162 cm.$^{-1}$ They can be represented by the equation:

$$\nu = \begin{matrix}(16359)\\(16197)\end{matrix} + \{336.8\,(v' + \tfrac{1}{2}) - 1.04\,(v' + \tfrac{1}{2})^2\} \\ - \{314.8\,(v'' + \tfrac{1}{2}) - 1.25\,(v'' + \tfrac{1}{2})^2\}$$

The highest observed v' is 6; the highest v'' is 4. In each state the convergence is slow and ω_e large, indicating rather tightly bound states (2 to 3 volts). The rotational structure appears very dense and complex. It is difficult to account for the apparent doublet structure, since neutral As_2 should have only odd multiplicities. The spectrum is conceivably due to As_2^+. No attempt is made to fit it into the scheme of table 1.

ANTIMONY

The absorption spectrum of Sb_2 was first studied by Naudé (13), who used a quartz tube in a furnace at temperatures below 1100°C. He found two systems: one in the range 2842 to 3315 A.U., one between 2200 and 2318 A.U. From the analysis of the former he finds the constants of the ground state and of an upper state at 32,027 cm.$^{-1}$ (D in table 1). The spectrum extends only to $v'' = 7$, and a reliable extrapolation to dissociation cannot be made. Rough extrapolation gives $D_0(X) = 32{,}000$ cm.$^{-1}$ Since the values of $D_0(X)$ of Bi_2 and As_2 are known much more accurately, and since $\omega_e(X)$ and $k(X)$ of Sb_2 fit in smoothly, it will be better in arranging the states of Sb_2 to interpolate a value of $D_0(X)$ for Sb_2. This gives $D_0(X) = 22{,}700$ cm.$^{-1}$ (figure 2), which has been used in calculating D_0 for the other states of Sb_2.

The upper state of this system shows perturbations in its vibrational structure. Although extended to $v' = 17$, there is no indication of convergence, ΔG varying erratically between 207 and 228 cm.$^{-1}$ If we assume that this most prominent system corresponds to the similarly perturbed, strong systems of P_2 and As_2, it is ${}^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ with ${}^1\Sigma_u^+$ from ${}^2D + {}^2P$. In this case $D_0(D) = 15{,}800$ cm.$^{-1}$, a reasonable value in comparison with the corresponding states of As_2 and Bi_2.

The second system of $Sb_2(F \leftarrow X)$ could not be analyzed with the available data. The observed intervals and its appearance at low temperature show that it involves the ground state.

H. A. Schultz has, in this laboratory, recently photographed the absorption and thermal emission spectrum of Sb_2. He used a carbon-tube furnace in an atmosphere of nitrogen, which can be heated to 2100–2200°C. He obtained in absorption the two systems photographed by Naudé and two new weaker systems in the visible spectrum. These appear in absorption when the temperature of the molten antimony is above 1300°C. Above 1700°C. both systems are strong in thermal emission. One system extends from 4500 to 6000 A.U., the other from 6000 to 7500 A.U. Both involve the ground state. They fit the equations:

$$\begin{aligned} A \longleftrightarrow X\colon\ & 14991 + 217.2\,(v' + \tfrac{1}{2}) - 0.44\,(v' + \tfrac{1}{2})^2 \\ & \qquad - 270.1\,(v'' + \tfrac{1}{2}) - 0.65\,(v'' + \tfrac{1}{2})^2 \\ B \longleftrightarrow X\colon\ & 19069 + 216.8\,(v' + \tfrac{1}{2}) - 0.40\,(v' + \tfrac{1}{2})^2 \\ & \qquad - 269.6\,(v'' + \tfrac{1}{2}) - 0.563\,(v'' + \tfrac{1}{2})^2 \end{aligned}$$

The constants of the upper states and the distribution of intensity in the two systems are surprisingly similar. Each extends to $v' = 10$, $v'' = 10$. The analysis is supported by the isotope effect.

In accounting for A and B the available states from suitably low atomic pairs are ${}^3\Sigma_u^+$ from ${}^4S + {}^4S$ and ${}^3\Pi_u$ and ${}^3\Sigma_u^+$ from ${}^4S + {}^2D$. In combining with $X(^1\Sigma_g^+)$, these violate $\Delta S = 0$, not improbable in Sb_2. Two interpretations are suggested: (1) A is $^3\Sigma_u^+$ from $^4S + {}^4S$, B is $^3\Sigma_u^+$ (or $^3\Pi_u$) from $^4S + {}^2D$, $^3\Pi_u$ (or $^3\Sigma_u^+$) (repulsive) from $^4S + {}^2D$ is responsible for the perturbations observed in D, as assumed in P_2 and As_2. Against this interpretation is the fact that it requires $D_0(A)$ to be only 7700 cm.$^{-1}$, while by a long extrapolation it is about 27,000 cm.$^{-1}$ (2) The LS coupling has become so large that Hund's case *c* holds. In case *c*, either the atomic J values are maintained in the molecule or a J is formed of L and S for the molecule as a whole, and the projection (Ω) of the J's (or J) on the axis characterizes the state. The designations $^3\Pi$, $^3\Sigma$, etc., lose meaning. Now in ^2D of Sb the interval is 1342 cm.$^{-1}$; in ^2P it is 2069 cm.$^{-1}$ Thus the frequency differences associated with electronic motions are several times the vibration frequencies in Sb_2, and case *c* is therefore a possibility. The states arising from a given pair of atomic J's have been discussed by Mulliken (9). $^4S_{3/2} + {}^2D_{5/2,\,3/2}$ would give several 1_u and 0_u^+ states capable of combining with X and perturbing D. On this interpretation the similarity of states A and B would suggest that they might form a wide "doublet" of two similar case *c* states, A from $^4S_{3/2} + {}^2D_{3/2}$, B from $^4S_{3/2} + {}^2D_{5/2}$. In this case $D_0(A)$ is 16,200; $D_0(B)$ remains 13,500. With the available information it is hardly worth while to discuss this possibility in detail.

There is some evidence for a repulsive state near the perturbed state D. Although the absorption is very strong in this region, it is difficult to photograph the bands distinctly. Naudé also reports that the system is very sensitive to the temperature and pressure of the vapor. An overlying continuum ($C \leftarrow X$) could cause these difficulties.

BISMUTH

The absorption spectrum of Bi_2 (16) consists principally of four systems of bands with discrete structure and a region (near 3100 A.U.) of strong continuous absorption. The four systems are: (1) A system in the visible extending from 4500 to 7900 A.U. ($B \leftarrow X$). (2) A system between 2600 and 2900 A.U., in which the absorption is more intense than in the visible system but which could not be extended to high v in either state. The upper state is perturbed. The system is probably $D \leftarrow X$ and has its counterpart in every molecule of the group. (3) A far ultra-violet system (< 2250 A.U.) corresponding in general appearance to the $F \leftarrow X$ system of Sb_2. (4) A violet system (4000 to 4200 A.U.), appearing only with dense vapor at temperatures greater than 1000°C., which is a transition between excited states, probably $E \leftarrow B$.

The heat of dissociation $D_0(X)$ is obtained most reliably from extrapolation of the upper state (B) of the visible system. The atomic states are so widely spaced and the extrapolation sufficiently short that there can be no question that B dissociates into $^4S + {}^2D_{5/2}$, if, as assumed throughout,

X dissociates into ${}^4S + {}^4S$. This interpretation leads to $D_0(X) = 13{,}735$ cm.$^{-1}$

In the bismuth atom the doublet intervals (4019 cm.$^{-1}$ in ${}^2D$, 10,505 cm.$^{-1}$ in ${}^2P$) are of the same order of magnitude as the molecular binding energies. It is therefore quite probable that case c obtains in the molecule and the term designations of table 1 have little meaning. The absence of state A, observed in Sb_2, may well be due to the fact that it lies beyond 8000 A.U., the limit of the region photographed. The continuum near 3100 A.U. is due, presumably, to a repulsive state C arising from ${}^4S$ and one component of ${}^2D$. It would thus correspond to the repulsive or shallow states perturbing state D in P_2, As_2, and Sb_2. On the present assignment C lies below D in Bi_2 and the perturbations in D must be ascribed to other states.

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ELECTRONIC ENERGY TRANSFERS BETWEEN IODINE AND OTHER MOLECULES[1]

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Resonance fluorescence of atoms and molecules is quenched in the presence of foreign gases. The case of mercury has long been studied because of the simplicity of the emission and absorption process which gives rise to the fluorescence. These results have been a considerable aid in the understanding of photochemical processes.

Among molecular fluorescences the simplest and most examined is that of iodine vapor (2). The quenching of iodine fluorescence excited by white light has been measured for various gases. It is most interesting to observe that argon, hydrogen, nitrogen, oxygen, chlorine, and iodine are rather efficient in deactivation of iodine molecules, the order of efficiency being that given.

At first sight complete deactivation would seem to be a rather improbable act. It is known that a shift from electronic to translational energy of collision is unlikely except in small amounts. This is well illustrated by the work of Franck and Wood (1), where iodine fluorescence excited by the 5462 mercury line was practically undiminished in total intensity, although considerably altered in wave-length distribution in the presence of 10 mm. of helium. Helium being able to take only small amounts of energy in the form of translation, there is little tendency to total deactivation.

In considering the removal of the electronic-vibrational energy of iodine by vibrational excitation of the foreign gas we run into the same difficulty. Unless there is a fortuitous correspondence of vibrational levels between the colliding molecules, there is still a considerable amount of energy which must be transformed to kinetic form.

However, there are two facts which point the way toward the answer to the problem. Turner showed that the iodine vapor illuminated with light of wave length greater than the convergence limit showed the presence of

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iodine atoms. Furthermore the kinetics of reactions involving the halogens have the same form above and below the convergence limit. Thus the deactivation process must result in atom formation.

The situation is represented graphically in figure 1, where are drawn the potential energy curves for the normal and excited states of iodine. Between the two there is an energy gap where only totally repulsive states,

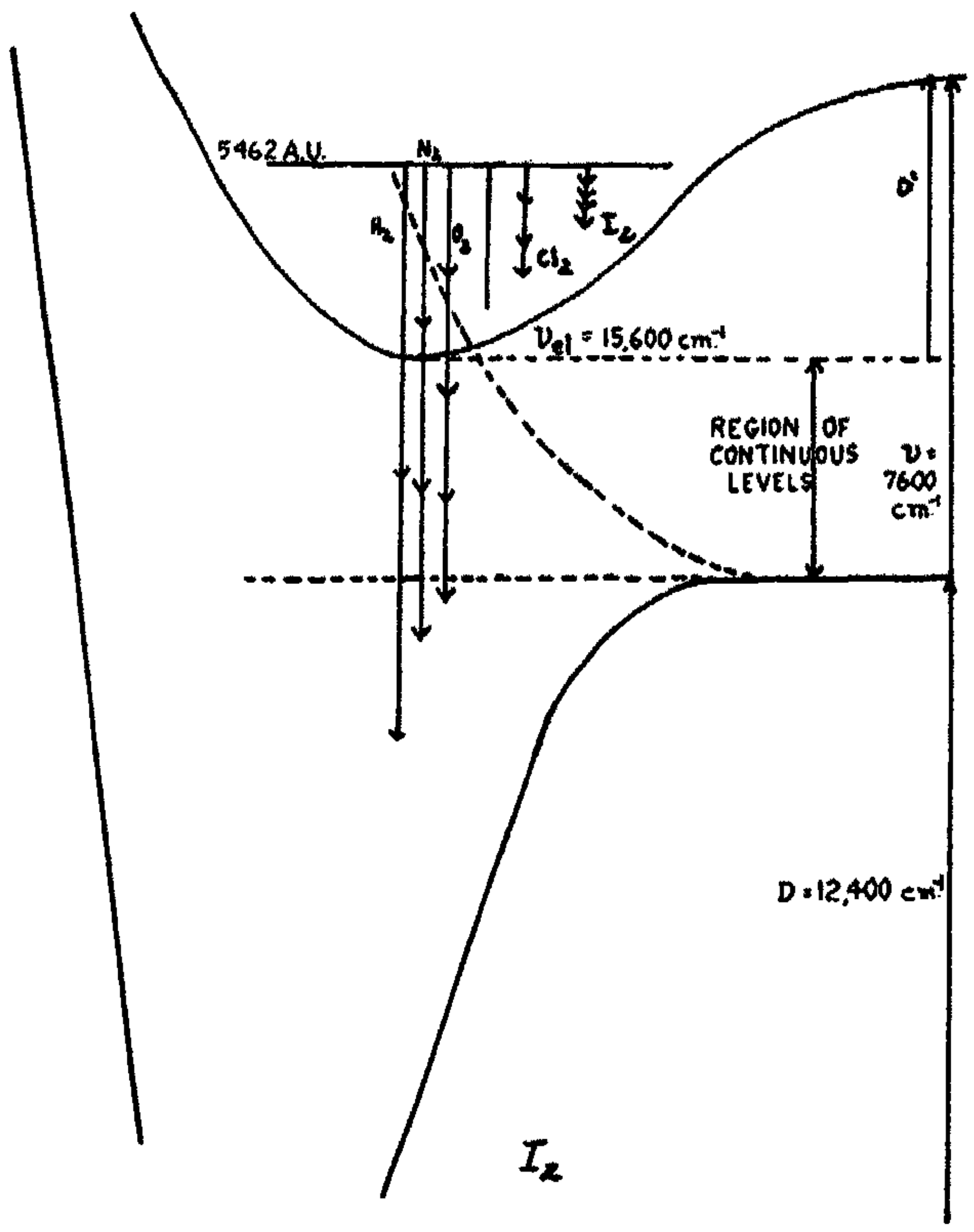

FIG. 1. Potential energy curves for the normal and excited states of iodine

with a continuous series of energy states, are possible. Such a state is shown by the dotted line.

This explains the quenching results, since we are at once freed from any necessity of correspondence in energy levels, with one exception. There must exist levels in the quenching molecule which will lower the energy of the iodine molecule to the energy range of the continuous states. In other words

$$15{,}600 \text{ cm.}^{-1} > E_{el} - E_{vib} > 12{,}400 \text{ cm.}^{-1}$$

where E_{el} is the energy of the excited iodine molecule and E_{vib} a vibrational level of the quenching molecule.

A simple calculation shows that hydrogen will have either zero or one such level for the different ranges of white light excitation, nitrogen one or two, oxygen two or three, chlorine and iodine a much larger number. This is thus the order of increasing efficiency: the greater the number of levels, the higher the quenching efficiency. This would seem to be a rather better explanation than the generally accepted one of deactivation to the normal state, with greater efficiency the more electronegative the gas.

A more exact treatment, involving the breadth of levels and collision frequency, is defeated in effect by a lack of knowledge of collision cross sections.

It is also interesting to observe that in a recent paper Rabinowitch and Wood (3) showed that the recombination of iodine atoms was affected by hydrogen, nitrogen, and oxygen with increasing efficiency. It is obvious that a similar argument might apply to this case.

SUMMARY

The quenching efficiencies of iodine fluorescence can be accounted for only by the assumption that the deactivation results in dissociation, which is also in agreement with other results.

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INTERMOLECULAR FORCES RESPONSIBLE FOR PRESSURE BROADENING OF BAND LINES[1]

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It is well known that spectral lines are broadened and slightly changed in frequency when the pressure of the gas surrounding the absorbing or emitting atoms or molecules is raised (16). The object of the present note is to indicate how quantitative measurements of the broadening of the rotational fine-structure lines of molecular spectra upon increase in the density of the same or of foreign gas molecules may yield information as to the nature and magnitude of the intermolecular forces involved. We shall confine our remarks to this ordinary pressure broadening of all the band lines. There are, in addition, interesting and important effects of pressure on the rotational lines broadened by predissociation or by rotational dissociation.

Cases of very marked and rapid increase in the width of the lines of infra-red vibration-rotation absorption bands with increasing pressure of the gas or vapor in the absorption tube should have our chief attention. For we are concerned then with the chemically important normal state of the molecule, and the large line width can only be assigned to extra-large van der Waals forces. These forces must be made up in considerable part, as we shall show below, of dipole interactions,—evidence of incipient association. Furthermore, the breadths of these lines may be very accurately measured by photometering spectrograms taken with the high dispersion of large grating spectrographs. Advantageous, too, is the favorable ratio of frequency units to Ångström units near the extreme end of the photographic infra-red region.

From the trend in the line-width variation in the range of low gas pressures one can by extrapolation obtain the "zero-pressure" line width, which is determined largely by the slit width and other adjustments of the spectrograph. The contributions from so-called natural line width and from Doppler broadening are negligible. It should be emphasized that for pressures under, say, 1 atmosphere, the rate of increase of line breadth

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with pressure as determined by two different investigators will in general be somewhat different, owing to their different zero-pressure line widths.[2] For the most accurate comparison of relative pressure broadenings for various gases, all apparatus conditions should be kept constant.

If the van der Waals interactions producing the pressure broadening of band lines are due to foreign perturbing molecules which have no permanent electric moment, theory (15) and experiment (20) both show that the shifts and breadths of the lines are about the same as for atomic lines. These dispersion forces bring about a mutual polarization of the interacting molecules, and the resulting effects are practically independent of the rotational and vibrational state of the absorber. For example, lines of the $^1\Pi \rightarrow {}^1\Sigma$ AlH band in absorption are all uniformly and symmetrically broadened by H_2, the half-widths of the lines increasing at a rate of 0.24 cm.$^{-1}$ per atmosphere of H_2 pressure. The corresponding half-width increase for the 2537 A.U. mercury resonance line is 0.41 cm.$^{-1}$ per atmosphere of H_2.

Dispersion forces are also the predominant broadening influence for infra-red vibration-rotation band lines upon increase in pressure in the absorption column of any gas or vapor whose molecules have no permanent polarity or are but slightly polar. For, although the perturbing molecules are of the same kind as the absorbers, resonance interaction should be small, owing to the limitations on the resonance process imposed by the rotational selection rules. Since most of the molecules, both perturbers and absorbers, have rotational states at or near the most probable ones for the existing temperature, it might be possible that lines due to transitions between these most densely populated rotational levels would be appreciably affected by resonance interaction.[3] As to the predominance of dispersion forces in the van der Waals interactions between weakly polar molecules, London (14) has shown that even for as strong a dipole gas as hydrogen chloride the dispersion effect is considerably larger than the Debye induction effect and the dipole direction effect.

A number of investigators have noted that methane (7, 5, 19) at and above atmospheric pressure and acetylene (8, 13, 9, 17) at atmospheric pressure exhibit in the photographic infra-red absorption bands with quite sharp rotational lines, while Herzberg and Spinks (10) observed by inspection that the second harmonic band of hydrogen chloride at 1.15μ too had sharp lines, although the absorbing gas was at approximately atmospheric pressure. On the other hand, ammonia (4), methyl alcohol (1, 12) and especially hydrogen cyanide (2, 6, 11; see note 2), to cite but a few examples,

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[2] The details of these measurements will be discussed in a note to be submitted by Professor Herzberg and the writer to *The Physical Review* in the near future.

[3] This possibility will be elaborated upon in a note by H. Margenau and the writer in a forthcoming issue of *The Physical Review*.

have been shown to have at atmospheric pressure vibration-rotation absorption bands with considerably broadened lines. Photometric study[2] of some of Herzberg's spectrograms reveals that the lines of the methane and acetylene bands indeed have half-widths nearly equal (about 0.51 cm.$^{-1}$)[4] and but little broader than the indicated apparatus line width for zero gas pressure. The hydrogen chloride lines, however, although sharp, have half-widths on the average about 0.08 cm.$^{-1}$ greater than the methane and acetylene line widths. Chao estimates the ammonia absorption lines to have a width of about 0.88 cm.$^{-1}$ at atmospheric pressure and with no detectable variation with rotational quantum number. And, finally, the lines of the hydrogen cyanide band at 1.04μ have at this same pressure an average half-width of about[4] (2, 6, 11; see note 3) 1.4 to 1.5 cm.$^{-1}$

To what intermolecular forces may these pressure broadenings in excess of the methane line widths, which indicate the breadths assignable to collision broadening and dispersion forces, be attributed? Since these molecules have dipole moments μ increasing from 1.03×10^{-18} for hydrogen chloride to 1.44×10^{-18} for ammonia and finally to 2.5–2.6×10^{-18} for hydrogen cyanide, the excess line breadths which increase in this same order might well be due to dipole interactions. Now energy expressions for dipole–dipole interaction usually involve[5] μ^4, and the μ^4 ratio for HCN: HCl is about 40:1. There is no exact agreement between this ratio and that for the excess pressure broadenings for these two molecules, but the comparison does indicate that dipole interaction is largely responsible for the effect. It must be remembered, too, that dispersion forces and dipole forces are not necessarily additive.

The question of the possible variation of this dipole pressure broadening with the rotational quantum number J is of interest. For the hydrogen cyanide band the observation of Herzberg and Spinks was that the broadening decreases with increasing molecular rotation, whereas Cornell and Watson concluded that their photometrically determined line half-widths showed a random variation with J about the mean values at each pressure. Closer inspection of the latter's data, as well as the recent measurements[2] of the plates of Herzberg and Spinks, however, indicate to the writer that the lines of both low and high J values are somewhat narrower than the more intense lines at and near the maximum of the rotational energy distribution. Consideration of the effect of molecular rotation on dipole forces does indeed indicate that this sort of a variation of pressure broadening with J might be observed if the dipole interaction is quite strong.[3] For, according to London's work on the interaction between rotating dipoles (14), there is repulsion if for the total angular momenta l and k of

[4] These figures are from the measurements of the writer alone. They have not as yet been checked by Professor Herzberg.

[5] See reference 15, p. 266.

the two dipoles $|l - k| > 1$, attraction if the two are in the same rotational state, and resonance degeneracy if $|l - k| = 1$. The numerical coefficients in the energy perturbation equation are the largest, $-\frac{1}{2}$, for $l = k$, have the same sign for $|l - k| = 1$, and are of opposite sign if $|l-k| > 1$ with decreasing magnitude for increasing values of $|l - k|$. And since the majority of both absorbing and perturbing molecules are in rotational states at or near the most probable value of J, there should be a somewhat larger number of absorber–perturber pairs with the same $J \cong J_{\text{max.}}$ experiencing the largest perturbation of their energy levels from these forces. This possibility should have more attention on both the theoretical and experimental sides.

Becker (3) has measured line half-widths in the first harmonic band of hydrogen chloride at 1.74μ at various hydrogen chloride pressures, using of course different experimental technique. Despite this difference in method it seems apparent that the lines of this band display a larger pressure broadening (about 0.7 cm.$^{-1}$ increase per atmosphere) than do those for the second harmonic band of hydrogen chloride as mentioned above. To explain this discrepancy one must apparently take into account the possible variation of μ with internuclear distance (18). This distance would be larger for the upper state of the second harmonic, the smaller pressure broadening for the latter then indicating a decrease in μ for hydrogen chloride for internuclear distances $r > r_e$. This would possibly answer the question of whether μ_{HCl} increases or decreases with r for r values near r_e, a question which intensity data alone cannot answer. Such variations of μ with internuclear distance make the whole problem rather complex. This could also possibly be the explanation of the fact that the lines of the water vapor bands at 9400 A.U., 11350 A.U., etc. show, according to recent results of S. D. Cornell in this laboratory, a somewhat smaller increase in line breadth with increase in vapor pressure than would be expected if the effective μ is as large as 1.87×10^{-18}.

It would seem as if further quantitative work on the pressure broadening of near infra-red bands of these and other strongly polar molecules should supply considerable information on the nature of the van der Waals forces involved. The spectra of the not too heavy molecules which have associative tendencies should receive particular attention. It should form a most sensitive means of detecting incipient association and of learning some of the details of the process.

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THE PUZZLE OF RARE-EARTH SPECTRA IN SOLIDS[1]

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It is well known that crystals of rare-earth salts are often characterized by sharp absorption or emission lines. The understanding of the precise nature of these lines, i.e., their spectroscopic classification and pedigree, is a matter of considerable interest to chemists and physicists, since these lines are intimately associated with the binding of the rare-earth atoms in the solid state, and so their analysis may provide us with information on crystalline forces. Such study is, of course, to be distinguished from that of gaseous atomic spectra, which tell us nothing about interatomic forces. Any acceptable interpretation of rare-earth solid spectra must be compatible with two other lines of evidence: (a) magnetism and (b) specific heats. The reconciliation of the different facts is far from easy, and so I have referred to the entire subject as a "puzzle" as far as existing knowledge is concerned. Practically all rare-earth salts are trivalent, so that all our questions relate to the behavior of the trebly ionized atom in solids.

It is now generally conceded, I believe, that the ground states of the trivalent rare-earth ions are of the form $4f^x$, where $x = 1$ for Ce^{+++}, 2 for Pr^{+++}, ... 13 for Yb^{+++}. Besides the very definite magnetic evidence to this effect, the recent beautiful spectroscopic work of Lang (13) shows conclusively that the ground state of the free Ce^{+++} ion is $4f\,^2F_{5/2}$, despite the fact that extrapolation by the irregular doublet law from the less enhanced spectra would appear to favor $5d$. Thus we can regard it as definite that the lower level in rare-earth absorption belongs to $4f^x$. The classification of the upper level is more of a question. There are two possibilities, which I shall term respectively the excitation and non-excitation hypotheses. In the former, the upper state belongs to a different configuration from the ground state, and is presumably often of the form $4f^{x-1}5d$ or $4f^{x-1}5g$. In the non-excitation hypothesis, on the other hand, the upper state belongs to the same configuration, $4f^x$, as does the ground state, and differs from it only in the value of the collective azimuthal

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quantum number L or in the spin S, the individual l's being the same. With the excitation hypothesis, the transition is due to ordinary dipole radiation, whereas with the non-excitation hypothesis, we have to deal with a forbidden transition, which is not allowed by the Laporte selection rule (that the algebraic sum of the individual l's must change by an odd integer (6)), but which is allowed with faint intensity if one considers quadrupole or magnetic dipole radiation, or distortion by crystalline fields. In my opinion the non-excitation hypothesis advocated by Freed (10), Tomaschek (23), and others, is the correct one in the case of the *sharp* lines, for the reasons given below.

EVIDENCE THAT THE RARE-EARTH LINES REPRESENT FORBIDDEN TRANSITIONS

According to this hypothesis, sharp lines should not be found for salts involving cerium or ytterbium, since the configurations $4f$ and $4f^{13}$ each yield one value of L, and hence one orbital level, whereas two are needed, namely, an upper and a lower level. Actually the sharp lines are missing for both the cerium and ytterbium salts. This argument has been particularly stressed by Freed (10). Of course, lines due to excited configurations should still be permitted in cerium and ytterbium, but the excited states reside on the outside of the atom, and are not sheltered from disturbing interatomic forces. Hence it is commonly supposed that they can have broad, diffuse Stark effects, and indeed intense diffuse absorption bands are found in cerium and ytterbium salts in the ultra-violet, ascribable (10) to excitation of an electron to $5d$.

A second argument is furnished by considerations of intensity. At first thought one might opine the contrary, as forbidden lines are often undetectable in gaseous spectra. However, we are dealing with the solid, the high density of which enhances the intensity by a factor a million or more, and so even feeble violations of the selection principle should give rise to perceptible radiation. Actually, the measurements of Becquerel (3) and others (23, 11) reveal in Pr^{+++} and Nd^{+++} an intensity about a millionth as great as one would expect for ordinary dipole radiation. Also it is particularly striking that in Pr^{+++} and Nd^{+++} the sharp lines in the visible do not show up at all as resonance centers in rotary dispersion, showing that their intensity is exceedingly low (11, 17). Instead the dependence on wave length is so slight that the strong centers due to $4f-5d$ must be far out in the ultra-violet.

We must, however, mention that the opposite interpretation, the excitation hypothesis, is maintained by Spedding (21). His most telling argument is perhaps that chromium and other salts of the iron group show sharp structures despite the fact that here the $3d$ electrons are to a considerable extent on the outside of the atom, and so not sheltered from interatomic fields. Hence mere sharpness does not imply interior location of the orbit. A possible, though admittedly only conjectural, answer is that the spectroscopic manifestations of the coupling between vibration and electronic motion may be more complicated when there is a change in electron configuration. In diatomic spectra, for instance, electron bands show much more prolific vibrational structure than do vibration bands in which the electron structure does not change. Conceivably there is a similar situation in the complexes found in solids. The sharp lines in chromium, etc., are due to forbidden transitions $3d^3 - 3d^3$ not involving a change in electron configuration, and so could be sharp according to this idea.

POSSIBLE CAUSES OF NON-VANISHING INTENSITY FOR THE FORBIDDEN TRANSITIONS

Why should the forbidden lines be visible at all, faint though they may be? There appear to be the following alternative explanations: (I) quadrupole radiation; (II) magnetic dipole radiation; and (III) electric dipole radiation, caused by distortion of the electronic motion by the crystalline fields, so that the selection rules for the free atom no longer apply. III differs in this respect from I and II, as I and II are effects characteristic even of free atoms. Not all crystalline fields are adequate to produce III. It is necessary that the field not have a center of symmetry, i.e., not be holohedral, as otherwise the wave functions would retain their even-odd classification as regards reflection in the origin, and the Laporte rule that only even and odd terms can combine (i.e., that $\Delta\Sigma_i l_i$ must be an odd integer) would remain rigorous. Even if there is a center of symmetry at the equilibrium position, obviously this property is lost when the atom starts vibrating, as is shown in figure 1. One can therefore distinguish between the two following forms of III: (IIIa) The crystalline field does not have a center of symmetry even at the equilibrium position; (IIIb) The departures from holohedral symmetry are due entirely to atomic vibration.

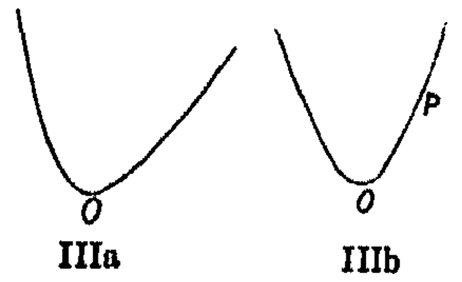

FIG. 1. In IIIa, the potential curve is unsymmetrical with respect to the equilibrium position O of the nucleus. In IIIb, there is symmetry with respect to the nucleus as origin if it is at O, but not if vibration carries it to some other point P.

It is of interest to ascertain whether I, II, IIIa, or IIIb is the proper explanation, as information is thereby communicated as to the nature of the interatomic forces, vibrational coupling, etc. Perhaps all the causes enter at the same time, and the spectrum is obviously then of great complexity. One would like a detailed x-ray analysis of the positions of the individual atoms in the rare-earth crystals, as this would definitely tell us to what extent the crystalline field has a center of symmetry at the equilibrium position of the rare-earth atoms. Unfortunately, it appears impossible to obtain this information, as x-ray experimentalists cannot locate the hydrogen and oxygen atoms because of their light masses. In the case of $Sm_2(SO_4)_3 \cdot 8H_2O$, Zachariasen (25) has located the position of the samarium atoms by x-ray analysis, and their arrangement is such that there cannot be holohedral symmetry as far as the part of the crystalline field due to Sm–Sm forces is concerned. However, this is not the important part, as the samarium atoms are at large distances from each other because of the intervening waters of hydration. More important are the forces due to nearby oxygen atoms, and conceivably they may be grouped with nearly perfect cubic symmetry. Crystals like $Sm_2(SO_4)_3 \cdot 8H_2O$, to be sure, belong to the monoclinic system, for which a center of symmetry is not to be expected, but this fact does not preclude the symmetrical clustering of oxygen atoms about the samarium atom. It is thus conceivable that the hemihedral portion of the crystalline field results entirely from distant atoms and is of subordinate importance.

It is sometimes convenient to expand the crystalline potential $V_{\text{crys.}}$ in terms of the displacement x_i, y_i, z_i of a typical 4*f* electron from the equilibrium position of the nucleus, so that

$$V_{\text{crys.}} = \Sigma_i\{A_0 + A_1x_i + B_1y_i + C_1z_i + A_2x_i^2 + B_2x_iy_i + C_2y_i^2 + \cdots + A_3x_i^3 + \cdots + A_4x_i^4 + B_4x_i^3y_i + \cdots\} \qquad (1)$$

or in polar coördinates

$$V_{\text{crys.}} = \Sigma_i\{A_0 + r_if_1(\theta_i, \varphi_i) + r_i^2f_2(\theta_i, \varphi_i) + r_i^3f_3(\theta_i, \varphi_i) + \cdots\} \qquad (2)$$

where the summation is to be taken over all of the 4*f* electrons in the atom. The expression 1 or 2 is a sort of Hartree potential for the electron, except that now the field is due to the entire crystal rather than simply the single atom itself. If the field has a center of symmetry, the odd powers in *r* are absent.

ALLOWED TRANSITIONS

The transition probability for ordinary electric dipole radiation is (4)

$$\sigma = 64\pi^4e^2\nu^3q^2/3hc^3 \qquad (3)$$

where ν is the frequency of the radiation in question, and q is the matrix amplitude for the transition. If it is an allowed one, q^2 is of the order of magnitude of the mean square radius r^2 of the orbit, given by

$$r^2 = \iiint \psi^2 r^2 dv \qquad (4)$$

To estimate the expression 4, we use a $4f$ wave function

$$\psi = Ar^3 e^{-Zr/4a_0}$$

for a hydrogenic atom of effective charge Ze. Here a_0 has its customary significance

$$a_0 = h^2/4\pi^2e^2m$$

The value of Z is to be so determined as to yield the proper binding energy. This energy is known for the $4f$ state only in Ce^{+++}, where (13) it is 296,197. cm.$^{-1}$ The corresponding value of Z is 6.6, and equation 4 yields

$$r = (360\ a_0^2/Z^2)^{\frac{1}{2}} = 1.53 \times 10^{-8}\ \mathrm{cm.}^{-1} \qquad (5)$$

If ν is 20,000 cm.$^{-1}$, the approximate value for visible light, one then has

$$\sigma = 1.3 \times 10^8\ \mathrm{sec.}^{-1} \qquad (6)$$

We now proceed to estimate the rough magnitude of the transition probability σ for various types of forbidden transitions.

FORBIDDEN TRANSITIONS

I. Quadrupole radiation

For a quadrupole transition, the expression which replaces expression 6 is (4)

$$\sigma_{\mathrm{I}} = 32\pi^6\nu^5e^2Q^2/5hc^5 \qquad (7)$$

Here Q is the "quadrupole amplitude", which is comparable dimensionally with the mean square radius of the orbit. However, the numerical factors which cannot be estimated from dimensional considerations are more important than in the dipole case. Namely, examination of the more precise formulas for Q given, for instance, in Condon and Shortley's[2] book shows that for a $4f \rightarrow 4f$ transition, Q^2 is usually considerably smaller than r^4 as defined in equation 4, and is sometimes even less than $r^4/100$. We shall therefore for our qualitative purposes take

$$Q^2 = r^4/10 \qquad (8)$$

Then if $\nu = 20{,}000$ cm., expression 7 becomes

$$\sigma_{\mathrm{I}} \sim 4\ \mathrm{sec.}^{-1} \qquad (9)$$

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[2] Reference 4, pp. 252–5; the important fact is that on p. 255 the quantity G of Condon and Shortley is considerably smaller than their S_3/e, which corresponds to our r^2.

II. Magnetic dipole radiation

Besides ordinary electric dipole radiation, there can also be magnetic dipole radiation (5), which, unlike the former, connects states of similar Laporte symmetry. The resulting transition probability is

$$\sigma_{II} = 64\pi^4\nu^3M^2/3hc^3 \tag{10}$$

where M is the matrix element of the magnetic moment connecting the states in question. If we neglect spin-orbit interaction, the matrix elements M will vanish except between components of the same multiplet, whereas we require them to exist between different multiplets. For example, in Pr^{+++} there are elements joining $f^2\,{}^3H_4$ and $f^2\,{}^3H_5$, but not $f^2\,{}^3H_4$ and $f^2\,{}^1G_4$. There will, however, be elements of the desired type if we allow for spin-orbit interaction, which prevents L and S from being rigorously "good quantum numbers". The resulting values of M are of the order of magnitude $\alpha\beta$, where β is the Bohr magneton $he/4\pi mc$, and α is the portion of the wave function which is of extraneous L or S. The order of magnitude of α is $\Delta\nu/\nu$, where $\Delta\nu$ is the multiplet width and ν is the interval between different multiplets. A reasonable estimate of α seems to be 1/10, as $\Delta\nu$ is between 1000 and 10,000 cm.$^{-1}$, while ν is between 10,000 and 100,000 cm.$^{-1}$ Then expression 10 becomes

$$\sigma_{II} \sim 2 \text{ sec.}^{-1} \tag{11}$$

Comparison of expressions 9 and 11 shows that there is not much difference in the importance of quadrupole and magnetic dipole radiation. The situation is thus quite different from that in light atoms like oxygen, where the magnetic radiation is less significant because the spin-orbit interaction is much smaller than in the rare earths (5).

III. Electric dipole radiation due to distortion by crystalline fields

As already stated, the interatomic forces in solids create a non-vanishing transition probability σ_{III} even for forbidden lines if the crystalline fields make the wave functions lose their rigorous even-odd classification. A typical wave function for the ion in the crystal may be expressed as a linear combination

$$\psi = \psi_0^g + \Sigma_i a_i\psi_i^g + \Sigma_i b_i\psi_i^u \tag{12}$$

of the wave functions ψ_i of the free ion. The superscripts g and u denote respectively even and odd Laporte symmetry, and the sums are respectively over all the even and odd atomic states, which together yield a complete orthogonal set of wave functions. For simplicity, we have supposed that there are an even number of electrons, so that the original unperturbed wave function ψ_0 for the given $4f^n$ state is even. The order of magnitude of the amplitude q involved in expression 3 is

$$\int \psi' x \psi'' dv = \Sigma_i \{\int \psi_0^{g\prime} x b_i'' \psi_i^u dv + \int b_i' \psi_i^u x \psi_0^{g\prime\prime} dv\}$$
$$\sim b_i \int \psi_i^g x \psi_j^u dv \sim b_i r \quad (13)$$

Here we have made use of the fact that a matrix amplitude for an allowed transition connecting an even and odd state is comparable with the quantity r defined in expression 4. Perturbation theory shows that $b_i = V_{\text{hem.}}/h\nu'$, where $V_{\text{hem.}}$ is a matrix element of the hemihedral part of the crystalline field, i.e., the portion which does not contain a center of symmetry. The formula for the transition probability becomes

$$\sigma_{\text{III}} \sim (64\pi^4 e^2 \nu^3 r^2/3hc^3)(V_{\text{hem.}}/h\nu')^2 \sim \sigma_{\text{allowed}}(V_{\text{hem.}}/h\nu')^2 \quad (14)$$

Here ν' must not be confused with ν, and is the frequency interval separating $4f^s$ from excited states of opposite Laporte symmetry. Its order of magnitude is $\nu' \sim 10^5$ cm.$^{-1}$

IIIa. Naturally unsymmetrical fields

First let us consider fields which do not have a center of symmetry even at the equilibrium position. Such fields are doubtless somewhat smaller than the main portion of the crystalline field, so we take $V_{\text{hem.}} \sim 10$ cm.$^{-1}$ Then expression 14 gives

$$\sigma_{\text{IIIa}} \sim 1 \text{ sec.}^{-1} \quad (15)$$

IIIb. Dissymmetry caused by vibration

In expression 1, x_i, y_i, z_i are the coördinates of the electron relative to an origin taken at the equilibrium position of the nucleus. Evidently if the nucleus vibrates, we have

$$x_i = x_i' + X, \qquad y_i = y_i' + Y, \qquad z_i = z_i' + Z \quad (16)$$

where x_i', y_i', z_i' are the coördinates of the electron relative to the moving nucleus, and X, Y, Z are those of the nucleus relative to its equilibrium position. If the crystalline field has a center of symmetry, expression 1 will contain no odd powers of x_i, y_i, z_i, i.e., no terms of the form $x_i^s y_i^t z_i^u$, where $s + t + u$ is an odd integer. However, when the substitution (16) is made, odd powers of x', t', z' will appear. Then expression 1 becomes

$$V_{\text{crys.}} = \text{even terms in } x_i' y_i' z_i' + \Sigma_i \{2A_2 x_i' X + 2B_2 y_i' Y + \ldots$$
$$+ 4A_4 x_i'^3 X + \ldots\} \quad (17)$$

The breakdown of the Laporte selection rule is contingent upon the existence of odd powers of x_i', y_i', z_i' rather than of x_i, y_i, z_i, as the relevant symmetry is for the reflection in the nucleus as origin. The odd part of expression 17 is clearly of the order of magnitude R/r compared with the main, even crystalline potential, which we will denote by $V_{\text{hol.}}$. Here R

is the root mean square amplitude of nuclear vibration, and r is defined as in expression 4. So in expression 14 we now take

$$V_{\text{hem.}} \sim (R/r)\, V_{\text{hol.}} \tag{18}$$

To estimate R, we use the relation

$$2\pi^2\mu\omega^2R^2 = \tfrac{1}{2}\, hv\omega \tag{19}$$

where ω is the vibration frequency, v is the vibrational quantum number, and μ is the effective reduced mass for the vibrating cluster (SmO_6, PrO_6 etc.). Now μ is comparable with the mass m_r of the rare-earth ion, so that we shall replace μ by m_r. In fact, μ would be identical with m_r if the oxygen atoms were rigidly connected to the rest of the crystal, so that they could not move. Actually, the connection is sufficiently stiff so that for local modes of vibration μ is closer to m_r than, say, the mass of six oxygen atoms. If we take $\omega \sim 100$ cm.$^{-1}$, $V_{\text{hol.}} \sim 100$ cm.$^{-1}$, then by expressions 19, 18, and 14 we have $R = \frac{1}{2} \times 10^{-9}$ cm., and

$$\sigma_{\text{IIIb}} \sim \tfrac{1}{10}\ \text{sec.}^{-1} \tag{20}$$

COMPARISON WITH EXPERIMENT

The transition probabilities observed by Becquerel and others in praseodymium and neodymium are of the order 10 to 100 sec.$^{-1}$ Our estimates of intensity due to any of the four causes I, II, IIIa, IIIb (equations 9, 11, 15, 20) all agree sufficiently with observation, as our calculations, admittedly rough, may easily be in error by a factor of 10 or 100. Much greater precision does not appear feasible at present, as it would require not only better knowledge of the wave functions of free rare-earth ions than now available, but also unknown exact information on the distortion of the outer orbits by the crystalline field. The one safe conclusion is that no one of the alternatives I, II, IIIa, IIIb can at present be ruled out on the basis of intensity, although IIIb does appear rather faint. Possibly lines exist due to all the causes; if so, one can readily see why the spectral phenomena observed by Spedding always present a more complicated front than do the magnetic data. More exact knowledge of crystalline forces can alone determine whether the hemihedry is really as important as assumed in IIIa. Decision between the various alternatives will probably be possible only when a detailed spectroscopic classification and Zeeman data become available for the various energy levels in the solid spectrum.[3] Then one can tell whether the effective selection rules and the Zeeman patterns are characteristic of quadrupole radiation, magnetic dipole

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[3] Tentative attempts at classifying rare-earth spectra in solids have already been made by Tomaschek (Physik. Z. **33**, 878 (1932)) and by Ellis (Phys. Rev. **49**, 875 (1936)); the subject, however, seems to be still in an uncertain state.

radiation, or neither, and whether there is coupling to the vibrational structure of the type demanded by IIIb, which will be described more fully below. With the quadrupole hypothesis I, changes of more than two units in L or J are forbidden (also $J = 0 \rightarrow J = 0, 1$; $L = 0 \rightarrow L = 0, 1$). With magnetic dipole radiation L or J cannot change by more than one unit (also $J = 0 \rightarrow J = 0$, $L = 0 \rightarrow L = 0$ are absent). No such exclusions are found according to IIIa or IIIb. If the fourth-order terms in the potential (1) are the important ones, then changes of L or J are permitted up to and including 5 units[4] according to IIIa and 4 units according to IIIb.

THE SPECIAL CASE OF GADOLINIUM, EUROPIUM, AND TERBIUM: INTERSYSTEM COMBINATIONS

In gadolinium, the ground state $f^7\,{}^8S$ is the only octet belonging to the configuration f^7. In europium and terbium, the ground level is the only septet of f^6 or f^8. Hence the lines for these ions must be intersystem combinations as well as forbidden by the Laporte rule. They can hence exist only in virtue of spin-orbit interaction. The estimates (9, 15, 20) of intensity due to I, IIIa, IIIb must consequently all be reduced by a factor $\alpha^2 \sim 1/100$, and become respectively 10^{-2}, 10^{-2}, 10^{-3} sec.$^{-1}$ For explanation of the factor α see the discussion in connection with equation 10. No reduction is necessary in our estimate of 2 sec.$^{-1}$ for magnetic dipole radiation, as equation 11 already includes the factor α^2. Magnetic dipole radiation thus appears somewhat more important than the other causes in gadolinium, europium, and terbium. Similar remarks apply to lines in any other rare earths that are intersystem combinations.

THE MYSTERY OF THE EXTRA LEVELS

Many of the levels reported by Spedding (20) seem to fit rather well into the general scheme of the crystalline field. In some cases, however, there are states which cannot possibly be interpreted as Stark levels, for more levels would be required than could be obtained by a crystalline field of whatsoever symmetry. A notable example is samarium, where levels are found by Spedding (19) at 0, 160, 188, 225, and perhaps 245 cm.$^{-1}$, although group theory shows that because of the inevitable Kramers (12) twofold degeneracy the ${}^6H_{5/2}$ state characteristic of the normal Sm^{+++} ion cannot possibly split into more than three levels under the influence of a crystalline field. Also levels are reported (18) at 0, 37, 53, 79 cm.$^{-1}$ for

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[4] Changes by five units are possible because a fourth-order field mingles states differing in L or J by up to four units, and this mixing effect is to be added to the unit changes permitted in ordinary free dipole radiation. With IIIb the permitted changes are one unit less, because only third-order terms in x', y', z' will appear in the odd part of 17, when expression 1 is of the fourth order in x, y, z.

$GdCl_3 \cdot 6H_2O$, and at 0, 21, 41 cm.$^{-1}$ for $Eu_2(SO_4)_3 \cdot 8H_2O$ (15), although an S state (^8S ground state of Gd^{+++}) doubtless does not split appreciably and a state with $J = 0$ ($^7F_0$ ground state of Eu^{+++}) manifestly can have only one component. There are three possible explanations of the extra levels.

1. They may be purely spurious, and due to some sort of a misclassification.

2. Some excited state may be depressed in energy so that it is comparable energetically with Stark components of the ground state. Following Spedding, we shall term such a potential deep-lying excited state an electronic isomer. In Sm^{+++} the isomer would presumably be some multiplet component of ^6H with $J > \frac{5}{2}$, and in Eu^{+++} some component of ^7F with $J > 0$.

3. The extra levels are somehow to be identified with vibration. By this we do not mean that any of the levels are purely vibrational, but rather that there is a certain interplay between vibrational and electronic motion, making the vibrational levels partake a little of the nature of crystalline Stark levels, and *vice versa*, so that the distinction between the two is lost. The agreement between observed and computed magnetic susceptibilities will not be destroyed, as one can show that both the specific heat and paramagnetic susceptibility are nearly the same as though the interplay were forgotten.

We shall not examine possibility 1, as it involves appraisals of spectroscopic technique and empirical analysis into energy levels which we do not feel competent to make. Also it seems to be belied by the consistency with which extra levels are reported. The alternative 2 is entirely incompatible with magnetic data,[5] as well as with recent work on the spectra of free rare-earth ions. Recent spectroscopic measurements by Albertson (2) on configurations of Sm, Sm^+ which differ from Eu^{+++} only by addition of one or two unimportant $6s$ electrons, show that the multiplet intervals assumed by Miss Frank in her magnetic calculations (9) on Eu^{+++}, which were made before the spectroscopic data were available, are substantially correct.[6] Analogous information is not yet available for Sm^{+++}, but analogy to Eu^{+++} leaves but little doubt that the multiplet intervals assumed by Miss Frank in Sm^{+++} are also reasonable, and that there is no low-lying electronic isomer.

We must, however, mention that specific heat data, if we can rely on them literally, would seem to indicate that the extra levels are due to some kind of electronic isomer rather than to vibration. Ahlberg and Freed (1) have assumed that vibrational effects cancel out in comparing the specific heats of gadolinium and samarium salts, so that their difference records

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[5] For a general discussion of the magnetism of the rare-earth group see Chap. IX of reference 24, also references 16 and 9.

[6] This point will be discussed more fully in a future paper by Miss Frank.

the purely electronic contribution. The measured difference agrees better with the assumption of four than three crystalline levels, whereas we have seen that not more than three are permitted unless an electronic isomer is introduced. However, the agreement with three levels is fair,[7] and the differential specific heat is hard to measure accurately, as it is very small relative to that of either gadolinium or samarium. For instance, C_p is 60 cal. per mole at 100°K. for $Gd_2(SO_4)_3 \cdot 8H_2O$, and 62.2 for $Sm_2(SO_4)_3 \cdot 8H_2O$, whereas the difference is only 2.2. Quite apart from possible experimental error, it is conceivable that the vibration frequencies of the two salts may be slightly unlike, more than one would conjecture from the mere mass difference in the cation. The perturbation effect discussed in fine print below gives rise to precisely this situation. So it seems dangerous to draw definite conclusions from specific-heat data at the present time.

Our preference is for possibility 3, in which coupling between vibration and electronic motion is hypothecated. It will be realized if our effect IIIb is the proper explanation of the intensity of some of the lines. Namely, if we use I, II, or IIIa to account for the intensity, the strong lines are those in which the vibrational quantum number is unaltered. With IIIb it is easily seen (see below) that the most probable transitions are those in which the vibrational quantum number v changes by one unit. The observed frequencies are then not ν_0, but rather $\nu_0 \pm \omega$, where ω is the vibrational frequency, and ν_0 is the frequency which would be obtained were the vibrational part of the energy neglected. In this event, the electronic energy levels cannot be obtained correctly without allowing for the vibrational modulation, and when allowance is not made for this fact, vibrational levels may be misinterpreted as crystalline levels. We do not believe that IIIb is the main cause of intensity, but it is quite possible that some radiation of this type is mixed in with the others, just enough to cause confusion and give the apparent extra levels.

To prove that in IIIb the effective frequencies are $\nu_0 \pm \omega$ rather than ν_0, we note that in equation 17 the terms which are odd in x, y, z and which are needed to break down the Laporte rule are linear in the vibrational coördinates X, Y, Z. (Higher powers of X, Y, Z would be smaller and hence less important.) The non-vanishing matrix elements of X, Y, Z involve changes of one unit in the appropriate vibrational quantum number (which is in general different for X, Y, and Z). Hence the significant part of equation 17 couples together states differing by one unit in v. Consequently the odd part of equation 12 is composed of terms differing by one unit in v from the main even part ψ_0^0. Now since x', y', z' are diagonal operators in v, a non-vanishing value of the transition amplitude 13 is obtained only if the odd part of ψ' contains terms of the same vibra-

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[7] Cf. figure 4 of Miss Frank's second paper (9).

tional quantum number as the main part of ψ'', or *vice versa*. Hence ψ_0' must differ by one unit in v from ψ_0''. The situation may be likened in some ways to that in radiation theory. Just as in the latter the coupling of the electronic motion to the ether causes electron transitions to be accompanied by changes of one quantum unit in the radiation harmonic oscillators, so in our theory the vibration-rotation coupling causes transitions to be accompanied by changes of one unit in the vibrational quantum number.

There may also be the following effect, which may be regarded as a variant of IIIb. It is well known that in the band spectrum of carbon dioxide, there is a resonance effect (7,8), whereby two close-lying levels share their properties with each other, owing to perturbing matrix elements connecting them. In consequence the two states, so to speak, lose their identity. In this way, both of them are able to combine with other states by means of the same selection rules and be manifested in the Raman effect, whereas without the perturbation, only one of the two levels would be detectable. Similarly in our case it may happen that a vibrational level (for example, a level in which one quantum of vibration is excited) happens to fall very near a crystalline Stark level in which no vibration is excited. If there is appreciable perturbation coupling connecting the two levels, then obviously they can make the same combinations with other states. In this way the number of apparent crystalline Stark levels is doubled as far as spectroscopic observation is concerned.

We are thus led to investigate when there can be appreciable matrix elements connecting a vibrational and a Stark state. The requisite perturbing potential must be linear in the vibrational coördinates, as higher powers are too small to be important. The connected levels then differ by one unit in some vibrational quantum number. The perturbing potential must be even in x_i', y_i', z_i', as two different Stark components of the same electronic level have the same Laporte parity. It thus might seem that only a hemihedral crystalline potential could be effective, as odd powers of x_i, y_i, z_i give rise to even powers of x_i', y_i', z_i' and *vice versa*, when one makes the substitution $x = x_i' + X$, etc., and retains only linear terms in X, Y, Z. If $V_{\text{hem.}} \sim 10$ cm.$^{-1}$, the matrix elements thus arising are of the order $V_{\text{hem.}}(R/r) \sim$ 0.3 cm.$^{-1}$, and hence too small to be important. This conclusion, however, is on the basis of a "one-atom treatment," wherein only the paramagnetic ion vibrates. If instead the whole cluster (e.g., SmO_6) is included as a dynamical unit, it can be shown that certain modes of vibration give rise to even terms in x_i', y_i', z_i' regardless of whether the potential has a center of symmetry. Our considerations on this subject, to be amplified elsewhere, are closely related to those which were presented in a rather different connection and terminology by Jahn and Teller at the April, 1936, meeting of the American Physical Society. In consequence there can be matrix elements of the order $V_{\text{hol.}}(R/r) \sim 3$ cm.$^{-1}$ Levels separated by such an amount will lose all their identity, and those separated by ten times this amount will become sufficiently mixed so that combinations permitted for one level will also be allowed for the other with an intensity about 1/100 as great.

DIGRESSION ON THE IRON GROUP

Our discussion has been intended primarily for the rare earths, but can easily be adapted to the study of the sharp lines emitted by chromic salts and other salts of the iron group in the solid state. The main difference is that the crystalline potential is about one hundred times larger, and so the estimate 20 of the transition probability IIIb must be increased by a factor 10^4. There are no great changes in the estimates 9 and 11 for quadrupole and magnetic dipole radiation. The careful x-ray analysis of Lipson and Beevers (14) shows that in chrome potassium alum, the field surrounding the chromic ion has a center of symmetry, so that here hypothesis IIIa must be discarded. Because of the large crystalline field, the resonance effect discussed above is adequate to merge two levels separated by 300 cm.$^{-1}$ or so. Perhaps this fact may explain the apparent electronic isomer reported by Spedding and Nutting (22) in chrome alum at 38 cm.$^{-1}$, which is quite incomprehensible if taken literally, since magnetic data show conclusively that only one electron state is inhabited. The interaction between electronic and vibrational motion seems to furnish a clue to the understanding of the interesting Zeeman measurements (22) of these authors and of the magnetic behavior of vanadium and titanium salts, as I shall discuss elsewhere.

CONCLUSION

The sharp lines in the rare earths are forbidden lines violating the Laporte rule. They probably do not originate in any one cause, but are rather to be attributed to a variety of effects, viz., quadrupole radiation, magnetic dipole radiation, and radiation created by crystalline fields in which the requisite departures from a center of symmetry are either present at the equilibrium position or caused by atomic vibrations. It appears likely that there is some interplay between vibration and electronic motion, as otherwise it is very hard to understand the extra levels reported by Spedding.

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A COMPARISON OF SOME ULTRA-VIOLET ABSORPTION SPECTRA OF POLYATOMIC MOLECULES WITH THOSE OF DIATOMIC MOLECULES[1]

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INTRODUCTION

In solving the numerous problems in the field of molecular structure, the methods of spectroscopy must be considered as among the most powerful tools at the disposal of scientists. X-ray and electron diffraction will, at least in the case of simple molecules, furnish information concerning the geometrical distribution of nuclei in molecules in the gas phase, and the added information obtained from the facts of inorganic and organic chemistry will in most cases permit the assignment of a spatial arrangement to a given molecule. It is possible, in the case of diatomic molecules, to predict the various possible electronic states by using the method of molecular orbitals. Once the various possibilities are known, detailed spectrum analyses permit an assignment of numerical energy values to the various states. An extension of the method of molecular orbitals to polyatomic molecules has been made, so that here again the possible spectroscopic states (at least for the simple molecules) may be predicted with certainty. However, while the principles governing electronic transitions in polyatomic molecules have been formulated (10, 17), the detailed applications of these ideas have been slow, largely because of the scarcity of adequate experimental data and partly because the enormous superficial complexity of these spectra seems to preclude the assignment of a unique distribution of energy levels. Only in very few cases have rotational analyses of electronic bands of polyatomic molecules been made, and it is not probable that many more will be accomplished in the near future. The applications of spectroscopy have been confined, therefore, to Raman spectra and to the infra-red and give information only concerning the ground electron state. Attempts to correlate frequencies

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[1] Presented at the Symposium on Molecular Structure, held at Princeton University, Princeton, New Jersey, December 31, 1936 to January 2, 1937, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society.

of diatomic molecules with those observed when groups containing the same atoms are present in a polyatomic molecule (7) may be of interest in showing that force constants for the bonds are similar, but would seem to give little definite information concerning electronic states.

From an experimental standpoint the difficulties in treating polyatomic electronic spectra are obvious. Numerous possibilities of predissociation exist in a molecule with many bonds, so that in many cases even spectroscopic apparatus of a hitherto unattained resolving power might show only diffuse bands. Furthermore, with many modes of vibration the number of allowed vibration transitions may be quite large, even assuming a rigorous application of the selection rules of Herzberg and Teller. It is true, fortunately, that the Franck–Condon principle often restricts the obvious bands to a few members of one type of progression, so that spectra of an unexpected simplicity are sometimes observed. Finally, it now seems certain that very frequently the apparent complexity of these spectra is to be ascribed to a more or less complete intermixing of the bands from several different electron transitions, so that detailed analyses become very difficult. For these and other reasons the obtaining of definite information from these spectra must be accomplished by methods which are not always infallible, and which do not have their counterparts in treating diatomic molecules. We will survey in a rapid fashion the type of information which one can obtain in a few cases.

I. THE CARBONYL GROUP IN ALDEHYDES AND KETONES

The electronic structures of aldehydes and ketones have been discussed by Mulliken (18). Recently Henri (7) has contrasted prominent frequency differences observed in the ultra-violet spectra and infra-red and Raman spectra for these substances with values of ω_e for various states of carbon monoxide. He has concluded that the electron states of the latter must resemble closely those of the former.

The electronic configuration of carbon monoxide in its normal (${}^1\Sigma^+$) state is (16)

$$KK(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2$$

This configuration would resemble a Lewis structure with three electron-pair bonds between the two atoms (:C:::O:). The ω_e value for the normal state of carbon monoxide is 2168.9 (31), which does not correspond to the frequency of the carbonyl group. The low excited states of carbon monoxide may be represented probably by adding a $v\pi$ electron to CO^+ (16). The configuration of the latter in its lowest state is probably $KK(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)\ {}^2\Sigma^+$. The ω_e value of CO^+ in its lowest known state is 2211 cm.$^{-1}$, which differs but little from that of normal CO, although it is higher, indicating that the $x\sigma$ electron exerts perhaps a slight anti-bonding action. The effect of the $v\pi$ electron will be anti-bonding, and the ω_e value of CO in its lowest excited ($^3\Pi$) state (excepting the K state for which the evidence is somewhat uncertain (14)) is 1739.3. This corresponds quite closely to the carbonyl frequency observed in the infra-red and Raman spectra of aldehydes and ketones (1744 in formaldehyde, 1720 in the aliphatic aldehydes, 1710 in the aliphatic ketones. The latter figures differ by scarcely more than the experimental error among the various homologs (11)).

When one compares the electronic configuration of the $a^3\Pi$ state of carbon monoxide with the electronic configuration of formaldehyde, one notices several important differences (even aside from the difference in symbolism which is necessitated in the consideration of polyatomic molecules). If the structure given for this state of carbon monoxide is correct, there are six bonding electrons ($(y\sigma)^2(w\pi)^4$), three electrons which are essentially non-bonding ($(z\sigma)^2(x\sigma)$) and one anti-bonding electron ($v\pi$), whereas in formaldehyde the structure probably consists (18) of four carbon–oxygen bonding electrons (although these electrons and other electrons play some part in the bond and are partly carbon–hydrogen bonding), four electrons which are primarily carbon–hydrogen bonding. (although they are not all localized completely in these bonds), two electrons largely on the oxygen, which are non-bonding, and two more which are non-bonding or slightly anti-bonding (these electrons are again largely but not entirely localized on the oxygen atom). In contrast to the normal state of carbon monoxide which has a very small dipole moment (28), the carbonyl group possesses a considerable moment and the oxygen atom is quite negative (29).

Unless one says that merely by accident the effect of the anti-bonding electron so nearly counterbalances the effect of a bonding electron that in both the $a^3\Pi$ state of carbon monoxide and in the carbonyl group one has really the equivalent of a typical double bond, there seems to be little reason for believing that the bonds in the two cases are similar. The agreement between the two frequencies may not have much theoretical significance. Some further support for this point of view is found from ionization potentials. The ionization potential of carbon monoxide is 14.1 volts (30), while the electronic term value of the $a^3\Pi$ state is 6 volts (31). Therefore the ionization potential of carbon monoxide in this state is about 8 volts, which is considerably lower than that observed for aldehydes and ketones, either as convergence limits of Rydberg series or by electron impact (23, 2, 20). The negative charge on the oxygen in the carbonyl group should tend to lower rather than raise the ionization potential.

When one turns his attention to the ultra-violet absorption spectra of aldehydes and ketones, one encounters the difficulty of ascertaining which frequency differences are to be ascribed to the carbonyl group. In reality the assignment of such frequencies will have to be done in the same manner as for the Raman effect, i.e., by the accumulation of a sufficiently large body of data to render certain the comparison of the frequencies in the various homologs.

No satisfactory vibration analysis of the near ultra-violet bands of formaldehyde has yet been published, although the ideas of Gradstein (6) concerning the fluorescence may give the clue to the correct solution of the problem. Dieke and Kistiakowsky (1) have carried out a rotational analysis of six of the near ultra-violet bands. These bands are all of a type such that the electric moment is perpendicular to the axis of symmetry, but the authors state that there are bands of another type in the same spectral region, for which the electric moment is parallel to the axis of symmetry. It seems probable, therefore, that more than one upper electron state is involved, a fact that would render the attainment of a correct vibration analysis exceedingly difficult. Although the details of this analysis are still lacking, a series of prominent bands, probably forming a progression, shows a frequency difference between the first and second members of 1187 cm.$^{-1}$ (8, 9).[2] The question arises as to whether the frequency of the carbonyl group in its first excited state is nearly the same in other ketones and aldehydes.

While in all probability the carbonyl electron structure is practically the same in all ketones and aldehydes, the symmetry properties of no one of these compounds will be as simple as that of formaldehyde. The rotations of parts of the molecule such as methyl groups must be considered in any complete derivation of selection rules. Nevertheless, the upper electron states of aldehydes and ketones may be expected to have many characteristics in common, and one will expect to find progressions based on carbon-oxygen vibrations in all of their spectra. The complexity of the molecules as a whole will, however, affect the appearance of the spectra and may render the characterization of any definite frequency differences very difficult. It is undoubtedly not sufficient to take differences between absorption maxima as being necessarily characteristic frequencies of vibration in the upper state. In the near ultra-violet absorption spectra of aldehydes and ketones, relatively few substances give sharp enough bands so that any progressions (even prominent ones) can be designated with certainty.

Turning our attention again to carbon monoxide, one finds that the $a^3\Sigma$ state has a value of ω_e equal to 1182 (31). The considerable decrease in ω_e from that of the ground state may be taken to indicate that one of

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[2] Professor Kistiakowsky (private communication) states that this difference is observed also in D_2CO.

the strongly bonding electrons has been excited to an anti-bonding orbital. This state is probably based on that of the ion

$$KK(z\sigma)^2(y\sigma)^2(w\pi)^3(x\sigma)^2\ {}^2\Pi$$

The additional electron may be $(v\pi)$ in carbon monoxide $(a^3\Sigma)$, thus weakening the bond. The decrease in frequency from 1700 to less than 1200 in the carbonyl group upon excitation indicates that a bonding electron is also involved in this transition. Here again, however, there does not seem to be a very close resemblance between the electron state of the carbonyl group and that of carbon monoxide.

In the far ultra-violet aldehydes and ketones again show characteristic absorption, but the data in this region are relatively scarce. Detailed data on formaldehyde in the long-wave Schumann region have not been published, although the spectrum has been photographed by Price (23). However, other ketones and aldehydes have been photographed in this region of the spectrum. All or nearly all of them show a frequency difference between prominent bands of approximately 1200 cm.$^{-1}$, and although the values are not as constant as those obtained by the Raman spectrum for the carbonyl group, it seems probable that this is a frequency characteristic of carbonyl compounds in excited electronic levels. In a few compounds another frequency of about 1050 cm.$^{-1}$ is also noticed. This may possibly be another carbonyl frequency, indicating perhaps that more than one upper electron state is involved in the bands between 1800 and 2000 A.U.

It seems probable, therefore, that the carbonyl frequency for the bands in the long-wave Schumann region is little different from that for the upper state of the near ultra-violet bands. The absorption coefficients for these compounds in the region 1800 to 2000 A.U. are very much higher than in the near ultra-violet, although not as high as for bands at still shorter wave lengths. It is not impossible that these are allowed transitions, but involving essentially the same bonding electron as in the near ultra-violet. The bond strength in any case seems to be about the same for the two upper states.

At still shorter wave lengths carbonyl compounds show still further electron transitions, some with exceedingly high probabilities, as evidenced by the fact that the absorption coefficients are in general very high. Some frequency differences might possibly be ascribed to the carbonyl group, but detailed analyses of these spectra are lacking. In at least two cases Rydberg series have been found (23, 2, 20), predicting ionization potentials between 10 and 11 volts, in good agreement with electron-impact values. Ionization results undoubtedly from the removal of a $2p_yb_2$ non-bonding oxygen electron. It is significant, perhaps, that the bands forming the Rydberg series are, in general, unaccompanied by bands separated by frequencies which could reasonably be ascribed to the carbonyl group. Excitation of the non-bonding electron should affect the bond strengths and interatomic distances relatively little (unless it goes into a bonding or anti-bonding orbital), and hence an application of the Franck–Condon principle would lead to the prediction of the greatest intensities in the 0,0 bands.

TABLE 1

Frequencies characteristic of the carbonyl group

COMPOUND	FREQUENCY IN GROUND STATE (RAMAN OR INFRA-RED)	UPPER STATE FREQUENCY (NEAR ULTRA-VIOLET)	UPPER STATE FREQUENCY (ABOUT 1900 A.U.)	REFERENCES
CO	(2167.4) ($^1\Sigma^+$) (1739.3) ($a^3\Pi$)	(1182) ($a'^3\Sigma$)	(1182) ($a'^3\Sigma$)	(31)
H_2CO	1744	1187		(11, 8, 9)
CH_3CHO	1715	1150*	(1160)	(11, 5, 27)
CH_3COCH_3	1706	1198 (?)	1192 1052 (?)	(11, 21)
$CH_3COC_2H_5$	1711	†	1281 (may be 1187)‡	(11, 4)
Cyclopentanone	(1715)		1245	(27, 26)
Cyclohexanone	1714		1160	(19, 26)

* This frequency is obtained as the first difference between peaks on a microphotometer curve. There is no assurance that it represents the difference between the zero and first vibration levels of the upper state. The same may be said for other aldehydes and ketones in the near ultra-violet, with the exception of formaldehyde and acetone.

† This substance shows no discrete structure in the near ultra-violet, although a careful search for such structure was made in this region. However, it does show a strong fluorescence which would indicate the presence of such a structure. A study of this fluorescence may furnish a clue to the problem.

‡ The band chosen as the 0,0 band for this substance apparently consists of three parts with a maximum separation of about 100 cm.$^{-1}$

Note: Eastwood and Snow (5) have measured the absorption spectra of several aliphatic aldehydes in the near ultra-violet and, by averaging frequency differences between maxima for each substance, have shown that there is a prominent frequency characteristic of all of these compounds varying between 1021 and 1107 cm.$^{-1}$ This method of averaging frequency differences in a progression will, of course, give an average lower than the difference between the first two members. Moreover, differences between absorption maxima need not correspond to a definite difference in frequency in either the upper or lower states.

In table 1 one finds a summary of some of the data concerning the frequencies most properly ascribed to the carbonyl group. Carbon monoxide has been included for comparison, although, as pointed out, the electron states of this molecule are not related too closely to those of the carbonyl group.

From the summary presented in table 1 we find that, whereas the frequency of the carbonyl group is not as constant from one compound to another in upper electron states as it is in the ground state, nevertheless there is a frequency in the neighborhood of 1200 cm.$^{-1}$ which is probably to be ascribed to a carbon-oxygen valence vibration in the upper electronic level.

It is rather surprising that the difference in intensity distribution should be so marked between the two states, since the frequency, and hence the force constants, are approximately the same in both upper states. In the near ultra-violet the intensities are low on the long wave end and increase in a progression, while in the region about 1900 A.U. the bands taken as the 0,0 bands are the most intense, and the progressions contain only about four members at most before a region of almost complete transparency is encountered. An application of the Franck-Condon principle would indicate that the two upper configurations have quite different dimensions in the vibrationless state. The products of photochemical reaction (at least in the case of acetone (13)) seem to be identical for the two regions of absorption but, as pointed out by Mulliken (18), this fact seems to have relatively little bearing on the problem at hand. No precise assignment of electronic structures to the upper states is possible. Both involve the change of a bonding electron, but probably in the near ultra-violet the electron involved has much more influence on the carbon-hydrogen or carbon-carbon bonds than does the electron involved at 1900 A.U.

In conclusion, it seems to be a coincidence without any particular theoretical implications that the frequencies of the carbonyl group agree fairly well with those of certain states of carbon monoxide, although this point of view may be altered as more is known about the states in question.

II. OTHER GROUPS

In the Raman spectra of compounds possessing typical double bonds between atoms of elements in the first period of the periodic table (carbon, nitrogen, and oxygen especially), one always finds a frequency of the order of magnitude of 1600 to 1700 cm.$^{-1}$ Examples are the typical carbon-carbon double bond frequency near 1660 or 1670 (12) and the carbonyl group mentioned above. It is not surprising that one of the states of C_2 should have a frequency near this figure. In fact the ground state $(A^3\Pi_u)$ has an ω_e of 1642 (32). The electron configuration of this state bears some resemblance to that of carbon atoms in the double bond, but the correspondence is not 1 to 1. The bond strength would not be expected to be identical with that observed in unsaturated hydrocarbons. Ultra-violet absorption spectra of quite a number of unsaturated hydrocarbons have been investigated, but detailed vibration analyses have not been made. In ethylene (24) an upper state frequency of about 1340, which may be a carbon–carbon frequency, has been observed. In the *cis*- and *trans*-dichloroethylenes frequencies between 1400 and 1450, probably characteristic of the double bond, have been found (15). None of the known spectroscopic states of C_2 has ω_e values near these figures, although theoretically additional states are capable of existence, some of which might conceivably have such frequencies. In any case there is no basis at present for a correlation of the spectroscopic states of C_2 with those of the carbon–carbon double bond.

The upper state frequency of 1000 to 1100 cm.$^{-1}$ observed (4) in organic compounds containing the —N=O group (25) is relatively close to that of nitric oxide in the $B^2\Pi$ state (33).

Triple bonds between atoms of these elements give rise to frequencies in the neighborhood of 2100 and 2200 cm.$^{-1}$ Examples are the frequency of the ground state of carbon monoxide referred to above, the frequency 1975 in acetylene, the frequencies between 2089 and 2201 observed in HCN, ClCN, BrCN, and ICN, respectively, and the frequency 2224.1 in nitrous oxide (34). In acetylene an upper state difference of about 1760 (24) is observed, which lies in the region of double-bond frequencies and does not differ greatly from the ω_e of one of the states of C_2 ($B^3\Pi_g$). In hydrogen cyanide the upper state frequency of about 900 (23) (which may possibly not be a bond-stretching frequency) does not correspond to that in any of the known states of CN. The same may be said for nitrous oxide, where the upper state difference of about 550 is too low for a bond-stretching frequency (3). This molecule may possibly not be linear in the upper state.

In conclusion, therefore, it seems quite evident that the correlation between electron states and frequencies of diatomic molecules and the same atoms when they form a group in a polyatomic molecule cannot be carried very far, although some more or less accidental agreements in frequency are observed. However, characteristic frequencies of groups are obtained for upper electron states just as they are for the ground states as observed in Raman and infra-red spectra.

SUMMARY

1. The electron states of carbon monoxide and of the carbonyl group are contrasted and the dissimilarities pointed out. The agreement between the frequencies probably does not indicate that the types of bond are identical.

2. The frequencies of certain other characteristic bonds in the normal and excited electron states are compared with those of diatomic molecules. Little accurate experimental information is available, but the correlation cannot be carried very far.

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ON THE ULTRA-VIOLET ABSORPTION SPECTRUM OF DIBORANE[1]

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Much attention has been paid recently to the structure of the B_2H_6 (diborane) molecule. Particularly Mulliken (2) has discussed in considerable detail the electronic structure of this molecule. By the courtesy of Professor Stock of the Technische Hochschule in Karlsruhe we obtained a very pure sample of this gas and have investigated its ultra-violet absorption spectrum down to about 1550 A.U.

EXPERIMENTAL

For experiments in the ordinary ultra-violet a quartz tube 15 cm. long with flat windows fused on to each end was used. In the Schumann region this was replaced by a quartz tube of 20 cm. length with extremely thin hemispherical quartz windows (4) fused on to it, which are transmittant down to 1550 A.U.

The first tube was sealed off after it had been filled in the Karlsruhe laboratory with the pure gas at approximately atmospheric pressure. For comparison spectrograms the gas could be frozen out in a side tube. The second tube was arranged in such a way that the gas could be continuously streamed through it during the exposure, going from one trap to another of suitable temperatures. The pressure used in this case varied from 0 to 40 mm. Precautions were taken to avoid contamination of the pure sample obtained from Professor Stock. Mercury valves were used to avoid contact with stopcock grease, and the quartz tube was joined to the glass apparatus by way of long ground joints not greased but only covered with picein outside.

A hydrogen discharge tube served as source of continuous background for the absorption experiments.

The ordinary ultra-violet spectrum down to 1900 A.U. was investigated with high dispersion (3rd order of the Darmstadt 3m grating, dis-

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persion 1.7 A.U. per millimeter). The Schumann region could only be investigated with the small dispersion of a Cario-Schmidt-Ott fluorite spectrograph (1) (dispersion at 1800 A.U. equal to 20 A.U. per millimeter; at 1600 A.U., 12 A.U. per millimeter).

RESULTS

The spectrograms taken in the ordinary ultra-violet showed an increasing continuous absorption with decreasing wave lengths starting from about 2200 A.U. at atmospheric pressure and 15 cm. absorbing length. There is no sharp wave-length limit. On the contrary the absorption fades out very slowly to longer wave lengths and would certainly extend to wave lengths > 2200 with longer absorbing lengths or higher pressures. Even with the high dispersion used, above 1900 A.U. there is no indication of discrete absorption bands. The absorption is entirely continuous.

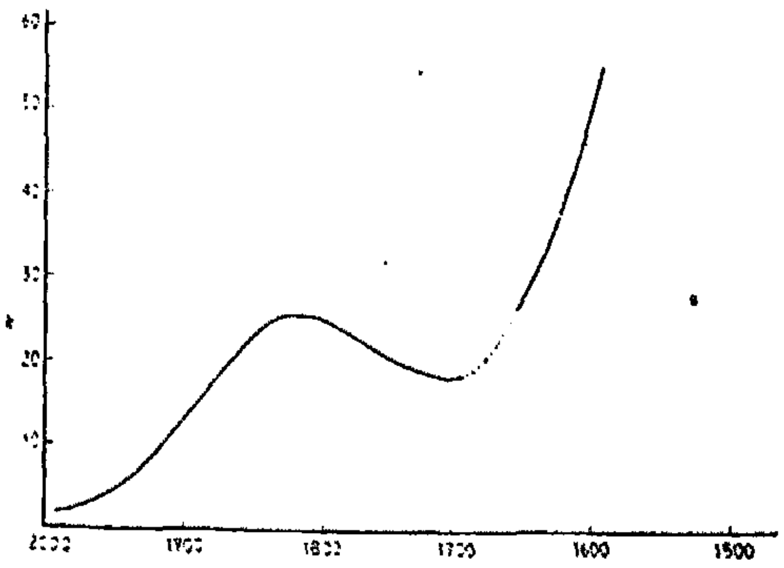

FIG. 1. Absorption coefficient of diborane in the Schumann region. The dotted part is more uncertain than the rest of the curve. Because of a numerical error the ordinates should be multiplied by 0.875.

In the Schumann region the continuous absorption further increases until it comes to a maximum at about 1820 A.U. and then diminishes. Owing to the much smaller dispersion used in this region we cannot be quite so sure about its continuous character, but in view of the lack of any indication of discrete bands at the long wave-length limit it seems highly improbable that the continuous spectrum observed in the Schumann region is not a true continuum. After a minimum at about 1700 A.U. the absorption rises again, now much steeper, until about 1550 A.U., the limit of the region observed. Also this absorption appears to be continuous. But of course below 1650 this cannot be stated with certainty, because here the many-line-spectrum of hydrogen sets in, which makes a decision more difficult. No irregularities in the absorption of the various H_2 lines have however been observed, so that if there is discrete absorption it is at any rate not very conspicuous.[2]

One spectrogram taken with the small fluorite spectrograph at 10 mm. diborane pressure was photometered with a Koch-Goos registering microphotometer and compared with a spectrogram taken at zero diborane pressure on the same plate. The resulting curve for the absorption coefficient, k, of diborane is given in figure 1. As no intensity marks were available the curve does not claim any great accuracy, but is intended only to give a rough idea of the absorption coefficient and of its order of magnitude. However, the curve shows clearly that there are two distinct regions of continuous absorption, the short wave-length one being much stronger than the long wave-length one. The absorption is given according to the formula

$$I = I_0 \cdot e^{-k \cdot l \cdot c}$$

where I_0 and I are the intensities before and after passing the tube, l the length of the tube, and c the concentration in moles per liter. It is seen that for the first continuous absorption k is about 25, whereas for the second it is about 50 or larger, the maximum being outside the region investigated.

It was observed that the windows of the absorption tube became more and more opaque to light of short wave lengths in the course of the investigation of diborane, evidently owing to some film of a solid product of decomposition of the diborane under the action of light. The occurrence of this photodissociation of diborane is in harmony with the continuous character of the absorption spectrum.

DISCUSSION

The two continuous absorption spectra found for diborane obviously prove the existence of at least two different excited electronic levels of the molecule. The first of these is unstable; the second probably is too, but might also be a stable state.

According to Mulliken the electronic ground state of diborane is a ${}^1A_{1g}$ state, i.e., the electronic eigenfunction is symmetrical with respect to all symmetry elements of the molecule (assuming symmetry D_{3d}). The electron configuration is given (omitting the carbon 1s electrons) by

$$[sa_1]^2[sa_1]^2[\sigma + \sigma, a_{1g}]^2[\pi e]^3[\pi e]^3 \qquad (1)$$

For an explanation of the symbols the reader is referred to Mulliken's paper (2). There are a number of other electronic states arising from the

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[2] With the same spectrograph and light source we could easily detect an H_2S band near 1580 A.U., in spite of the discontinuous background in that region.

same electron configuration. These, as well as the states of the configurations

$$[sa_1]^2[sa_1]^2[\sigma + \sigma,a_{1g}][\pi e]^4[\pi e]^3 \tag{2}$$

$$[sa_1]^2[sa_1]^2[\pi e]^4[\pi e]^4 \tag{3}$$

must, according to Mulliken's theory, lie rather low, below about 1 volt. Therefore none of them can be identical with the upper states of the two ultra-violet absorption continua observed.

For the discussion of the possible upper states of the ultra-violet absorption of diborane it seems useful first to consider the molecules ethane (C_2H_6) and ethylene (C_2H_4), both of which show some similarities to diborane (B_2H_6). Ethane has in all probability the same symmetry as diborane but has two more electrons, whereas ethylene, though it has not the same symmetry, has the same number of electrons as diborane.

The ground state of ethane, according to Mulliken, is (omitting carbon 1*s* electrons)

$$[sa_1]^2[sa_1]^2[\pi e]^4[\pi e]^4[\sigma + \sigma,a_{1g}]^2 \ {}^1A_{1g} \tag{4}$$

i.e., the incomplete shells of diborane are filled. Thus there is only one low-lying state of ethane.

In ethylene all degeneracies are removed, owing to its smaller degree of symmetry. Therefore though it has the same number of electrons as diborane, all shells are closed in the ground state and there are no neighboring states of similar energy. It is described by

$$[s + s,a_{1g}]^2[s - s,b_{1u}]^2[y\ b_3]^2[y\ b_2]^2[\sigma + \sigma,a_{1g}]^2[x + x,b_{3u}]^2 \ {}^1A_{1g} \tag{5}$$

The first excited states of ethane arise in all probability from a transfer of an electron from the $[\sigma + \sigma,a_{1g}]$ or $[\pi e]$ orbital to a three-quantum state $[3sa_1]$. This accounts for the fact that ethane starts to absorb only at 1600 A.U.

Similar excited states with a three-quantum electron are possible for ethylene. But, besides, other excited states arise from higher two-quantum orbitals. Mulliken (3) has explained the two observed electronic band systems of ethylene at 2000 and 1750 A.U. as due to transitions to one of each group of excited levels.

It seems very probable that the second, short wave-length diborane absorption also corresponds to a transition to a three-quantum state:

$$[sa_1]^2[sa_1]^2[\sigma + \sigma,a_{1g}]^2[\pi e]^3[\pi e]^2[3sa_1] \tag{6}$$

However it is hardly possible to explain the longer wave-length absorption of diborane in the same way as that of ethylene, in spite of the near agreement of the energies of the states above the ground state. The excited two-quantum states of ethylene correspond to the various diborane states which lie very near to the ground state, owing to degeneracy of the $[\pi e]$ orbital and the fact that the two $[\pi e]$ orbitals do not appreciably interact in diborane.[3]

Therefore the first ultra-violet absorption of diborane has either to be interpreted as a transition to one of the numerous states arising from configuration 6 other than the upper state of the second absorption or as a transition to a state of the configuration

$$[sa_1]^2[sa_1]\,[\sigma + \sigma, a_{1g}]^2[\pi e]^4[\pi e]^3 \qquad \cdot(7)$$

i.e., a transition of an inner electron similar to the well-known transitions in diatomic molecules like CN, N_2^+, and others. This is an additional possibility for diborane which, as can be seen from configurations 4 and 5, does not exist for ethane or for ethylene.

Both states 6 and 7 should be stable because the number of bonding electrons is the same as in the ground state. But predissociation into the various dissociation products $BH_3 + BH_3$, $B_2H_4 + H_2$, or others may be so strong as to give a completely continuous spectrum.

With the material at present available it is not possible to decide definitely between the two possibilities discussed above.

SUMMARY

The ultra-violet absorption spectrum of diborane has been investigated down to 1550 A.U. Two regions of continuous absorption have been found, extending from 2200 and 1700, respectively, to shorter wave lengths. These correspond to transitions to two different excited states, the possible electron configurations of which are discussed on the basis of Mulliken's theory.

In conclusion we wish to express our sincere thanks to Prof. Stock and his assistants for the supply of the pure diborane used in this investigation. The experiments were carried out at the Physikalisches Institut der Technischen Hochschule, Darmstadt, Germany.

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[3] The only possibility for a higher two-quantum excited state is

$$[\pi e]^{-1}\,[\sigma - \sigma, a_{2g}]$$

which, however, very probably lies above configuration 6 and has also to be considered as a three-quantum state (cf. reference 3).

REMARKS ON THE PHOTOCHEMISTRY OF POLYATOMIC MOLECULES[1]

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I. INTRODUCTION

In a recent discussion (18) of photosynthesis in plants K. Wohl arrives at the following conclusion: The assumption made up to now that the photochemical part of photosynthesis is described by

$$\text{Chlorophyll} + 4h\nu + CO_2 + 3H_2O \rightarrow H_2CO + 2H_2O_2 + \text{chlorophyll} \quad (1)$$

cannot be reconciled with the facts, since the energy supplied by the absorption of 4 quanta of red light is too small. He uses as wave-length 680 mμ, the long wave-length limit within the absorption of chlorophyll which still gives photosynthesis, and finds the energy of four such quanta to be about 20 kg-cal. per mole smaller than the energy difference between initial and end products. The difference in free energy is also found to be slightly greater than the energy supplied by the photons. Assuming, as has always been done hitherto, that the energy differences alone are the determining quantities in a photochemical reaction and that one can neglect the contribution from thermal energy at room temperature, he has to reject the possibility of the chemical reaction 1. The problem whether the assumption generally made, that the thermal energy plays no rôle in photochemical reactions at room temperature, is also valid for polyatomic molecules able to give fluorescence, has not yet been investigated. This and its possible application for the problem of photosynthesis make it worthwhile to undertake a systematic discussion. We treat first the general case, then briefly its application to photosynthesis, and leave the mathematical proofs to the appendix.

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[1] Presented at the Symposium on Molecular Structure, held at Princeton University, Princeton, New Jersey, December 31, 1936 to January 2, 1937, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society.

II. GENERAL DISCUSSION

We start out with photochemical reactions in the gaseous state and limit ourselves mainly to room temperature.

Of course it has long been known that the primary photochemical reaction might be followed by all kinds of secondary ones. We discuss here, however, the special case (not mentioned before) where the secondary reaction is endothermic and follows the primary one in a very short time.

The usual view, mentioned in the introduction, has its origin in the case of photochemical reactions of diatomic molecules in the gaseous state, where it is entirely justified.

If a light quantum is absorbed having insufficient energy to dissociate the molecule, the excited state will last 10^{-8} to 10^{-7} sec. The molecule has thermal energy in its degrees of freedom of translation and rotation, but the first are completely, the second almost (i.e., except for the centrifugal expansion) useless for dissociation. In the single degree of oscillation, there might be, at room temperature, at the utmost 1 or 2 quanta (see appendix, a), which however are so small that they affect the dissociation energy very little, so that the real limit of the photochemical process might be lifted by 1/20 of a volt or less for 200°C. One can of course gain more energy if one makes use of the few molecules having more quanta. They are (at least partly) responsible for the absorption at the long wavelength side of the main absorption band, which absorption is however very weak, because of the small number of such molecules. The lifetime of the optically excited molecule, however, is too small to acquire more vibrational energy by collision with other molecules[2] (see appendix, f), and therefore, if the light quantum is too small, it is lost (by reëmission or collisions of the second kind) before a reaction can occur.

The situation is quite different for very large molecules in the gaseous state or in solutions in which fluorescence is possible. It is still true that, as far as the primary transition into the excited state is concerned, the vibrational energy of not more than one eigen-vibration, i.e., about 1 or 2 vibrational quanta, can be used in general, so that if the light energy is smaller than the heat of dissociation, the system gets into an excited state below the dissociation. But while it is in that state, there is now a good chance that it may get enough thermal energy into the bond that has to break.

The energy necessary to supply the difference between bond strength and optically excited states gets into the important bond through fluctuations between different vibrations (Wigner and Polányi (17)). The time required increases strongly with the amount of the necessary energy and

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[2] At 1 atmosphere pressure the time to acquire by collision 4 kg-cal. per mole is 10^{-7} sec., and correspondingly longer at lower pressures.

depends in addition somewhat on the particular form of this complex (see appendix, c). Energies between 2.4 and 9.2 kg-cal. per mole might occur within 0.5×10^{-8} sec. in the bond through interference. The range 2 to 9 kg-cal. is so large because some particular configuration of the molecule might be necessary to make dissociation possible (steric hindrance). In general, 7 kg-cal. is an average value.

As mentioned before, the lifetime of the excited state is too short for any considerable amount of energy to be supplied by collision in the gas, even at 1 atmosphere. Therefore, the molecule must be large enough to contain sufficient thermal energy in its normal state; i.e., it must have, for a thermal energy of 7 kg-cal., at least $7 : 0.002 \times 300 = 12$ useful degrees of freedom.[3]

There is, however, an important difference between this case and the usual case of a purely thermal reaction. In the latter, the reaction rate falls off at low gas pressures, because the energy supply through collisions is then not sufficient to keep up the number of molecules with higher thermal energy. The higher the number of degrees of freedom, the later will this falling off come, according to theories of Polányi, O. K. Rice, and Kassel (10, 11).

Here however, the possession of the critical thermal energy, say 7 kg-cal., is not sufficient for decay; the molecule must also be excited optically. Now the combined reaction rate, photochemical excitation plus thermal reaction, is, with the usual light intensities, enormously slower than would be an entirely thermal dissociation with a heat of dissociation of 7 kg-cal. (which latter would proceed at room temperature with a reaction constant of $\sim 10^8$ sec.$^{-1}$). Therefore the energy supply by collision has all the time between optical excitations and will be amply sufficient even at very low pressures. If, for example, every molecule receives 10^3 quanta per second, which is very high, a pressure of 0.06 mm. would still be sufficient to keep up the supply.

In solutions, however, the latter problem does not come up at all. It is, on the other hand, difficult to decide which number of degrees of freedom a molecule in liquids has to have so that the fluctuation can occur un-

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[3] The equilibrium probability that an energy $> \Delta U$ resides in a certain bond is the same for the diatomic and for the large molecule. But the distribution is different. Disregard first the possibility of dissociation. Then (in gas of $\backsim$ 1 atmosphere pressure) the diatomic molecule will gain ΔU about $10^{10} \exp. -\frac{\Delta U}{RT}$ times a second, keep it 10^{-10} sec. and lose it again. In the polyatomic molecule, the bond will get the same energy $10^{13} \exp. -\frac{\Delta U}{RT}$ times a second and lose it after 10^{-13} sec.

If we now permit dissociation, the first time the molecule gains sufficient energy will permit dissociation; it is not a question of the whole time the molecule has the high energy, but of how long it has to wait for it.

hindered. We know very little about the forces between molecules in the liquid. If we could treat the whole liquid as one molecule, as far as vibrations are concerned, there would be no necessity of storing all the energy in the particular chemical molecule to be dissociated. That would mean that even a diatomic molecule, if dissolved, would under proper conditions (i.e., the right position and form of the absorption curve and the possibility of keeping excitation long enough, which shows in the presence of fluorescence) only need an optical energy which is by 7 kg-cal. less than the dissociation energy. On the other hand, it seems probable that the forces between molecules are several times less than the forces within molecules, so that the boundaries of molecules act as a kind of barrier preventing quite as effective interference of the elastic waves, i.e., for the same amount of energy, the accumulation in the bond will be less frequent. That means that we might expect even diatomic molecules in solution to react with an insufficient amount of photon energy, but only if the difference is less than 7 kg-cal.

Up to now, there was no mention of the difference in free energy between initial and end products. What rôle does it play? It determines the rate of the back reaction. Gaffron and Wohl (7) have recognized this, but have not given a quantitative discussion.

In chemical equilibrium the free energies of the initial and end products are equal. So are the forward and back reactions. If one diminishes the concentration of the end products, one does two things: (1) one diminishes the free energy of the end products, i.e., arranges the process so that there is a decrease in free energy when a reaction takes place from initial into end products, and (2) one diminishes the back reaction.

In other words, the free energy difference in a reaction occurring spontaneously measures the ratio between forward and backward reaction (see appendix, d).

For an actual calculation of the back reaction, one can either use the difference in free energy calculated for the concentrations as they actually occur, or one can use the free energy difference for standard conditions as they are found in the tables, and introduce the concentrations explicitly. The difference is, of course, purely formal; the latter method seems simpler.

If one uses the first method, the fraction of the products which is lost by back reaction is, for an uninterrupted process, according to equation 9 of the appendix

$$\exp - \frac{\Delta F}{RT}$$

if the forward reaction is purely thermal.

If the speed of the forward reaction is determined by light absorption at the rate $k_1'c_1$ instead of the thermal reaction

$$A' \exp - \frac{\Delta U}{RT}$$

the ratio lost by back reaction is

$$\frac{A'}{k_1'} \exp \frac{\Delta U - \Delta F}{RT}$$

or

$$\frac{A'}{k_1'} \exp - \frac{\Delta \phi}{RT} \qquad (4')$$

Therefore, in a photochemical reaction $\Delta F = 0$ has no immediate significance. The necessary difference in free energies depends on the strength of the light. From now on we use the second method.

Consider a dissociation

$$1 \rightarrow 2 + 3 \qquad (2)$$

Assume that the product 2 is not lost and will be present in amounts comparable to those of 1. The only way to slow up the back reaction in comparison to the forward reaction is to diminish the amount of 3. If we want the product of a photochemical dissociation to be available for subsequent reactions, photochemical or thermal, it is therefore necessary to withdraw the molecule 3 as fast as possible.

Up to now we have assumed that the thermal reaction following the primary photoreaction is a dissociation. If it is only an internal change, i.e., of such a nature that the back reaction is also monomolecular, the difference between the change in free energy and the change in total energy is a small one (9, 5), provided only one degree of freedom is involved. That is, if this difference is 1.5 cal. in the right sense, if the forward reaction is endothermic and the back reaction has no heat of activation, the speed of the back reaction would be 10^{10} to 10^{12} sec.$^{-1}$.

Only if a very large number of degrees of freedom were involved, if, for example, a very large number of vibrations would simultaneously go over into rotations, could we expect a considerable increase in entropy, and the back reaction would be correspondingly slow.

That means kinetically that many degrees of freedom would have to get into rather special positions, which is a slow process.

III. APPLICATION TO PHOTOSYNTHESIS

The application of these considerations to photosynthesis gives us a greater freedom in the hypotheses which we can make for possible steps of the photochemical reactions. One is not any more limited strictly to steps in which $h\nu \geq Q$, where Q is the heat of reaction. Thus it appears that the energy relations do not exclude the possibility that hydrogen peroxide and formaldehyde are formed as intermediate products by the absorption of 4 light quanta of 6600 A.U. On the other hand, special assumptions are necessary if one accepts this hypothesis. While other hypotheses may be preferable, one might just as well treat this one as an example for the application of our results.

Wohl calculates the energy necessary for this reaction to be 192 kg-cal. To find the energy of the light quanta, Wohl uses as wave length 6800 A.U., which gives 167.5 kg-cal. But the main absorption (12) lies at 6600, and the very weak absorption at 6800 might be due to molecules of high thermal energy, as explained at the beginning of section II. Warburg (16) also uses 6600 A.U. for his estimates. For this latter wavelength, the 4 quanta give 172 kg-cal. The missing 20 cal. might easily be supplied by thermal energy; this would necessitate about 5 kg-cal. per step. We can, however, expect about 8 to be available.

First, it might be possible to utilize about 1 kg-cal. from vibrational energy in the ground state. To wait for an additional 7 kg-cal. in the upper state the molecule needs a lifetime of somewhat more than 10^{-8} sec., if we take A to be 10^{13}.

Now Prins (12) has measured the total absorption of chlorophyll in the red and found an "electron number" of about 1/8, which would correspond to a transition probability from the excited state back to the normal state under fluorescence of

$$\frac{1}{T'} = \frac{1}{2} \times 10^7$$

That is, if fluorescence were the *only* possible way to get back to the normal state, the lifetime of the excited state would be $T' = 2 \times 10^{-7}$ sec. Even if we assume that only 5 per cent of the transitions give fluorescence (i.e., if the fluorescent light is 5 per cent of the absorbed light), the lifetime would still be 10^{-8} sec., the total transition probability being then twenty times as great as that under fluorescence alone.

We would therefore still have an activation energy of about 3 kg-cal. per step available.

Next, we have to ask whether the back reaction is too fast. Gaffron and Wohl (7) have already given some consideration to that matter, and believe that it presents great difficulties for equation 1.

Actually, we do get into difficulties if we assume that product 3 in the forward reaction, which we identify with hydrogen peroxide, is destroyed by a monomolecular reaction. If we assume that in the forward reaction we have a gain of 5 kg-cal. in the entropy per step under standard conditions (this 5 kg-cal. being one-fourth of the 20 kg-cal. which is the difference between total energy change and free energy change, according to

Wohl (18)), we find for the lifetime of product 2, say formaldehyde, equation 14 of the appendix. Let us now consider a case where the production of oxygen is about 1 per cent of the saturation value. According to Arnold and Emerson (1, 2, 3) we have then 4 quanta absorbed by a chlorophyll molecule every 2000 sec. (for half-saturation, they calculate 20 sec.). There is about 0.01 mole of chlorophyll per liter of cells (moles per liter are the units used for the standard free energy calculations), so that $2 \times 0.01 : 2000 = 10^{-5}$ mole hydrogen peroxide are produced per second per liter under these conditions. If we take the reaction destroying hydrogen peroxide to be the Blackman reaction, which has an average duration of 0.02 sec., and assume it to be monomolecular, we have $k_1^1 = 10^{-5}$, $k_3 = 50$ in equation 15 and therefore $c_3 = 2 \times 10^{-7}$ and the lifetime of formaldehyde comes out to be $\frac{1}{3} \times 10^{-3}$ sec., which is probably too short.

On the other hand it is not quite impossible that for moderately high concentrations of hydrogen peroxide, its destruction by catalase might be of zero order. Then we can calculate the rate of destruction of hydrogen peroxide from the time of this destruction, 0.02 sec. (Blackman reactions) and the amount of oxygen developed during a light flash, which amount is twice that of hydrogen peroxide decomposed. This amount of oxygen, Arnold and Emerson (1, 2, 3) find, is about 5×10^{-5} mm.³ of oxygen per flash per 1 mm.³ cell, or 5×10^{-6} mole of hydrogen peroxide decomposed per liter cell per flash, which decomposition lasts 0.02 sec. Therefore, the speed of decomposition is 2.5×10^{-4} moles per liter per second, which is sufficient up to an intensity at which it takes 40 sec. to have 4 quanta absorbed per chlorophyll molecule. At light intensities comparable with this one (which is very close to the value at half-saturation mentioned by Gaffron and Wohl), the influence of back reactions will become important. We will discuss this problem elsewhere in connection with other possibilities for the theory of photosynthesis.

The main result of this paper is the fact that in photochemical reactions of polyatomic molecules able to emit fluorescent light the thermal energy can contribute to a much greater amount than it was formerly assumed. One gains hereby a greater freedom for assumptions on possible intermediate steps in photosynthesis.

We wish to thank Professor E. Teller of George Washington University for helpful discussions.

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APPENDIX

(*a*) The probability that the molecule has, at the moment of light absorption, the necessary thermal energy (either as a whole, if it is diatomic, or in the particular bond, if it is polyatomic) is

$$\exp - \frac{\Delta U}{RT} \tag{2}$$

i.e., for $T = 300°$ Abs. and $\Delta U = 6.5$ kg-cal., 2×10^{-5}.

(*b*) The number of collisions which one molecule makes in a second with a kinetic energy larger than E is

$$Z = \exp - \frac{E}{RT} \tag{3}$$

where Z, the total number of collisions, is of the order

$$Z \sim 10^{10} \, p^{-1}$$

p being the total gas pressure in atmospheres.

Therefore, if $E = 6.5$ kg-cal. per mole, equation 3 has the value

$$2 \times 10^{5} \, p^{-1}$$

(*c*) The fraction of molecules dissociating thermally per second is

$$A \exp - \frac{\Delta U}{RT} \tag{4}$$

where ΔU is the minimum amount of energy needed, plus a possible heat of activation.

A depends slightly on the temperature, is on the average 10^{13} sec.$^{-1}$ but might vary between 10^{10} to 10^{15}, depending on the particular reaction.

Eyring and O. K. Rice and Gershinowitz have given detailed theories of A (4, 6, 8, 13, 14, 15).

If we want a molecule to dissociate in the average during the time $\alpha \times 10^{-8}$ sec., the following values of ΔU are permitted for 300° Abs.

$$\begin{array}{cc} A & \textit{Upper limit of } U \textit{ in kg-cal.} \\ 10^{10} & \left.\begin{array}{r} 2.8 \\ 7 \\ 9.6 \end{array}\right\} + 1.4 \log \alpha \\ 10^{13} & \\ 10^{15} & \end{array}$$

The general formula is

$$T = \alpha \times 10^{-8} = A^{-1} e^{\frac{\Delta U}{kT}}$$

(*d*) Consider the dissociation

$$1 \rightleftarrows 2 + 3 \tag{5}$$

Measure the concentrations in units of a standard state. Use circumflexes to denote quantities in that standard state, so that

$$\Delta \hat{F} = \hat{F}_1 - (\hat{F}_2 + \hat{F}_3) \tag{6}$$

is the charge in free energy in the standard state, as taken from the tables.

Then, if the velocities of the forward and backward reactions have the form

$$k_1 c_1;\ k_2 c_2 c_3 \tag{7}$$

we have, in well-known expressions

$$\ln \frac{k_1}{k_2} = \ln k = \frac{\Delta \hat{F}}{RT} \tag{8}$$

If the actual concentrations are c_1, c_2, c_3, we have

$$\ln \frac{k_1 c_1}{k_2 c_2 c_3} = \frac{1}{RT} \{\Delta \hat{F} + RT \ln c_1 - RT \ln c_2 - RT \ln c_3\} = \frac{1}{RT} \Delta F$$

where ΔF is the change in free energy in the actual reaction with the given concentrations.

(*e*) Consider a case in which the back reaction has no heat of activation, so that

$$k_1 = A \exp - \frac{\Delta U}{RT} \tag{4'}$$

Write

$$F = U + \Phi$$

i.e., with U_ν as the light energy

$$\Delta F = -U_\nu - \Delta U + \Delta\Phi \tag{10}$$

in the notation we have used. Therefore $\Delta\Phi$ (positive) is the amount of energy by which the free energy balance is more favorable to the reaction (in the standard state) than the total energy balance.

Therefore

$$\ln \frac{A}{k_2} = \frac{\Delta\Phi}{RT} \tag{11}$$

Now the life T_2 of a product molecule, i.e., the time before it recombines, is given by

$$\left(\frac{k_2 c_2 c_3}{c_2}\right)^{-1} = \frac{1}{k_2 c_3} \tag{12}$$

or

$$T_2 = \frac{1}{A} e^{\frac{\Delta\Phi}{RT}} c_3^{-1} \tag{13}$$

If, for example, $\Delta\Phi$ is 5 kg-cal. and $A = 10^{13}$, we have

$$T_2 = 10^{-10} c_3^{-1} \tag{14}$$

If product 3 is produced at the (photochemical) rate k_1^1 and destroyed by a third process at the rate $k_3 c_3$, we have

$$c_3 = \frac{k_1^1}{k_3}, \qquad T_2 = 10^{-10} \frac{k_3}{k_1^1} \tag{15}$$

In this formula an assumption is implied, namely, that if the whole forward reaction went thermally instead of part photochemically, part thermally, the velocity constant would be

$$k_1'' = k_1 \exp - \frac{U\nu}{RT} = A \exp - \frac{U\nu + \Delta U}{RT}$$

If a heat of activation ϵ'' is present in the back reaction, this increases the lifetime of product 2, making it

$$T_2 = \frac{1}{A} e^{\frac{\Delta\Phi + \epsilon''}{RT}} c_3^{-1} \tag{13'}$$

But at the same time it increases the energy necessary in the forward thermal reaction by the same amount.

(*f*) If the destruction of product 3, however, goes in a reaction of zero order (catalytic on the walls or on some catalyst present only in small amounts), we have to change the calculation leading to equation 15.

Assume it were known that C' moles of 3 are destroyed within t sec. Then the rate of destruction of unit concentration is

$$k_3' = \frac{C'}{t} \tag{16}$$

Then, the stationary concentration of product 3 is zero, if

$$k_3' > k_1'$$

while for

$$k_1' > k_3'$$

there is no stationary state, but the amount of product 3 present increases continuously (that is, if we neglect the back reaction) as production exceeds destruction.

THE CROSSING OF POTENTIAL SURFACES[1]

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The crossing of potential curves or surfaces is important if reaction mechanisms are discussed, particularly if activated states are involved. Thus in photochemistry both the chemical yield and the fluorescence will depend on the question whether the molecules can get from a higher potential surface to a lower one, transforming in this way electronic excitation energy into kinetic energy of atoms and finally into heat. We know that in both diatomic and polyatomic molecules this can happen in several ways through the change of position of an electron, as discussed by Franck and Haber (1), or through dissociation and re-composition of the molecules. It is our purpose to discuss a difference between diatomic and polyatomic molecules with respect to the question whether electronic energy levels as functions of the atomic configuration may cross.

It is well known that potential curves of diatomic molecules will not cross unless the two electronic states in question differ in some essential way. In fact two curves will cross only if the electronic states differ either in their symmetry properties or in their multiplicity or finally in the "position" of an electron which belongs to one atom or ion for the first curve but belongs to another atom or ion (sufficiently far removed from the first atom) for the second curve. These facts were first recognized by Hund (2), who supported his statement by the following argument: If two potential curves cross, the electronic state must be degenerate at the point of crossing. We should not expect, however, that degeneracy can be established by varying only one parameter, which would be of course the case if by varying the nuclear distance in a diatomic molecule we should as a rule encounter crossing points. Neumann and Wigner (4) have given the mathematical proof that Hund's qualitative argument is correct. The essence of this proof is as follows: We suppose that we already know the correct electronic proper-functions for all energy levels except for the two potential curves the crossing of which we want to investigate. Using for these last two the two arbitrary functions ψ_1 and ψ_2, which are chosen to

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be orthogonal to each other and to the other proper-functions, the matrix of the electronic energy will be diagonal except for the elements $a_{12} = a_{21}^*$. (The asterisk signifies the conjugate complex value; a_{12} is the matrix element $\int \psi_1 H \psi_2^*$, where H is the operator of the electronic energy.) Now the diagonal elements corresponding to ψ_1 and ψ_2, i.e., a_{11} and a_{22} are in general not equal, and also a_{12} will be different from zero. Degeneracy on the other hand would mean that $a_{11} = a_{22}$ and $a_{12} = 0$. By varying only one parameter we shall not expect that both these conditions can be satisfied.

From this reasoning it is evident that if more than one parameter can be varied degeneracy may occur. This will be the case for polyatomic molecules where the whole atomic configuration (and not only a single interatomic distance) can be varied. In general three parameters are necessary, since a_{12} may be a complex quantity and two parameters are needed to make both its imaginary and its real part equal to zero. The diagonal elements of the energy matrix are always real, and only one more parameter is necessary to get $a_{11} = a_{22}$.

If in our problem all magnetic forces may be neglected, which is justified for molecules containing no heavy atoms, then the electronic proper-functions can be chosen real. Therefore all matrix elements will become real, and only one parameter will be needed to obtain $a_{12} = 0$. In this case it will be sufficient to change two parameters in order to get a common point on the two energy surfaces which represent the dependence of the electronic energy on the atomic configuration.

If, on the other hand, the electronic spin becomes important, as will be the case whenever heavier elements are present, a_{12} will be complex and three parameters are needed to obtain crossing.

The crossing of energy surfaces which is thus shown to be possible is, however, of a different type from the simple crossing of two potential curves in diatomic molecules. Let us first investigate the case of light atoms where crossing is brought about by varying two parameters. It will then be sufficient to discuss the dependence of the surface from two parameters x and y. If we are only interested in the behavior of the surface in the immediate neighborhood of the crossing, then we may assume that all matrix elements will be linear functions of x and y. Furthermore we choose the coördinates and the electronic energy ϵ in such a way that the crossing should take place at $x = y = 0$ and $\epsilon = 0$. Finally we may choose the proper-functions in such manner that for $y = 0$ the energy matrix should be diagonal. The part of the energy matrix M which determines the crossing of the two surfaces will then be

$$M = \begin{pmatrix} \alpha_1 x + \beta_1 y & by \\ by & -\alpha_2 x - \beta_2 y \end{pmatrix}$$

If $a_1 = a_2$ and $\beta_1 = \beta_2$ the sum of the energies of the two surfaces will remain the same as in the crossing point, i.e., it will remain zero. Since we are not interested in the slope of the surfaces but only in the way they cross, we may simplify the problem by putting $a_1 = a_2 = a$ and $\beta_1 = \beta_2 = \beta$. The energy surfaces will now be determined by the secular equation

$$\begin{vmatrix} ax + \beta y - \epsilon & by \\ by & -ax - \beta y - \epsilon \end{vmatrix} = 0 \tag{1}$$

and we obtain for the electronic energy ϵ

$$\epsilon = \pm \sqrt{(ax + \beta y)^2 + (by)^2} \tag{2}$$

This means that the energy surface will be a double cone.

As an example for such an energy surface we may consider a degenerate electronic state of a molecule with trigonal symmetry (e.g., CH_3I). It can be shown (3) that the degeneracy will be split by the non-symmetrical atomic displacements (for instance, the displacement of the carbon atom perpendicular to the molecular axis). For the energy matrix and the splitting of the energy we shall obtain expressions similar to 1 and 2. But, owing to the symmetry of the problem, we have $\beta = 0$ and $a = b$ and the cone will become circular. Of course for such symmetrical molecules the crossing itself is caused by symmetry, whereas in the general case the crossing comes about at any point in which the parameters of the problem happen to have suitable values.

If magnetic forces cannot be neglected and three parameters (x, y, and z) must be used, then with simplifications similar to those introduced for the two-parameter case we obtain for the secular equation and energy values the expressions

$$\begin{pmatrix} ax + \beta y + \gamma z - \epsilon & by + icz \\ by - icz & -ax - \beta y - \gamma z - \epsilon \end{pmatrix} \tag{3}$$

$$\epsilon = \pm \sqrt{(ax + \beta y + \gamma z)^2 + (by)^2 + (cz)^2} \tag{4}$$

The internal motion of the molecule can be represented by a point moving on our potential surface. Each position of the point will correspond to a configuration of the atoms in the molecule. If, to begin with, the molecule is in a certain configuration and on a certain electronic energy level, and in the end is in the same configuration but on another energy level, then the point representing the internal motion must have crossed from one energy surface to another. We shall now investigate therefore with how great a probability a point moving on a surface as in expression 2 or 4 will cross over from one part of the double cone to the other.

For diatomic molecules the corresponding question, whether if two potential curves come close to each other the molecule will remain in one curve (adiabatic process) or whether in moving through the region of close approach it will jump over to the other potential curve (non-adiabatic process) has been solved by Zener (5) for the case in which the velocity of the molecule is sufficiently great. Then the nuclear motion can be treated according to classical mechanics, and it remains only to be seen how the electronic proper-function will change under the influence of the change of interatomic forces. Under such conditions Zener obtains for the probability, P, of transition between the two curves

$$P = e^{-\frac{2\pi\epsilon_{12}^2}{hqv}} \tag{5}$$

Here ϵ_{12} is half of the smallest energy difference at closest approach of the two curves; q is the difference of the slopes of the two curves at a sufficiently great distance from the point of closest approach;[2] v is the velocity with which the nuclear distance changes.

We may calculate the transition probability for our two-parameter case with the same simplifications and the same method as Zener used in treating the one-parameter case. We shall ascribe to the point on the energy surface (representing the internal motion of the molecule) a definite orbit. For this orbit two energy curves will be obtained on the two surfaces of the double cone. Then we can obtain the transition probability for this orbit from expression 5. In order to get the total transition probability for a wave function arriving from a certain direction to the crossing point we must, as we shall see later, take the transition probability for all orbits parallel to the momentum of the wave function and integrate.

If the wave arrives from the x direction then the orbits which we must take into account are given by y = const. In expression 5 we must insert for v the velocity with which the parameter x varies, for q the quantity $2a$ (from expressions 1 and 2) and for ϵ_{12} we must substitute by. Integrating over y we get the total transition probability

$$\bar{P} = \int_{-\infty}^{\infty} P dy = \int_{-\infty}^{\infty} e^{-\frac{\pi b^2 y^2}{hav}} dy = \sqrt{\frac{hav}{b^2}} \tag{6}$$

The expression has the dimension of a length[3] and it can be interpreted as the length of the aperture through which the point on the two-dimensional surface x, y can get over from one part of the cone to the other. Classically, i.e., for $h = 0$, this length is zero, as is evident at once, since in classical theory only an orbit going exactly through the apex $x = y = 0$ of the cone will give rise to a transition between the two surfaces.

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[2] It can be shown that near the point of closest approach the curves can be represented by hyperbolas; q is the angle of the two asymptotes.

[3] P is a pure number; a and b have the dimension energy/length.

If on the three-parameter surface given by expressions 3 and 4 a wave arrives at $x = y = z = 0$ from the x direction we must substitute again $2a$ for q, but ϵ_{12} will now be $\sqrt{(by)^2 + (cz)^2}$ and the integration must be carried out over both y and z. We shall then obtain for the total transition $\overline{\overline{P}}$

$$\overline{\overline{P}} = \int\int_{-\infty}^{\infty} P\,dy\,dz = \int\int_{-\infty}^{\infty} e^{-\frac{\pi(b^2y^2+c^2z^2)}{hav}}\,dy\,dz = \frac{hva}{bc} \tag{7}$$

$\overline{\overline{P}}$ has of course the dimension of an area.

We shall now prove the correctness of our procedure to calculate the transition probability for each orbit, and then integrate over the different orbits. Only the two-parameter case will be discussed; the three-parameter case is quite analogous.

Using for the electronic proper-functions ψ_1 and ψ_2, which are chosen to be the correct solutions for $y = 0$, we may write the Ψ-function which describes the behavior of the degrees of freedom x and y as well as the behavior of the electrons in the following form

$$\Psi = e^{\frac{2\pi i}{h}\int p_1 dx}\, C_1(x, y)\,\psi_1 + e^{\frac{2\pi i}{h}\int p_2 dx}\, C_2(x, y)\,\psi_2 \tag{8}$$

p_1 and p_2 are defined by

$$\begin{aligned} p_1 &= \sqrt{2m_x(E - ax - \beta y)} \\ p_2 &= \sqrt{2m_x(E + ax + \beta y)} \end{aligned} \tag{9}$$

m_x is the reduced mass belonging to the motion in the x direction and E is the electronic energy plus the kinetic energy belonging to the parameters x and y. The functions $C_1(x, y)$ and $C_2(x, y)$ remain to be determined from the Schrödinger equation. If the velocity with which the parameter x changes is sufficiently great, then $C_1(x, y)$ and $C_2(x, y)$ can be supposed to vary slowly as compared with the exponential factors in expression 8.

The classical expression for the kinetic energy of the heavy particles will be

$$E_{\text{kin}} = \frac{p_x^2}{2m_x} + \frac{p_y^2}{2m_y} \tag{10}$$

where p_x and p_y, m_x and m_y are the moments and reduced masses for the motions of the parameters x and y. No product terms p_xp_y occur in expression 10 if, as we shall suppose, the parameters x and y have been chosen to be orthogonal.

Substituting the operators $\frac{h}{2\pi i}\,\frac{\partial}{\partial x}$ and $\frac{h}{2\pi i}\,\frac{\partial}{\partial y}$ for p_x and p_y and using the matrix M for the electronic energy we obtain the Schrödinger equation

$$-\frac{h^2}{8\pi^2 m_x}\frac{\partial^2\Psi}{\partial x^2}-\frac{h^2}{8\pi^2 m_y}\frac{\partial^2\Psi}{\partial y^2}+M\Psi-E\Psi=0 \tag{11}$$

We now substitute equation 8 into equation 11. Because of the orthogonality of ψ_1 and ψ_2 their factors on the left-hand side of expression 11 must vanish. Furthermore in the approximation used here ψ_1 and ψ_2 may be regarded independent of x and y. We obtain therefore

$$\begin{aligned}&-\left(\frac{h^2}{8\pi^2 m_x}\frac{\partial^2}{\partial x^2}+\frac{h^2}{8\pi^2 m_y}\frac{\partial^2}{\partial y^2}\right)\left(e^{\frac{2\pi i}{h}\int p_1 dx}C_1(x,y)\right)\\&+(ax+\beta y-E)\,e^{\frac{2\pi i}{h}\int p_1 dx}C_1(x,y)+by\,e^{\frac{2\pi i}{h}\int p_2 dx}C_2(x,y)=0\\&-\left(\frac{h^2}{8\pi^2 m_x}\frac{\partial^2}{\partial x^2}+\frac{h^2}{8\pi^2 m_y}\frac{\partial^2}{\partial y^2}\right)\left(e^{\frac{2\pi i}{h}\int p_2 dx}C_2(x,y)\right)\\&+(-ax-\beta y-E)\,e^{\frac{2\pi i}{h}\int p_2 dx}C_2(x,y)+by\,e^{\frac{2\pi i}{h}\int p_1 dx}C_1(x,y)=0\end{aligned} \tag{12}$$

The largest contribution from the first term is obtained if all differentiations are carried out with regard to the quickly varying exponential factor alone. Because of expression 9 this contribution and the second term in equations 12 will cancel. The next greatest term which may be obtained by differentiating will be the one which we get if we once differentiate the exponential and once the factor $C(x, y)$. Since the exponential does not depend on y only the differentiation with regard to x will give rise to such a term. If the velocity is sufficiently high we may neglect all other terms obtained by differentiating and we have therefore

$$\begin{aligned}&-\frac{h}{2\pi i}\sqrt{\frac{2(E-ax-\beta y)}{m_x}}\,e^{\frac{2\pi i}{h}\int\sqrt{2m_x(E-ax-\beta y)}\,dx}\frac{\partial}{\partial x}C_1(x,y)\\&+by\,e^{\frac{2\pi i}{h}\int\sqrt{2m_x(E+ax+\beta y)}\,dx}C_2(x,y)=0\\&-\frac{h}{2\pi i}\sqrt{\frac{2(E+ax+\beta y)}{m_x}}\,e^{\frac{2\pi i}{h}\int\sqrt{2m_x(E+ax+\beta y)}\,dx}\frac{\partial}{\partial x}C_2(x,y)\\&+by\,e^{\frac{2\pi i}{h}\int\sqrt{2m_x(E-ax-\beta y)}\,dx}C_1(x,y)=0\end{aligned} \tag{13}$$

If we divide now by the exponential factor of the first term we obtain in the exponent a difference of square roots. For high velocity we have for the region close to the apex of the cone (which is the region where transitions happen)

$$E >> |\,ax+by\,|$$

We may therefore write

$$\sqrt{2m_x(E+\alpha x+\beta y)} - \sqrt{2m_x(E-\alpha x-\beta y)} \sim \sqrt{\frac{m_x}{2E}}\,2(\alpha x+\beta y) \quad (14)$$

The factor

$$\sqrt{\frac{m_x}{2E}}$$

is the reciprocal value of the velocity v at the point $x = y = 0$. If the velocity is sufficiently high, the factors

$$\sqrt{\frac{2(E-\alpha x-\beta y)}{m_x}} \quad \text{and} \quad \sqrt{\frac{2(E+\alpha x+\beta y)}{m_x}}$$

(which are not exactly equal to the classical velocities on the double cone) may also be substituted by v. Thus expression 3 can be written in the form

$$\begin{aligned} \frac{hv}{2\pi i}\frac{\partial}{\partial x}C_1(x, y) &= bye^{\frac{2\pi i}{h}\int 2(\alpha x+\beta y)\frac{dx}{v}}C_2(x, y) \\ \frac{hv}{2\pi i}\frac{\partial}{\partial x}C_2(x, y) &= bye^{-\frac{2\pi i}{h}\int 2(\alpha x+\beta y)\frac{dx}{v}}C_1(x, y) \end{aligned} \quad (15)$$

These equations contain y only as a parameter and they may be solved for each y = const. separately. If furthermore we introduce instead of x the time $t = \frac{x}{v}$ we obtain

$$\frac{h}{2\pi i}\frac{\partial}{\partial t}C_1(t, y) = bye^{\frac{2\pi i}{h}\int 2(\alpha x+\beta y)dt}C_2(t, y)$$

$$\frac{h}{2\pi i}\frac{\partial}{\partial t}C_2(t, y) = bye^{-\frac{2\pi i}{h}\int 2(\alpha x+\beta y)dt}C_1(t, y)$$

These, however, are the equations which Zener has solved, so that our procedure of taking his results and integrating over the different orbits y = const. is justified.

Apart from the types of crossing discussed here we may also expect for polyatomic molecules the simpler type of crossing in which only one parameter must be varied in order to arrive at a common point of the two surfaces. This will again be the case if the two energy states differ in symmetry, multiplicity, or electronic position. However, the difference in symmetry properties of the electronic proper-functions is less important for polyatomic molecules than for diatomic molecules, because in a diatomic molecule the change of interatomic distance does not destroy the molecular symmetry; for a polyatomic molecule, however, the whole symmetry is frequently destroyed by the internal atomic motion.

On the other hand we have for polyatomic molecules the special type of "conical crossing" discussed above. The transition probability for this type of crossing may become quite considerable. If we take for instance $v = 10^6$ cm. sec.$^{-1}$ and $a = b = 1$ e.v. per Ångström unit, we obtain from expression 6, $P = 0.6$ A.U. Of course the velocities may be for chemical reactions anything between 10^4 and 10^7 cm. sec.$^{-1}$ Much will depend on the magnitude of a and b. A large value for a and a small one for b, i.e., a cone which rises steeply in the direction of the incident waves but rises slowly perpendicularly to this direction will be favorable for the transition.

Even if the transition probability is relatively small, the transition from one surface to another may take place after a few periods of molecular vibration if the potential surface is such that the molecular configuration will keep returning into the neighborhood of the apex of the cone. This may be the case for many photochemical processes where the question is whether the molecule will go over through vibration into a lower energy surface before it radiates. Since when we are concerned with a transition from a higher to a lower potential surface the apex of the cone will frequently be the lowest point of the upper surface and since the vibrational energy might easily be dispersed between the many internal degrees of freedom of a polyatomic molecule, the probable values for the parameters x and y will be close to zero. Although in such cases the velocity may become too small and our method of calculation may therefore be inapplicable, still the orders of magnitude will be given by expressions 6 and 7. We shall then get a transition in a short time because though expressions 6 and 7 show that the transition probability decreases for small velocities this will be compensated by the fact that for small kinetic energies the molecular configuration will return more frequently to the crossing point.

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THE NATURE OF THE HYDROGEN BOND. II

THE RÔLE OF RESONANCE. GENERAL CONSIDERATIONS[1]

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The hydrogen bond (3), first recognized as a general phenomenon by Latimer and Rodebush (9), seems to be the object of renewed interest, as evidenced by the recent appearance of several papers on the subject (5, 2, 6, 7, 8, 3, 1, 4). However, the nature of the hydrogen bond is not yet clear, owing largely, no doubt, to the lack heretofore of a suitable definite experimental criterion to indicate its presence in a molecule or complex.

Sidgwick (10) deduced the presence of hydrogen bonds in several molecules and complexes. His arguments were based upon the abnormal physical properties of such molecules compared to related ones where no such bonds presumably exist. Physical properties such as association, solubility, volatility, tendency to form complexes, etc., were considered.

Hilbert, Wulf, Hendricks, and Liddel (5, 6) point out that the physical properties of some molecules containing hydrogen bonds may not always be sufficiently striking in comparison to normal molecules to enable one to come to any definite conclusion. They therefore suggest an alternative experimental criterion based upon the fact that some molecules supposedly containing hydrogen bonds do not give characteristic OH absorption bands in the infra-red.

In this paper the idea is set forth that neither the criterion based upon physical properties nor the one based upon infra-red absorption measurements is entirely satisfactory.

Various structural formulas representing the hydrogen bond have been proposed. If A and B denote two atoms, one of which is rather strongly electronegative, such as oxygen or fluorine, and the other is carbon, nitrogen, oxygen, or fluorine, then such formulas as $A^-H^+B^-$, $A-H-B$, and $A-H\rightarrow B$ have been proposed for the bond in question. From a quantum-

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[1] Presented at the Symposium on Molecular Structure, held at Princeton University, Princeton, New Jersey, December 31, 1936 to January 2, 1937, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society.

mechanical standpoint a resonance formula[3] is to be preferred. But whatever their precise nature all chemical bonds possess the property in common that their formation lowers the potential energy of the system, i.e. an energy, the heat of dissociation, must be supplied to break the bond.

The potential energy of molecules containing hydrogen bonds should therefore be lower than that of the corresponding molecules without these bonds. A class of molecules ideally suited to test this point are the ortho, meta, and para derivatives of benzene. Owing to geometrical considerations one would not expect substituents in the 1,3- or 1,4-positions in the benzene ring to be joined by bonds. If one grants for the moment that the isometric ortho, meta, and para molecules have the same energy, providing there is no additional bond formed between substituents in the 1,2-position, then if there is such a bond formed the heat of formation of the ortho derivative should be greater (or the heat of combustion less) than for the corresponding meta and para compounds. This difference

TABLE 1

Heat of combustion for various disubstituted benzene molecules

MOLECULE	Q
	kg-cal. per mole
o-Dinitrobenzene	703
m-Dinitrobenzene	697
p-Dinitrobenzene	695
o-Nitrotoluene	897
m-Nitrotoluene	893
p-Nitrotoluene	889
o-Nitrobenzoic acid	735
m-Nitrobenzoic acid	729
p-Nitrobenzoic acid	728
o-Nitroacetanilide	974
m-Nitroacetanilide	970
p-Nitroacetanilide	968
o-Nitrophenol	689
m-Nitrophenol	684
p-Nitrophenol	686

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[3] If ψ_1 represents the state $A^-H^+B^-$, ψ_2 the state A—H B, and ψ_3 the state A H—B, the wave function for the complex, ψ, will in general be a linear combination of ψ_1, ψ_2, and ψ_3. The structural formula corresponding to the wave function ψ is termed a 'resonance formula.' If the coefficient of ψ_1 is nearly zero, and the coefficients of ψ_2 and ψ_3 equal, the formula for the complex may, *over a time average*, be represented as A--H—B.

should be a measure of the strength of the bond. Hence thermochemical data should provide information concerning the presence of hydrogen bonds. Now according to the infra-red absorption criterion the measurements of Hilbert, Wulf, Hendricks, and Liddel indicate the presence of this bond in *o*-nitrophenol, and its absence in the meta and para derivatives.

Table 1 gives the thermochemical data for some disubstituted benzene compounds.

The data given in table 1 are for the compounds in the solid state. The thermal values should be corrected for the transition to the gaseous state, but this will not change the *difference* in heats of combustion for ortho, meta, and para derivatives by more than 1 kg-cal.

Data for four disubstituted benzenes other than the nitrophenols are given in order to determine the relative energies of the isomers in the absence of hydrogen-bond formation. This bond presumably does not exist in any of these compounds and, of course, certainly not in dinitrobenzene.

It is seen that in all these molecules the meta derivatives are about 5 kg-cal., and the para compounds about 7 kg-cal., more stable than the corresponding ortho compounds. Now the significant point is that *m*-nitrophenol is *also* 5 kg-cal. more stable than the ortho derivative, in spite of the fact that the latter supposedly contains a hydrogen bond.

p-Nitrophenol is 3 kg-cal. more stable than the ortho compound, which, for some unapparent reason, is under the average for the other para compounds. The lower stability of the ortho derivatives is undoubtedly largely due to the greater steric repulsion between substituents in the ortho position.

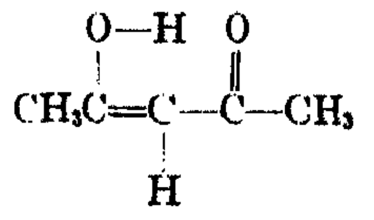
It must be concluded, therefore, that the thermochemical data at hand do not provide any evidence for a hydrogen bond in *o*-nitrophenol. If a bond exists it is not more than 1 or 2 kg-cal. strong, and this energy may be accounted for by dipole–dipole attractions, which will be discussed below, so that there is no necessity for assuming a hydrogen bond in this case. Consequently it appears that the infra-red criterion is not consistent with the thermal data, and if one defines a bond in terms of energy it does not seem that the presence or absence of the characteristic OH band *always* affords a satisfactory criterion for the detection of a bond. The presence of a hydrogen bond would undoubtedly increase the stability of a compound by much more than 2 kg-cal. It is not implied that the infra-red data are in general inconsistent with the thermal data, but only that in some cases they may be so.

The presence or absence of a band in infra-red absorption is determined by such factors as the symmetry of the molecule and the change of electric moment associated with the fundamental modes of vibration of the molecule, and therefore it does not necessarily appear that the absence of the characteristic OH band must be interpreted in terms of the formation of a hydrogen bond.

The 'abnormal' physical properties used by Sidgwick as evidence of hydrogen-bond formation in certain ortho derivatives can probably be explained upon the basis of the different dipole moments of ortho, meta, and para compounds. It is known that such properties as boiling points, tendency towards association, solubility, etc., are dependent in part upon the magnitude of the dipole moment of the molecule in question. For example, part of the energy represented by the heat of vaporization of a liquid must be expended in overcoming the attraction between dipoles as well as that due to van der Waals' forces. Sidgwick implicitly assumes that interactions between atoms generally result in the formation of electron pair bonds, but bonds arising from electrostatic sources such as ions and dipoles are of course also possible.

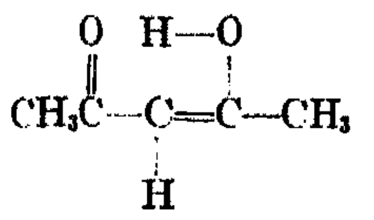
In nitrophenol the OH group has a moment with the negative end of the dipole towards the oxygen, and the nitro group has the negative end of its moment directed away from the nitrogen. Consequently there is a certain amount of attraction between the dipoles which would give rise to a weak dipole–dipole bond, if one chooses to consider such attraction a bond. It could hardly be considered a hydrogen bond, however, and to consider such bonds in chemistry in general would only complicate matters unduly.

The question now arises as to a suitable definition and experimental test for a hydrogen bond. It is suggested that it is a bond, the energy of which is derived from the so-called resonance energy of quantum mechanics, the electron of a hydrogen atom constituting part of the resonating system. For example, the conventional structural formula for the enol form of acetylacetone is



$$CH_3\overset{\overset{\textstyle O-H}{|}}{C}=\underset{\underset{\textstyle H}{|}}{C}-\overset{\overset{\textstyle O}{\|}}{C}-CH_3$$

but an equally satisfactory way of drawing the bonds is



$$CH_3\overset{\overset{\textstyle O}{\|}}{C}-\underset{\underset{\textstyle H}{|}}{C}=\overset{\overset{\textstyle H-O}{|}}{C}-CH_3$$

Owing to the resonance energy between these two states, and other excited and polar states, the molecule will be more stable than corresponds to the conventional formula, and the increase in stability may be taken as the energy of the hydrogen bond.

It follows from the definition just given that, unlike other bonds, the energy of the hydrogen bond will not be at all constant but will be a function of the molecule. These molecules are simply additional illustrations of the principle that it is not always a good approximation to represent a system by a single state, i.e., by a definite way of drawing the bonds, as was assumed in classical theory. The best known molecule for which this is true is of course benzene. Another example is dimeric acetic acid, discussed in Paper I.

It also follows from the above definition that an experimental criterion for the presence of a hydrogen bond in a molecule involves a determination of the heat of combustion or heat of formation, and a comparison of this value with that to be expected for this molecule without the hydrogen bond, the greater stability, if any, representing the energy of the bond.

The above ideas will be expanded and calculations of the energies of molecules which are supposed to contain hydrogen bonds will be carried out, both from quantum-mechanical theory and from the existing thermochemical data. This will appear in forthcoming publications with R. H. Gillette.

SUMMARY

The previously suggested experimental criteria for the presence of hydrogen bonds in molecules, both the method of Sidgwick, based upon abnormalities in physical properties, and the one of Hilbert, Wulf, Hendricks, and Liddel, based upon the absence of characteristic OH absorption bands in the infra-red, are not satisfactory in that they are not always consistent with the thermochemical data. A hydrogen bond is then defined as one the energy of which is derived from the resonance energy of quantum mechanics, the electron of a hydrogen atom being part of the resonating system. This leads to an experimental test, in which thermochemical data are used to determine the energy of the molecule.

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ON THE PHOTOGRAPHIC INFRA-RED SPECTRUM OF METHYLACETYLENE (ALLYLENE) AND THE C–C SINGLE BOND DISTANCE[1]

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In a series of investigations of the absorption spectra of simple polyatomic molecules in the photographic infra-red we have included methylacetylene (CH_3C_2H) for investigation because it seems interesting from two points of view: (1) As it was to be expected that the molecule represents a symmetrical top its investigation could serve as a check on the theory of the rotational structure of symmetrical tops in general which, so far, in the photographic infra-red, had been rather unsatisfactory. (2) As all the other nuclear distances in the molecule except the C–C single bond distance were known from the investigation of other molecules, it was hoped to obtain an accurate value for the C–C single bond distance from the moment of inertia of methylacetylene, which can be determined spectroscopically.

EXPERIMENTAL

The absorption tubes, grating spectrograph, infra-red plates, etc. were the same as in several previous investigations (10, 11). The methylacetylene was prepared from propylene bromide and potassium hydroxide.

QUALITATIVE DISCUSSION OF THE METHYLACETYLENE BAND AND OF THE STRUCTURE OF THE MOLECULE

In the whole photographic infra-red up to 12,000 A.U. only one absorption band was found. It was at 10,304 A.U., quite near to the strong band

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[1] Presented at the Symposium on Molecular Structure, held at Princeton University, Princeton, New Jersey, December 31, 1936 to January 2, 1937, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society. A preliminary report on this subject appeared in Physik. Z. **36**, 625 (1935).

of ordinary acetylene at 10,370 A.U. It is reproduced in figure 1. The acetylene band appears on the spectrogram as an impurity. In the first order of the Darmstadt 3m grating the fine structure of the methylacetylene band was unresolved, but as seen from figure 1 it is fairly well resolved in the second order. It consists of a simple *P* and *R* branch as well as a line-like *Q* branch. In addition there is another much weaker "line" at the long wave-length side of the *Q* branch and possibly a still much weaker one further to longer wave lengths. The presence of the latter is not quite certain, owing to strong overlapping by the fine structure of the main band. As will be discussed below, these two additional lines are the *Q* branches of two other bands different from the main band, to which we shall now confine our attention.

As is seen from figure 1 the *P* branch is resolved completely, the *R* branch only partly, owing to the convergence of the lines to shorter wave lengths. The *Q* branch of course is unresolved because nearly all lines fall on the same spot. It can be seen from inspection, and is confirmed by actual measurements (cf. below), that there is no irregularity in the two resolved branches. Thus there can be no doubt that this band really consists only of a *simple P, R, and Q branch.*

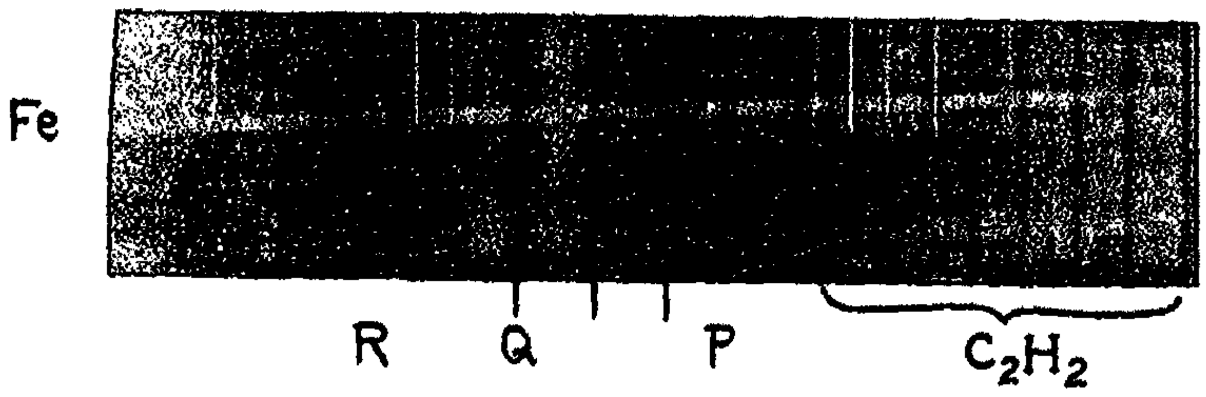

FIG. 1. Methylacetylene band at 10,304 A. U. The R branch is not resolved in the reproduction, although it is clearly resolved on the original plate, except at the end where the lines come too close together.

An absorption band of such a simple structure as found here for methylacetylene can only be explained by the assumption that the absorbing molecule is a symmetrical top, or at least very nearly so. Linearity, of course, is quite out of the question. Apart from obvious chemical reasons this is also impossible from purely spectroscopic reasons. As has also been observed by Gänswein and Meeke (6) for other derivatives of acetylene the $CH_3—C\equiv C—H$ band lies very close to the strongest acetylene band. There can therefore be no question but that it corresponds to the same transition as for acetylene, namely, $3\nu_{C-H}$, i.e., the second overtone of the C—H valence vibration. As this is a vibration parallel to the axis of the molecule the band could not have a *Q* branch if the molecule were linear.[2] The weakness of the band lines near the origin is another spectroscopic argument for non-linearity of the molecule (cf. below). Conversely, the actual occurrence of a strong *Q* branch, in addition to a simple *P* and *R* branch, proves that the molecule is a symmetrical top with a non-vanishing moment of inertia about the figure axis. The only plausible way in which this can be realized is that the four atoms C—C≡C—H are arranged on a straight line and that the three hydrogen atoms of the methyl group are symmetrically arranged about this line. The band structure is then also in harmony with the fact that the band corresponds to a || vibration.

If the molecule were slightly bent it would still be approximately a symmetrical top and therefore would give the same band structure. Such a slight angle however seems very unlikely, but would not change in any serious way the following conclusions. Any appreciable angle in the C—C≡C—H line would, however, alter the structure of the band fundamentally. Thus we may conclude from the spectrum that the four atoms C—C≡C—H are at least very nearly on a straight line.

We have not found any ⊥ band of methylacetylene corresponding to a ⊥ vibration of the CH_3 group, though such bands have been found by one of us (12) for the methyl halides.

QUANTITATIVE EVALUATION OF THE ROTATIONAL CONSTANTS AND OF THE MOMENT OF INERTIA

Table 1 gives the wave numbers of all the lines of the *P* and *R* branches which could be measured, as well as the wave numbers of the center and the head of the main *Q* branch. Though the head is not very pronounced and can therefore not be very accurately given, it is obviously this head which represents the zero line of the band.

The numbering of the lines in the *R* and *P* branches is not quite obvious, owing to the extreme weakness of the lines near the origin, which makes it impossible to measure them. The numbering was found in the following way: A formula of the type $\nu = a + bm + cm^2$ was fitted to the lines of the *P* branch and extrapolated to include the lines of the *R* branch. There was only one way in which this could be done. Thus the number of lines not measured between the *R* and *P* branches was obtained. One of the calculated lines in this gap coincided as nearly as could be expected with the head of the main *Q* branch, so that it was to be considered as the zero line and thus the numbering of all the other lines was given.

The rotational energy of a symmetrical top is given (3) by

$$F = \frac{E_r}{h\nu} = BJ(J + 1) + (A - B)K^2 \qquad (1)$$

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[2] Apart from that, perpendicular bands which have a *Q* branch constitute only the weakest bands of linear molecules in the photographic infra-red, whereas the methylacetylene band is the strongest in this region.

TABLE 1

Wave numbers of the band lines

J	P BRANCH	R BRANCH
2		9703.95
3		04.53
4	9700.26	05.11
5	9699.53	05.87
6	98.87	06.36
7	98.31	06.89
8	97.75	07.36
9		07.88
10		08.43
11	96.00	08.92
12	95.35	09.43
13	94.70	09.97
14	94.11	10.47
15	93.42	10.92
16	92.80	11.41
17	92.19	11.90
18	91.51	12.35
19	90.85	12.84
20	90.20	13.30
21	89.50	13.80
22	88.83	14.33
23	88.14	14.77
24	87.46	15.15
25	86.76	15.58
26	86.07	15.96
27	85.38	16.38
28	84.69	
29	84.01	Main Q branch
30	83.35	head: 9702.55 cm.$^{-1}$
31	82.48	center: 9702.30 cm.$^{-1}$
32	81.87	
33	81.22	
34	80.51	
35	79.82	
36	79.20	
37	78.33	
38	77.58	
39	76.83	
40	75.99	
41	75.23	
42	74.35	
43	73.62	

where K is the quantum number of the rotation about the figure axis, J the quantum number of the total angular momentum, $B = \frac{h}{8\pi^2 cI_B}$, and $A = \frac{h}{8\pi^2 cI_A}$, where I_A and I_B are, respectively, the moments of inertia about the figure axis and about an axis perpendicular to it. For a || band $\Delta K = 0$ and $\Delta J = 0, \pm 1$. For the previously discussed model of methylacetylene we have $B \ll A$. For a || vibration of the ≡C—H group B will change slightly in going from the ground state to an excited vibrational state, whereas A, i.e., the moment of inertia about the figure axis, remains practically constant. Owing to this and to the rule $\Delta K = 0$, we may neglect the second term $(A - B)K^2$ of equation 1 for the discussion of the structure of a || band. Thus we have the same formulae as for a linear molecule. We obtain the rotational constant B'' for the ground state, as for linear molecules, from the combination differences

$$\Delta_2 F''(J) = R(J-1) - P(J+1) = 4B''(J+\tfrac{1}{2})$$

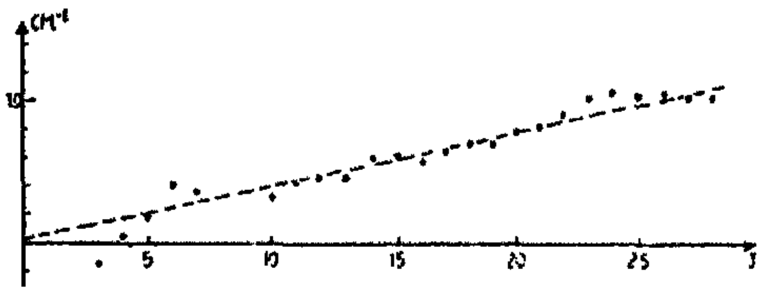

FIG. 2. $\Delta_2 F(J) - 4\tilde{B}(J+\frac{1}{2})$

Figure 2 gives the observed $\Delta F''(J)$ values after $4\tilde{B}(J+\frac{1}{2})$ with $\tilde{B} = 0.275$ has been subtracted. From the slope of the straight line through the origin the correction is found which has to be applied to $\tilde{B}$ in order to obtain the true rotational constant B''. A value

$$B'' = 0.28458 \pm 0.00010 \text{ cm.}^{-1}$$

is obtained. Changing B'' by only ± 0.00010 would give a straight line, which would leave all observed points below or all above itself except the five points with lowest J, which are known to be inaccurate owing to the weakness of the corresponding lines. Thus ± 0.0001 is a safe estimate of the possible error. The B value for the upper state was derived from the $R(J) + P(J)$ values (11) and found to be

$$B' = 0.28217 \pm 0.00010 \text{ cm.}^{-1}$$

The difference of B' and B'' gives for the rotational constant α_{CH} (change of B per vibrational quantum of the C—H vibration)

$$\alpha_{CH} = 0.00080 \text{ cm.}^{-1}$$

The moment of inertia of the molecule in the vibrationless state about an axis through the center of gravity perpendicular to the figure axis follows from B'' as

$$I''_B = 97.15 \times 10^{-40} \text{ or } 98.09 \times 10^{-40} \text{ g.cm.}^2$$

depending on the choice of the two values for h now in use ($h = 6.544$ or 6.607×10^{-27} erg. sec.).

The influence of the term with K^2 in equation 1 consists in the fact that each line with a certain value of J really is a superposition of J lines with different $K (K = 0, 1, 2, \ldots J)$, which coincide very nearly because of the equality of A in the upper and lower state.[3] As the number of superimposed lines increases with J it is to be expected and is indeed observed that the lines with small J are rather weak, comparatively weaker than in a similar band of a linear molecule (cf. above).

In the acetylene spectrum weaker bands accompanying the main bands were found which, as could be definitely shown by varying the temperature, are due to transitions in which in both the upper and the lower state of the main band a small perpendicular vibration is excited (4, 5, 11). At ordinary temperatures the percentage of molecules in the first excited state of a vibration of the order of 500 cm.$^{-1}$ is already sufficient to give a noticeable absorption. It is therefore not surprising to find similar subsidiary bands for methylacetylene. This is evidently the way in which the second weaker Q branch with head at 9697.06 and center at 9696.72 cm.$^{-1}$ is to be interpreted. The smallest frequency of methylacetylene is, from Raman data (8), 336 cm.$^{-1}$ Therefore the theoretical intensity ratio of the main and subsidiary band is (allowing for the factor 2 due to the degeneracy of the vibration) about 4:1, which does not contradict a visual estimate of the intensity ratio of the two Q branches (cf. figure 1). The distance between the two Q branches, 5.49 cm.$^{-1}$, is a measure of the interaction between the deformation frequency 336 and the C—H vibration 3300 cm.$^{-1}$, the interaction term x_{ik} in the expression for the vibrational energy levels being $\frac{1}{3} \times 5.49 = 1.83$ cm.$^{-1}$ The much weaker and doubtful Q branch at 9691.5 cm.$^{-1}$ may correspond to the second smallest vibrational frequency of the ground state, 643 cm.$^{-1}$

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[3] Owing to the fact that K^2 occurs with the factor $A - B$ there will, however, be a slight difference in the position of the lines with different K and equal J which is of the same order as the difference of the various lines with different J of the Q branch. As the Q branch is rather sharp it is not surprising that the individual lines of the P and R branch are also fairly sharp. But owing to this effect it will probably be impossible to resolve the end of the R branch (high J) even with higher dispersion than we used.

THE NUCLEAR DISTANCE OF THE C—C SINGLE BOND

If a, b, c, and d are the nuclear distances in the methylacetylene molecule, as indicated in figure 3, and φ is the angle of the C—H direction with the figure axis, the moment of inertia of the molecule about an axis perpendicular to the figure axis through the center of gravity is

$$I_B = m_C b^2 + m_H(b + a)^2 + m_C c^2 + \tfrac{3}{2} m_H d^2 \sin^2\varphi + 3m_H(c + d\cos\varphi)^2 - \frac{[(3m_H + m_C)c + 3m_H d\cos\varphi - (m_C + m_H)b - m_H a]^2}{3m_C + 4m_H} \qquad (2)$$

where m_H and m_C are respectively the masses of the hydrogen and the carbon atoms. From this equation c, the nuclear distance of the C—C single bond can be evaluated, if a, b, d, and φ are known.

Recently the nuclear distances C—H and C≡C in acetylene have been determined very accurately by investigating C_2HD as well as C_2H_2, with the result r_0 (C—H) = 1.057 A.U. and r_0 (C≡C) = 1.204 A.U. (9, 10).

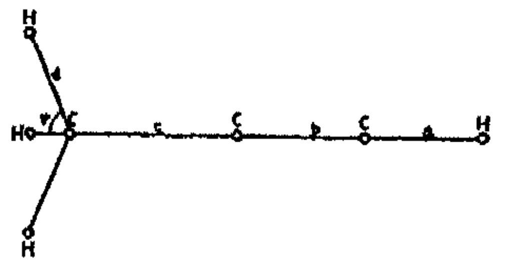

FIG. 3. The methylacetylene molecule

These values are believed to be accurate to ± 0.001 A.U. For hydrogen cyanide (HCN) in a similar way, but quite independently, the C—H distance was found to be the same as in acetylene within ± 0.003 A.U., whereas in methane the C—H distance turned out to be 1.093 A.U. (7).

It seems to be very probable that the C≡C and C—H distances in the acetylene group of methylacetylene are very nearly the same as in acetylene itself, and that the C—H distance in the methyl group as well as the angles in this group are very nearly the same as in methane. Thus we assume for methylacetylene: a = 1.057 A.U., b = 1.204 A.U., d = 1.093 A.U., φ = 70°32′. Using these values one obtains for the C—C single bond distance in methylacetylene

$$c = 1.463 \text{ A.U. or } 1.466 \text{ A.U.}$$

depending on whether the old or new set of values for the Avogadro number and for h is accepted. The possible error of c brought about by the error in I_B is certainly smaller than ± 0.002, very probably within 0.001 A.U. However an appreciably larger error may arise by a deviation from the assumed values for a, b, d, and φ.

In order to show the dependence of c on the other distances and the angle, table 2 gives the c value when changing each of the values of a, b, d, and φ. As is seen from this table, a 1 per cent change in the C—H distance a only gives a change of ± 0.001 A.U. in c. But a change of the C—H distance as high as 1 per cent in going from acetylene to methylacetylene seems extremely improbable, because there is nothing changed in the vicinity of this ≡C—H group and also because of the close coincidence of the C—H distance in acetylene and hydrogen cyanide. The value r (C—H) = 1.057 ± 0.001 A.U. must be considered as characteristic for the distance of a hydrogen atom from a carbon atom with a triple bond.

Similarly a change in the C—H distance of the methyl group by 1 per cent only produces a change of c by ± 0.001 A.U., whereas a change of the C≡C distance by 1 per cent produces a change of c by ± 0.009 A.U. Also in these cases a change of as much as 1 per cent does not seem very likely, even though one cannot give as convincing arguments as for a being unchanged.

TABLE 2

C—C bond distances for varied other distances and angles in the methylacetylene molecule

a	b	d	φ	c
A.U.	*A.U.*	*A.U.*		*A.U.*
1.057	*1.204*	*1.093*	*70°32′*	1.463 normal
1.067	1.204	1.093	70°32′	1.462
1.047	1.204	1.093	70°32′	1.464
1.057	*1.214*	1.093	70°32′	1.454
1.057	*1.194*	1.093	70°32′	1.472
1.057	1.204	*1.103*	70°32′	1.461
1.057	1.204	*1.083*	70°32′	1.464
1.057	1.204	1.093	*75°32′*	1.481
1.057	1.204	1.093	*65°32′*	1.445

One may perhaps not be quite as sure about the constancy of the angle in going from methane to methylacetylene. A change of only ±5° produces a change in c of ± 0.02 A.U. Usually, it is true, it is assumed that the tetrahedral angle is rather constant for compounds of carbon. If that is so a limit of error ± 0.005 A.U. may be given for the C—C single bond distance given above which would include small differences in a, b, d, and φ (below ± 1°) from the normal values in acetylene and methane, respectively. A definite answer to the question whether the angle is the same as in methane could be obtained if it were possible to investigate the spectrum of CD_3C_2H, which would give a similar band at about the same wave length. Its moment of inertia would give a second equation for the two unknowns c and φ.

If the assumed constancy of interatomic distances is correct[4] the value c for the C—C distance in methylacetylene derived above would constitute an accurate general value for the C—C single bond distance applicable also to other molecules. For some molecules other than methylacetylene this distance has been determined by electron diffraction. The most recent investigations have given $r(C—C) = 1.51 \pm 0.05$ for acetaldehyde (Ackermann and Mayer (1)) and $r(C—C) = 1.50 \pm 0.02$ for propane (Bauer (2)). Though these values are a little higher than our spectroscopic value they do not seem to be incompatible with it, owing to their rather large possible errors. It has to be pointed out that the electron-diffraction values for the C—C distance also depend partly on the assumption of constancy of interatomic distances. But if this assumption holds true our value for the C—C single bond distance is certainly more accurate than the electron-diffraction value, because it is based on the very accurately measured value for the moment of inertia of methylacetylene.

SUMMARY

The photographic infra-red absorption of methylacetylene ($CH_3—C\equiv C—H$) has been investigated. One band at 10,304 A.U. of simple type (*P*, *Q*, and *R* branch) has been found whose structure proves that the four atoms $>C—C\equiv C—H$ are on a straight line. The analysis of the band gives a very accurate value for the moment of inertia of the molecule in its ground state, $I_B'' = 97.15 \times 10^{-40}$ g.cm². From this the C—C single bond distance can be calculated if it is assumed that the other internuclear distances are the same as in acetylene and methane, respectively. A value $r_0(C—C) = 1.462 \pm 0.005$ A.U. is obtained. The possible error given includes small deviations of the other distances from their values in acetylene and methane up to ±1 per cent and a deviation in angle of the C—H direction to the figure axis from the tetrahedral angle up to ±1°.

The experiments underlying this paper were performed at the Physikalisches Institut der Technischen Hochschule Darmstadt (Director: Prof. H. Rau). We wish to express our thanks to the firm Agfa for supplying us with their excellent infra-red plates.

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[4] It has of course to be admitted that the constancy of interatomic distances for different compounds is not by far as certain as for the nuclear distances for isotopic molecules such as C_2H_2 and C_2HD, where any deviations are certainly much smaller than 1 per cent.

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RAMAN SPECTRA OF AMINO ACIDS AND RELATED COMPOUNDS. II

GUANIDINE AND UREA DERIVATIVES[1]

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The structure of guanidine and urea and their derivatives has long been a matter of debate among chemists, in spite of the small size and apparent simplicity of these molecules. The study of Raman spectra should be of aid in recognizing the nature of the chemical bonds involved and in evaluating their force constants, also in throwing some light on the type of symmetry present in the molecules. For this purpose, the Raman spectra of guanidine and methylguanidine hydrochlorides, methylurea, thiourea and thioacetamide have been determined; that of urea is already known (2, 5). Qualitative polarization measurements have also been made for the Raman lines of guanidine hydrochloride. Even when not quantitative, such measurements are often of value in assigning frequencies to modes of molecular vibration.

Taken in conjunction with observations from other sources, especially x-ray diffraction data, the observed Raman spectra appear to permit the drawing of some definite conclusions regarding the structure of the molecules. Further consideration also indicates that the formate ion, whose spectrum has been previously determined (2), bears a close resemblance in molecular symmetry to the other molecules and ions here considered. Tentative analysis of its Raman spectrum is undertaken with a result which may be of more general significance in throwing light on the structure of the ionized carboxyl group in other acids.

EXPERIMENTAL METHODS

The experimental technique employed for exciting the Raman spectra was essentially the same previously described (2), being modeled closely on that developed by R. W. Wood. Exposures were always taken in filtered light. To isolate the 4047 mercury line, a dilute solution of sodium nitrite

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[1] Presented at the Symposium on Molecular Structure, held at Princeton University, Princeton, New Jersey, December 31, 1936 to January 2, 1937, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society.

(about 0.02 saturated in a layer 30 mm. thick) was used to remove all lines below 4000 A.U., and Corning red-purple ultra glass (2 mm. thick) to remove the 4358 line and all lines of longer wave length. To transmit 4358 A.U., removing 4047 and all shorter wave lengths, a dilute solution of *p*-nitrotoluene in alcohol was employed (1). Exposures were taken with both filters for every substance examined except thiourea and thioacetamide. In aqueous solution these substances decompose, under the influence of light, giving a very fine cloudy precipitate (sulfur ?), which produces such intense continuous background as to mask the Raman lines. These solutions were, therefore, studied using very short exposures at very high light intensities, using either the *p*-nitrotoluene solution or dilute sodium nitrite (without the purple glass) as a filter. The Raman tube was watched carefully and, as soon as the cloudy precipitate began to form, the exposure was stopped (generally after about ten minutes). Under these circumstances a fairly satisfactory spectrum of thiourea was obtained, but the spectrum found for thioacetamide is certainly incomplete.

Further details concerning the substances studied will be found in table 2, which gives a complete list of the spectra obtained.

DISCUSSION

The observed spectra, including that of urea, which has been previously studied, are listed in table 2 and shown graphically in figure 1. The general similarity in the spectrum of urea and of the guanidonium ion is obvious and striking, as might indeed have been expected from their general structural likeness. The close similarity between methylurea and the methylguanidonium ion is also immediately apparent. Thiourea shows a spectrum closely analogous to that of urea, but with most of the frequencies displaced to lower values. The incomplete spectrum of thioacetamide indicates the close relationship of this substance to thiourea. The general character of the spectra, taken in conjunction with what is known of the chemistry of these substances, indicates that these molecules all belong to a closely related group.

In the more detailed discussion of these spectra which follows, two considerations are important. Both experiment and theory have shown (3) that only compounds containing covalent bonds give rise to Raman frequencies, at any rate in the range with which we are here concerned (> 300 cm.$^{-1}$). Thus the Raman spectrum of guanidine hydrochloride is the spectrum of the guanidonium ion, $^{+}C(NH_2)_3$. Moreover, in a first approximation, the NH_2 group may be treated as a single vibrating unit, urea and the guanidonium ion being considered for purposes of calculation as tetratomic molecules. The NH_2 group, like the CH_2 group, may of course be expected to give rise to characteristic internal valence and deformation frequencies, which must be allowed for in the analysis of the observed spectra.

The most striking feature in the very similar spectra of urea [$O{=}C(NH_2)_2$] and the guanidonium ion [$^+C(NH_2)_3$] is the intense line which lies in both cases almost exactly at 1000 cm.$^{-1}$ It should be noted that the oxygen atom in urea has virtually the same mass as the NH_2 groups, so that if the strength of the bonds is similar, the type of symmetry in the two compounds is not very unlike. Closer examination shows, however, that the spectrum of the guanidonium ion is distinctly simpler than that of urea, suggesting a higher type of molecular symmetry in the former. Thus the line at 1170 cm.$^{-1}$ in urea has no counterpart in the spectrum of the guanidonium ion, and the one fairly strong line at 533 in the guanidonium ion is replaced by two weaker lines at 521 and 584 in urea. This may well represent the splitting of a doubly degenerate frequency due to a reduction of the symmetry of the molecule. Such a distinction between the two compounds should not be expected from the classical formulas, according to which urea was generally written as shown in formula I, and the guanidonium ion as shown in formula II.

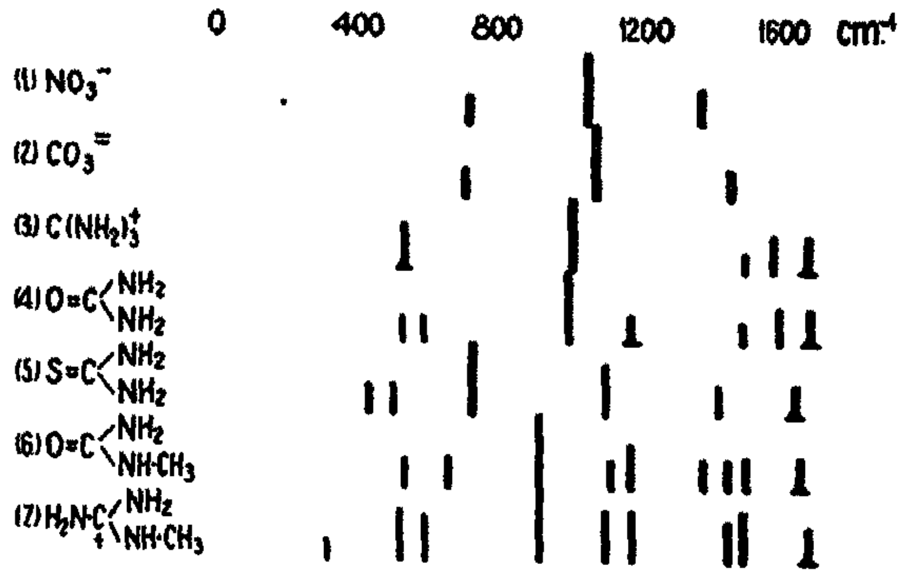
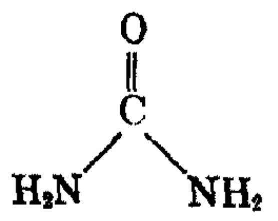


FIG. 1. Raman spectra of (1) the nitrate ion, (2) the carbonate ion, (3) the guanidonium ion, (4) urea, (5) thiourea, (6) methylurea, (7) the methylguanidonium ion. The height of the Raman lines indicates roughly their relative intensities. A broad line is indicated by broadening at the base. The lines above 1600 cm.$^{-1}$ may be due, at least in part, to the water used as solvent.



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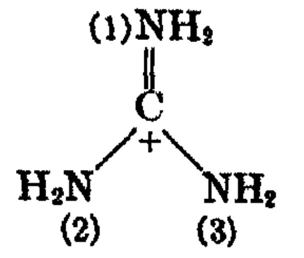
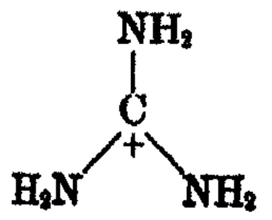


II

Treating the NH_2 groups as unit masses, and assuming that all the bonds lie in one plane, each of these structures should possess a twofold symmetry axis (symmetry C_{2v}). This indeed appears to harmonize with the observed spectrum in the case of urea (although the classical formula probably requires a revised interpretation). For the guanidonium ion, however, it has been shown on other grounds that the classical formula is in need of revision. In formula II a double bond is shown as joining the carbon to nitrogen atom 1. If it were attached instead, however, to either atom 2 or 3, the three resulting structures would be completely equivalent. Under these circumstances, as pointed out by Pauling, Brockway, and Beach (8), complete resonance between all these possible structures should occur, the resulting ion possessing trigonal symmetry (symmetry D_{3h}), the carbon and the nitrogen atoms being all coplanar:



III

This is exactly analogous to the structures already demonstrated (9) for the carbonate and nitrate ions. The three C—N bonds are all equivalent, and in strength probably approach more nearly to double than to ordinary single bonds. The x-ray diffraction measurements of Theilacker (10) on the guanidonium halides are entirely in harmony with this picture, the results indicating the complete equivalence of the three C—N bonds. The low carbon-nitrogen distance (about 1.18 A.U.) indicates that the bond is a very strong one.

A molecule showing this type of symmetry should give rise to three Raman frequencies (9, 12): one totally symmetric and polarized, ν_1, and two degenerate frequencies which are depolarized, ν_2 and ν_3 ($\rho = 6/7$). (A fourth, asymmetric frequency is Raman-inactive, although present in infra-red absorption.) Polarization measurements show the intense line at 1008 cm.$^{-1}$ to be highly polarized, while those at 533, 1566, and 1662 are almost completely depolarized. ν_1 is therefore 1008 cm.$^{-1}$, while 533 certainly corresponds to one of the degenerate frequencies (ν_2). ν_3 may be represented either by the very weak line at 1480, or by one of the somewhat stronger lines at 1566 or 1662. One of these frequencies probably represents a deformational vibration of the NH_2 group, and that at 1662 may be partly due to the weak water band present in this range. Any definitive assignment of these three frequencies is impossible on the basis of the present data.

The force constants of the C—N bonds can, however, be approximately calculated if the guanidonium ion be treated as a valence force system (6). On this assumption, the binding constant, f, is uniquely determined in terms of the frequency ν_1 and the mass of the NH_2 group, and is found to be 9.54×10^5 dynes cm.$^{-1}$. Using this value and the observed value of ν_2 (533 cm.$^{-1}$), we may then solve for d, the deformation constant of the C—N bond, and also calculate the third frequency, ν_3. Comparable calculations may also be made for the NO_3^- and CO_3^{--} ions, and the results are summarized in table 1.

It is apparent that the calculated values of ν_3 for the nitrate and carbonate ions are grossly in error. This discrepancy indicates the inadequacy of the assumptions involved in a valence force system to account for the behavior of a molecule of this type. It is therefore impossible to use these calculations to decide which of the observed frequencies corresponds to ν_3 for the guanidonium ion. It is perhaps significant, however, that the calculated f values are much closer to those generally typical of double bonds (10 to 12 × 10^5) than to those of single bonds (4 to 5 × 10^5),—a result entirely in harmony with the expectations from Pauling's theory.

Urea unquestionably possesses a lower degree of symmetry than the guanidonium ion. This conclusion follows both from the Raman spectrum and from the x-ray diffraction measurements of Wyckoff and Corey (14), which show the carbon–oxygen distance to be markedly lower than the carbon–nitrogen distance. As would have been inferred from the classical formula, the symmetry is undoubtedly C_{2v}; the molecule should give rise to six fundamental frequencies, all present in the Raman spectrum, three polarized and three depolarized (12). An attempt to analyze the spectrum of urea on this basis has already been made by Kohlrausch and Pongratz (5), who have pointed out the inadequacy of the assumptions involved in a valence force treatment as applied to a system of this sort. In their treatment, they assume (as would follow from the classical formula) that the C—N bonds have the strength of single bonds only. According to Pauling, Brockway, and Beach (8), however, resonance between the C═O and the two C—N bonds is nearly complete; hence the C—N bonds are probably closer to double than to true single bonds in strength. On no assumption, however, does the oversimplified valence force picture give anything approaching a quantitative description of the facts.

TABLE 1

Frequencies and force constants of the carbonate, nitrate, and guanidonium ions

ION	ν_1 (OBSERVED)	ν_2 (OBSERVED)	ν_3 (OBSERVED)	ν_3 (CALCULATED)		d
CO_3^{--}	1065	714	1438	1985	10.65 × 10^5	1.115 × 10^5
NO_3^-	1050	720	1360	1870	10.36 × 10^5	1.16 × 10^5
$C(NH_2)_3^+$	1008	533	$\left\{\begin{matrix}1480\\1566\\1662\end{matrix}\right\}$?	1820	9.54 × 10^5	0.578 × 10^5

Thiourea

The spectrum of this substance is of exactly the same type as that of urea. The powerful line at 732 corresponds to the symmetrical vibration at 1000 in urea; and the two weaker lines at 418 and 487 in thiourea appear to be the exact analogues of those at 521 and 584 in urea. Not only is the sulfur atom more massive than oxygen, but the carbon to sulfur distance in thiourea, 1.64 A.U., (13) is much greater than the carbon to oxygen distance in urea. Furthermore, the force constant of the C=S bond is probably much less than that for the C=O bond in urea, since its value for C—S in methyl mercaptan is only about three-fifths of that for C—O in methyl alcohol (4). As with urea, however, no quantitative description by a valence force system is possible.

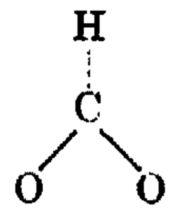
The very similar molecule, thioacetamide, in which the symmetry has been destroyed by replacing one NH_2 by a CH_3 group, shows as its principal vibration a frequency (714 cm.$^{-1}$) very close to that of thiourea.

Methyl urea and the methylguanidonium ion (see figure 1)

These two substances possess Raman spectra extraordinarily alike, indicating that the pattern of molecular structure in the two is essentially identical. Evidently the difference between the C=O bond in the one compound and the C—NH_2 bond in the other is very slight as compared with the disturbance of symmetry introduced by the presence of the methyl group in both compounds.

The formate ion

Since there is no obvious basis for distinguishing between the two oxygens in the ionized carboxyl group, resonance between them is probably complete, and the two C—O bonds and C–O distances should be identical. On this assumption, the formate ion,



IV

possesses a twofold axis of symmetry (symmetry group C_{2v}) and is thus closely analogous to urea or to (unpolymerized) formaldehyde. The Raman spectrum of the ion has been previously determined (2), and consists of the following lines (in cm.$^{-1}$): 772 (1), 1072 (1), 1351 (6), 1386 (1), 1611 (0), 2123 (1b), 2734 (2b), 2823 (6b). The figures in parentheses indicate roughly the relative intensities of the lines; that at 1611 may be due to the water used as solvent.[2] For comparison, a calculation has been made of

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[2] Venkateswaran (11) has reported a spectrum for the formate ion differing from this in some important respects. The spectrum reported here was obtained from two sodium formate solutions, prepared from pure formic acid made by two different firms. The two spectra agreed completely, and the results are therefore believed to be trustworthy. The problem is, however, being further investigated.

the vibrations of a valence force system of this type (6), assuming $f_{C-O} = 10^6$ dynes cm.$^{-1}$ (nearly as in the carbonate ion), $f_{C-H} = 4.5 \times 10^5$, and taking the deformation constants for these bonds as $d = 0.21 \times 10^6$ and $d^1 = 0.6 \times 10^5$, respectively. The C-H distance was taken as 1.08 A.U.; C-O as 1.29 A.U.; and the angle between the two C—O bonds as 125° (7). The calculated spectrum was 413 (*P*), 1270 (*P*), 1375 (*D*), 1960 (*D*), 2903 (*P*). Depolarized frequencies ($\rho = 6/7$) are denoted by *D*; polarized ones by *P*. (One depolarized frequency, which should be active in the Raman spectrum, is not given by the calculation.) Quantitative agreement, of course, is not to be expected, but the general features of the observed spectrum are roughly reproduced. The two very intense lines at 1351 and 2823 in the observed spectrum are probably highly polarized, and should correspond in type to the calculated frequencies 1270 and 2903. Further studies on the spectra of this and related compounds, including polarization measurements, are now being undertaken, in order to test more rigorously the interpretation here tentatively developed.

SUMMARY

1. The Raman spectra of thiourea, the guanidonium ion, the methylguanidonium ion, methylurea, and thioacetamide have been determined. All of these compounds, and also urea, give spectra of closely related type.

2. The spectrum of the guanidonium ion indicates that it possesses trigonal symmetry, like the carbonate and nitrate ions, as would be expected from the theory of resonance and from x-ray diffraction data. Urea and thiourea possess a lower degree of symmetry (twofold axis).

3. It is concluded that because of resonance, the formate ion should possess a twofold symmetry axis, similar to that in unpolymerized formaldehyde. A tentative analysis of its Raman spectrum is suggested on this basis.

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TABLE 2

Observed Raman spectra

COMPOUND	FORMULA	SOURCE	SOLUTION USED	VALUES
1. Thiourea	$S{=}C(NH_2)_2$	Eastman	9 per cent solution in water; saturated	$\Delta\nu$ = 418 (0) (e); 487 (1) (k, e); 732 (6) (k, i, f, e); 1099 (4b) (k, e); 1406 (1vb) (e); 1628 (½vb) (e) (water?)
2. Guanidine hydrochloride	$C^+(NH_2)_3\overset{-}{Cl}$	Eastman	60 per cent solution in water + 0.1 *N* HCl	$\Delta\nu$ = 533 (3) (k, i, e); 1008 (8) (k, i, g, f, e); 1480 (½) (k, e); 1566 (1b) (k, e); 1662 (1b) (e) (water?); 3251 (2vb) (k); 3354 to 3461 (6vb) (k) (water); 3615 (1b) (k?)
3. Methylguanidine hydrochloride	$(H_2N)_2\overset{+}{C}(NHCH_3)\overset{-}{Cl}$	Hoffman-La Roche	50 per cent solution in water + 0.3 *N* HCl	$\Delta\nu$ = 327 (½b) (e); 511 (4b) (k, i, e); 599 (3b) (k, i, e); 915 (8) (k, e); 1095 (3b) (k, i, e); 1176 (3b) (k, e); 1435 (2) (k, e); 1470 (4) (k, e); 1671 (1vb) (e) (water?); 2835 (3) (k); 2956 (6b) (k, e); 3021 (3b) (k, e)

4. Methylurea..............	$(NH_2)CONHCH_3$	Eastman, m.p. 101–2°C.	45 per cent solution in water (marked fluorescence, strong continuous background)	$\Delta\nu$ = 527 (1) (k, e); 666 (1) (k, e); 917 (6) (k, e); 1103 (1) (k, e); 1163 (2) (k, e); 1365 (1) (k, e); 1426 (1) (k, e); 1478 (1) (k, e); 1644 (1vb) (e) (water?); 2909 (0) (k); 2940 (3) (k, e, f)
5. Thioacetamide............	CH_3CSNH_2	Eastman	20 per cent solution in water (spectrum incomplete)	$\Delta\nu$ = 722 (4) (k, e); 1044 (1) (e); 1431 (½b) (e); 1492 (½b) (e); 2921 (1b) (e)
6. Urea.....................	$O{=}C(NH_2)_2$		In water	See references 2 and 5

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* For each Raman line is given: (1) its frequency shift in cm.$^{-1}$; (2) in parentheses, its estimated relative intensity; "b" denotes a broad line, "vb" very broad; (3) the mercury lines exciting it; Kohlrausch's notation (reference 4, p. 19).

THE RAMAN EFFECT OF DEUTERIOAMMONIA[1,2]

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INTRODUCTION

The apparatus developed in this laboratory (3) has been used to study the Raman spectrum of gaseous heavy ammonia,[3] ND_3. An improvement introduced by us consisted of a cylindrical aluminum reflector surrounding the eight mercury-neon lamps. To the end of the reflector was attached a 3-in. pipe leading to an air blower which permitted fair control of the temperature.

EXPERIMENTAL RESULTS

The sample of heavy ammonia was contained in a Raman tube of 250-cc. capacity at a pressure of about 900 mm. of mercury. Because of the limited amount of the sample only two Raman frequencies of the four expected could be obtained in spite of the very long exposure times used. One of the frequencies found could be photographed in five days, and a ten-day exposure yielded the other line. Our results are in agreement with the findings of Silverman and Sanderson (8) in the infra-red, as seen in table 1. The value of the N-D vibration (ν_1) given in table 1 is the mean of ten observations (see table 2). The frequency shift (ν_3) corresponding to the doublet obtained by Amaldi and Placzek (1) for light ammonia at 933.8 and 964.3 cm.$^{-1}$ was much more difficult to measure. The mean position was determined on one plate which resulted from a ten-day exposure. It is seen that the values of the fundamental frequency ν_1 found in the infra-red and in the Raman spectrum are in good agreement. It seemed impractical to make further effort to obtain the other two lines, since their intensity was likely to be extremely low, because the change in polarizability during the motion of the atoms involved in these two de-

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[1] Presented at the Symposium on Molecular Structure, held at Princeton University, Princeton, New Jersey, December 31, 1936 to January 2, 1937, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society.

[2] This article is based upon part of a thesis to be presented to the Faculty of the Graduate School of the University of Minnesota by F. T. Wall in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] We wish to thank Professor H. S. Taylor of Princeton University for a sample of ND_3.

generate frequencies is very small. This situation is similar to the case of methane studied by MacWood and Urey (5).

THE THEORY OF SMALL VIBRATIONS APPLIED TO ND_3

By means of the method of small vibrations, it is possible to obtain expressions for the fundamental frequencies of a molecule (for example, ND_3) in terms of the force constants, masses, and geometric properties (2, 4, 7). Assuming a potential function of the form

TABLE 1

Fundamental frequencies of ND_3

FREQUENCY	INFRA-RED (6)	RAMAN LINES	THEORETICAL
	cm.$^{-1}$	*cm.*$^{-1}$	*cm.*$^{-1}$
ν_3	748	786 (?)	722
ν_4	1191		1190
ν_1	2420	2420.0	2377
ν_2	2556		?

TABLE 2

The value of ν_1

EXPERIMENT NO.	Hg-EXCITING LINE		FREQUENCY SHIFT
	A.U.	A.U.	*cm.*$^{-1}$
1(a)	4047		2419.5
1(b)		4358	2418.7
2(a)	4047		2420.1
2(b)		4358	2419.5
3(a)	4047		2419.3
3(b)		4358	2420.9
4(a)	4047		2420.8
4(b)		4358	2420.4
5(a)	4047		2420.8
5(b)		4358	2419.9
Average			2420.0

$$V = \tfrac{1}{2}k_{\mathrm{ND}}(x_1^2 + x_2^2 + x_3^2) + \tfrac{1}{2}k_{\mathrm{DD}}(y_{12}^2 + y_{23}^2 + y_{31}^2) \tag{1}$$

the equations of motion can be written

$$\begin{aligned}
\ddot{x}_1 &= ax_1 + bx_2 + bx_3 + cy_{12} + 0 + cy_{31} \\
\ddot{x}_2 &= bx_1 + ax_2 + bx_3 + cy_{12} + cy_{23} + 0 \\
\ddot{x}_3 &= bx_1 + bx_2 + ax_3 + 0 + cy_{23} + cy_{31} \\
\ddot{y}_{12} &= fx_1 + fx_2 + 0 + 4gy_{12} + gy_{23} + gy_{31} \\
\ddot{y}_{23} &= 0 + fx_2 + fx_3 + gy_{12} + 4gy_{23} + gy_{31} \\
\ddot{y}_{31} &= fx_1 + 0 + fx_3 + gy_{12} + gy_{23} + 4gy_{31}
\end{aligned} \tag{2}$$

where x_i is the displacement of the distance N–D$_i$ from equilibrium and y_{ij} is the displacement for the distance D$_i$–D$_j$.

The constants have the values

$$a = -\left(\frac{1}{m_0} + \frac{1}{m_1}\right)k_{\mathrm{ND}}$$

$$b = -\frac{1}{m_0}k_{\mathrm{ND}}\cos\theta$$

$$c = -\frac{1}{m_1}k_{\mathrm{DD}}\cos\phi$$

$$f = -\frac{1}{m_1}k_{\mathrm{ND}}\cos\phi$$

$$g = -\frac{1}{2m_1}k_{\mathrm{DD}}$$

where m_0 = mass of the nitrogen atom, m_1 = mass of the deuterium atom, θ = angle between two valence bonds, and ϕ = angle N–D–D = $\pi/2 - \theta/2$. k_{ND} and k_{DD} are the force constants.

Assuming simple harmonic vibrations, i.e.,

$$\begin{aligned} \ddot{x}_i &= -n^2x_i \\ \ddot{y}_{ij} &= -n^2y_{ij} \end{aligned} \tag{3}$$

where $n/2\pi$ = frequency, then one arrives at a determinantal equation which reduces to

$$\begin{aligned} &[n^4 + (a + 2b + 6g)n^2 + (6ag + 12bg + 4cf)]\cdot \\ &\qquad [n^4 + (a - b + 3g)n^2 + (3ag - 3bg - cf)]^2 = 0 \end{aligned} \tag{4}$$

There will be six roots for n^2, two single roots and two double roots, the double roots corresponding to degenerate vibrations.

ASSIGNMENT OF TYPE OF VIBRATIONS TO THE FREQUENCIES

Introducing the values of the above frequencies back into equations 2 and taking into account equations 3, it is possible to find the types of vibrations associated with the different frequencies. This is done by finding the ratios of the displacements by making use of the substituted equations (2).

For the non-degenerate frequencies it is seen that

$$x_1 = x_2 = x_3;\ y_{12} = y_{23} = y_{31} \tag{5}$$

and that

$$\frac{x_1}{y_{12}} = -\frac{n^2 + 6g}{2f} \tag{6}$$

From equation 5 it is seen that the non-degenerate vibrations are totally symmetrical, with the nitrogen atom moving along the axis of symmetry. From equation 6 we find that the ratio of displacements is positive for a value of n^2 greater than $-6g$, since f is negative. The higher frequency has such a value that the ratio is positive and for the lower frequency the ratio is negative. Hence for the higher frequency the motion is such that the deuterium atoms move nearly along the valency bond directions, and for the lower frequency they move in a direction somewhat perpendicular to the valency bonds.

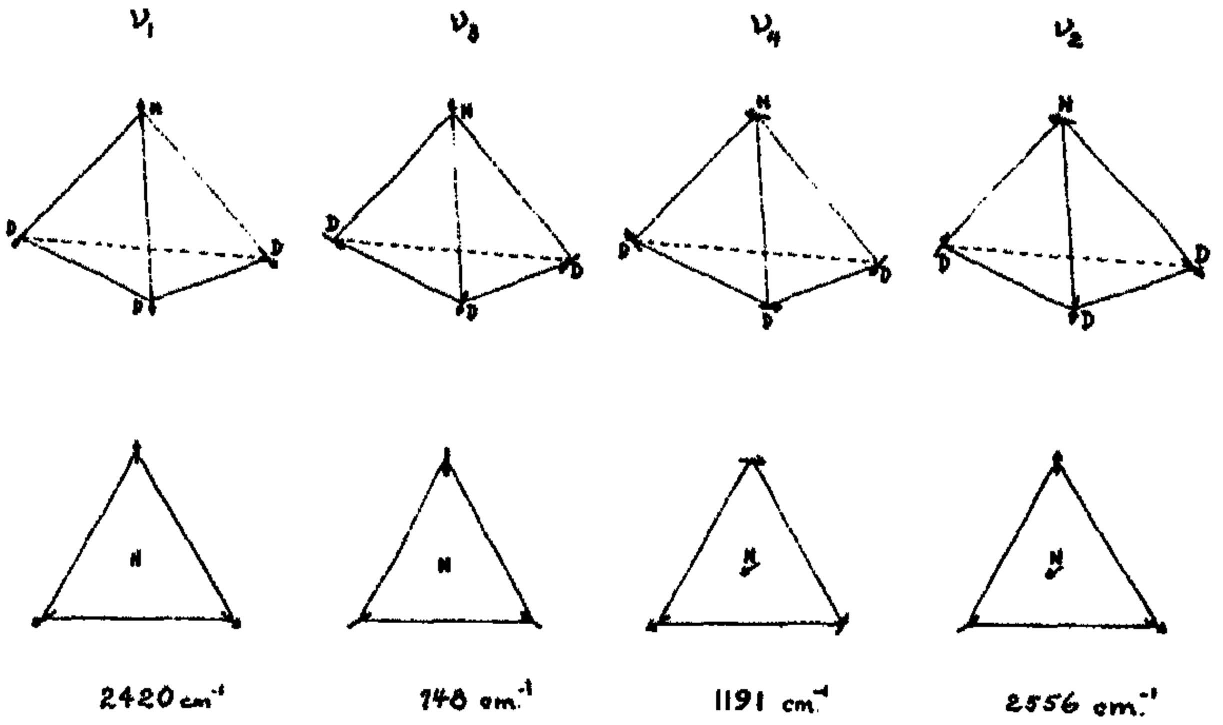

FIG. 1. Fundamental frequencies of deuterioammonia. ν_1 and ν_3 are non-degenerate, totally symmetrical vibrations; ν_2 and ν_4 are degenerate vibrations.

For the degenerate vibrations it is not possible to find all of the ratios of displacements, but the following information is available:

$$x_1 + x_2 + x_3 = 0 \text{ and } y_{12} + y_{23} + y_{31} = 0$$

Also

$$\frac{x_3}{y_{12}} = \frac{x_2}{y_{31}} = \frac{x_1}{y_{23}} = \frac{n^2 + 3g}{f}$$

For the lower degenerate frequency, as the distance between the nitrogen atom and one deuterium atom lessens, the distance between the other two deuterium atoms lessens also, but for the higher degenerate frequency, the signs of these displacements are opposite.

In the degenerate vibrations, the nitrogen atom moves transversely to the axis of symmetry, while the deuterium atoms move unsymmetrically along or transversely to the valence bond directions, depending upon whether the frequency is high or low.

Using the expression for the frequencies of the ND_3 type molecule we have recalculated three of the four frequencies for heavy ammonia, making use of the observed values for light ammonia (8) and the ratio of the force constants given by Howard (4). The calculated values are found in table 1. The agreement between the experimental and calculated values of the frequencies is about as good as can be expected, taking into account the approximations involved.

SUMMARY

The Raman spectrum of deuterioammonia, ND_3, has been studied. The results check satisfactorily with the infra-red spectrum. A method of allocating types of motions of atoms to the fundamental frequencies has been illustrated in some detail. This is done by finding the ratios of the displacements of the atom from equilibrium for a given vibrational frequency.

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ENTROPY AND THE SYMMETRY OF THE BENZENE MOLECULE[1]

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Deitz and Andrews (6) in 1932 made the first attempt to decide a question of molecular structure by a thermal-spectroscopic determination of symmetry number. In spite of the handicap of incomplete data and of a vibrational analysis made with the roughest sort of approximations, their effort produced the very reasonable value of six for the symmetry number, σ, of benzene. Definition of the symmetry number and the method of combining thermal and molecular information for the computation of σ are presented in detail in the paper of Deitz and Andrews.

Since 1932, much theoretical and experimental work has been carried out with the object of clearing up the problem of the internal frequencies of benzene. In addition, deficiencies in accuracy of the low temperature thermal data have lately been removed by Ahlberg, Blanchard, and Lundberg (1). Accordingly it is now possible to make a much more reliable calculation of σ for benzene.

The symmetry number of the particular type of molecule present in a gaseous system enters the expression furnished by statistical mechanics for the entropy, S_g, of that system. If all the components of this expression except σ can be evaluated, we can determine σ by an experimental evaluation of the entropy of the gas. The calculation of S_g requires a considerable amount of molecular information, namely the molecular weight, the moments of inertia, the complete set of vibrational frequencies, and the symmetry number. Granted a knowledge of all these items except σ, and given experimental access to S_g, σ becomes easily determinable. The moments of inertia can be computed without difficulty when geometrical data are available for the molecule. The essentially important item is therefore the complete set of vibrational frequencies, and the determination of this set by analysis of spectroscopic data on benzene is our chief problem.

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The experimental data available for a determination of the thermal value of S_g are quite satisfactory. A survey of the estimated reliabilities of these thermal data leads to the conclusion that, barring the possibility of undiscovered transitions and of anomalous behavior of the heat capacity below 2°K., the thermal entropy of gaseous benzene at the boiling point is in error by about 0.5 per cent.

THE VIBRATIONAL FREQUENCIES OF BENZENE

The frequencies of the benzene molecule have been the object of much widely varied study, particularly since the discovery of deuterium. The number of investigators of this compound in the different fields of molecular spectroscopy has been quite large. The spectroscopic data have been summarized quite thoroughly by Ingold et al. (9). The values of Raman and infra-red frequencies which we have utilized are in essential agreement with those in the summaries. In addition the fact that benzene possesses particularly high symmetry has incited several theoretical attacks (3, 19, 21, 22) on the vibrational forms of the molecule. The most complete theoretical study is that of Wilson (21). In this paper Wilson not only obtained normal coördinates for the vibrations of benzene, but in addition suggested a simple and plausible potential system on the basis of which the equations for actual frequencies were worked out. These equations are quite helpful in interpreting observed frequencies, and are especially valuable for estimation of those frequencies which are not observable.

The benzene molecule possesses thirty degrees of vibrational freedom, of which ten are non-degenerate and ten doubly degenerate. The twenty distinct frequencies have modes of vibration which are predetermined by the symmetry of the molecule. The actual modes have been given by a number of investigators (9-VIII, 11, 20, 21). Of the twenty frequencies, four are obtained from the roots of a quartic equation, three from a cubic, five pairs from the roots of five quadratics, and three from the single roots of three linear equations. Wilson's article gives the explicit equations for all frequencies save those coming from the quartic and cubic. These latter he leaves in the form of secular determinants. The determinants have been expanded by Kohlrausch (11), whose expansion we have been able to check except for one considerable discrepancy: the first term in the coefficient of λ in the cubic as given by Kohlrausch is twice too large.

The evaluation of five of the six force constants of the Wilson potential scheme has been carried out by Kohlrausch for benzene and benzene-d_6. K and q (see table 1) may be obtained directly from frequencies ν_1 and ν_2 (Wilson's notation) and h from ν_{10}. k and H require more complicated determination, since the observable frequencies involving them derive from the quartic and cubic equations. Kohlrausch has evaluated k by assigning to the unobservable frequency ν_{13} a definite value of 1000 cm^{-1}.

We agree with this assignment and will list the arguments in its favor later on.

Kohlrausch used a graphical method for obtaining H from the quartic. His method seemed rather dubious to us, and we therefore devised several approximation methods of solving the four relationships between the force constants and the frequencies of the quartic. The approximation methods yielded values of q and k in good agreement with those found in other ways. The constant K, however, turned out to be somewhat lower than its value as found from ν_1 and ν_2, and H appeared to be rather too high. It is probable that the quartic is an equation of restricted validity, because of the overly simplified form of the potential function. H was therefore evaluated from the cubic, the frequencies of which are observable in the infra-red. The values of H we obtained from benzene and benzene-d_6, respectively, are in good agreement. On the other hand, Kohlrausch reports an increase of some 15 per cent in H for benzene-d_6 over that for benzene. This apparent increase is doubtless due to his interpretation of the infra-red band at 1440 cm.$^{-1}$ in benzene-d_6 as a fundamental, which interpretation may have been expedited by the previously mentioned error in the λ-term of the cubic. If this fundamental is identified with the 1330 cm.$^{-1}$ band, the value of H for benzene-d_6 lies within about 2 per cent of that for benzene. This assignment is supported by the calculated ratio for the benzene–benzene-d^6 shift, which can be determined with the help of Teller's unpublished theorem concerning isotopic vibrational shifts (see reference 9-VIII).

There are eleven frequencies in benzene which are observable in the Raman effect or in infra-red absorption. These eleven frequencies, constituting *nineteen* of the thirty vibrational degrees of freedom, are listed in table 1, with the corresponding calculated values. The only notable departure of calculated from observed frequency occurs in ν_{11}, where the discrepancy is as large as 15 per cent. The disagreement is puzzling, for there seems to be no explanation for the failure of the Wilson potential scheme for this particular mode of vibration. The failure of the assumed potential system under such apparently favorable circumstances indicates that one must not be too sanguine about the calculation of unobserved frequencies.

The remaining eleven degrees of freedom are represented by nine unobservable frequencies. These nine frequencies may be divided into the five non-degenerate vibrations which take place in the plane of the ring, and the four vibrations, two of which are degenerate, that do not preserve the plane of the ring as an element of symmetry.

The force constants involved in the five planar vibrations, namely K, q, k, and H, can be determined from the observable frequencies. Accordingly the calculation of these unobservable frequencies by means of Wilson's equations is possible. We have made such a calculation using the values of K, q, and k listed in table 1. In addition we felt that it would be worthwhile to attempt to improve the value of the constant H by taking into account repulsion between adjacent hydrogen atoms. H can be considered as made up from several components, namely the "directed" C—H valence bond, repulsion between the hydrogen atom and the two carbon atoms nearest the carbon atom to which the hydrogen atom is bound, and repulsion between neighboring hydrogens. The first two components may be considered to remain fairly constant from one vibration form to the next, and thus may be said to determine the "basic value" of H. The remainder of H is composed of hydrogen–hydrogen repulsion, which varies greatly from one vibrational mode to another. In the planar bending frequency ν_3, for example, the hydrogen–hydrogen distance does not change, whereas in ν_9 or ν_{18} the distance alters quite significantly.

TABLE 1

Frequencies in benzene and force constants involved in vibrations

FREQUENCY NUMBER	DEGENERACY	BENZENE		BENZENE-d_6		OBSERVED IN
		Calculated	Observed	Calculated	Observed	
1	1	992.6*	992.6	946.6*	946.6	Raman effect
2	1	3061.5*	3061.5	2292.0*	2292.0	Raman effect
6	2	608	606.4	580	581.6	Raman effect
7	2	3107	3048.3	2324	2266.8	Raman effect
8	2	1645	1595	1616	1555.4	Raman effect
9	2	1170	1176.0	863	869.8	Raman effect
10	2	849.7*	849.7	662*	662	Raman effect
11	1	783	670	580	503	Infra-red
18	2	1030	1025	800	813	Infra-red
19	2	1480	1477	1330	1333	Infra-red
20	2	3080	3077	2294	2294	Infra-red

FORCE CONSTANT	VALUE IN 10^5 DYNES PER CM.		FORCE CONSTANT	VALUE IN 10^5 DYNES PER CM.	
	Benzene	Benzene-d_6		Benzene	Benzene-d_6
K (C—C stretching)	7.58	7.62	H (C—H bending in plane)	0.76	0.78
q (C—H stretching)	5.05	5.11	h (C—H bending out of plane)	0.34	0.34
k (C—C—C bending)	0.65	0.65	κ (C—C bond torsion)	0.23	0.23

* These frequencies were used for direct calculation of force constants.

The repulsion between the hydrogens bound to adjacent carbon atoms can be calculated fairly well from Morse's equation (15) after the manner of Eyring (7). The Morse expression does not include van der Waals or ionic forces. The latter we neglect, and the contribution of the former is calculated by the well-known equation of London (13). The net contribution of hydrogen–hydrogen interaction to *H* for the various modes of vibration is:

Vibration No.	3	9	14	18
Contribution of repulsion, in 10^6 dynes per contimeter	0	0.11	0.17	0.11

It is thus apparent that the effect of repulsion may be considerable. The "basic value" of *H*, which is to be used to calculate ν_3, is obtained by subtracting 0.11 from the value of *H* furnished by ν_9 and ν_{18}. *H* for ν_{14} then results from the addition of 0.17 to the basic value.

Calculated values of the five planar unobservable frequencies are listed in table 2. The "τ-ratio" given by Teller's theorem is tabulated with the τ's obtained from our calculated frequencies. The agreement of the τ's does not assure the correctness of the calculated frequencies, but it does indicate that frequency product ratios are not incorrect.

TABLE 2

Calculated frequency values

FREQUENCY NUMBER	PRESENT PAPER			KOHLRAUSCH		INGOLD		TELLER'S τ	
	Value of *H*	C_6H_6	C_6D_6	C_6H_6	C_6D_6	C_6H_6	C_6D_6	Theoretical	Calculated
3	0.65	1190	930	1258	1058	1240	940	1.29	1.28
12		1008	960	1000	948	766	730		
13		3063	2294	3056	2296	3062	2294	1.41	1.40
14	0.82	1854	1844	1852	1842	1720	1640		
15	0.82	1145	816	1094	838	1145	820	1.41	1.40

It is readily seen that the three independent calculations are in good agreement. The one real discrepancy in the table is the disagreement on ν_{12}. Ingold and coworkers place this frequency at about 770 cm.$^{-1}$ Their evidence is of a wide variety and in some respects convincing. They estimate the ratio ν_{12}/ν_6 as $\sqrt{8/5}$ on the assumption that the only force constant involved is *k*. This ratio leads to the calculated value of 766 cm.$^{-1}$ for ν_{12}. To support their value, they offer the extremely faint Raman line found by Grassman and Weiler (8) at 781, and in addition the strong infra-red band at 773. Further evidence appears in the resonance emission spectrum, in which bands indicating a fundamental at 765 appear. The expected shift for deuterium of about 35 cm.$^{-1}$ shows up approximately on the Raman effect, in which the frequency appears at 750; the infra-red maximum, however, changes by only 20 cm.$^{-1}$ In resonance emission, moreover, the deuterium frequency drops to 707, which is 60 cm.$^{-1}$ away from the benzene frequency. These latter benzene-d_6 values thus mitigate somewhat the force of the evidence presented by the benzene spectra.

In opposition to these arguments, it may be offered that it is a rather doubtful procedure to make the simplifying assumptions which are necessary to obtain the ratio $\sqrt{8/5}$ for ν_{12}/ν_6, especially so since ν_6 is the root of a quartic equation. Furthermore if a value of 1000 cm.$^{-1}$ is assumed for ν_{12}, the resultant k is identical with that obtained by solving the quartic equations for k by either of two approximation methods. The experimental evidence submitted by Kohlrausch likewise bears weight: mono-, *m*-di-, and symmetrically tri-substituted benzenes show in the Raman effect a strong, *polarized* line at 1000 cm.$^{-1}$ which has a surprisingly constant value and which is undoubtedly a totally symmetrical vibration. These latter characteristics indicate that the frequency arises from a vibration form such as that for ν_{12}. This frequency appears in benzene-d_1 at 1008 cm.$^{-1}$, which must be quite close to the actual value for benzene. The decision is not an easy one to make, but we feel that the evidence rather favors the assignment ν_{12} = 1000 cm.$^{-1}$

There is one additional discrepancy in table 2, which appears in the values for ν_{14}, but these frequencies are quite high, and an error of 100 cm.$^{-1}$ has very slight effect on the entropy calculations. The evaluation of the planar unobserved frequencies is therefore rather satisfactory for our purposes.

The four out-of-plane distortion frequencies account for six degrees of freedom. These frequencies involve a carbon–carbon bond torsion, resistance to which is measured by the force constant κ. No precedent for the value of κ exists, but if it be assumed that it is of the same order of magnitude as other bending constants, it should lie somewhere in the range 10^4-10^5 dynes per centimeter, and the frequencies involving it should be among the very lowest in benzene. This presumption has led some investigators to attribute the frequency of approximately 160 cm.$^{-1}$, which has appeared in certain electronic spectra, to fundamental vibrations of the out-of-plane type. Several investigators, however, have found a line in the Raman spectrum of benzene at 406 cm.$^{-1}$ The existence of this line cannot be doubted; its interpretation is therefore essential to a complete picture of the vibrational scheme. This interpretation may be one of several alternatives: the line may be a fundamental or some type of combination tone. We will mention presently evidence against the 160 cm.$^{-1}$ fundamental which appears to rule out the possibility that the line is an overtone or combination of lower frequencies. Assignment to a difference tone is reasonable, but no allowed combination of the lower benzene frequencies (606, 670, 850) with higher frequencies will produce 406 cm.$^{-1}$ with the possible exception of $\nu_3 - \nu_{10}$. It seems highly doubtful that a line violating the selection rules should be able to break through the further barriers of the Boltzmann factor and of the low intensity of combination tones in general. Difference tones involving only fundamentals of 1000 cm.$^{-1}$ or higher are unlikely because of the very small value of the Boltzmann factor.

There is also constructive evidence that 406 is a fundamental. It is true that these distortion frequencies should not appear in the Raman effect as fundamentals, but there is a possibility that in the force fields of a liquid, the selection principles are abrogated to some extent. An alternative explanation might be that the line is due to a molecule such as $C^{13}C^{12}_5H_6$ or C_6H_5D, both of which possess the proper symmetry to allow the nonplanar frequencies to appear in the Raman effect. In this connection, it should also be pointed out that the closely related molecule of pyridine, C_5H_5N, which also possesses this symmetry (C_{2v}), exhibits at 404 cm.$^{-1}$ a Raman line of somewhat less than moderate intensity (12). This line in pyridine has an intensity which is rather larger than one would expect from a difference tone.

Further evidence is furnished by a frequency shift of 790 cm.$^{-1}$ found by Cuthbertson and Kistiakowsky (5) and by Ingold and Wilson (9-VI) in the resonance emission spectrum of benzene. This shift corresponds to a possible fundamental at 395 cm.$^{-1}$, and as Ingold and Wilson point out (9-VI, p. 966), the fundamental might be attributed to one of the out-of-plane frequencies. Corresponding evidence for benzene-d_6 is lacking.

TABLE 3

Frequencies calculated from Wilson's equations

FREQUENCY NUMBER	DEGENERACY	BENZENE	BENZENE-d_6
4	1	538	395
5	1	1520	1480
16	2	406	314
17	2	1160	1070

Ingold and associates (9-III) have reported tentatively a doubtful frequency at 337 cm.$^{-1}$ in the Raman spectrum of benzene-d_6. This line may correspond to the 406 frequency in benzene, although it is conceivable that 337 cm.$^{-1}$ is the difference frequency $\nu_3 - \nu_{10}$.

On the basis of the preceding evidence, the frequency 406 cm.$^{-1}$ in benzene is attributed to one of the two low frequencies ν_{16} or ν_4. Somewhat arbitrarily we make the assignment $\nu_{16} = 406$. ν_{16} should be lower than ν_4, and by making this assignment we have obtained a value for the force constant κ which is reasonably close to those of the other bending constants. The frequencies listed in table 3 are those calculated from Wilson's equations. The value of κ used was 0.23×10^5 dynes per centimeter, and that of h was 0.34×10^5.

STATISTICAL CALCULATIONS

The results given in tables 1, 2, and 3 have been used to calculate a spectroscopic value of S_g. The moments of inertia were determined from the geometry of the molecule, the C–C distance being taken as 1.40 A.U. and the H–H distance as 1.14 (10, 18). The results of the calculations are listed in table 4. In obtaining the entropies in table 4, nuclear spin has been ignored and the contribution of electronic levels in benzene above the non-degenerate ground state has been neglected.

TABLE 4

A. Entropy of benzene vapor at 1 atmosphere from statistical mechanics

ENTROPY OF	BENZENE		BENZENE-d_6	
	298°K.	353.2°K.	298°K.	353.2°K.
Translation	38.98	39.83	39.21	40.05
Vibration	4.75	7.01	7.55	10.50
Rotation	25.72	26.23	26.31	27.07
Symmetry term: $-R \ln \sigma$ ($\sigma = 12$)	−4.93	−4.93	−4.93	−4.93
Total	64.52	68.14	68.14	72.69

Moments of inertia in gram-cm.^{2}:
Benzene: $A = 148.6 \times 10^{-40}$; $C = 297.2 \times 10^{-40}$
Benzene-d_6: $A = 180.7 \times 10^{-40}$; $C = 361.4 \times 10^{-40}$

B. Thermal entropy of benzene vapor at 1 atmosphere

ENTROPY OF	RANGE	REFERENCE	TEMPERATURE OF VAPOR	
			298°K.	353.2°K.
Solid	0°–90°K.	(1)	10.89 ± 0.2	10.89 ± 0.2
	90°–M.p.	(17)	20.00 ± 0.2	20.00 ± 0.2
Fusion	M.p. = 278.5°K.	(2, 17)	8.43 ± 0.0	8.43 ± 0.0
Liquid	278.5°–298°K.	(17)	2.15 ± 0.0	2.15 ± 0.0
	298°–253.2°K.	(2, 17)		5.83 ± 0.05
Vaporization		I.C.T. and 14	27.36 ± 0.15	20.85 ± 0.05
Compression			−4.16 ± 0.05	
			64.67 ± 0.6 E.U	68.15 ± 0.5 E.U

The agreement of spectroscopic and thermal entropies indicates definitely a symmetry number of 12, i.e., benzene must have plane hexagonal symmetry. An assumed σ of six would lead to disagreement in the entropies of about 1.4 E. U.

It seems appropriate at this point to consider the validity of the sort of calculation which we have made. In the first place, the method requires thermal data of considerable accuracy. In the present instance, the thermal data are trust-worthy, probably more so than is indicated by the liberal estimate of error of 0.5 E. U. Even if the error is 0.5 E. U., however, one can still decide between 6 and 12 for the symmetry number. It is presumed that the thermal data are free from such orientation effects in the crystalline state as have been found by Giauque (4) for carbon monoxide and other molecules. These effects make the thermal entropy too low, and hence always lead to a value of σ which is too high. There seems to be no reason to suspect that such effects are actually present in crystalline benzene.

Secondly, the method necessitates a complete vibrational analysis, that is, a knowledge of all frequencies and degeneracies. We can summarize our analysis in this fashion:

(1) The eleven observed frequencies accounting for nineteen degrees of freedom are known accurately enough so that the error in the vibrational entropy due to uncertainty in these frequencies is less than 0.5 E. U. at 298°K.

(2) The five planar unobserved frequencies all lie above 1000 cm.$^{-1}$, with the possible exception of ν_{12}. Hence the error in the entropy because of inaccurate knowledge of these vibrations is hardly more than 0.05 E. U. If ν_{12} has a value in the region around 770 cm.$^{-1}$, the error rises to 0.2 E. U. at the most.

(3) Because the preceding sources of error are small, it is seen that the entire analysis rests on the assignment of ν_{16} to the 406 frequency. If the assignment is correct, the calculated value of ν_4 is probably not far wrong. The other torsional frequencies are quite high, and while they may be considerably in error, their contribution to the entropy is slight. Assuming the assignment is correct, the error in the entropy due to the out-of-plane frequencies may be roughly set at 0.4 E. U., bringing the total possible error to 0.5–0.6 E. U.

If ν_{16} does not have the value of 406 in benzene, we are faced with a number of alternatives:

(1) ν_{16} may be *higher* than 406. The vibrational entropy then lies somewhere between the listed value and about 2 E. U. lower. This possibility would indicate a minimum symmetry number of about six.

(2) If ν_4 instead of ν_{16} has the frequency 406 the vibrational entropy is *increased* by an entropy unit or so, and the disagreement with experimental values becomes marked. In this eventuality, a symmetry number of twelve is definitely indicated, with the additional discrepancy between theory and experiment perhaps to be attributed to trouble in the crystalline state.

(3) If it be assumed that ν_4 or ν_{16} is to be identified with the 160 cm.$^{-1}$ frequency found in electronic spectra, then unless the theory is completely meaningless, there must be *three* degrees of freedom 200 cm.$^{-1}$

or lower. These would make an entropy contribution of some 5 E. U. and cause a discrepancy with experiment of more than 3 E. U. at 298°K. For this reason the possibility of a fundamental frequency in benzene as low as 160 cm.$^{-1}$ seems definitely ruled out.

In conclusion it may be recalled that a symmetry number of twelve is compatible with the best evidence of x-ray and electron-diffraction studies on benzene. The theories of the electronic structure of the benzene ring likewise predict planarity. It may further be remarked that hydrogen–hydrogen repulsion can be shown to be too weak to warp the C—H bond out of the ring plane if the bending constant h calculated from ν_{10} or ν_{11} be made the basis of the calculation. The evidence we have presented is in agreement with all these structural arguments, and, while it is not entirely conclusive, it strongly indicates a plane structure of symmetry D_{6h}.

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SOME PROPOSALS CONCERNING NOMENCLATURE AND SYMBOLS FOR POLYATOMIC MOLECULES[1]

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I. INTRODUCTION

The desirability of a more or less standardized nomenclature for describing the spectra and especially the energy levels of polyatomic molecules hardly needs much argument. If different writers agree in their language and symbols, clarity and economy of effort result both in the writing and in the reading of papers. Further, a properly chosen systematic nomenclature for molecular energy levels greatly facilitates the understanding and discussion of their combining properties. By "combining properties" are here meant the selection and polarization rules governing transitions involving radiation (both ordinary and Raman spectra), the selection rules governing perturbations and predissociation, and such correlation rules as may apply to dissociation and other processes. Finally, an orderly nomenclature assists in the proper comprehension of the subject as a whole.

One might, however, question whether the time is yet ripe for a stabilization of nomenclature. One might ask: do not most of the questions of nomenclature come up only in connection with higher states of vibration, and especially with excited electronic states, which are of relatively little interest to most people as yet, and about which no one yet knows very much? This question has force, but nevertheless the writer is inclined to think that it is not too soon to begin at least a discussion of the subject. Spectra involving higher states of vibration, and excited electronic states, are now being increasingly investigated, especially in the photographic infra-red, and in the ultra-violet. Further, an understanding of these higher states is important in connection with activation energies and with photochemical reactions. Hence, a number of proposals are here submitted for discussion. It is hoped that the present paper may also have some value in facilitating the presentation of certain topics in the theory

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of polyatomic spectra, and in the discussion of the energy levels of certain molecules.

As compared with diatomic molecules, the nomenclature problem for polyatomic molecules is inherently much more complicated. The differences between the two cases may be summarized as follows. (1) Polyatomic molecules include molecules of a great many different types of symmetry, with the problem of nomenclature in some respects a new one for each type. Diatomic molecules really comprise merely two special cases of this general problem (with symmetries $C_{\infty v}$ and $D_{\infty d}$). (2) In polyatomic molecules, classification and nomenclature are needed for vibrational levels and for electronic-vibrational levels, whereas in diatomic molecules this is unnecessary, since there is only one possible type of vibration. (The vibrational wave functions are all of the type Σ^+ for heteropolar, Σ^+_g for homopolar diatomic molecules.) (3) In lesser measure, there is a similar increase in complexity of type for rotational levels. (4) In polyatomic molecules, intermediate and generalized cases, including cases where classification according to an equilibrium type of symmetry breaks down more or less, are common.

In the present paper, attention will be confined mainly to vibrational and electronic properties of molecules, largely leaving aside questions of rotational and nuclear-permutation properties for the time being.[2] Just one or two simple proposals concerning rotational states will be made. Further, no attempt will be made to cover exhaustively all aspects and special cases of vibrational and electronic classification.

II. COMPLETE WAVE FUNCTION

For the *complete* wave function of every molecule, two properties always exist which can be easily designated: (1) the property now universally designated in atoms and diatomic molecules by assigning a quantum number J; (2) the property according to which every wave function (at least if non-degenerate) can be classified as either even or odd with respect to an inversion of all coördinates at the center of gravity. In atoms this second property is called *parity*, and the two kinds of levels are called *even* and *odd*, while in diatomic molecules they are called + and − (the terms even and odd then being reserved for another property, of electronic levels alone). There seems to be no reason why the symbol J should not be universally used for the resultant angular momentum quantum number, and the symbols + and − to indicate the parity of the complete wave function, for all polyatomic molecules.

Further, it would be logical to extend the diatomic use of the symbol K to polyatomic molecules. In diatomic molecules, K is the same thing as

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[2] In this connection cf. especially reference 4.

J in case the resultant electronic spin S is zero, and the two symbols can then be used interchangeably. When, however, S is greater than zero, but is loosely coupled to the remaining edifice of nuclear and electronic orbital angular momentum vectors, the resultant of the latter is designated by K; K and S then combine vectorially to give J. This use of K might well be extended to all polyatomic molecules in which the spin is zero or loosely coupled. In this connection, it may be noted that loose spin coupling is expected to be much more the usual rule in the polyatomic than in the diatomic case. On the other hand, the case $S = 0$, where J can be used just as well as K, has hitherto been much more common in practise in polyatomic than in diatomic spectra,— largely because of the relatively greater emphasis on infra-red and Raman work.

The only objection to the use of K here proposed is that K is now often used (e.g., in NH_3) to designate the component of nuclear angular momentum around an axis of symmetry. It would seem, however, that some other symbol, e.g. P or Q, could be substituted for the latter purpose,— perhaps P for ordinary rotational angular momentum, Q for angular momentum associated with a degenerate vibration.

III. ELECTRONIC WAVE FUNCTIONS AND ORBITALS

As an approximation which in ordinary cases is useful, the complete wave function ψ of a polyatomic molecule can be written as a product of factors, as follows (a final factor ψ_{cg} for the motion of the center of gravity is omitted):

$$\psi = \psi_{el}\psi_{v}\psi_{r}\psi_{nu\ sp} \tag{1}$$

The factors are respectively called the electronic, vibrational, rotational, and nuclear spin wave functions. More accurately, one may write

$$\left.\begin{aligned}\psi &= [(\psi_{el}\psi_{v} + \psi^{1}_{ev})\,\psi_{r} + \psi^{1}_{evr}]\psi_{nu\ sp}\\ &= (\psi_{ev}\psi_{r} + \psi^{1}_{evr})\,\psi_{nu\ sp} = \psi_{evr}\psi_{nu\ sp}\end{aligned}\right\}(2)$$

Here ψ^{1}_{ev} and ψ^{1}_{evr}, respectively, represent corrections for mutual interactions between electronic and vibrational motions, or between electronic-vibrational motions and nuclear rotational motions.

The factor ψ_{ev} may be called the *vibronic* wave function, the factor ψ_{evr} the rovibronic wave function. While "vibronic" wave function may sound disagreeable at first, it is important to have a name for ψ_{ev} (see section V), and the writer has sought in vain for a better one of reasonable simplicity.

The classification of the complete electronic wave functions of atoms and of diatomic molecules into types is well known. Instead of "types" it will be convenient to refer to *species* (cf. the German "Rasse", often applied to a class of electronic states of a molecule).

The nature of the classification into electronic species, in diatomic molecules as well as in atoms, depends on the nature of the spin-orbit coupling. It will be convenient to refer to the usual types of coupling as *normal coupling*. Normal coupling in atoms is usually called Russell-Saunders, or L, S coupling. In diatomic molecules it includes Hund's cases a and b and intermediate cases.[3] In most polyatomic molecules normal coupling will resemble Hund's diatomic case b, but in some (especially linear) molecules, will include also cases like Hund's diatomic case a.

In atoms and diatomic molecules, for normal coupling, each electronic species is denoted by a *species symbol* (^1S, $^1S^\circ$, $^2P^\circ$, ^2D, $^3D^\circ$, etc. for atoms; $^1\Sigma^+$, $^1\Sigma^-$, $^2\Sigma^+$, $^2\Pi$, etc., for heteropolar diatomic molecules; $^1\Sigma^+_g$, $^1\Sigma^+_u$, $^2\Pi_u$, $^3\Sigma^-_g$, etc., for homopolar diatomic molecules). Each species symbol implies a particular value of each of the angular momentum quantum numbers L and S (atoms), or Λ and S (diatomic molecules); but it also implies certain other properties (the even or odd property, in atoms; the property denoted by + or − in diatomic Σ states; the even or odd ($_g$ or $_u$) property in states of homopolar diatomic molecules). Fundamentally, each species symbol can be taken to indicate certain properties of form and symmetry of the wave function ψ_{el}. In addition to electronic species, one may often distinguish electronic *sub-species*, which are indicated by final subscripts. The latter refer to different possible relative modes of orientation of spin and orbital angular momenta.

For polyatomic molecules, classification of electronic states into species can also be carried out, and symbols for the species for normal coupling have been devised.[4] Examples of species symbols are: ^1A, $^1A_1$, $^1B_2$, $^3B_1$, $^2A_1'$, $^2A_1''$, ^1E, $^3E_*$, ^2T, $^3T_1$. Hitherto no good sub-species symbols have been developed; they are not likely to be needed as often as in atoms and diatomic molecules, because in polyatomic molecules the spin usually is only loosely coupled to the rest of the molecule. In linear polyatomic molecules, to be sure, they will often be needed; but for such molecules, the electronic species and sub-species and their symbols are exactly the same as for diatomic molecules. It should be noted that the numerical and other subscripts appearing in such symbols as $^1A_1$, $^1B_2$, $^3E_*$, etc., do *not* denote sub-species. They are parts of the species symbols, which are

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[3] See the writer's paper in Section I of this Symposium in regard to diatomic molecules.

[4] See reference 2. The electronic species symbols there introduced are nearly the same, except for addition of superscript prefix to denote the multiplicity, as the *vibrational* species symbols previously developed by G. Placzek (Marx' *Handbuch der Radiologie*, Vol. VI/2). The principal change has been the substitution of T where Placzek used F, with the idea of avoiding confusion with the atomic species symbol F. Another change, of doubtful value, has been the substitution of E_* and E_{**}, for Placzek's E^+ and E^-. See also L. Tisza (3) in regard to the classification of vibrations and vibrational species.

more complicated here than for atoms and diatomic molecules; in regard to the reasons for this, see below.

Although in atoms and diatomic molecules angular momentum properties can be used to a large extent in characterizing electronic species, this is hardly true at all in polyatomic molecules, other than linear ones. As a result, the language of group theory is particularly useful in characterizing species. In polyatomic molecules as well as for atoms and diatomic molecules, the group theory approach, introduced particularly by Wigner, appears to be the most natural and penetrating one. Although to some people this may make the matter seem formidable, the writer knows no simpler way to gain a good understanding of the necessarily rather great variety of wave-function types which exists in the field of polyatomic molecules.

In judging the suitability of the species symbols now in use for polyatomic molecules, one should bear in mind that a new classification and, in principle, a new set of symbols must be set up for each different type of molecular symmetry. (Fortunately, however, the number of distinguishable species decreases with diminishing symmetry, being finite except for atoms and diatomic and linear molecules.) In practise, it would be too great a burden on the memory, and would require too many alphabets, if we tried to develop a distinctive set of simple symbols for each polyatomic symmetry. Instead, it has seemed wise to use a restricted number of somewhat cumbersome but more or less self-explanatory symbols, and frequently to permit the same formal symbol to appear for species belonging to different symmetries. For instance, $^1A_1$ is used to denote, for each of several different symmetries, the respective most symmetrical species of ψ_{el}. If we extended the same system to include atoms and diatomic molecules, the ^1S species of atoms and the $^1\Sigma^+$ and $^1\Sigma^+_g$ species of diatomic molecules would also be labelled $^1A_1$. Such a system tends to cause confusion when, but only when, molecules of different symmetry are discussed simultaneously; in this eventuality, an extra index might be attached to the species symbol to indicate the symmetry. For atoms and diatomic molecules, however, because of their predominant importance, it is certainly good that we have distinctive sets of symbols.

In general, A and B have been used for orbitally non-degenerate species, E for species having twofold, T for those having threefold, orbital degeneracy;[4] while subscript and superscript suffixes have been used to designate other characteristics of the form of ψ_{el}. A perhaps desirable improvement in the species symbols would be the replacement of the numerical subscripts (1, 2, and rarely 3) by literal subscripts (a, b, and c). That would make it less likely that the subscripts would be confused with the *sub-species* subscripts used for atoms and for diatomic and linear molecules. Aside from this and a few other possible minor changes, the writer is inclined to think that the present system of electronic species symbols for polyatomic molecules is a satisfactory one.

When electron-configuration approximations are used—as is nearly always the case—in discussing electronic structures of atoms or molecules, a symbol is needed for each of the *orbitals* used in making up the electron configuration. Thus for atoms we have $1s$, $2s$, $2p$, and so on, and for diatomic molecules such symbols as $1s\sigma$, $2s\sigma$, $2p\pi$, and so on, $\sigma_g 1s$, $\sigma_u 2p$, etc., or $\sigma 1s$, $\sigma^* 1s$, $\sigma 2p$, etc. Each such symbol is made up of a *particular* or individual and a *species* symbol. For atomic orbitals the possible species are symbolized by s, p, d, f, and so on, for heteropolar diatomic molecular orbitals by σ, π, δ, ϕ, and so on, and for homopolar diatomic orbitals by σ_g, σ_u, π_u, π_g, δ_g, and so on. The *species* symbols ought to be, and are, definitely fixed and standardized, but (for diatomic molecules) the *particular* symbols are more varied and less standardized. The species symbols for orbitals are the same as those for electronic states except that (1) small letters are used in place of capitals, (2) the multiplicity superscript is omitted, and (3) sometimes other superscripts are omitted because unambiguous (e.g., the $^+$ is omitted in σ^+, since σ^- is impossible).

For polyatomic molecules, the relation of species symbols for orbitals to those for electronic states is just the same as in the case of atoms and diatomic molecules. As has been noted already, the species symbols for polyatomic molecules are more cumbersome than for atoms or diatomic molecules, but it hardly seems desirable to attempt to simplify them, unless possibly for a few special cases of particularly important types of symmetry. Because of the variety and complexity of polyatomic molecules, relatively complicated and varied *particular* symbols have been used in describing their orbitals. There appears to be no point in trying to standardize these at present.

IV. VIBRATIONAL WAVE FUNCTIONS AND VIBRATION MODES

Although the Schrödinger equations for ψ_v of equations 1 and 2 are entirely different from those for ψ_{el}, nevertheless both are characterized by the same formal types of geometrical symmetry. As a consequence, ψ_v can be classified according to exactly the same formal system as ψ_{el}, and the same species symbols can be used for both, except that for the *vibrational species*, no multiplicity superscript is included.

It might of course be argued that, since the vibrational and electronic wave functions are entirely different things, they should be classified by different symbols. The writer is of the opinion that this is unnecessary, and that it would be undesirable for the following reasons: (1) the multiplicity superscript is adequate to distinguish an electronic from a vibrational species symbol; (2) the use of nearly the same symbols here promotes understanding much more than it causes confusion; (3) understanding and classification of vibronic wave functions (ψ_{ev}) is greatly facilitated (cf. section V) by having a common basis of symbolism for ψ_{el}, ψ_v, and ψ_{ev}.

It sometimes happens, of course, that one wishes to speak of electronic species without specifying multiplicity. In that event, they can, if necessary, be distinguished from vibrational species by adding a subscript prefix, as, for example, ${}_eA_1$ for an electronic A_1 species, ${}_vA_1$ for a vibrational A_1 species.

At present, the vibrational species symbols introduced by Placzek and used by Tisza differ slightly[4] from the electronic species symbols used by the writer. In the writer's opinion, it would be desirable that *exactly the same* symbols, aside from the multiplicity index of course, should be used in the two cases. If this idea is carried out, the whole set of symbols should be gone over carefully at the same time for possible minor improvements.

Following out the formal analogies between ψ_{el} and ψ_v, it is convenient to define the term ***vibrational configuration*** in analogy to "electronic configuration." By vibrational configuration is meant the detailed state of vibration of the molecule, in so far as it can be described by stating the number of quanta (i.e., the quantum number) with which each of various normal modes of vibration is excited. Such a description is of course only an approximate one, and often fails badly, being defective to the extent that normal coördinates are unsuitable for describing large vibrations. These defects are sometimes less, sometimes more, serious than the rather similar limitations to which electron configuration descriptions are subject.

We may now proceed to set up vibrational configuration symbols in analogy to electron configuration symbols, as follows: let each normal-mode-of-vibration symbol in the former correspond to an orbital symbol in the latter, and let the number of quanta with which a given vibration mode is excited be indexed in the same way as is the number of electrons which occupy a given orbital.

Different normal modes of vibration, or the corresponding normal coördinates, can be classified according to species, just as orbitals are. As was shown by Wigner,[4] the possible *modal species* (i.e., vibration-mode species) are formally of exactly the same kinds as are the vibrational (i.e., the vibrational wave function) species, even though the classification of modal species is based on classical mechanics, that of vibrational species on quantum mechanics.

We now have the formal relation, which may be stated in the form of a proportion—modal species: vibrational species : : orbital species : electronic species. The same kind of relation can be set up also among the respective symbols. We then note, among other things, that where vibrational and electronic species are denoted by capital letters, modal and orbital species are denoted by corresponding small letters.

Something must now be said about the relations between a vibrational configuration and the corresponding vibrational states. Formally, these are similar to the relations between electron configurations and corresponding electronic states, even to the existence of a rough analogy of non-equivalent and equivalent electrons to singly excited and multiply excited modes of vibration. An important difference, however, is that for the vibrations, unlike the electrons, there is no spin nor any Pauli principle. (To be sure, there *are* nuclear spins and there *is* a nuclear Pauli principle, but these take effect only when we consider the complete wave function, not just ψ_v.) The rules for determining the resultant vibrational state or states corresponding to any given vibrational-species configuration have been fully worked out by Tisza (3); the formally somewhat similar rules for electron configurations and states have been given by Bethe and the writer.[4]

The foregoing considerations can be made clearer by considering an example. The linear symmetrical molecule CO_2 will serve very well, even though its symmetry ($D_{\infty d}$) is the same as that of homopolar diatomic molecules and so is not altogether typical of polyatomic cases. CO_2 has two non-degenerate and one twofoldly degenerate normal modes of vibration. We may classify these by using the same symbols as for orbitals of homopolar diatomic molecules, since the formal characteristics of symmetry are the same in the two cases. The vibration modes, then, are: one σ_g of frequency about 1340 cm.$^{-1}$ (symmetrical valence vibration); one σ_u of frequency about 2350 cm.$^{-1}$ (antisymmetrical valence vibration); and one π_u of frequency about 668 cm.$^{-1}$ (deformation vibration, with twofold degeneracy). The main characteristics of each mode of vibration are neatly summarized by its species symbol.

Suppose now we give the vibrational configuration and state-species symbols for all of the lowest few vibrational states of CO_2. In most cases, the proper vibrational (state) species symbol or symbols will be obvious, but if not, one can resort to the methods of Tisza, or to detailed examination of the wave functions. The lowest state (zero vibration) is clearly of the type $\Sigma^+{}_g$, and might be written

$$(\sigma_u)^0\ (\sigma_g)^0\ (\pi_u)^0,\ \Sigma^+{}_g,$$

or perhaps simply N, $\Sigma^+{}_g$, where N indicates *normal* state. The next state in order of energy is

$$\pi_u,\ \Pi_u$$

after which we have a close group of three levels, including the famous pair of perturbed levels. The cause of this is that the configuration $(\sigma_u)^0\ (\sigma_g)^1\ (\pi_u)^0$ has nearly the same energy as $(\sigma_u)^0\ (\sigma_g)^0\ (\pi_u)^2$. The former of these configurations should give a single vibrational state of species $\Sigma^+{}_g$, the latter *two* states, a $\Sigma^+{}_g$ and a Δ_g (the Δ_g has of course a twofold degeneracy). Following the general rule that any two vibrational states of the same species tend to perturb each other, the assumed σ_g, Σ^+_g and $(\pi_u)^2$, Σ^+_g states interact, strongly as it happens, giving as a result two, actual, Σ^+_g states, one of considerably lower and one of considerably higher energy than the original assumed pair of states. The Δ_g, however, being of a different species, is undisturbed. The final results may be summarized by writing

$$(\sigma_g, \pi_u^2), \Sigma^+_g; \pi_u^2, \Delta_g; (\pi_u^2, \sigma_g), \Sigma^+_g$$

Next in energy come states derived from the two configurations $\sigma_g\pi_u$ and π_u^3. The former should give one Π_u state, the latter one Π_u and one Φ_u. Again a strong perturbation occurs, this time between the two Π_u states, leaving the Φ_u unaffected. As a result we have, in order of increasing energy,

$$(\sigma_g\sigma_u, \pi_u^3), \Pi_u; \pi_u^3, \Phi_u; (\pi_u^3, \sigma_g\sigma_u), \Pi_u$$

After these, the next state is

$$\sigma_u, \Sigma^+_u$$

and so on.

It will be seen that the vibrational configuration symbols here describe simply and explicitly the nature of the vibration, while the vibrational species symbols for the overall state are of great value in showing where perturbations occur. The rigorous selection rules for infra-red or Raman bands are also expressed extremely easily in terms of these species symbols. For instance in the case of infra-red bands, the selection rules are: $\Delta Q = 0, \pm 1; {}_g \leftrightarrow {}_u$. ($Q = 0$ for Σ, 1 for Π, 2 for Δ, 3 for Φ, and so on). According to these selection rules, infra-red absorption from the normal state N, Σ^+_g can lead only to Π_u or Σ^+_u states, e. g. to those given above. It seems to the writer that the general use of symbols such as those here suggested would appreciably facilitate both the analysis and the understanding of infra-red spectra, and, when combined with similar symbols for electronic levels, also of ultra-violet spectra.

Our example of CO_2 is too simple in one respect to illustrate fully the matter of vibrational configuration symbols. In CO_2, each normal vibration mode belongs to a different species, so that modal species symbols suffice in setting up vibrational configurations. This, however, is not usual. Another, still very simple, example will illustrate the point. Consider the water molecule, which has symmetry C_{2v}.[5] Of its two modes

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[5] Strictly speaking, the vibrational Schrödinger equation for H_2O and similar cases has only the symmetry C_s (one plane of symmetry) rather than C_{2v} (two perpendicular planes and an axis of symmetry). However, the use of species symbols based on the C_{2v} classification is not really wrong, involving nothing worse than some superfluities, and on the other hand is desirable (see section V), because the electronic Schrödinger equation has symmetry C_{2v} and so requires C_{2v} species symbols for ψ_{el}.

of vibration, two belong to the species a_1 (symmetrical modes), one to b_2 (antisymmetrical mode). In writing vibrational configurations, some *particular* symbol must now be combined with the species symbol to distinguish between the two a_1 modes. Following Mecke, one might write νa_1 (symmetrical valence frequency) and δa_1 (deformation frequency); further, νb_2 or simply b_2 (unsymmetrical valence frequency). If, for instance, these frequencies were excited with 2, 1, and 3 quanta respectively, we should have

$$(\nu b_2)^3(\nu a_1)^2\delta a_1,\ B_2$$

In more complicated molecules, the distinction between types ν and δ will often be insufficient or too inaccurate, and additional (e.g., $\nu_1, \nu_2, \ldots \delta_1, \delta_2, \ldots$), or other, particular symbols for indexing individuals of a species will be needed.

If the physical nature of a vibration mode is not known, its wave-number might be used instead of ν or δ or the like, e.g.,

$$(1830\ b_2)^3\ (1720\ a_1)^2\ (810\ a_1),\ B_2$$

In highly excited vibrational states, and in some cases even for lower states, vibrational configurations should often cease to be usable, corresponding to a failure of normal coördinates as a usable approximation. The CO_2 perturbations discussed above illustrate the beginning of this case. In higher vibrational states, perturbations will tend to get stronger and more common. Finally, only the vibrational species symbols will retain their meaning. These will be significant until, or unless, rotational perturbations get very strong.

VI. VIBRONIC WAVE FUNCTIONS

An examination of the nature of vibronic wave functions (ψ_{ev} of equation 2) and their classification is of interest in connection with the higher excited states of molecules, and also helps to make clearer the nature of the vibrational and electronic classifications. In ordinary cases, the Schrödinger equations for ψ_{el}, ψ_v, and ψ_{ev} for a given molecule all have the same geometrical symmetry and this is the equilibrium symmetry of the nuclear configuration. As a direct consequence, the same formal species classification can be used for ψ_{el}, ψ_v, and ψ_{ev}, except of course that ψ_{el} and likewise ψ_{ev} have a multiplicity classification not present for ψ_v. The geometrical symmetry which appears in the Schrödinger equations enters, of course, through the potential energy functions, which may be denoted by U_{el}, U_v, and U_{ev} for ψ_{el}, ψ_v, and ψ_{ev} respectively.

Referring now to equations 1 and 2, it is important to note that if the factoring is of the following character, the correction term ψ_{ev}^1 can ordinarily be kept very small:[6]

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[6] Cf. reference 1.

$$\psi_{ev}(q, Q) = \psi_{el}(q, Q)\psi_v(Q) + \psi^1_{ev}(q, Q) \tag{3}$$

Here q stands for electronic coördinates and Q for normal or other coördinates specifying the displacements of the nuclei from equilibrium during vibration. The major term $\psi_{el}\,\psi_v$ in equation 3 can be approximated, with gain in simplicity but loss in exactness, by writing

$$\psi_{ev}(q, Q) = \psi_{el}(q, Q_e)\psi_v(Q) + \psi^{1e}_{ev}(q, Q) \tag{4}$$

Here Q_e stands for the equilibrium values of the vibrational coördinates (all zero if we use normal coördinates). In equation 3, for a given electronic state, the form and even the symmetry of ψ_{el} depend on the parameters Q, while in equation 4 they correspond to the case of equilibrium. Correspondingly, U_{el} for equation 3 is U_{el} (q, Q), but for equation 4 it is $U_{el}(q)$, i.e., $U_{el}(q, Q_e)$.

In setting up the classification and species-symbols for ψ_{el}, deriving electronic selection rules, and so on, one usually deals primarily with ψ_{el} as defined by equation 4. Also in writing and studying systematically the electron configurations of different molecules, it usually suffices to classify the orbitals and the electronic states according to the equilibrium symmetry.

Passage from the approximate equation 4 to the more exact equation 3 definition of ψ_{el} is, however, often important, for example in showing the possibility of the occurrence with low intensity[6] of electronic transitions which are not allowed by the selection rules of ψ_{el} for the equilibrium symmetry. With the equation 3 definition, we must in general establish several different classifications and several different sets of species-symbols for a given ψ_{el},—one for each possible type of symmetry which $U_{el}(q, Q)$ may take on through variation of Q. This is generally not a difficult matter in practise, since the classifications and symbols for $Q \neq Q_e$ usually are fairly simply related to those for $Q = Q_e$.

In spite of the variable symmetry and selection rules for ψ_{el} in equation 3, and consequent complications[6] for ψ_v selection rules in electronic transitions, matters are comparatively simple for ψ_{ev} itself. The geometrical symmetry of $U_{ev}(q, Q)$ is always perfectly definite, and so are the species-symbols and selection rules for ψ_{ev}.[7] Given the vibronic selection rules, we can go back (cf. the "product" rule in the next paragraph) and get the vibrational selection rules for any specified electronic transition. (The possibility or probability of the *latter* may first be examined by a consideration of ψ_{el} according to equations 3 and 4.)

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[7] It can be shown that U_{ev} (q, Q) always belongs to the same formal geometrical symmetry type as $U_v(Q)$ or as $U_{el}(q, Q_e)$, although the actual symmetry operations are defined differently in the three cases, here involving both q's and Q's, but involving only Q's *or* q's in the other respective cases.

In the usual case where the species-symbols for $\psi_{el}(Q_e)$, ψ_v, and ψ_{ev} correspond to the same geometrical symmetry, the correct symbol or symbols for ψ_{ev} can be immediately determined as "products" of those for $\psi_{el}(Q_e)$ and ψ_v; the necessary "multiplication tables" of symbols are most easily explained and expressed in group theory language. For this product relation it is particularly convenient that one does not need to know the ψ_{el} symbol for any other symmetry than that which it has for $Q = Q_e$.

In exceptional cases, ψ_{ev}, ψ_v, and $\psi_{el}(Q_e)$ do *not* all correspond to the same symmetry. One rather trivial case of this kind has been disposed of in footnote 5. More serious cases occur when there is more than one equivalent equilibrium configuration for the nuclei, and when at the same time the potential barriers between these equivalent configurations are sufficiently low. Examples are C_2H_6, NH_3; an otherwise similar case where the potential barrier is too high is CH_3I.

Let us consider more carefully the cases of NH_3 and CH_3I. Here $\psi_{el}(Q_e)$ is necessarily classified according to the species-symbols of symmetry C_{3v}, since both of the two equivalent equilibrium configurations Q_e have that symmetry. If we consider sufficiently small vibrations and neglect the tunnel effect, i.e., the possibility of passage through the potential barrier, the normal modes of vibration, and ψ_v, can also be classified according to the C_{3v} species-symbols. A similar statement then applies to ψ_{ev}.

The method of description just outlined is adequate for all ordinary purposes in the case of CH_3I. For NH_3, however, because of the much lower potential barrier between the equivalent equilibrium configurations, it will not do except as a possible stage of approximation. Rigorously, U_v and U_{ev} for NH_3 (and for CH_3I) have symmetry D_{3h}. $U_{el}(q, Q)$, however, has symmetry C_{3v} for $Q = Q_e$; its symmetry is D_{3h} only when Q is such (let us call this Q_0) that the nitrogen atom is at the center of an equilateral H_3 triangle.

The product rule for species-symbols cannot be applied in the usual way in the circumstances here outlined, but it can be applied if we determine the species-symbol of ψ_{el} not for $Q = Q_e$ but for $Q = Q_0$. Corresponding to this, a new way of approximating ψ_{ev} is convenient here, replacing equation 4:

$$\psi_{ev}(q, Q) = \psi_{el}(q, Q_0)\psi_v(Q) + \psi^{1b}{}_{ev}(q, Q) \tag{5}$$

Equation 3, of course, is still applicable just as in other cases.

In the approximation of C_{3v} symmetry (neglect of tunnel effect), the normal electronic state of NH_3 is of the species $^1A_1$, and the normal modes of vibration may be described as νa_1, δa_1, νe, and δe. The two a_1 modes are non-degenerate, while the e modes each have two-fold degeneracy. The mode in which the nitrogen atom and the H_3 plane move toward each other is δa_1. In order of increasing energy, the vibrational energy levels, with their vibrational configurations, are:

$$N,A_1;\ \delta a_1,A_1;\ \delta e,\ E;\ (\delta a_1)^2,A_1$$

and so on.

In the usual discussion, one says next that each of the vibrational levels just mentioned has a further degeneracy factor of two, corresponding to the two equivalent Q_e's; but that because of tunnel effect this degeneracy is removed, so that each level is split into two components called α and β. From the standpoint of rigorous classification, however, a more satisfactory and simpler treatment here is to recognize at the outset that C_v really has symmetry D_{3h}. It is then readily shown, for instance by comparison with the hypothetical case of an NH$_3$ molecule with symmetry D_{3h} for Q_e,[8] that the vibrational levels in order of increasing energy are as follows:

$$N,A_1';\ A_2'';\ A_1';\ A_2'';\ E';\ E'';\ A_1';\ A_2''$$

and so on.

It is somewhat difficult here to give vibrational configurations, because the normal coördinate δa_1 of C_{3v} rapidly loses significance at high quantum numbers. If the molecule in equilibrium were plane (symmetry D_{3h}),[8] the levels with their vibrational configurations would be as follows (except that perhaps the positions of the E levels would be somewhat different):

$$N,A_1';\ \delta a_2'',\ A_2'';\ (\delta a_2'')^2,\ A_1';\ (\delta a_2'')^3,\ A_2'';\ \delta e',\ E';\ (\delta e')(\delta a_2''),\ E'';$$
$$(\delta a_2''),^4\ A_1';\ (\delta a_2'')^5,\ A_2''$$

and so on. For the actual case of NH$_3$, however, the close approximation of the levels to those for symmetry C_{3v} which exists if the δa_1 mode is excited only slightly might be indicated as follows:

$$N,A_1';\ N,A_2'';\ \delta a_1,A_1';\ \delta a_1,A_2'';\ \delta e,E';\ \delta e,E'';\ (\delta a_1)^2,A_1';\ (\delta a_1)^2,A_2''$$

and so on. The symbols here are mixed, the vibration-mode symbols belonging to C_{3v} and the state-symbols to D_{3h}. In the case of the last two levels given, the indicated vibrational configuration $(\delta a_1)^2$ is of only very rough significance.

The classification according to symmetry D_{3h} has the advantage of giving in a simple way the correct vibrational selection rules, special rules as to α and β levels then being unnecessary. Further, the D_{3h} classification is the natural one when the δa_1 vibration is excited with more than two quanta. Also, for any given electronic and vibrational state, the vibronic state is easily determined by the product rules of D_{3h}.

In concluding this section, mention should be made of the occasional possible need of distinguishing between electronic and vibronic symbols,

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[8] This case is probably realized in *excited* electronic states of NH$_3$.

which are exactly alike in form according to the proposals made here. Suppose, for example that we want to talk about ${}^1A_1$ electronic and ${}^1A_1$ vibronic states. The former could be written ${}_e{}^1A_1$, the latter ${}_{ev}{}^1A_1$, in this case.

VII. ISOTOPIC MOLECULES

Some special questions of nomenclature arise when different isotopes of some element are present in a single molecule (cf., e.g., CH_3D). Under these circumstances, $U_{el}(q, Q_e)$ has to a very high degree of approximation the same symmetry as for a molecule in which all the atoms of the given element belong to a single isotope (cf. e.g., CH_4). Hence, for all practical purposes, $\psi_{el}(q, Q_e)$ is the same, and should be classified according to the same symmetry, for all isotopes of the given molecule. Selection rules for electronic transitions, to the approximation that $\psi_{el}(q, Q_e)$ may be used for $\psi_{el}(q, Q)$, are determined accordingly.

For $\psi_v(Q)$ and $\psi_{ev}(Q)$, however, substitution of one isotope for another may of course make radical changes in form and classification. Likewise, ψ_{el} and its selection rules are affected, usually in a minor way, if one goes beyond the equation 4 approximation to $\psi_{el}(q, Q)$ of equation 3.

The ways in which the classifications of energy levels change, and in particular the ways in which degenerate levels often split up in going from a relatively symmetrical molecule to an isotope molecule with a less symmetrical configuration of nuclear masses, are easily determined in connection with the symbols here discussed for ψ_v and ψ_{ev}, using their group theory definitions.

VIII. PREDISSOCIATION AND PERTURBATION TYPES

In polyatomic molecules, predissociation and perturbations can occur in a confusing variety of ways. It is the writer's feeling that a suitable nomenclature would be of real value in making the situation more readily intelligible. A twofold classification of all types of perturbations or predissociations, as follows, appears to serve the purpose. Each type may accordingly be classified (1) as homogeneous, heterogeneous, or (if we are dealing with electronic or vibronic states with normal spin-orbit coupling) intersystem[3]; (2), as electronic, vibrational, or vibronic.

Homogeneous and heterogeneous perturbations are respectively defined as perturbations in which two states of the same or of different species perturb each other.[3] If the two states belong to the same electronic and vibrational species, but are not identical in *electron configuration*, we may speak of homogeneous electronic perturbations. If they belong to the same identical electronic state, and are alike in vibrational *species* but differ in vibrational *state* (i.e., vibrational configuration), we may speak of homogeneous vibrational perturbations. If they belong to the same vibronic species, yet differ in respect to electronic and vibrational species, we may speak of homogeneous vibronic perturbations. The term "homogeneous vibronic perturbations" could also be used in a broader sense to include *all* the homogeneous cases just defined.

Definitions similar to the preceding apply also to predissociation, although certain questions need then to be answered as to the classification of states in which some of the vibrational degrees of freedom are unquantized. It should also be borne in mind that no sharp line can always be drawn between homogeneous predissociation and simple dissociation.

A heterogeneous electronic perturbation may be defined as a perturbation between two states differing in electronic species, and either (a) alike in vibrational species or (b) different in vibrational *and in vibronic* species. (The case of two states differing in electronic and vibrational species, yet alike in vibronic species, fits under the heading of homogeneous vibronic perturbations given above. It might, however, also be classified here under heterogeneous electronic perturbations.) Heterogeneous vibrational perturbations involve vibrational levels of different species but belonging (*a*) to a single electronic state, or (*b*) to different electronic states of the same species. The four cases just considered may all be classified as heterogeneous vibronic perturbations in a broad sense; there appears to be no need for this category in a special restricted sense.

In regard to the probability of occurrence of heterogeneous perturbations in polyatomic molecules, much of the theory remains to be developed. In general, however, heterogeneous perturbations might be characterized as rovibronic perturbations, since their occurrence depends on the term ψ^1_{evr} in equation 2.

In the cases of electronic and of vibronic, but not of vibrational, perturbations and predissociation, intersystem as well as homogeneous and heterogeneous types may be distinguished.[3] These are like the homogeneous types except that there is a difference in multiplicity between the two mutually perturbing states.

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SOME ASPECTS OF INVESTIGATIONS OF MOLECULAR STRUCTURE OF ORGANIC COMPOUNDS[1]

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The spectroscopic methods for determining molecular structure, capable in general of furnishing the most precise data, become rapidly less effective as the complexity of molecules under investigation increases. With the present-day equipment very few molecules more complex than those having two heavy atoms in addition to hydrogens can be exhaustively studied spectroscopically, and recourse must be had to other methods if the knowledge of their structure is not to be postponed indefinitely. Such methods have been devised to attack the problem from several directions, but the scope of the present article precludes the possibility of even mentioning all of them briefly. Instead, attention will be concentrated on only those which have shown themselves useful in the study of molecular structure of matter in the form of dilute gases, when interactions between and mutual orientations of molecules can be neglected.

The most important questions of molecular structure, from the point of view of a chemist, are the geometric distribution of charge and mass, the forces between atoms when these are at near-equilibrium distances, and the energies necessary to separate the molecules into two or perhaps three free radicals with rupture of one or at the most two chemical bonds.

Among methods for determining the geometric relations within molecules, the electron scattering in gases and the dipole-moment determination have received most attention in the past, but other methods, such as x-ray scattering by gases, electric double refraction, and the fine structure of x-ray absorption edges (24, 36), will undoubtedly be developed to a more general usefulness than is the case at present.

The numerous successes of the dipole-moment studies in elucidating molecular structure are so familiar by now that no time will be devoted to their description. Instead some of the shortcomings may be considered. The most fundamental of these, which can hardly be overcome without utilizing results obtained by other types of work, is that only a very sche-

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matized representation of the real dissymmetry of electric charge distribution in molecules can be obtained by this method. Undoubtedly some of the difficulties encountered in using dipole data for quantitative calculations of molecular configuration are to be attributed to this cause. Therefore, a combination of dipole-moment data with results of experiments on electric double refraction and on depolarization of Raleigh scattering should enhance their value greatly, giving a more refined picture of the charge distribution. It is unfortunate that the latter measurements, when performed on gases, are difficult technically and no great reliance can be placed on the results, as is best shown by discrepancies found when comparing results of different workers (10). The use of data obtained with liquids, on the other hand, is doubtful for theoretical reasons. In fact, in recent years the evidence is accumulating that, in the case of dipole moments at any rate, the effect of liquid state is not to be neglected even in dilute solution with non-polar substances as solvents (49, 16; cf. also 9).

The interpretation of molecular structure with the aid of dipole data suffers further from the mutual, not-too-easily-calculated polarization effects of dipoles, as is demonstrated, for instance, by chloroform for which large deviations from tetrahedral angles were deduced until proven otherwise by the electron-diffraction measurements (44). This and other instances suggest that in cases of some complexity one should regard interpretations which are offered on the basis of dipole studies alone with some caution, until substantiated by other methods.

The x-ray diffraction by gases offers in principle the possibility of determining the complete charge distribution within a molecule. However, the practical development of this method has shown that a rather simplified electron distribution must be assumed in advance in order to interpret diffraction patterns in terms of the interatomic distances (6, 12). Thus, in practice, this method does not offer advantages over electron diffraction but instead has disadvantages, some of a purely technical nature but others more fundamental, connected with the circumstance that the diffraction of x-rays is caused by electrons only and hence the assumed electron distribution within each atom affects considerably the evaluated interatomic distances in the molecules. This is demonstrated again by the case of chloroform already mentioned (6, 12). The use of electrons of high energy eliminates the last complication to some extent, because now the scattering is done mainly by the nuclei. It apparently enables one to treat atoms composing the molecule as points, a procedure adopted by most of the investigators in the field and one which yielded results in agreement with those calculated with the aid of more complete theoretical treatment. This problem has been discussed in detail by Pauling and Brockway (32) and convincing evidence was offered in favor of the simplified procedure; nevertheless some doubts can arise as to whether, in discussing more complex molecules, the approximations introduced may not occasionally lead to substantially wrong results.

Perhaps it would be of some interest to study thoroughly by the x-ray diffraction method some simple molecules, the internuclear distances of which have already been accurately determined with the aid of electron diffraction. In this manner it may become possible to obtain more detailed description of the molecular electron distribution laws than that contained in a direct application to molecules of the Thomas-Fermi distribution or that of the self-consistent field, as derived for free atoms.

An appreciable shortcoming of both the x-ray and the electron diffraction methods is their inability to determine with any accuracy the positions of hydrogen atoms in the molecule. In the absence of this information one is forced at present to assume that the internuclear distances between hydrogens and the atoms to which they are bonded, as well as the bonding angles, depend only on the bonding atom and are not influenced by the rest of the molecule. The latter assumption receives indirect support from the observation that the tetrahedral angles are well conserved with carbon, irrespective of the kind of atom attached to it; the bond angles on oxygen also remain rather constant (44). On the other hand, the observed moments of inertia of formaldehyde (13) suggest strongly that either the bond angles between hydrogens and carbon or their distance apart are quite different from the values now commonly accepted, following Pauling (31).

Other internuclear distances, according to the results of the experiments on electron diffraction, are not always constant for a given pair of atoms even though the simple chemical structural formulas may indicate the same bonds between these atoms. An interpretation of the observed variations is due to Pauling, Brockway, and Beach (33), who attribute them to the resonance between several electronic structures of the molecules. They construct first an empirical curve which relates the internuclear distance of two carbon atoms in certain compounds with the amount of resonance between single and double bonds, as evaluated by the method developed by Pauling. On this curve are then fitted other less well known compounds in general agreement with the predictions of the theory. The resonance theory calculations appear thus to supply more reliable information in this matter than is the case with the bonding energies, but this is not astonishing in view of the greater complexity of the latter problem.

The subject of interatomic forces is still completely dominated by the spectroscopic methods, and it is rather doubtful whether others will be found in the near future to replace them effectively. However, the present situation is far from being completely satisfactory, because of the unavoidable shortcomings of the spectroscopic work. Very promising appears the supplementing of it by the studies of the heat capacities of gaseous molecules down to rather low temperatures. In the hands of Eucken (14) such combination has led to the evaluation of a number of vibrational frequencies not accessible to measurement otherwise. The adopted experimental method for the heat capacities is unfortunately open to some criticism. Indeed, because of grave disagreement with other (thermal equilibrium and thermochemical) data (21, 41, 45), one is led now to believe that either in the case of ethane or in that of ethylene some considerable errors have crept into this work.

It seems rational to divide the subject of the bonding energies of organic compounds into two parts and to consider first their absolute values in the approximation that a given pair of atoms has always the same bonding energy regardless of the other parts of the molecule. Unfortunately the knowledge of these bonding energies is so uncertain at present that many important chemical problems, among which should be mentioned the mechanism of the thermal decomposition, must await better data to be finally decided.

The approach to the problem of bonding energies is being made from two directions. By essentially physical methods attempts are being made to determine the total energy necessary to separate organic molecules into free atoms. Since the dissociation energies of hydrogen, oxygen, and possibly nitrogen are now accurately known and, of course, the heats of formation of organic compounds from the elements can be readily obtained from the combustion data, one needs only to know the heat of sublimation of carbon to have the desired answer. This, in turn, may be determined directly or calculated from the heat of dissociation of carbon monoxide. Unfortunately these two avenues of approach lead to widely divergent results. The latest direct figure of Marshall for the heat of sublimation of carbon is 177 Cal. (26). Errors suspected in other work of this type have been eliminated by Marshall, and much more reliance can be placed in it than in values deduced (47) from earlier measurements, which almost invariably were obtained at such high temperatures that the temperature scale is considerably in doubt.

The heat of sublimation of carbon calculated from the dissociation energy of carbon monoxide, as given by Herzberg (9.09 e.v.), is 125 Cal., thus in striking disagreement with the value given earlier. It is true indeed that, while each of the spectroscopic determinations of the heat of dissociation of carbon monoxide[2] (11, 18, 39, 42) claims a very high accuracy, the agreement between different determinations is not particularly good. However, a general trend of decreasing spectroscopic values can be noted in the last few years, and the acceptance of the direct heat of sublimation would bring the dissociation energy of carbon monoxide back into the days

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[2] D_{CO} = 9.09 e.v. (Herzberg (18)); D_{CO} = 8.41 e.v. (Brons (11)); D_{CO} = 8.40 e.v. (Schmid and Gerö (42)); D_{CO} = 9.11 e.v. (Rosen (39)).

of quadratic extrapolation of vibrational energy levels (11.4 e.v.). This value seems to be entirely out of the question, because predissociation has been observed at much lower energies (9.66 e.v.) of the molecule. A reconciliation of the two methods is hardly possible, and it is only as a vague possibility that one may entertain the idea that the direct value does not measure the reversible heat of sublimation. Perhaps the sublimation process leads to the formation of carbon vapor atoms in the ^5S state and not in the normal, because in graphite carbon is tetravalent. But if one corrects the 177 Cal. by the energy difference between the normal (^3P) and the ^5S states, which according to Bacher and Goudsmit (2) is some 100 Cal., one does not get a good agreement either. Also, this mechanism would require an extremely low accommodation coefficient for the ordinary carbon vapor on graphite surfaces. On the whole it is thus apparent that no satisfactory choice can be made at present. Considering the two figures as extremes, one arrives at an average bond strength in methane of either 100 Cal. or 87 Cal., while for the carbon–carbon bond in ethane the values are 84 Cal. and 56 Cal. The latter figures presuppose that the carbon–hydrogen bonds are the same in ethane as in methane. All of them have been calculated on the assumption that the state of the free carbon atom is the ^3P state. This procedure differs from that of Norrish (27) and others who calculated bond energies from the ^5S state of carbon, but in view of the theoretical calculations of Van Vleck (46) and Voge (48) the use of this state seems to be of no advantage. However, in view of these calculations (and some still further improved ones which are certain to follow), the chemical significance of the above bonding energies is rather small. It appears, namely, that the average bonding energy in methane is not identical with the energy necessary to separate the first hydrogen atom, this being the question in which the chemist is particularly interested. By analogy one may conclude that in ethane, also, the energy necessary to break the carbon–carbon bond, leaving the methyl groups intact, is not identical with one of the above figures even if it happens to be derived from correct original data. Noteworthy it is, however, that according to Voge the CH_2 radical is not particularly more stable than is CH_3.

All this suggests that the more direct determinations of the energies required to break an organic molecule into two radicals are very essential. Unfortunately not many such data of even semiquantitative nature are available. The heat of dissociation of cyanogen into CN radicals (20) has been measured. Against this figure, as representing the average carbon–carbon bond strength, the criticism must be leveled that unknown amounts of resonance energy in the original molecule[3] and in the CN radi-

[3] Professor Pauling suggested to the writer that this value may be twice as large as found experimentally in butadiene, hence about 5 Cal.

cals may make it quite unrepresentative. In several papers the energy needed to separate the first hydrogen from methane has been estimated from reaction-rate data (8, 17). Without entering into detailed discussion it may be mentioned that these figures range between 95 and 110 Cal. F. O. Rice (38) and coworkers have estimated bond energies from the activation energies in reactions forming free radicals at high temperatures and low pressures. Essentially these figures (ca. 74 Cal. for C—C and ca. 95 Cal. for C—H) were used by Rice and Herzfeld (37) to calculate chain mechanisms for the decomposition of some organic compounds at lower temperatures. Since, however, the work of Patat and Sachsse (29, 30) strongly suggests that chains are much less frequent than supposed by Rice, one may venture to conclude that the true bond energies are higher than those figures.

Altogether, one is forced to admit that the knowledge of the absolute strengths of even the most common bonds in organic compounds is still very uncertain. The situation is much more encouraging in regard to the relative bond strengths or, more correctly, in regard to the relative stability of certain groups, since experimental data of this type can seldom be utilized to deduce with certainty even relative single bond energies.

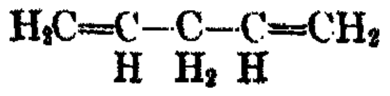
In discussing resonance energies of organic compounds, Pauling (35, 34, 19) has used a simplifying assumption that the bond strengths are constant, except for additional stabilization caused by resonance, either with other homopolar or with ionic electronic structures of the molecules. This assumption has been criticized by Serber (43) on theoretical grounds, while Eyring (15) earlier concluded that in the case of carbon-hydrogen bonds considerable variations are to be expected due to other substituents on the carbon atom. These effects, in brief, may be called steric effects. Experimental evidence obtained by Rossini (40) from heats of combustion of saturated hydrocarbons, where resonance phenomena should be at their minimum, indicates that the bonds are not constant. His data can be accounted for, however, by variations of bonding strength not exceeding a few per cent of the total bonding energy. In fact, they can be represented as variations in energy of the carbon-hydrogen bonds alone, in which case a decrease of about 1 Cal. from methane to ethane and of another 1 Cal. for the secondary hydrogens on propane must be assumed. This is in qualitative accord with calculations of Eyring, but it does not explain better than qualitatively heats of hydrogenation of various normal olefins (21, 41, 45), unless the strength of the double bond is also assumed to be dependent on other substituents. This, however, would spoil the simplicity of the interpretation, and on the whole no definite conclusion can be reached. Certain it is from these calorimetric observations that the energy content per carbon atom increases in the methane series as the atoms become embedded in a longer chain. In the ethylene series, on the other hand, the energy content decreases as the double bond is surrounded by more alkyl groups. In both these instances only the immediate surroundings of the group in question are of importance, and the effect does not extend appreciably over carbon chains more than two atoms long. This is also true of the interaction of two double bonds present in the same molecule (22) and of a variety of other phenomena, such as ultra-violet absorption spectra of two active groups in the same molecule (1), ionization constants of halogen substituted organic acids (25, 28), rates of esterification of aliphatic esters (7), etc.

In conformity with the breakdown of the original assumption of constant bonding energies, calculations of Pauling and coworkers on the magnitude of the resonance energy, made by a semi-empirical method using benzene as the reference scale, have been found to be only qualitatively correct. Thus in the case of aryl substituted ethanes Bent (3, 4, 5) and coworkers conclude, on the strength of rather convincing if not altogether quantitative evidence, that only about half of the observed apparent weakening of the ethane bond is to be attributed to the resonance in the trisubstituted-methyl free radicals. The other half must be assigned to steric hindrance in the ethane, and represents therefore a real weakening of this bond. That alkyl (and also aryl) groups show considerable "steric hindrance" even at larger distances is demonstrated also by the difference in energy content of the *cis*- and *trans*-butenes-2 (45, 21, 41) or that of *cis*- and *trans*-stilbenes (23).

In other conjugated double bond compounds with open-chain or ring structure the resonance stabilization energy has also invariably been found smaller than predicted by Pauling, values between 1.5 and 3 kg-cal. resulting for a simple conjugated system of two double bonds (1) against the calculated (35, 34, 19) value of about 8 kg-cal. In obtaining these figures the entire difference between observed heats of hydrogenation and those calculated by the additivity rule from data on olefins has been attributed to resonance. Indication has been found, however, that a close proximity of double bonds results in their labilization, an effect not predicted by resonance calculations and one which may make the comparison of calculated and observed "resonance" energies somewhat meaningless.

The preceding remarks are not intended to imply that the resonance between several energetically possible electronic structures has not a most important effect on the stability and configuration of the resultant state of the molecule, thus affecting its reactivity and other properties. They merely point out that the calculations now available have been made with so many (inevitable) approximations that one can hardly expect anything better than a qualitative agreement with experimental data. This, however, is obtained in all cases studied thus far and may be demonstrated very convincingly on a series of compounds (I to V) studied recently in

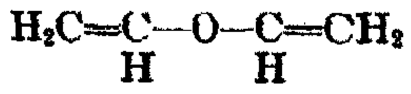
I



$H_2C{=}\underset{H}{C}{-}\underset{H_2}{C}{-}\underset{H}{C}{=}CH_2$

60.8

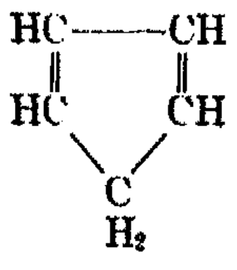
II



$H_2C{=}\underset{H}{C}{-}O{-}\underset{H}{C}{=}CH_2$

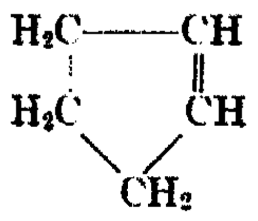
57.2

III



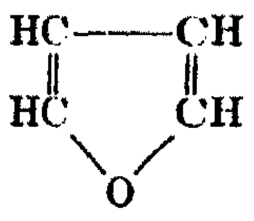
50.9

IV



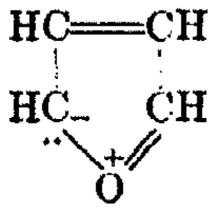
26.9

V



36.6

this laboratory, the heats of hydrogenation of which (to corresponding saturated compounds) are given below each structure. It will be noted on comparing compounds I and II that resonance, in which the unshared electrons of oxygen participate, stabilizes II to the extent of some 3 kg-cal. The closure of the ring on transition from I to III produces conjugation of two double bonds, giving again a stabilization energy of some 3 kg-cal., found by comparing III and IV. Most effective, however, is the closure of the ring in II, since V has stabilization energy of about 17 kg-cal. The reason for this has already been discussed by Pauling (35, 34) and has been attributed by him to a coöperation of polar structure of the type:



Other types of resonating structures have been considered by Pauling, but we shall not enter into a discussion of them. It is to be hoped that further theoretical work, by more refined methods, as well as the accurate thermochemical measurements now in progress in several laboratories, will bring complete and quantitative understanding of the resonance phenomena, which are probably more responsible than anything else for the varied behavior of a given functional group in different compounds so familiar to organic chemists.

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THE STRUCTURES OF THE FLUOROCHLOROMETHANES AND THE EFFECT OF BOND TYPE ON CHEMICAL REACTIVITY[1]

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The investigation of the structures of the normal valence compounds of the non-metallic elements was originally started for the purpose of studying their stereochemistry as shown by the bond angles observed in their compounds and the validity of a table of bond radii as indicated by observed bond distances. Results of the study of angles have shown (2) that in the chlorine and methyl derivatives of the first row elements the bond angles are never more than about three degrees larger than the tetrahedral angle (109°28′) observed in the symmetrical compounds of the AB_4 type. In oxygen fluoride (OF_2) as in water the bond angle is several degrees smaller than the tetrahedral value. The trifluorides and trichlorides of phosphorus and arsenic have angles from 101° to 104°.

Of greater importance in their relation to the chemical properties of substances are the bond distances. Several years ago Pauling and Huggins (8, 10) proposed a set of bond radii (table 1) whose sums represent the corresponding single-bond distances in compounds in which the fourth-group elements form four electron-pair bonds, the fifth group three, the sixth group two, and the seventh group one. The values for the fourth and seventh groups are half of the observed interatomic distances in the elements; the other values were obtained by interpolation with the aid of crystal structure data.

The validity of these radii is supported by the observed distances for the methyl compounds (5). The values of the bond distances observed in eleven of these compounds are compared with the corresponding radius sums in table 2. In no case is the difference as great as the experimental error.

These results show that a considerable degree of ionic character in

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covalent bonds does not have an appreciable effect on the bond distances. Although the radii were obtained from bonds between like atoms they are apparently also applicable to bonds between atoms of quite different electronegativities, as illustrated here for several compounds in which appreciable electric moments are observed.

TABLE 1

Normal covalent radii

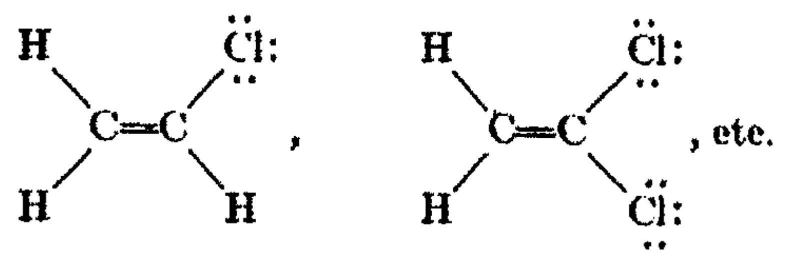
C	N	O	F
0.77	0.70	0.66	0.64
Si	P	S	Cl
1.17	1.10	1.04	0.99
Ge	As	Se	Br
1.22	1.21	1.17	1.14
Sn	Sb	Te	I
1.40	1.41	1.37	1.33

TABLE 2

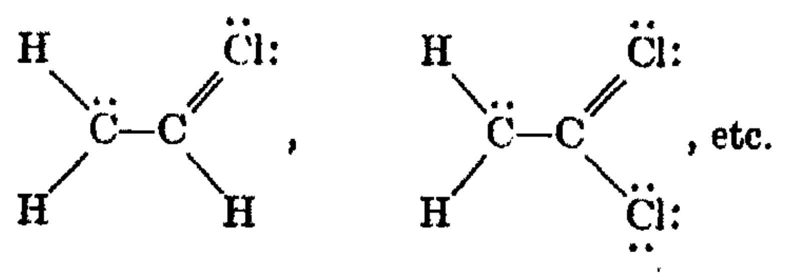
Bond distances and radius sums in methyl compounds

C—C	N—C	O—C	F—C
1.55 ± 0.02 1.54	1.47 ± 0.02 1.47	1.42 ± 0.03 1.43	1.42 ± 0.02 1.41
Si—C		S—C	Cl—C
1.93 ± 0.03 1.94		1.82 ± 0.03 1.81	1.77 ± 0.02 1.76
Ge—C			Br—C
1.98 ± 0.03 1.99			1.91 ± 0.05 1.91
Sn—C			
2.18 ± 0.03 2.17			

Application of the radii to substances containing multiple bonds has shown that a new kind of conjugation frequently exists. Reference may be made to the chloroethylenes (4) for which the conventional bond structures are represented with a double bond between the two carbon atoms and with single bonds connecting the chlorine and carbon atoms,



The observed carbon–chlorine distances in these six compounds are from 0.07 to 0.03 A.U. less than 1.76 A.U., the radius sum and the value observed in the chloromethanes, according to the number of chlorine atoms in the molecule. This shortening, which has also been observed in phosgene and thiophosgene, may be explained on the basis of contributions to the normal states of the respective molecules of structures in which the double bond is between carbon and chlorine,



An empirical quantitative relation between bond character and bond distance (4) has been worked out for all molecules in which the normal state is best represented as a resonance among several individual electronic structures such that a particular bond is single in one and double in another. Additional examples of substances of this type are benzene, graphite, cyanogen, carboxylic acids, carbonates, nitro compounds, nitrates, and many others.

The normal chlorides and fluorides of a number of the non-metals have also been measured (6, 1), and the observed distances are compared with the corresponding radius sums in table 3. The chlorides of silicon, germanium, tin, phosphorus, and arsenic and the fluorides of carbon, silicon, phosphorus, and arsenic show distances which are smaller than the respective radius sums by amounts which in most cases are several fold greater than the experimental error. The shortenings in the chlorides have been explained on the basis of the contributions of structures containing double bonds. Such structures are formed if a chlorine atom shares one of its extra electron pairs with the central atom. In the chlorides of the first row elements the existence of only four bond orbitals on the central atom prohibits this phenomenon; it will be noted that the shortening does not occur in carbon tetrachloride or in chlorine monoxide. The amounts of the shortenings observed in the other chlorides correspond to reasonable degrees of double-bond character.

The fluorides, on the other hand, show striking anomalies. In silicon tetrafluoride and phosphorus trifluoride the observed shortenings of 15 and 13 per cent below the respective single-bond distances are too great to be due to the contribution of double-bond structures because the maximum difference observed between single- and double-bond distances is 10 per cent. Carbon tetrafluoride, moreover, shows a 4 per cent shortening, although the existence of only four bond orbitals on the carbon atom prohibits its holding even one fluorine atom by a double bond and the other three by single bonds. That this decrease in distance is not due to the electrostatic attraction of the negative fluorine for the positive carbon

TABLE 3

Bond distances and radius sums in chlorides and fluorides

C–Cl 1.755 ± 0.005 1.76 0.00		O–Cl 1.68 ± 0.03 1.65 +0.03	
Si–Cl 2.00 ± 0.02 2.16 −0.16	P–Cl 2.00 ± 0.02 2.09 −0.09		Cl–Cl 1.983 ± 0.005 1.98 0.00
Ge–Cl 2.08 ± 0.03 2.21 −0.13	As–Cl 2.16 ± 0.03 2.20 −0.04		
Sn–Cl 2.30 ± 0.03 2.39 −0.09		Te–Cl 2.36 ± 0.03 2.36 0.00	I–Cl 2.315 ± 0.005 2.32 0.00
C–F 1.36 ± 0.02 1.41 −0.05		O–F 1.41 ± 0.05 1.30 +0.11	
Si–F 1.54 ± 0.02 1.81 −0.27	P–F 1.52 ± 0.04 1.74 −0.22		
	As–F 1.72 ± 0.02 1.85 −0.13		

atom is shown by the result given below for methyl fluoride in which the carbon–fluorine bond has the distance 1.42 A.U., only 0.01 A.U. larger than the normal single-bond distance. The appreciable difference in the carbon–fluorine bond distances in the two compounds, amounting to 0.06 A.U., indicates that the carbon–fluorine bond in carbon tetrafluoride is several thousand calories per mole stronger than in methyl fluoride, a fact which is related to the differences in the chemical properties of the substances.

I undertook the investigation of the fluorochloromethanes in order to discover the conditions governing the behavior of the carbon–fluorine bond and its effect on other bonds in the same molecule and also to find an explanation in terms of bond structure which would not only account for the chemical properties of the fluoromethanes but which might be applicable to the fluorine compounds of other elements. The compounds investigated include methyl fluoride, difluoromethane, and all of the fluorochloromethanes except trifluorochloromethane.

The structures of these molecules were determined from electron-diffraction patterns obtained from the gases. The experimental procedure has already been described (2) and the details of the interpretation of the photographs will be published separately. The results are collected in table 4 together with those previously obtained for the chloromethanes (11) and for carbon tetrafluoride (6, 1). The estimated probable errors indicate the relative certainty with which the various interatomic distances have been determined. In some of the compounds containing both chlorine and fluorine the fluorine–chlorine and chlorine–chlorine separations are given with smaller errors than those for the shorter distances. This is due to the fact that the theoretical diffraction patterns are less sensitive to changes in the distances between the atoms whose scattering powers are smaller.

In some of the cases, as indicated below, assumptions about the bond angles have been made which aid in fixing probable values for the smaller distances, but in every such case the ranges through which these distances may vary without causing pronounced disagreement between the theoretical and observed diffraction patterns are included within the limits of the assigned errors.

The FCF bond angle in difluoromethane is only slightly larger than the tetrahedral angle and is appreciably smaller than the corresponding ClCCl angle in dichloromethane. The high electronegativity of fluorine relative to hydrogen appears not to be an important factor in affecting the bond angles. Measurements on trifluoromethane would furnish an additional test of this point. The results on fluorotrichloromethane show that the fluorine–chlorine repulsion is less than the chlorine–chlorine repulsion; although the number of separations of each kind is the same, the bond angle for the first is 4° smaller than that for the second. In difluorodichloro-

TABLE 4

Structures of the fluorine and chlorine derivatives of methane

SUBSTANCE	C—F	C—Cl	F—F	Cl—Cl	Cl—F	∠FCF	∠ClCCl	∠FCCl
CH_3F	1.42 ± 0.02							
CH_3Cl		1.77 ± 0.02						
CH_2F_2	1.36 ± 0.02		2.23 ± 0.03			110° ± 1°		
CH_2FCl	1.40 ± 0.03	1.76 ± 0.02			2.59 ± 0.03			110° ± 2°
CH_2Cl_2		1.77 ± 0.02		2.93 ± 0.02			112° ± 2°	
CHF_2Cl	1.36 ± 0.03	1.73 ± 0.03	2.24 ± 0.04		2.56 ± 0.03	110½° ± 1°		110½° ± 1°
$CHFCl_2$	1.41 ± 0.03	1.73 ± 0.04		2.87 ± 0.03	2.56 ± 0.03		112° ± 2°	109° ± 2°
$CHCl_3$		1.77 ± 0.02		2.93 ± 0.02			112° ± 2°	
CF_4	1.36 ± 0.02		2.22 ± 0.03			109°28′		
CF_2Cl_2	1.35 ± 0.03	1.74 ± 0.03	2.21 ± 0.03	2.90 ± 0.03	2.52 ± 0.02	109° ± 2°	113° ± 2°	110° ± 2°
$CFCl_3$	1.40 ± 0.04	1.76 ± 0.02		2.91 ± 0.03	2.56 ± 0.04		111½° ± 1°	107½° ± 1°
CCl_4		1.755 ± 0.005		2.87 ± 0.02			109°28′	

methane the chlorine–chlorine bond angle is larger than either the fluorine–chlorine or fluorine–fluorine angle. These results together with comparisons with the chloromethanes support the conclusion that the fluorine–fluorine and fluorine–chlorine bond angles on carbon generally are about equal while the chlorine–chlorine angle is larger. This was assumed in the analysis of the measurements on difluorochloro- and fluorodichloromethane. It is evident that the repulsions which fix the halogen bond angles on carbon are determined chiefly by the relative sizes of the atoms and not by their relative electronegativities.

The carbon–fluorine bond distances listed in the first column of the table show that the difference originally observed between methyl fluoride and tetrafluoromethane occurs between other members of this series. A value close to 1.36 A.U. is observed for difluoro-, tetrafluoro-, and difluorodichloromethane. Difluorochloromethane also belongs to this group, for although the determination is less accurate the carbon–fluorine distance in this compound cannot be more than 0.02 or 0.03 A.U. greater than 1.36 A.U. A value of about 1.41 A.U., on the other hand, is observed for methyl fluoride, fluorochloromethane and fluorodichloromethane. Only in the case of fluorotrichloromethane is the uncertainty in the determination as large as the difference between the two values for the carbon–fluorine distance; here the existing evidence supports the larger value and this compound, too, probably belongs to the second group. The striking feature in this classification is that the methane derivatives containing two or more fluorine atoms fall into the first and those containing only one fall into the second group.

The value 1.41 A.U. is the sum of the single covalent radii for carbon and fluorine. Since it is observed in methyl fluoride, and the methyl compounds in general (5) have the normal values for single covalent bonds, it is probable that the carbon–fluorine bonds in the second group of compounds represent the normal type of such bonds. The bonds in the first group of compounds are then about 4 per cent shorter than the normal value. This shortening interpreted in terms of bond energies indicates that a carbon–fluorine bond in the first group is about 8000 or 10,000 calories per mole stronger than one in the second group.

The carbon–chlorine bond distances in the second column of table 4 show that in most of these compounds the bond has the normal distance, 1.76 A.U., observed in the chloromethanes. In particular the chlorine bonds in fluorochloromethane and fluorotrichloromethane are not shortened. It is to be noted, however, that there is a possible effect in the two compounds having two fluorine atoms on the carbon. The shortening is small and uncertain in any event, and we may conclude that if there is any strengthening of the carbon–chlorine bond it is much less pronounced than the strengthening observed in some cases in the carbon–fluorine bond.

The chemical properties of the fluorochloromethanes and fluorochloroethanes have been reported by Midgley and Henne. They have studied the influence of fluorine atoms in the molecule on the reactions in which chlorine (or bromine) is substituted by fluorine. The following quotation from their recent survey (7) shows the very close relation between the structural anomalies observed above and the chemical behavior of these compounds: " . . . The presence of a lone fluorine atom in an aliphatic molecule produces an unstable compound, which shows a great tendency to liberate hydrogen fluoride. In contradistinction, compounds having a halogen atom on the carbon bearing the fluorine are more stable. The presence of two fluorine atoms on the same carbon is attended with (1) a very great increase of the strength of the carbon–fluorine bonds; (2) a strengthening of the linking of any third halogen atom that may be present on this same carbon; and (3) a great increase of the stability of any halogen atoms present on adjacent carbon atoms."

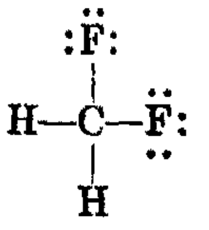
The structural data are in accord with these conclusions. The shortening and strengthening of the carbon–fluorine bond are found to occur in the methane derivatives having two or more fluorine atoms on the carbon atom. Accepting the chemical evidence for the effect on chlorine as a third halogen atom, we know from the observed bond distances that the strengthening of the carbon–chlorine bond is considerably less than that of the fluorine bond. Among fluoromethanes and fluorochloromethanes the very great increase in stability occurs only in those having two or more fluorine atoms, the differences between methyl fluoride and the monofluorochloromethanes being much less.

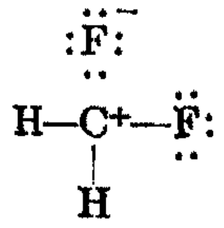
An explanation of the structural and chemical properties of the fluorine derivatives of aliphatic compounds can be developed from the assumption that on account of its great electronegativity fluorine has a tendency to take the shared electron pair from the carbon atom and become a negative ion. When this ionic character of the bond is high the fluorine atom is reactive; a decrease in the ionic character will make the fluorine atom less reactive.

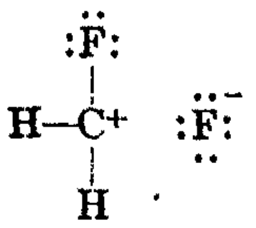
The saturated monofluorides with the exception of the first four in the series of normal alkyls lose hydrogen fluoride spontaneously. According to the foregoing postulate the ionic character of the fluorine bond in these compounds is so pronounced that the separation into a negative fluoride ion and a positive alkyl ion actually occurs; the latter then loses a proton and is transformed into an olefin. All of the saturated monofluorides are hydrolyzed quite easily by concentrated acids and bases. In basic solutions the high concentration of hydroxyl ions favors the formation of the carbon–oxygen bond, which has less ionic character than the fluorine bond, and the alcohol is formed. The splitting off of hydrogen fluoride observed in acid solutions may be attributed to an increase in the tendency of the fluoride ion toward a complete separation from the alkyl group due to the high concentration of hydrogen ions and the alkyl ion again becomes an olefin molecule.

The ionic character of the carbon–fluorine bond is decreased when another group is present in the molecule which tends to reduce the relative electronegativity of the carbon and fluorine atoms. This will occur in general when one of the hydrogens is substituted by a more negative group, and under these circumstances the fluorine compound should be more stable. This increase of stability is observed in the fluorine compounds containing other halogens. The ionic character and reactivity of the carbon–fluorine bond may be decreased by the presence of a negative atom on the adjacent carbon as shown by the stability of monofluoroethanol and monofluoroacetic acid. It will be noted that in the fluorochloro compounds both halogen atoms are less reactive than in the respective mono derivatives. This mutual effect is probably due to the increase in the negativity of the carbon atom occurring on the substitution of either halogen into the molecule containing an atom of the other so that both carbon–halogen bonds have less ionic character and reactivity than in their respective monohalogen parents.

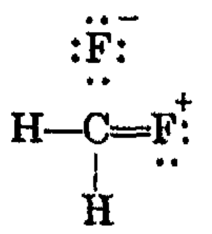
The very marked increase in stability when the second substituent is fluorine we attribute to an additional effect. If the normal state of difluoromethane is represented in terms of the individual electronic structures, whose resonance together determines the properties of the substance, the three structures I, II, and III would be expected by analogy to methyl fluoride to contribute to the normal state of the molecule, II and III giving ionic character to the carbon–fluorine bonds.

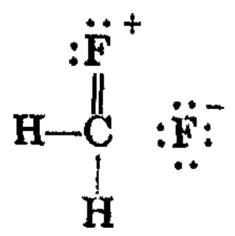

I


II


III

In addition, however, the two structures IV and V have low energy values and can make a significant contribution.

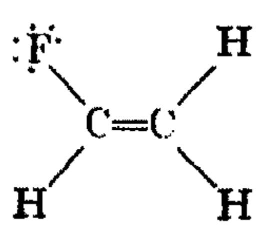

IV


V

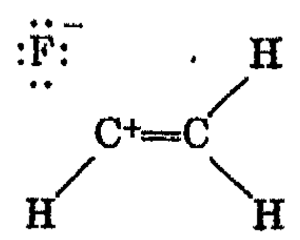
In these structures one fluorine atom is able to form a double covalent bond by sharing one of its extra pairs with carbon, on which a bond orbital has been released by the other fluorine atom which has assumed an ionic form. These structures making equal contributions to the normal state would strengthen and shorten the carbon–fluorine bonds. With the aid of the relation between bond distance and double-bond character (9) the observed shortening can be accounted for by a 10 per cent contribution from each of IV and V. This formulation is applicable only to the molecules having two or more fluorines on one carbon, a distinction which agrees with the experimental evidence.

Double-bond character of the bonds between halogen atoms and non-first-row atoms has already been well established; for these heavier atoms, which have a larger number of orbitals in the valence shell, there is no such restriction on double-bond formation as there is for carbon. The shortening effect of double-bond character is not found in the monofluorochloromethanes presumably because chlorine has not the great electronegativity which would allow the assumption of an extreme ionic form in these compounds.

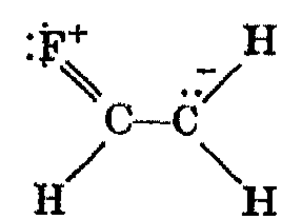
In fluoroethylene, also, the greater stability may be explained by the contribution of some double-bond character to the carbon–fluorine bond. Here as in the chloroethylenes (4) one of the important structures has a single bond between the carbon atoms and double bond to the halogen. The representation for fluoroethylene is the following:



I



II



III

Measurements should show that the carbon–fluorine bond in this molecule is shortened without the presence of a second fluorine atom. When other halogen atoms are present the same effect would occur, although more structures would contribute to the normal state. We can predict that there is not the great difference in the stability of the mono- and di-fluoroethylenes that is observed in the corresponding saturated compounds.

The decreased reactivity of chlorine in the fluorochloromethanes is apparently due chiefly to the effect of the fluorine in decreasing the ionic character of the carbon–chlorine bond. In the difluorochloromethanes there is some evidence of double-bond character in the chlorine bond, but to a much lesser extent than in the fluorine bonds. The stabilizing effect of two fluorines on chlorine attached to the adjacent carbon atom is accounted for by the increased negativity of the carbon and the lesser ionic character of the chlorine bond.

The foregoing discussion has assumed that chemical reactivity is dependent upon (1) the degree of ionic character in bonds which are largely covalent and (2) the contribution of double-bond character to single bonds. From the chemical data it appears that the second effect has the more pronounced influence on reactivity. From the structural data it appears that the second effect has much the greater influence on the bond distances. Indeed the change in distance with ionic character must be very small. This conclusion is supported by the observed carbon–nitrogen bond distances in cyanides and isocyanides (3) which have the same value in spite of the difference in the ionic character of the bonds. That great differences in chemical reactivity may follow small changes in structure has been discussed theoretically by Sutton and Pauling (12).

The explanation offered for the methanes does not solve the question of the abnormal shortening in the phosphorus and silicon fluorides. The 3 to 5 per cent shortenings observed below the *double-bond* values for these compounds have not yet been explained. The contribution of triple-bond structures is not very plausible, in view of the small tendency which second row elements have toward triple-bond formation. It is evident from the foregoing results, however, that the mixed halides of phosphorus and silicon should be investigated for variations in the fluorine bond distances.

The kindness of Dr. Midgley and Dr. Henne of the Midgley Foundation and of Mr. R. J. Thompson of Kinetic Chemicals, Inc., in supplying the materials is gratefully acknowledged. To Professor Linus Pauling I am indebted for the benefit of many consultations and suggestions.

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IONIZATION AND DISSOCIATION OF MOLECULES BY ELECTRON IMPACT[1]

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Among the methods available for experimental study of molecular structure an important place is occupied by that one which uses a mass spectrograph to study the kind of products formed when molecules are struck by electrons of known energy. In the following paper we wish to give some illustrations of work done in this field including a brief account of some new results recently obtained which will be published in detail elsewhere.

By a mass spectrograph is meant any apparatus embodying a combination of electric and magnetic fields which sorts out the ions formed in a source according to the value of the ratio of mass to charge of the ion, enabling a measurement of the ratio to be made and also a measurement of the relative number of ions of each kind as conditions in the source are varied. Research in this field started about twenty years ago, and was at first directed to study of atomic ionization processes and to study of isotopes. In a few years the importance of the mass spectrograph for studies of molecular structure was recognized independently by H. D. Smyth in Princeton and Hogness and Lunn in Berkeley.

A good review of the field up to about five years ago is found in a paper by Smyth (14). For a rational classification of the various types of spectrographs with illustrations of their applications reference may be made to a recent paper by Bleakney (3). More recent reviews of the experimental material have been prepared by de Groot and Penning (5) and also by Sponer (15).

I. RESULTS OBTAINED WITH DIATOMIC MOLECULES

Most of the ideas involved in the application of mass spectroscopy to studies of molecular structure are illustrated by considering in detail the well-studied case of molecular hydrogen. In figure 1 there are plotted the potential energy curves for a number of electronic states of the hydro-

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gen molecule, neutral and singly and doubly ionized. Of these we are most sure of the uppermost, that for doubly ionized H_2, for this is merely two protons and therefore curve e is simply the function e^2/r representing the Coulomb interaction of the two particles. Curve a is for the normal state of neutral H_2, as obtained from band spectra using the moment of inertia, the vibration frequency, and the heat of dissociation to fix the main features of the curve. Curve b is for the repulsive $^3\Sigma$ state of neutral H_2, first calculated by Heitler and London, and recently calculated more exactly by James, Coolidge, and Present (9). This new calculation puts the curve several volts lower than the first-order perturbation calculation of Heitler and London, in the region of nuclear separations near the

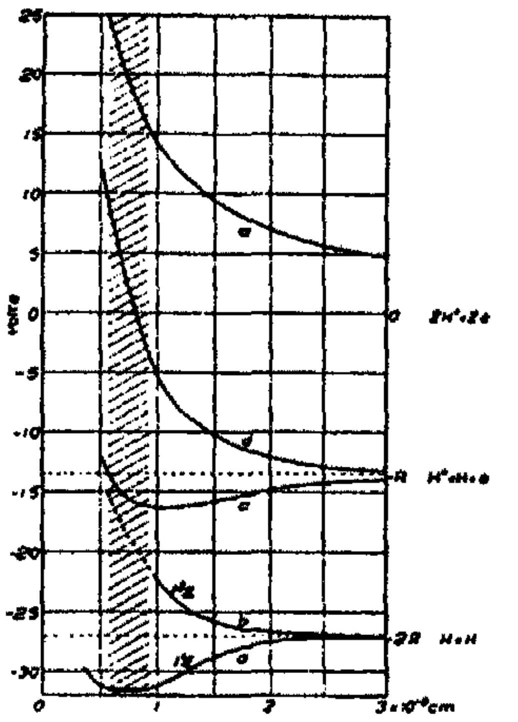

FIG. 1

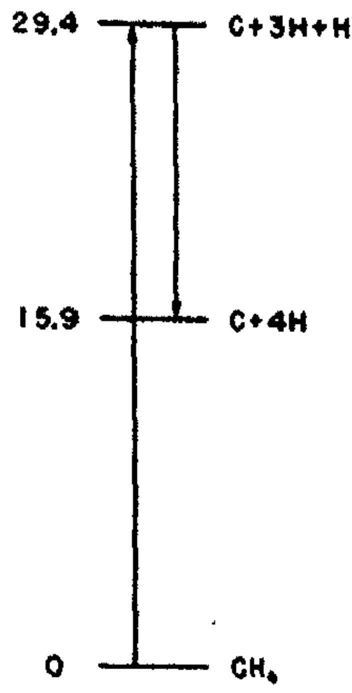

FIG. 2

FIG. 1. Potential energy curves for a number of electronic states of the hydrogen molecule.

FIG. 2. Energy level deduced from the 29.4 volt appearance potential of H^+

nuclear separation for the normal state. Curves c and d correspond, respectively, to the stable and unstable electronic states of H_2^+ that are based on combination of a proton and a normal hydrogen atom (12, 18). In addition, a complete diagram would show a large number of curves corresponding to various electronically excited states of H_2 and H_2^+, but these are not of interest here.

In considering the processes which may be expected to occur when electrons strike normal hydrogen molecules, we are guided by an idea which has come to be known as the Franck-Condon principle (6, 4). This is simply a recognition of the fact that light quanta or electrons transport a negligibly small amount of momentum for a given amount of energy as compared with the momentum which the massive nuclei possess when they have the same amount of energy. Therefore the distribution of momentum of the heavy particles of a nucleus and their instantaneous positions will be essentially the same after an electron impact (or light quantum emission or absorption) as it is before. Hence among transitions that are energetically possible, the most probable will be those that call for least change in the positions and momenta of the massive nuclei.

This is indicated on the diagram by the shaded vertical region extending up from the minimum of the curve for the normal electronic level. The width of this region is the amplitude of the zero-point vibrational motion. We consider the effect of striking hydrogen molecules with electrons whose energy is gradually increased. To excite the molecule to vibration without making an electronic change would call for direct communication of momentum to the nuclei by the electron, which is extremely improbable. As the voltage is increased above 4.4, transitions to the repulsive state become energetically possible, but at first are of vanishing probability for the energetically possible transitions would call for a large abrupt change in the nuclear separation. Only as the voltage gets up to about 10, where the repulsive curve enters the shaded area, do favored transitions become energetically possible. Molecules making such transitions find themselves in an unstable electronic state with some 6 volts more energy than necessary for dissociation, so they dissociate at once into two normal hydrogen atoms each having about 3 volts of kinetic energy. A critical potential is observed in this region, which may be interpreted in this way, but of course the mass spectrograph cannot check the details since the products are not charged. Chemically such atoms should be extremely reactive, for they have a translational energy of the order of 75 kg-cal. per mole.

Between 15 and 16 volts the shaded region is crossed by the curve for the normal electronic state of H_2^+, so this is where we have to expect appearance of the molecular ion. Since the minimum of the curve does not lie in the shaded region, we expect that as the energy of the electrons is increased above 16 volts the most probable mode of formation of H_2^+ will be by transitions which give the ions some vibrational energy. As the repulsive part of curve c is still within the shaded area at a level of 18 volts, which is enough for simultaneous ionization and dissociation of the molecule into a proton and a normal hydrogen atom, we may expect to observe a slight yield of atomic H^+ ions at this voltage.

An interesting confirmation of these views is afforded by some hitherto unpublished results obtained by Mr. J. A. Hipple in this laboratory. For electron voltages just above 18 volts he compared the yield of monatomic and diatomic ions in hydrogen and in deuterium. The electronic potential energy curves for the two molecules are the same to within the accuracy needed here. But the greater mass of deuterium reduces the zero-point energy of vibrations in the normal electronic state, with corresponding reduction in the zero-point amplitude of vibration. Therefore the shaded region should be drawn but $2^{-\frac{1}{2}}$ as wide for deuterium as for hydrogen. This should considerably reduce the yield of atomic ions as compared to molecular ions from transitions to curve c. This is exactly what was found experimentally. Using 22-volt electrons Hipple found the ratio $H_2^+/H^+ = 104$, while in heavy hydrogen the corresponding ratio is $D_2^+/D^+ = 292$.

As the voltage is increased to about 30 volts, we come to the place where curve d enters the shaded region. At this place transitions to curve d may occur, which result in formation of atomic hydrogen in the normal state and protons, each with about 7 volts of kinetic energy. Curiously enough this energy happens to coincide with the energy needed for complete dissociation of the hydrogen molecule (4.4 plus twice 13.5 volts), and so this critical potential was at first attributed to such a process. That our interpretation is the correct one was shown by Bleakney (1) by experiments which demonstrated that the protons produced in this process have kinetic energy. More exact studies of the processes in which the ions are formed directly with kinetic energy have been made by Lozier (10) and, for corresponding processes in nitrogen, oxygen, and carbon monoxide, by Tate and Lozier (16, 11). Finally at some 45 volts energy for the impacting electron we come to the place where the simple Coulomb potential energy curve for the H_2^{++} molecule (f) crosses the shaded area. At these voltages electron impact will be able to strip off both electrons from the hydrogen molecule, leaving the two protons at the same distances as they were in the original molecule in the first instant. They then move out, changing their approximately 18 volts of potential energy into kinetic energy, which is equally divided between them because of their equal mass.

This account of what happens in hydrogen has been given in full, for it represents most of the ideas and is so satisfyingly complete in its correlation of theory and experiment. Moreover, processes of this kind gave the first definite experimental evidence for the reality of the repulsive potential energy curves that were obtained from quantum-mechanical calculation of electronic states.

Similar studies have been made for other simple diatomic molecules with, however, the difference that in the other cases one cannot say so much about the potential curves from theory, owing to the difficulty of the calculations involved. The method gives us information supplementary to that obtained from molecular spectra about the potential energy curves leading to stable molecular states, and also additional rough information about the location of repulsive potential energy curves. A recent compilation of collision data has been given by Sponer (15).

II. POLYATOMIC MOLECULES

As is the case with every method of molecular structure study, the problems presented by studies of polyatomic molecules with the mass spectrograph are considerably more complicated than for diatomic molecules.

The method of electron collisions is not a universal one since it, like all the other methods, tells only a small part of the story of molecular structure, but this small part is nevertheless a significant and useful one. It is primarily concerned with the number of ways in which a molecule may be broken up, the energies necessary for these transformations, and the probabilities of their occurrence. Since a review of this whole field is not feasible at this time, we will confine our discussion to a few carbon compounds. It is a remarkable fact that all or almost any combination of the valence bonds of a molecule may be broken by a single electron impact if the transformation is energetically possible. As an illustration we cite the case of benzene. Nier[2] found that as the result of a single impact all the hydrogens may be stripped off, leaving a C_6^+ ion. This result is somewhat surprising, since, according to the Franck-Condon principle, the energy ($\backsim$ 35 volts) must first go into an electronic excitation.

The chief difficulty with the interpretation of the results when the mass spectrograph is applied to the study of polyatomic molecules is the lack of information on what happens to the neutral particles. In addition to the discrete energy levels to which they may be excited, there is the possible continuum of translational kinetic energies which serve to obscure the final potential energies of the products. The situation is not hopeless, however, as the analysis given below will indicate. Fortunately the states of the hydrogen atom and molecule are well known, and the first excited state of the hydrogen atom is so far above the ground state that excited states of this atom in dissociated products of molecules containing hydrogen atoms are seldom a cause of misinterpretation. It is to be remembered that the ionization potentials represent the minimum electron energy at which the particular ion in question appears. It is therefore natural to assume, if there is no evidence to the contrary, that the products of ionization are in the lowest electronic states. The question of the vibrational state is however a different matter, since it involves nuclear motions which respond slowly to changes in bond energies.

Although it is undoubtedly true that the Franck-Condon principle restricts the vibrational transitions which accompany an electronic change in a polyatomic molecule, the situation is here so much more complicated that the principle is not of much help. In a polyatomic molecule containing N atoms there are $3N - 6$ internal degrees of freedom for the nuclear

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[2] Private communication from Dr. A. O. Nier.

motion, so in place of a potential energy curve as in the diatomic case we shall have a potential energy surface giving the energy as a function of the $3N - 6$ internal coördinates of the nuclear frame of the molecule. There will be one such surface for each electronic state of the molecule. At present we know almost nothing about such surfaces except in the few cases which have been studied by Eyring, Polányi, and others in connection with problems of chemical kinetics. The analysis of Raman and infra-red vibration spectra gives us information about the shape of the surface of the lowest electronic state in the neighborhood of its minimum, and we may hope to learn about excited states from analysis of electronic band systems of polyatomic molecules.

The picture then is this: By appropriate choice of coördinates in a $(3N - 6)$ dimensional configuration space the motions of the nuclear frame will be the same as the motion of a single mass point in the configuration space moving under the forces described by the potential energy surface. Before being struck by an electron the representative mass point is moving on the potential energy surface of the normal electronic state. This means it is performing small oscillations around the minimum of this surface. The electron impact changes the electronic state, substituting a new potential energy surface to govern the mass point's motions. The mass point then begins to move on the new surface starting from the initial configuration that corresponds to the initial state before impact. The ensuing motion has much greater possibilities for complexity than in the diatomic case, with the general result that a process of dissociation that is energetically possible is much more likely to occur.

It is tempting to try to make progress by assuming some gross oversimplifications of the surfaces in the absence of better information. Thus in methane the H-H distance is greater than in normal H_2 or H_2^+. Does this mean that if H_2^+ is formed by electron impact in methane it will necessarily be formed with vibrational energy? At first sight it might seem that we could reason thus: From the fact that H_2^+ appears at all we know that two C—H bonds are broken in the excited electronic state of the CH_4^+ complex from which it is produced. If the bonds are broken we might neglect the forces between C and H altogether and assume the force between the two hydrogen atoms to be the same as in normal H_2^+. In that case we could use the curves of figure 1 to make a definite estimate of the amount of vibrational energy in the H_2^+ produced.

In a first draft of this paper we had analyzed the data for methane that are discussed below, from this point of view. It appears on going over the matter more carefully that such arguments are too inaccurate to be of value. This is emphatically brought out below in the striking contrast between the processes of forming C_2^+ in C_2H_2 and C_2N_2, respectively.

Experimental results for methane

The ions produced by electron impact in methane were studied with a mass spectrograph of the type described by Bleakney (2). The positive ions observed, together with their relative intensities and their appearance potentials, are shown in table 1. In addition, several negative ions were found, which will be described in a later paper.

The positive ions were all observed using first a tungsten filament and later an oxide-coated, equipotential cathode, run at about 1000°C., as source of electrons, the relative intensities of the first five ions being the same in both cases, while the intensities of the last three were not recorded with the tungsten filament. The relative intensities, furthermore, were all found to be unchanged by changes in pressure, electron current, and filament temperature over wide ranges. Hence we may say that each ion is produced by the single impact of an electron with a methane molecule, and that none is the result of primary thermal dissociation of methane at the cathode, as was thought to be the case in the experiments of Hogness and Kvalnes (8).

TABLE 1

Positive ions formed in methane

m/e	ION	PER CENT OF TOTAL IONIZATION (ELECTRON ENERGY = 50 VOLTS)	APPEARANCE POTENTIALS *volts*
16	CH_4^+	50.7	13.1 ± 0.4
15	CH_3^+	39.5	14.4 ± 0.4
14	CH_2^+	4.2	15.7 ± 0.5
13	CH^+	1.7	23.3 ± 0.6
12	C^+	0.6	26.7 ± 0.7
3	H_3^+	0.005	25.3 ± 1.0
2	H_2^+	0.3	27.9 ± 0.5
1	H^+	3.0	22.7 ± 0.5 29.4 ± 0.6

The errors quoted in the last column of table 1 are estimated probable errors which we believe to be quite conservative. Argon, introduced into the instrument simultaneously with the methane, was used to correct the observed electron energy scale for contact potentials, etc., in measuring the appearance potentials of CH_4^+, CH_3^+, CH_2^+, CH^+, and C^+, while helium and a slight impurity of hydrogen were used as calibrating gases for H_3^+, H_2^+, and H^+.

Interpretation of data on methane

Our chief guide in selecting most probable processes to explain the observed appearance potentials is the heat of dissociation of methane into atoms in the gaseous state $D(\mathrm{CH_4})$. This quantity is obtainable from thermochemical data, using the following cycle:[3]

$$\begin{aligned}
\mathrm{C(s)} + \mathrm{2H_2} &\rightarrow \mathrm{CH_4} + 18.24 \text{ kg-cal.} = 0.79 \text{ volts}\\
\mathrm{4H} &\rightarrow \mathrm{2H_2} + 207.6 \text{ kg-cal.} = 9.00 \text{ volts}\\
\mathrm{C(g)} &\rightarrow \mathrm{C(s)} + 140 \pm 30 \text{ kg-cal.} = 6.1 \pm 1.3 \text{ volts} \equiv \lambda_0
\end{aligned}$$

$$\mathrm{C(g)} + \mathrm{4H} \rightarrow \mathrm{CH_4} + 366 \pm 30 \text{ kg-cal.} = 15.9 \pm 1.3 \text{ volts} \equiv D(\mathrm{CH_4})$$

The very large uncertainty in the value of the heat of sublimation of carbon λ_0 is estimated by Bichowsky and Rossini from data up to 1934, and most values that have been proposed since that time (11, 7, 13)[4] fall within it.

H^+ *at 29.4 volts*

On the assumption that 29.4 volts is the minimum energy required for the reaction $\mathrm{CH_4} \rightarrow \mathrm{C} + \mathrm{3H} + \mathrm{H^+}$, we obtain $D(\mathrm{CH_4}) = 15.9 \pm 0.6$ volts or 366 ± 14 kg-cal. by subtracting the ionization potential of H (13.5 volts) from 29.4 volts (figure 2). This gives $\lambda_c = 6.1 \pm 0.6$ volts or 140 ± 14 kg-cal. We could assume that $\mathrm{CH_4}$ molecules do not dissociate completely in yielding H^+ ions at this minimum energy. In this case we should also have to assume that the products of dissociation have some kinetic or excitational energy in order not to arrive at values of $D(\mathrm{CH_4})$ and λ_c which are too high. Since the reaction first proposed does not require the latter assumption it is the preferred explanation. If in this reaction the products possess kinetic energy when formed, the values obtained for $D(\mathrm{CH_4})$ and λ_c represent upper limits to the true values of these quantities.

H^+ *at 22.7 volts*

If we are correct in taking 29.4 volts as the minimum energy required to dissociate completely the methane molecule with ionization of one of the hydrogen atoms, the only energetically possible reactions which could account for the formation of an H^+ ion at a minimum energy of 22.7 volts are:

$$\mathrm{CH_4} \rightarrow \mathrm{CH_3} + \mathrm{H^+};\ \mathrm{CH_4} \rightarrow \mathrm{CH_2} + \mathrm{H} + \mathrm{H^+};\ \mathrm{CH_4} \rightarrow \mathrm{CH} + \mathrm{H_2} + \mathrm{H^+}$$

---

[3] Values are taken from Bichowsky and Rossini's *Thermochemistry of Chemical Substances*, Reinhold Publishing Corp., New York (1936). This provides an excellent summary of the values obtained for the heat of sublimation of carbon (λ_0) up to January 1, 1934.

[4] In the two papers referred to in reference 13, it is suggested that C(s) → C(g) ^5S at 7.57 volts or 177 kg-cal. Since the ^5S state is 4.3 volts or 100 kg-cal. above the normal ^3P state of the carbon atom, this would mean that C(s) → C(g) ^3P at 3.34 volts or 77 kg-cal. Unless the transition $^5S \rightarrow {}^3P$ by collisions even at high pressure has an extraordinarily low probability, it is highly improbable that in the determinations by the vapor pressure method the energy measured is that for the process C(s) → C(g) ^5S, but rather for C(s) → C(g) ^3P.

The energy required for the corresponding reactions where H^+ is replaced by H is 22.7 − 13.5 = 9.2 volts. Since it is known that it takes about 4.0 volts to break a C—H bond this means that the kinetic or excitational energies of the products of dissociation are respectively: 9.2 − 4.0 = 5.2 volts; 9.2 − 8.0 = 1.2 volts; 9.2 − (12.0 − 4.5) = 1.7 volts. The first of these values seems too high, so either the second or third reaction is probably the correct one. The reasoning by which one obtains $D(CH_4)$ = 17.2 volts, assuming the second reaction, is shown in figure 3. If the products of dissociation have 1.2 volts of excitational or kinetic energy this value is in accord with the 16.0 volt value.

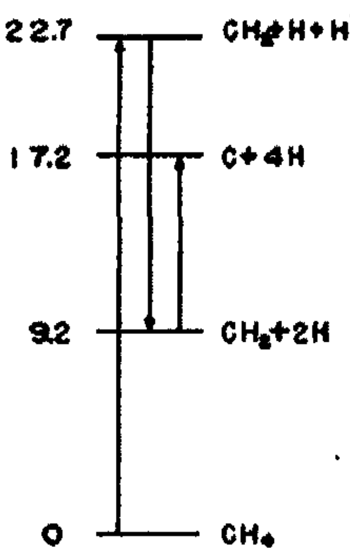

FIG. 3

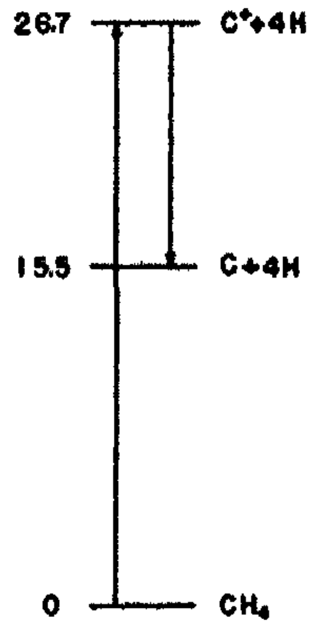

FIG. 4

FIG. 3. Energy levels deduced from the 22.7 volt appearance potential of H^+
FIG. 4. Energy level deduced from the appearance potential of C^+

H_2^+ *and* H_3^+

The simplest interpretation of the observed appearance potential of H_2^+ ions is that 27.9 ± 0.5 volts is the minimum energy required for the reaction $CH_4 \rightarrow H_2^+ + C + 2H$. Subtraction of the ionization potential of H_2 (15.4 volts) and addition of the heat of dissociation of H_2 (4.5 volts) yields $D(CH_4) = 17.0 \pm 0.5$ volts or 389 ± 12 kg-cal., whence $\lambda_c = 7.1 \pm 0.5$ volts or 163 ± 12 kg-cal. provided the products are formed in their normal states without kinetic energy. These values being somewhat above the upper limits for $D(CH_4)$ and λ_c set by the 29.4 volt appearance potential of H^+, we are inclined to attribute about a volt of kinetic or excitational energy to the products of dissociation $H_2^+ + C + 2H$.

Since H_3^+ ions are apparently formed along with negative ions they will not be discussed here but will be treated elsewhere.

C^+

C^+ ions are well explained by the assumption that 26.7 ± 0.7 volts is the minimum energy necessary to dissociate completely a methane molecule and to ionize the carbon atom. If the C^+ ion is unexcited and none of the products acquires kinetic energy as a result of a dissociation, we get $D(CH_4) = 26.7 - 11.2 = 15.5 \pm 0.7$ volts or 357 ± 16 kg-cal., where 11.2 volts is the ionization potential of carbon (figure 4). This gives $\lambda_c = 5.7 \pm 0.7$ volts or 131 ± 16 kg-cal. If the products dissociate with energy these are upper limits to the true values.

CH^+

Values of $D(CH_4)$ and the ionization potential of CH may be obtained simultaneously by combining the observed appearance potential of CH^+ ions formed from methane with that of these ions formed from acetylene. The latter quantity has been measured by Tate, Smith, and Vaughan (17) as 22.2 ± 0.5 volts. Let us denote the former quantity by $A(CH^+)$ and the latter by $A'(CH^+)$, and let us assume the reaction responsible for the appearance of CH^+ ions at these minimum energies to be $CH_4 \rightarrow CH^+ + 3H$ and $C_2H_2 \rightarrow CH^+ + C + H$. Let us also denote a heat of dissociation by D, an ionization potential by I, and the energy evolved in the formation of a gram-mole of a substance from its elements in their standard states by Q. If the products of dissociation are formed without kinetic or excitational energy in both reactions we have:

$$
\begin{aligned}
& I(CH) = A(CH^+) + D(CH) - D(CH_4) \\
& \qquad = A'(CH^+) + D(CH) - D(C_2H_2) \\
\text{also} \quad & D(CH_4) = Q(CH_4) + 2D(H_2) + \lambda_c \\
\text{and} \quad & D(C_2H_2) = Q(C_2H_2) + D(H_2) + 2\lambda_c \\
\text{Hence} \quad & A(CH^+) - A'(CH^+) = D(CH_4) - D(C_2H_2) \\
& \qquad = Q(CH_4) - Q(C_2H_2) + D(H_2) - \lambda_c \\
\text{or} \quad & \lambda_c = Q(CH_4) - Q(C_2H_2) + D(H_2) + A'(CH^+) - A(CH^+) \\
& \quad = 0.79 + 2.34 + 4.50 + 22.2 - 23.3 \\
& \quad = 6.5 \pm 0.8 \text{ volts or } 150 \pm 18 \text{ kg-cal.}
\end{aligned}
$$

This gives $D(CH_4) = 16.3 \pm 0.6$ volts or 376 ± 18 kg-cal. and also gives $I(CH) = 10.9 \pm 0.8$ volts. Since these values of $D(CH_4)$ and λ_c are reasonable, it appears that the assumed reactions are probably correct, and that if the products of dissociation have excitational or kinetic energies when formed they have about the same amount in the two cases.

CH_2^+, CH_3^+, *and* CH_4^+

Little can be said by way of correlating the appearance potentials of these ions with known quantities. Simple considerations show that at a minimum energy of 14.4 ± 0.4 volts a CH_3^+ ion must be formed in accordance with the reaction $CH_4 \rightarrow CH_3^+ + H$. This means that the ionization potential of CH_3 is less than or equal to $14.4 - 4.0 = 10.4$ volts, according as the CH_3^+ ion and H atom are formed with or without energy. Similarly, the observed appearance potential of CH_2^+ ions leads to the conclusion that the ionization potential of CH_2 is less than or equal to $15.7 - 8.0 = 7.7$ volts if a CH_2^+ ion is accompanied by two H atoms or is less than or equal to $15.7 - (8.0 - 4.5) = 12.2$ volts if it is accompanied by an H_2 molecule.

Acetylene and cyanogen

A few remarks will now be made concerning possibilities of interpretation of the data of Tate, Smith, and Vaughan (17) for acetylene and cyanogen. They find that C_2^+ appears at 23.8 ± 0.3 in acetylene and at 18.6 ±0.5 in cyanogen. From Bichowsky and Rossini, using $\lambda_0 = 5.8$ volts, we get 14.6 volts and 16.7 volts for the atomic heats of formation of acetylene and cyanogen respectively. The diagram, figure 5, will show the relations involved. The simplest interpretation in each case is to suppose that C_2^+ is accompanied by two hydrogen or two nitrogen atoms, dissociated, unexcited, and without kinetic energy in each case. But that leads to discordant values of the ionization potential of C_2 from the two sets of data, namely 14.7 from acetylene and 7.3 from cyanogen. The difference between these two values, 7.3 volts, agrees almost exactly with the 7.4 volt heat of dissociation of N_2. If we suppose C_2^+ is accompanied by N_2 in the case of nitrogen, but by 2H in the case of hydrogen, we get concordant values of 14.7 and 14.8 for the ionization potential of C_2^+ in the two cases.[6]

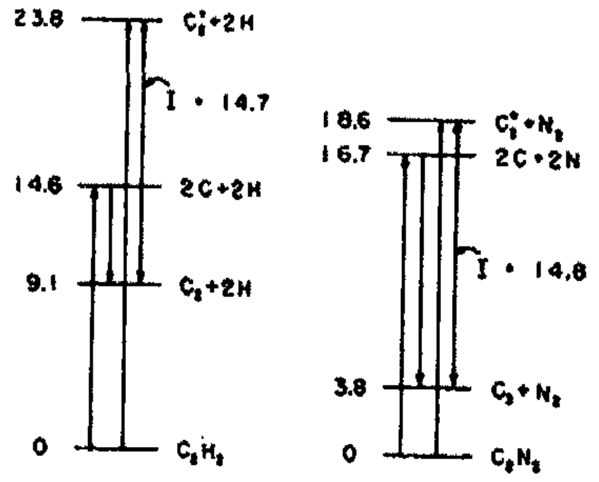

FIG. 5. Deduction of the ionization potential (I) of C_2 from the appearance potentials of C_2^+ in C_2H_2 and C_2N_2.

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[6] This agrees with the rough value 12 ± 2 obtained by Kallmann and Rosen (Z. Physik **61**, 332 (1930)) from a study of electron transfer processes involving the C_2^+ ion formed in C_2N_2 and absorbed in other gases.

CONCLUSION

The preceding remarks have shown that information of value for molecular structure problems can be obtained by the mass spectrograph. The importance of a great deal of further work is obvious. All of the simpler organic molecules lend themselves to studies of the type here reported for methane, and a program of such work is being planned in this laboratory.

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BOND MOMENT AND ELECTRONEGATIVITY[1]

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One of the fondest hopes of the early investigators of dipole moments was that they would give a quantitative means of evaluating the electronegativities of atoms in molecules so often used to explain chemical behavior. Difference in the values of dipole moments associated with chemical bonds A—B and A—C would seem to measure the difference in the electronegativities of B and C. If, however, the molecule containing the bond is polyatomic, the assignment of a constant value to the moment of the bond may be uncertain or impossible. Although values, more or less incorrect but not without usefulness, have been calculated for the moments associated with a number of bonds in polyatomic molecules, it has been shown (17) that a bond moment is merely a measure of the electrical asymmetry of a certain section of a molecule and is affected by the environment of the section. If the moment found for a bond in one environment is used for the same bond in a different environment, quite erroneous conclusions may be drawn. A group attached to a benzene ring may give a moment markedly different from that produced by its attachment to an aliphatic group, and the differences in moment thus arising have been correlated with the orienting influences of the groups upon substitution in the benzene ring (21). The large mutual inductive effects and consequent lowering of moments of two or more dipoles attached to the same atom in the substituted methanes have been pointed out (18). The moment of a group which is the resultant of a number of moments of varying size, one or two usually predominating, may, through the insulation of its component dipoles, be less dependent upon the rest of the molecule than that of a single large dipole like that occasioned, for example, by the presence of a halogen atom. The effect of extramolecular environment upon the weakly screened halogen bond moments of diatomic molecules is interestingly shown by the much higher values found for the hydrogen

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halides (5) and iodine monochloride (6) in solution than in the vapor state (9).

TABLE 1

*Group moments** ($\times 10^{18}$)

GROUP	C_6H_5-	CH_3-	C_2H_5-	ANGLE
—CH_3	0.35 G	0 G	0 G	180°
	0.4 L			
—H	0 G	0 G	0 G	0°
—OCH_3		1.30 G	1.14 G	55°
	1.23 L		1.29 L	
—OC_6H_5	1.14 L	1.23 L	1.28 L	59°
—SCH_3	1.27 L	1.40 L	1.57 L	(70°)
—NH_2	1.53 L	1.23 G	1.2 G	
—I		1.59 G	1.90 G	0°
	1.30 L	1.6 L	1.9 L	
—Br	1.70 G	1.78 G	2.02 G	0°
	1.52 L		2.0 L	
—Cl	1.72 G	1.86 G	2.03 G	0°
	1.55 L			
—F	1.57 G	1.81 G	1.92 G	0°
	1.43 L			
—OH		1.68 G	1.70 G	62°
	1.56 L	1.66 L	1.7 L	
—CH_2Cl		2.03 G	2.05 G	67°
	1.85 L		2.1 L	
—$CHCl_2$	2.04 L	1.98 L	2.06 L	48°
—CCl_3	2.11 L	1.57 L		0°
—$COOCH_3$	1.9 L	1.74 L	1.74 L	
—CHO	2.75 L	2.70 G	2.4 L	58°
—$COCH_3$	3.00 G	2.84 G		58°
	2.90 L	2.74 L	2.76 L	
—NO	3.18 L			
—CN	4.39 G		4.09 G	0°
	3.92 L	3.4 L	3.4 L	
—NO_2	4.21 G	3.42 G		0°
	3.95 L	3.08 L	3.2 L	

* These moment values are calculated, for the most part, from the values in the Appendix of Fuchs and Wolf's *Dielektrische Polarisation, Hand- und Jahrbuch der Chemischen Physik*, Akademische Verlagsgesellschaft M.B.H., Leipzig, 1935, and from data in the references given therein.

Because of the importance of the moments associated with groups in considerations of molecular structure, it has seemed desirable, while assembling material for the examination of bond moments, to show as well the best values now available for the moments of the molecules in which the more important groups are attached to a benzene ring, a methyl group, and an ethyl group. Table 1 gives these groups in the first column, the moments in the three succeeding columns, and the approximate angle which the plus to minus direction of the resultant dipole makes with the bond between the carbon and the atom of the group attached to it. There is some uncertainty in the angles other than 0°, and those of three groups are omitted because their uncertainty appears excessive. The values given are based upon considerations of dipole moment and valence angles given by electron diffraction. The values given in column four for ethyl compounds are reproduced merely to show the effect of the carbon chain on the total moment, which will slightly alter the angle shown in column five when the difference between the methyl and ethyl compound is appreciable. The effect of any chain more than two carbons away is so small as to be negligible, the moments of longer chain compounds being usable in column four when that of the ethyl compound is not available. Although the values marked G, determined for the gaseous state, are the true moment values, the usually slightly different values marked L, obtained from measurements in solution, are reproduced even when the gas values are available, as they may give more nearly correct results when used in combination with other measurements made in solution. The variation in value from non-polar solvent to solvent is not negligible in accurate measurements, but is usually much less than the difference between solution and vapor.

The moment associated with one bond alone is obviously obtainable directly only in the case of diatomic molecules. Knowledge of valence angles obtained from spectroscopic investigations and particularly from electron diffraction measurements (3) has made possible the calculation of bond moments in triatomic and tetratomic molecules such as H_2O, NH_3, PCl_3, $AsBr_3$, etc. It must be borne in mind, however, that each value thus obtained contains the inductive effects of the other bond dipoles in the molecule. An electronegativity scale was prepared from bond moments obtained in this way by J. G. Malone (10) and M. G. Malone and Ferguson (11), hydrogen being taken as zero for reference. As our knowledge of valence angles has advanced since these calculations were made, most of the bond moments have been recalculated in the present work. The values of H—As and H—P calculated by Malone are used unchanged. Because of the small dipole moments of arsine and phosphine, a considerable error in the valence angles assumed would not change the values of the bond moments greatly. The valence angle in phosphorus tribromide is assumed to be the same as that found for the trichloride, and the angle, indistinguishable from this, found for arsenic trichloride is used for the other arsenic trihalides and for the antimony trihalides. The assumptions are almost certainly warranted in the phosphorus and arsenic compounds, and the possible error resulting in the values for the antimony bond angles is probably no greater than that caused by the unusually large error in the moment values for the antimony trihalides.

The hydrogen bond moments in the second column of table 2 give an electronegativity scale referred to hydrogen as zero, which parallels in arrangement of the elements, as pointed out by Malone, the scale established by Pauling (15) on the basis of excess bond energies and, as pointed out by Mulliken (12), the scale established by him on the basis of electroaffinities. The phosphorus bond moments in the fourth column are almost calculable from the differences in the hydrogen bond moments, e.g., (H—I) − (H—P) = 0.02, observed P—I = 0; (H—Br) − (H—P) = 0.42, observed P—Br = 0.36; (H—Cl) − (H—P) = 0.67, observed P—Cl = 0.81. However, as the difference in size and polarizability of the two atoms diminishes and changes sign, the departure from the relations existing among the hydrogen bond moments increases. The departures are greater in the arsenic compounds than in the phosphorus and still greater in the antimony compounds, the difference (Sb—Cl) − (Sb—I) being 1.8 as compared to 0.65 for (H—Cl) − (H—I). The differences (As—Br) − (As—I) = 0.49 and (As—Cl) − (As—I) = 0.86 are but little higher than the directly measured, though not very accurate, I—Br and I—Cl differences, which in turn are close to those calculated from the hydrogen bond moments.

TABLE 2

Bond moments ($\times 10^{18}$)

BOND	MOMENT	BOND	MOMENT	BOND	MOMENT	BOND	MOMENT	BOND	MOMENT
H—As	0.10	C—C	0						
H—P	0.36	C=C	0			I—Br	0.4		
H—I	0.38	C≡C	0			I—Cl	0.8		
H—S	0.68	H—C	0.3	P—I	0	As—I	0.78	Sb—I	0.8
H—Br	0.78	C—I	1.29	P—Br	0.36	As—Br	1.27	Sb—Br	1.9
H—Cl	1.03	C—Br	1.48	P—Cl	0.81	As—Cl	1.64	Sb—Cl	2.6
H—N	1.31	C—Cl	1.56			As—F	2.03		
H—O	1.53	C—F	1.51						
		C—O	0.86	Cl—O	0.73				
		C=O	2.4	Cl→O	2.3				
		C≡N	3.6						

The Cl—O moment, determined from the measured moment of chlorine monoxide, is 0.2 higher than the value calculated as the difference (H—O) − (H—Cl), thus falling in line well with the other bond moments which have been discussed. The bond moment inadequately represented as Cl → O is roughly obtained by taking the moment of chlorine dioxide (20), 1.69×10^{-18}, as the resultant of two equal bond moments making an angle

137° ± 15° with each other (1, 2). The best representation of chlorine dioxide (1) is given by the two formulas

$$:\underset{\cdot\cdot}{\ddot{O}}:\underset{\cdot\cdot}{\overset{\cdot\cdot\cdot}{Cl}}:\underset{\cdot\cdot}{\ddot{O}}: \text{ and } :\underset{\cdot\cdot}{\overset{\cdot\cdot\cdot}{O}}:\underset{\cdot\cdot}{Cl}:\underset{\cdot\cdot}{\ddot{O}}:$$

resonance occurring between the two. As these require a considerable excess of positive electricity on the chlorine and of negative on the oxygen, strong polarity is required of the chlorine-oxygen bond, as shown by the large moment 2.3 in contrast to the small moment of the ordinary covalent Cl—O bond in chlorine monoxide.

In a previous discussion of the moments of the molecules of the phosphorus, arsenic, and antimony halides (17), it was shown that increasing moment for a given halogen resulted from increasing shift of the electrons in the positive atom toward the positive end of the dipole, which amounted to a lengthening of the dipole or the formation of a secondary dipole acting in the same direction with consequent increase in the total moment. As no such increase can occur in the hydrides, where the positive end of the dipole lies toward the proton, it is obvious that increasing polarizability of the atom toward which the positive end of the dipole lies will cause increasing discrepancies between the observed moments and those calculated from hydride bond differences, the observed moments being the larger. The same considerations should apply to the Cl—O moment, where, however, the observed moment is larger than that calculated from hydride bond differences by an amount no larger than the possible uncertainty in the values.

Mulliken (13) has formulated an expression for the dipole moment of a bond A—B between atoms A and B as follows:

$$\mu_{AB} = Q_B r - 4ezabS + \mu_S$$

in which Q_B $(= -Q_A)$ is the net charge on atom B, r is the distance between the centers A and B, e is the electronic charge, z is the distance from the midpoint of the line A—B of the electric center of the moment given by the "homopolar dipole" term $4ezabS$, a, b, and S are the quantities connected with the two independent orbitals ϕ_A and ϕ_B by the equations,

$$\phi_{AB} = a\phi_A + b\phi_B$$

and

$$S = \int \phi_A \phi_B dv$$

and μ_S is the secondary moment induced in the non-bonding electrons. Positive μ is taken as corresponding to polarity A^-B^+, and positive z is taken as the direction A → B. Q_B can be calculated approximately according to Mulliken from the equation

$$Q_B/e = -Q_A/e = (P_A - P_B)/3 - (P_A - P_B)^3/48$$

in which P_A and P_B are the "absolute electroaffinities" on Pauling's electronegativity scale (15). The equation for μ_{AB} would seem to offer a means of estimating bond moments quantitatively. Unfortunately, however, the values of the homopolar term and of the secondary induced moment μ_S are commonly of the same order of magnitude as the first term Q_Br. The large errors probable in their calculation, together with the smaller error in the first term, accumulate in the sum or difference of the terms, so that the absolute value of μ_{AB} calculated by this equation must as a rule be very uncertain. The equation should, however, be useful in explaining or predicting differences in moment between bonds for which the first term can be calculated and the relative values of the second and third terms estimated from knowledge of the radii and polarizabilities of the atoms A and B. The second and third terms evidently do not vary in such a way as to throw any of the bond moments in table 2 hitherto discussed out of the order required by Pauling's electronegativity series as well as by our knowledge of the chemical behavior of the elements. The hydrogen bond moments in the second column of table 2 form a consistent electronegativity series of the elements, although the differences between the successive values do not parallel those on Pauling's electronegativity scale. Quite aside from the other two terms of the equation, mere uncertainty in the values of the moments can account for a large part of the discrepancies. As the sign of the homopolar term is such that the positive end of its dipole is always directed toward the larger atom, this term, which decreases the moment in the hydrogen bonds, reverses its sign in the P—Cl, As—Br, and Sb—I bonds and increases the moment very slightly in these bonds and more in the As—F, Sb—Br, and Sb—Cl bonds, thus adding to the effect of changing μ_S in increasing the moment and introducing discrepancies in the differences of the bond moments as compared to those in the hydrogen bond moments. It would appear from this that the difference (As—F) − (As—Cl) = 0.39 should be greater than the difference (H—F) − (H—Cl), which would mean that the H—F bond moment should be slightly smaller than the value 1.42 calculated by adding 0.39 to the H—Cl bond moment 1.03. On the other hand, because of the small size of the fluorine atom, the homopolar dipole term should effect less reduction in the moment than in the H—Cl bond, which would tend to make the moment greater than 1.4. In order to fall in the order given by Pauling's electronegativity scale and by our knowledge of the chemistry of fluorine, the H—F moment should be greater than the value 1.53 found for H—O. The homopolar dipole and the induced secondary dipole may account for the discrepancy, but it appears probable that the H—F moment is larger than the value 0.8 roughly estimated from Kirkwood's calculation (8) and consistent with the fact that the moment of methyl fluoride is lower than that of methyl chloride.

Consideration of the bonds involving carbon has been postponed until examination of the other bond moments should show that a reasonable basis for their discussion exists. Although the moment of a bond between like atoms is normally zero, it has seemed worth while to list the zero moments of the single, double, and triple carbon-carbon bonds, obtained directly from the zero moments of the ethane, ethylene, and acetylene molecules (19), in which the symmetry of the molecules causes the moments of the C—H bonds to cancel one another. When the unsaturated bonds are unsymmetrically located in their molecules, inductive or electromeric effects or both give rise to small moments.

The other carbon bond moments are all obtained from the moments of molecules to which the moments of H—C bonds contribute. It has been concluded (17) that the H—C moment is probably no greater and, in many cases less, than moments due to induction or electromeric effects. In early work on bond moments incorrect reasoning led to a value of 0.4×10^{-18} for the H—C moment, the positive end of the dipole lying toward the hydrogen, an assumption universal in dipole moment literature until recently. Fuchs and Wolf (7) have decided from a number of indications, none of them conclusive, that the negative end and not the positive end of the dipole lies toward the hydrogen. Trieschmann (24) has reached the same conclusion from a consideration of the moments of chloroform and methylene chloride, obtaining 0.41 for the H—C bond from the chloroform moment and −0.78 from the methylene chloride moment. As the mean of these two widely differing and altogether inaccurate values is −0.19, he concludes that the negative end of the dipole is toward the hydrogen, a conclusion which must be regarded as quite unwarranted by his conflicting results, even if his disregard of inductive effects between the C—Cl bond moments did not invalidate the method. Timm and Mecke (22) have calculated the size of the H—C moment from the intensity of absorption of the H—C bonds for a number of halogen-substituted methanes, ethanes, and acetylenes, finding it to be 0.3 to 0.4×10^{-18}, and have followed Fuchs and Wolf in assuming the negative end of the dipole to lie toward the hydrogen.

In applying Mulliken's equation to the H—C bond μ_S is taken as zero, since there are no non-bonding electrons in either atom except the inner pair in carbon, for which the polarizability is very small. The approximate constancy of the H—C moment is indicated by the fact that Timm and Mecke find that the influence of a neighboring halogen atom upon it is relatively small. The first term of the expression for the moment is easily calculated to be 0.96×10^{-18}. The second term has been calculated from values of z, S, and a and b obtained from S and Q by the equations

$$a^2 + b^2 + 2Sab = 1$$

and

$$Q_B/e = a^2 - b^2$$

The values of S and z were calculated by Dr. J. O. Hirschfelder in the following manner. The overlap integral between carbon and hydrogen may be computed, using the approximate eigenfunction for carbon,

$$\psi_C = \tfrac{1}{2}\psi_C(2s) + \frac{\sqrt{3}}{2}\,\psi_C(2p\sigma_z)$$

where $\psi_C(2s)$ and $\psi_C(2p\sigma_z)$ are, respectively, the eigenfunctions for the $2s$ state of carbon and the $2p\sigma$ eigenfunction referred to the C—H axis as origin (25, 26). Both the $2s$ and $2p$ eigenfunctions are taken so that they have the same sign as the eigenfunction for hydrogen in the region of their maximum overlap. In order to estimate the magnitude of the carbon-hydrogen overlapping, hydrogen-like eigenfunctions were used for the carbon in which the nucleus was shielded by the Pauling-Sherman size-screening constants (16), the effective nuclear charges for the $2s$ and the $2p$ electrons in carbon respectively, $Z_{2s} = 3.96e$ and $Z_{2p} = 3.09e$, being obtained. That such eigenfunctions give only a rough estimate of the charge distribution, and a particularly rough one for the $2p$, has been pointed out in the literature (23, 4); and this is borne out by the fact that a greater overlap was obtained for H with the $2s$ than with the $2p$, i.e.,

$$\int\psi_H\psi_C(2s)d\tau > \int\psi_H\psi_C(2p)d\tau$$

which is contrary to the notion that a $2p$ electron can overlap the eigenfunction of another atom more than a $2s$, because it has its charge distribution concentrated in a small solid angle (14). Using the C—H separation of 1.12 the following values were obtained:

$$\int\psi_C(2s)\psi_H d\tau = 0.515$$
$$\int\psi_C(2p\sigma_z)\psi_H d\tau = 0.475$$
$$\int\psi_C\psi_H d\tau = 0.668 = S$$

In the Mulliken sense, the location of the center of the homopolar dipole term is at that plane x_0 at which:

$$\int_{x=-\infty}^{x=x_0}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi_C\psi_H\,d\tau = \int_{x=x_0}^{x=\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi_H\psi_C\,d\tau$$

Calculating these integrals for the midpoint of C—H and for the plane $x_0 = 0.4a_0$, and measuring x from the midpoint of C—H positive when it is closer to H than to C:

$$\int_{x=0}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi_C(2s)\psi_H\,d\tau = 0.26 \qquad \int_{x=0}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi_C(2p)\psi_H\,d\tau = 0.41$$

$$\int_{x=0.4a_0}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi_C(2s)\psi_H\,d\tau = 0.10 \qquad \int_{x=0.4a_0}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi_C(2p)\psi_H\,d\tau = 0.28$$

from which it is ascertained by linear interpolation that the plane x_0, containing the center of the homopolar dipole, is 0.73 A.U. from the carbon atom and 0.39 A.U. from the hydrogen atom. z is therefore 0.17 A.U. a and b are calculated as 0.47 and 0.64, respectively. The homopolar dipole term consequently has the value 0.66×10^{-18} and the total moment of the H—C bond a value $(0.96 - 0.66) \times 10^{-18} = 0.3 \times 10^{-18}$, the positive end of the dipole being toward the hydrogen. This value is in excellent agreement with the spectroscopically obtained moment, which Timm and Mecke (22) assumed to be acting in the opposite direction. Although the accuracy of the calculation is not as great as this excellent agreement might seem to indicate, it is sufficient to give strong indication that the positive end of the H—C dipole lies toward the hydrogen and that the moment is not far from the size found spectroscopically. The value 0.3×10^{-18} is, therefore, assigned to the H—C moment which is listed in column three of table 2, where it is used to obtain the carbon bond values below it. As Pauling's electronegativity scale places carbon between sulfur and bromine, one would expect a value 0.7 instead of 0.3, which is the only hydrogen bond moment not falling in the order of the electronegativity scale. Presumably, the discrepancy is due to the smallness or absence of an induction effect, which would raise the total bond moment.

As the geometry of the tetrahedral molecule of the methyl halide, if undistorted, is such that the components of the three H—C moments are equivalent to one H—C moment in the carbon–halogen line, the carbon-halogen moment is obtained by subtracting 0.3 from the moment of the methyl halide. The C—I, C—Br, and C—Cl moments are in the same order as the corresponding hydrogen moments, although the differences between them are very much reduced, but the C—F moment is smaller than that of the C—Cl instead of larger as would be expected, and the C—O moment, which should be larger than the other single-bond moments except C—F, is much smaller. As a test of the accuracy of the C—O and H—O values, the one calculated from the moment of methyl ether and the other from that of water, the moment of methyl alcohol has been calculated, the H—C moment being taken as 0.3. If the oxygen valence angle is taken as 110°, the moment calculated is 1.58 as compared to an observed value 1.67, while, if the angle is 104°, the calculated value is 1.68. As the valence angle probably lies between 104° and 110°, the agreement between observed and calculated values is remarkably good. The C—O moment should be lower than the H—O moment by the amount of the H—C moment, 0.3. Actually, it is 0.67 lower, which is very nearly the difference that would exist if the H—C moment fell in its natural order between H—S and H—Br. The homopolar dipole term should decrease the H—O moment more than the C—O, but the induced moment term may be appreciably larger in the case of the H—O moment. This may or may not account for the discrepancy of about 0.4.

In contrast to the C—O moment, the carbon-halogen moments appear to be too large. In the hydrogen-halogen bond the moment is opposed by the homopolar dipole term, which tends to be larger the larger the difference between the atomic radii. In the carbon-halogen bond the larger radius of the carbon atom tends to reduce this homopolar dipole term and thus raise the moment, the increase being greatest in the iodide where the difference in radii is greatest and least in the fluoride where the difference in the radii is least. This reduction of the homopolar dipole term is in the right direction to account for the effect, but the greater electronegativity of the carbon tends to reduce the moments as compared to those of the hydrogen bonds. In terms of Pauling's electronegativity scale alone, the positive end of the C—I dipole would lie toward the iodine, as does the homopolar dipole, while μ_s must consequently act in the same direction, but the experimental values for both aliphatic and aromatic iodides show the C—I moment to be but slightly smaller than the C—F and C—Cl moments and acting in the same direction. The situation would be made worse if the H—C bond dipole had its positive end toward the carbon, since then the carbon moments would have to be larger than the values in table 2 by twice the amount of the H—C moment. The discrepancies in these carbon bond values are evidently not wholly explained by the terms of the Mulliken equation. They are probably due to inductive effects between the adjacent bond dipoles which have not thus far been accurately calculated, although rough estimates have been made for the halogenated methanes (18).

It is not to be expected that an electronegativity scale based upon energies should be identical with one based upon dipole moments, for potential energy may arise from shifts of charge which give compensating dipole moments and thus do not affect the total moment of the molecule. For considerations of reactivity, the scale based upon energy is obviously the one to use. Where the actual polarity or symmetry of charge distribution is required, the bond moment should be used. A very approximate parallelism between the two scales, which has been previously noted, is evident from consideration of the bond moments calculated here.

SUMMARY

The dipole moments associated with the more important substituent groups have been collected or calculated. These and other data are used to calculate the moments of a large number of bonds, which are examined in the light of Pauling's electronegativity scale and the factors contributing to the moments. All of the bond moments examined are consistent with these considerations except those involving carbon, which show discrepancies. Differences are obviously to be expected between an electronegativity scale based upon bond energies and one given by bond moments.

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REMARKS ON MOLECULAR STRUCTURE AND VAN DER WAALS FORCES[1]

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I. STRUCTURE OF THE BENZENE RING

If we examine the structure of graphite as determined by x-ray analysis, and also the structure of crystals such as benzene, naphthalene, anthracene, diphenyl, etc., we are very much disturbed to find relatively large holes in the lattice. These empty spaces seem always to occur on both sides of the flat benzene ring. A chemist is naturally distinctly unhappy about this situation, because he would much prefer to have these empty places between the molecules and planes of molecules filled with pieces of impenetrable matter of some sort, and thus explain how it is that the structure is kept from collapsing to a more compact configuration.

Assuming that such pieces or "bumps" of impenetrable matter do exist, one would like very much to know their size and shape. So in 1929–30, when I became interested in this question, I made a series of models, just as any other chemist would do, and tried to determine which one of the forms would give the best explanation of the available data on the structure of crystals of aromatic compounds. Figure 1 shows how the conception developed. Models A and B were crude attempts to indicate the position of electron orbits perpendicular to the plane of the ring. Model C represented a crater-like elevation protruding above and below the ring, and was supposed to represent the impenetrable volume (in the additive sense of Kopp) of the oscillating double bonds (in the sense of Kekulé). Models D and E, with cone and dome, were supposed to take into account electron orbits across the ring (such as Pauling's μ-orbits).

Of all of these forms, the "dome" model, E, was the most useful conception. When it was mounted (5) over the hexagonal rings in the flat layers of graphite, and the "hard surface" of the impenetrable dome was arbitrarily assigned a radius of 1.84 A.U., it was possible to account for the

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3.40 A.U. spacing between layer planes and for the type of superposition observed for the layers, and to give a satisfactory picture for the gliding of layers over one another. The dome of the benzene molecule was larger, as would be expected from its three-times larger electron content, and had to be assigned a radius of 2.45 A.U. A further refinement in the picture of the dome in benzene is given in figure 1F, showing regions of greater penetrability or of easier compression, around the base of the dome, between the carbon atoms. This feature appears in the molecule of tetraphenylmethane, as well as in the lattices of benzene, diphenyl, *p*-diphenylbenzene, and others.

It is desired to emphasize particularly that the basis for this conception of the benzene ring dome was, and is, *empirical*. It is true that the quantum-mechanical calculations in connection with benzene and other aromatic compounds by Hückel and especially by Pauling seem to support the idea. For instance, in a recent very beautiful paper, "The Diamagnetic Anisotropy of Aromatic Molecules," Pauling (8) says: "The remaining six *L* electrons, which give to benzene its characteristic electronic structure and properties, occupy orbital wave functions which are antisymmetric with respect to reflection in the plane of the nuclei. The probability distribution function for these electrons is large only in two ring-shaped regions, one above and one below the carbon hexagon. We may well expect that in these regions the potential function representing the interaction of an electron with the nuclei and other electrons in the molecule would be approximately cylindrically symmetrical with respect to the hexagonal axis of the molecule, the electron, some distance above or below the plane of the nuclei, passing almost imperceptibly from the field of one carbon atom to that of the next."

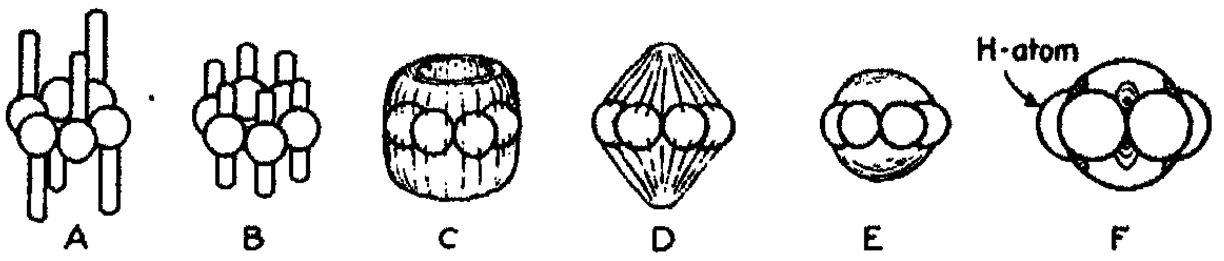

FIG. 1. Suggested shapes of space occupied by the "unsaturation" of the benzene ring

This is support for the conception of some sort of organized electron cloud over the carbon hexagon, with a cylindrical and ring-like symmetry. Further, one does not have to suppose that the shape which such an impenetrable region presents to approaching neighbor molecules is exactly the same as the prolate ellipsoid of magnetic susceptibility found by Krishnan (2) and his collaborators. The fact that the calculations of Pauling (9) and Wheland in another paper show that 80 per cent of the resonance energy of benzene comes from the Kekulé structures alone, might be interpreted in itself as support for such a form as that of figure 1C; but the 20 per cent of the total resonance energy that comes from the three excited canonical structures with bonds across the ring suggests justification for capping or bridging the Kekulé form to give an impenetrable dome, as in figure 1E.

Whatever the final results of the quantum-mechanical calculations may be, it is probably true, as has been shown (5) in a previous paper, that the addition of such a dome to the ring or rings of the molecule involved is necessary and sufficient to account for the observed arrangement in the lattices of aromatic compounds, and to reproduce the unit cell dimensions and space group.

Recently I have been constructing models for many other crystals of this sort, but since it is practically impossible to describe adequately these complicated three-dimensional structures without three-dimensional representation, I prefer to exhibit these models at the Symposium, if there is time and opportunity.

Once the usual habits followed by a few such molecules in establishing van der Waals contacts among themselves in the lattice have been clearly shown, it is not only likely that we can predict lattice structure without x-ray data, but also likely, when the number of hydrogen-to-hydrogen, hydrogen-to-dome, dome-to-dome contacts per molecule are counted, that we can assign proper values for van der Waals energies of separation to the various types of contact, and so construct on an additive basis a scheme for the explanation of heats of fusion and heats of sublimation and heats of solution, and also have the foundation for a prediction of solubility and of melting points.

II. FILMS AND SURFACE ENERGY

This conception of the size and shape of the benzene molecule gives us a satisfying explanation, as has already been shown (5) in a previous paper, of the surprisingly large area occupied by the phenol group (polar head) attached to a long, vertically oriented aliphatic chain, on a water surface. Figure 2 shows the setting. (The reader is looking down on the oil film.) The area, in the surface, occupied by the hydrocarbon chain is expected to be about 20 sq. A.U., but the benzene ring (OH group underneath, in the water) is found by Adam (1) and his collaborators to occupy an area of 24 sq. A.U. The arrangement shown is the closest possible packing and involves the use of a dome and a hydrogen atom of exactly the same sizes as in the benzene crystal lattice. The area of the rectangular cell is 48 sq. A.U., and with two molecules in the cell the predicted area of the phenol group is thus 24 sq. A.U.

Langmuir (3) has pointed out that the hydrocarbons from hexane to molten paraffin have substantially the same total surface energy, 46 to 48 ergs per cm.^{2}, as do also the alcohols, methyl alcohol, ethyl alcohol, etc., and has given as his reason for this "that the surface layer in both cases consists of CH_3 groups. With such substances as CH_3NO_2, CH_3I, we find that the surface energy is much greater than that of the hydrocarbons. This is due to the fact that the volume of the I or the NO_2 is so great that the surface cannot be completely covered by the CH_3 radicals. The forcing apart of these groups increases the surface energy."

Now we are probably justified in supposing that the formation of this surface paved with methyl groups is equivalent to an evaporation of the methyl groups from the liquid, or in this case partial evaporation, since the methyl groups (probably spinning) are still in fairly good contact around their edges with surrounding methyl groups in the surface layer of hydrocarbons and alcohols; that is, the methyl groups are only partially stripped of their van der Waals force contacts. From the data of heats of vaporization for the homologous straight-chain hydrocarbons it can readily be shown that the heat of vaporization for a mole of CH_3 at room temperature is about 2000 cal. or 8.4×10^{10} ergs, or about 14×10^{-14} ergs for an actual CH_3 group. There are approximately 5×10^{14} methyl groups in 1 sq. cm. of such a surface (area of hydrocarbon chain section = about 20 sq. A.U.), and hence the surface energy would be about 70 ergs per cm.^{2} if the methyl groups were in the completely evaporated condition. The fact that the surface energy is actually only 46 to 48 ergs per cm.^{2} may then be interpreted as an indication that the methyl groups are, on the average, only about two-thirds evaporated.

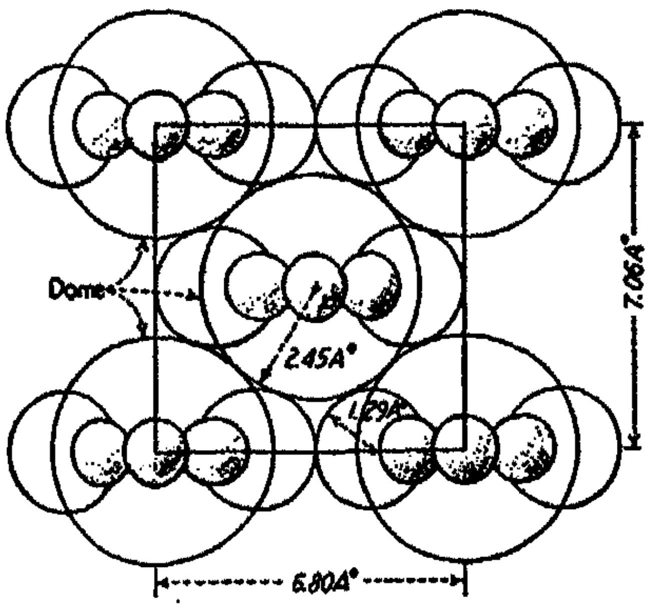

FIG. 2. Suggested packing for polar heads (phenol groups) in oil film

On the other hand, such liquid compounds as


p-chlorotoluene


p-nitrotoluene

and


p-cresol

with molecules "tilted up on edge" (to use Dr. Langmuir's expression) and thus oriented with the methyl groups in the surface layer, show much larger surface energies, 67.3, 65.2, and 70.0 ergs per cm.^{2}, respectively.

It is not unlikely that the packing of the *p*-cresol molecules, for example, in the liquid surface resembles that of figure 2. If we modify the setting to the extent of substituting methyl groups (represented as heavy circles) for the long hydrocarbon chains, we obtain figure 3. It will be seen that, even with the closest possible packing, the bulky domes of the benzene rings isolate the methyl groups from their neighbors, playing much the same rôle that Langmuir conceived for the I and NO_2. In view of the extremely rapid decrease in intensity of van der Waals forces with increasing distance (5th, 6th, or 7th power law), it may reasonably be supposed that the methyl groups are here practically completely stripped of van der Waals force contacts. Thus, from the calculation given in the preceding paragraph, we would expect a surface energy of about 70 ergs per cm.^{2} (as actually observed for *p*-cresol) were it not for the smaller population of methyl groups per unit area. There are only about 4×10^{14} of these (as compared with about 5×10^{14} per cm.^{2} in the case of the long-chain molecules), and the predicted surface energy for *p*-cresol would be about $4/5 \times 70$, or 56 ergs per cm.^{2} The difference between this and the observed 70 ergs per cm.^{2} is to be explained in terms of the slight stripping of van der Waals contacts from the upper regions of the dome and from the two hydrogen atoms in ortho positions to the methyl group.

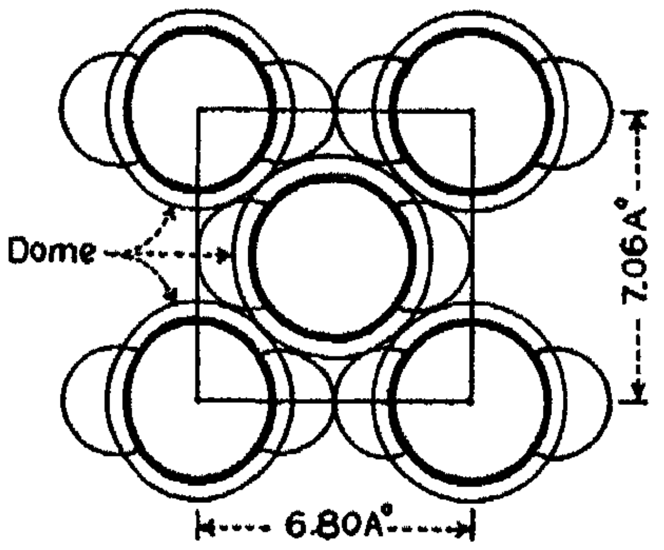

Fig. 3. Suggested spacing for methyl groups in surface layer

Indeed, the relatively large surface energies of aromatic compounds of this general type, ranging from about 60 to about 90 ergs per cm.^{2}, depending on the nature and positions of the polar groups, can probably be satisfactorily accounted for by the isolation, in the surface layer, of the upper portions of the benzene molecules and the topmost group which it bears.

III. MELTING-POINT BEHAVIOR OF MOLECULES WITH DOUBLE BONDS

Let us represent any typical organic molecule as a generalized brick-like form, figure 4. After a crystal lattice made up of such molecules has melted down completely, it seems clear that the total heat of fusion divided by the total number of molecules, or the average heat of fusion per molecule, is necessarily the energy required to cause the molecule to break away from the van der Waals forces holding it rigidly in the lattice, *around one-half of the molecule's surface*, namely at the three faces, *a*, *b*, and *c*. This is true no matter what the mechanism of the melting process may be. It is also probably true, furthermore, that the melting does actually proceed in just this way, i.e., by a breaking away of every individual molecule at its three faces, *a*, *b*, and *c*, first starting with the corner molecules in the crystal, and then proceeding regularly down the rows of molecules in the edges and faces of the crystal as new corners are produced. It is the exact identity of this repeated act of escape from the lattice that results in sharpness of melting point. Moreover, the escaping molecule must break away all at once at its three faces (and not step-wise, first from *a*, then *b*, and finally *c*, as probably happens in the evaporation of a liquid molecule).

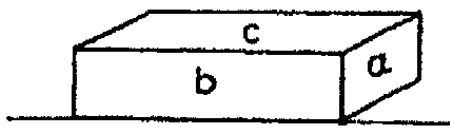

FIG. 4. Brick-shaped molecule

There are some interesting instances, however, of a "step-wise" escape of a molecule from a crystal lattice, in a somewhat different sense. In table 1 the melting point of stearic acid is given as 69.3°C. In melting out of the lattice, this molecule escapes as a whole. But if a double bond is introduced, say between the sixth and seventh carbon atoms, as in $\Delta^{6,7}$-oleic acid, thus

$$C—C—C—C—C—C{=}C—C—C—C—C—C—C—C—C—C—C—COOH$$

the situation becomes quite different. Around the double bond there is more room for rotation on bonds, and fewer van der Waals contacts to hinder free rotation on bonds, than in a normal hydrocarbon section. As a result the chain is flexible on each side of the double bond, and the left-hand portion (strictly hydrocarbon portion) of the molecule melts off first, in a manner shown in figure 5, b or c. Then as the temperature continues to rise, the right-hand section, containing COOH, finally melts, when it has acquired sufficient kinetic energy to break the much larger van der Waals forces holding it rigidly in the lattice.

Such a picture explains almost perfectly the observed melting points in table 1. In the case of substance 2 ($\Delta^{6,7}$-oleic acid), the C_6H_{11} or more

TABLE 1

Melting-point values

SUBSTANCE	FORMULA	MELTING POINT
		°C.
1. Stearic acid	$C_{17}H_{35}COOH$	69.3
2. $\Delta^{6,7}$-Oleic acid (*cis*)	$C_5H_{11}CH{=}CH(CH_2)_{10}COOH$	33-34
3. $\Delta^{9,10}$-Oleic acid (*cis*)	$C_8H_{17}CH{=}CH(CH_2)_7COOH$	16 (14?)
4. $\Delta^{12,13}$-Oleic acid (*cis*)	$C_{11}H_{23}CH{=}CH(CH_2)_4COOH$	Liquid
5. Linoleic acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	−18
6. Linolenic acid	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ or $CH_3(CH_2)_3CH{=}CHCH{=}CHCH{=}CH(CH_2)_7COOH$	Liquid at very low temperatures
7. Undecoic acid	$H(CH_2)_{10}COOH$	28.3
8. Caprylic acid	$H(CH_2)_7COOH$	16.5
9. Valeric acid	$H(CH_2)_4COOH$	−20

probably the $C_5H_{11}CH{=}C$ section melts off first, probably at a temperature corresponding roughly to that of hexane or heptane, and then the $H(CH_2)_{10}COOH$ section melts at a temperature of 33–34°C., corresponding closely to the melting point 28.3°C. for undecoic acid (substance 7 in the table). Similarly, $\Delta^{9,10}$-oleic acid melts at about 16°C., checking the melting point of caprylic acid, 16.5°C.; and $\Delta^{12,13}$-oleic acid is a liquid at room temperature, as one would expect from the fact that valeric acid melts at −20°C.

Molecules with two double bonds, like linoleic acid, would melt in three sections, and those with three double bonds, like linolenic, would melt in four sections. Furthermore, in these latter cases, we may expect that the melting point of the acid section will be much lower than usual because of the relatively violent kinetic disturbance to which the acid section would be subjected by the rest of the molecule, in the liquid phase.

This theory of melting-point behavior in molecules containing double bonds was suggested to me by one of my former students, Dr. Sherman E. Smith, and it is presented here with his permission. The theory can readily be extended to give a very satisfying explanation of these curious

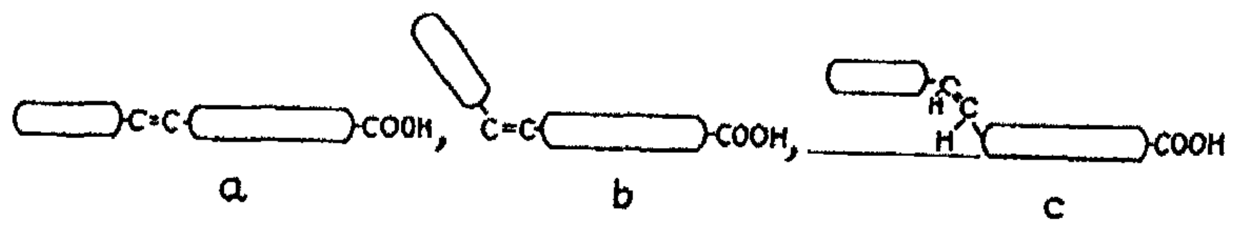

FIG. 5. Step-wise melting of molecule

melting points, not only for other acids, but for the chain hydro carbons themselves, and for certain aromatic molecules, and probably for all molecules possessing regions of marked flexibility.

It would be extremely interesting to test this theory, for example in the case of the oleic acids, by using the technique of Raman (10) and Ramdas for examining the quality of the light scattered from a reflecting surface. By selecting the proper crystal face, allowing a beam of sunlight to fall upon it, and gradually warming up the crystal from low temperature, one could determine whether the surface does in fact become minutely "roughened" at a definite temperature somewhat above the normal melting point of the more fusible section of the molecule. This temperature would be somewhat above the normal melting point because the surface would be appreciably roughened only when the sections of the molecules were lifted out all over the face of the crystal rather than merely at the corners.

IV. EXTERNAL AND INTERNAL VAN DER WAALS FORCES

Much study has been made of what may be called *external* van der Waals forces between one molecule and a neighbor molecule, but apparently little attention has been devoted to the play of similar *internal* forces among the atoms and groups of an individual molecule. Nevertheless this effect often is of great importance in controlling both physical and chemical properties.

One consequence of it, which might be of interest and which has never been referred to before, as far as I know, is in connection with the heat of combustion. When, for example, hydrocarbon molecules are burned in oxygen, the carbon and hydrogen atoms must not only be separated from one another along their chemical bonds, but the hydrogen atoms must be also separated against internal van der Waals forces, although the energy consumed in doing this would, of course, be small in comparison with the bond energies. Table 2 lists Rossini's (11) latest published values for the heats of combustion of some straight-chain hydrocarbons (gaseous).

TABLE 2

Heats of combustion (ΔH) at 25°C. for gaseous hydrocarbons

SUBSTANCE	FORMULA	ΔH	INCREASE IN ΔH FOR CH_2
		calories	
Methane	CH_4	−212,790	160,020
Ethane	C_2H_6	−372,810	157,760
Propane	C_3H_8	−530,570	157,370
n-Butane	C_4H_{10}	−687,940	157,330
n-Pentane	C_5H_{12}	−845,270	157,130
n-Hexane	C_6H_{14}	−1,002,400	157,000
n-Heptane	C_7H_{16}	−1,159,400	157,000
n-Octane	C_8H_{18}	−1,316,400	157,000
n-Nonane	C_9H_{20}	−1,473,400	157,000
n-Decane	$C_{10}H_{22}$	−1,630,400	157,000
n-Undecane	$C_{11}H_{24}$	−1,787,400	157,000
n-Dodecane	$C_{12}H_{26}$	−1,944,400	

It will be noted that the increase in ΔH per CH_2 becomes constant after hexane. This we might well expect, since once the gaseous molecule has become long enough to be coiled into a complete loop, the number of van der Waals internal contacts established by every further CH_2 group would be the same. Furthermore, it is readily to be seen, with the aid of a scaled three-dimensional model, that the improvement in internal contacting between hydrogen atoms becomes progressively less per CH_2, beginning with methane and ending with hexane. Consequently, the energy required to rupture all such van der Waals contacts (about 400 cal. in the case of hydrogen-to-hydrogen) should most certainly be taken into account in the calculation of energies of formation and of bond energies for these and other molecules.

That such straight-chain molecules are actually folded up, or coiled up, in the gaseous state can hardly be doubted. Langmuir (4) has predicted a globular or droplet-molecule from a consideration of the tendency to reduce surface energy to a minimum in the molecule's own surface, and one arrives at the same conclusion by adopting the procedure we are employing here, namely by counting the much larger number of hydrogen-to-hydrogen contacts that can be made in the coiled form as compared with the extended molecule. It has also been shown by calculation of the collision areas (7) of the gaseous molecules of *n*-heptane, *n*-octane, and *n*-nonane (from viscosity data) that the molecules are coiled.

In the liquid state, however, the situation is quite different. There, in contrast to the vapor state, the external van der Waals contacts must be reckoned with. It can be demonstrated that the sum total of internal and external van der Waals contacts (between hydrogen atoms) is much better with extended than with coiled molecules, mainly because of the better packing of the extended forms. On such *a priori* grounds, at least, we have every reason to believe that these molecules spend most of their lives extended to full length. We know, of course, that this is true in the crystalline state, and what little pertinent x-ray evidence there is for liquid hydrocarbons suggests also the extended shape.

The argument is worth following through into at least one other setting, namely in a system of randomly arranged macro-length chain molecules, as in the substance rubber. Here the external forces would play a relatively unimportant rôle because of the criss-crossing, and because of the hindrances to adjustment of position that are imposed by the entanglement of the thread-like molecules. If the structure is such that internal forces can come into play and can implement foldings, by bond rotation, between groups favorably placed at regular intervals along the chain, then we would expect the appearance of the various types of elastic behavior (6) shown by rubber-like substances.

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THE QUANTUM THEORY OF VALENCE[1]

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INTRODUCTION

"Valency," according to N. V. Sidgwick (5), "is a general term used to describe the power which atoms possess of combining with one another to form molecules." The concept of valence is thus one of the most important, if not the most significant, concepts in the correlation of those observations on the interactions of atoms and of molecules that constitute the science of chemistry. Our understanding of the nature of valence has undergone, during the past three decades, a profound change, which has been largely the result of discoveries in the field of atomic structure. The naïve picture of two little hard balls bound together by a "hook and eye" has been displaced, through the work of Kossel, G. N. Lewis, and Langmuir, by a classification of chemical bonds into covalent and electrovalent, or homopolar and heteropolar. We designate as covalent or homopolar those bonds in which we regard the two atoms as sharing pairs of electrons, as, for instance, in hydrogen, methane, etc., and as electrovalent or heteropolar those bonds in which the two atoms possess opposite electric charges, as, for instance, in sodium chloride and in ionic compounds in general.

While such a classification has proven extremely useful in the investigation of molecular structures and in the interpretation of their chemical properties, it is obvious that it lacks any quantitative aspect. By this we mean that the Lewis–Langmuir concept of the shared-electron bond does not enable us to derive the energy relations which govern the possible modes of interaction of atoms to form stable molecules.

What we are interested in fundamentally is the solution of this problem:

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Given two or more atoms for each of which we know the nuclear charge and electron configurations, what will be the result of their interaction? Fundamentally, the problem involves a determination of the total energy of the system of nuclei and electrons as a function of internuclear distance. For any two atoms A and B the energy as a function of internuclear distance may be of the form I or II shown in figure 1. In the first case we conclude that the repulsive force increases as the atoms are made to approach each other and that, consequently, no molecule formation will occur; in the second case, the attractive energy increases with decrease in distance of separation and passes through a minimum, which represents the energy of binding, to form a stable molecule.

While classical dynamics and the Bohr theory proved incapable of dealing with this problem, the advent of quantum mechanics has given us, at least theoretically, a method by which for the first time it is possible to make such calculations as are of interest in solving the problems of molecule formation. In 1927 Heitler and London published their now well-known discussion of the hydrogen molecule problem. While the actual results of their calculation gave a value for the energy of dissociation of hydrogen of 72.38 kg-cal. per mole, as compared with the observed value, 108.80 kg-cal. per mole,[2] even this partial success has encouraged subsequent investigators to apply the methods of quantum mechanics to this and similar problems of molecule formation and interaction.

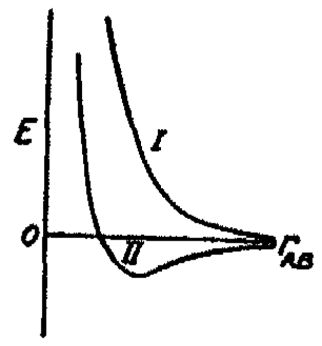

FIG. 1

The methods used and the results of these investigations have been reviewed recently in two extremely interesting publications, one by J. H. Van Vleck and A. Sherman (6) and the other by W. G. Penney (4). It is therefore not necessary in the present paper to enter into any detailed discussion of the mathematical technique involved in the calculation. To such aspects we shall refer only briefly. It is rather the logic and physical significance of these calculations that we shall attempt to consider in the following remarks.

FUNDAMENTAL CONCEPTS

As the most fundamental idea of quantum mechanics we must recognize the validity of Heisenberg's principle of indeterminism. For our present

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[2] This includes the "zero point" energy, which is 6.12 kg-cal. per mole.

purposes it may be stated in the form that precise determination of the kinetic energy of a particle at any instant is incompatible with a precise determination of the position of the particle at that instant. Since the potential energy of any system (V) is a function of the coördinates of the particles, and the total energy (E) is a constant for an atomic or molecular system, this means that it is impossible to associate instantaneous values of the kinetic energy (T) with simultaneous values of the coördinates. In other words, we cannot derive any conclusions with regard to definite orbits, and *consequently the only magnitude that we can calculate is the* relative density distribution as a function of the coördinates. This is the physical significance of the function $\psi\bar{\psi}$, which is derived from the solution of the Schrödinger equation for the system.

Let us consider, as an illustration, the hydrogen-like atom problem. This consists of an electron of charge $-e$, moving in the field due to a nucleus of charge $+Ze$. The potential energy function for the system is given by the relation

$$V = -Ze^2/r \tag{1}$$

where r is the distance of the electron from the nucleus. The corresponding Schrödinger equation has the form

$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}(E - V)\psi = 0 \tag{2}$$

where ∇^2 is the Laplacian operator, μ is the mass of the electron, and h is Planck's constant. We can write this in the form

$$H\psi = E\psi \tag{3}$$

where H is an operator defined by the relation

$$H = -\frac{h^2}{8\pi^2\mu}\nabla^2 + V = T + V \tag{4}$$

When written in this form, H is said to be the total energy operator while $-\frac{h^2}{8\pi^2\mu}\nabla^2 = T$ and V are the kinetic and potential operators, respectively.

Now it can be shown that if we consider any arbitrary function ϕ of the coördinates which is everywhere finite, then the so-called mean value of the energy integral

$$I = \int \bar{\phi}H\phi d\tau \tag{5}$$

is always greater (more positive) than the value of E_0, the lowest energy level for the system. The more closely the form of ϕ approaches the exact solution for ψ in equations 2 and 3, the lower the resulting value of I, and when ϕ is identical with ψ_0, the eigenfunction for the system corresponding to the lowest energy level, the value of I becomes equal to E_0, the corresponding eigenvalue. Consequently, we can express the solution in the form

$$E_0 = \int \bar{\psi}_0 H \psi_0 d\tau \tag{6}$$

where E_0 is a *minimum* obtained by varying ϕ (or ψ) in all possible ways.

Since the mean value of H for given ϕ is equal to the sum of the mean values of T and V, that is,

$$\bar{H} = \bar{T} + \bar{V}$$

and $\bar{T}$ is always positive while $\bar{V}$ is always negative, it is interesting to note the way in which the two "competing" terms modify the charge distribution going with the ϕ corresponding to the minimum energy. In the first place, one could minimize $\bar{T}$ to zero by setting ϕ = constant, but this would not give $\bar{V}$ its minimum value, since it would place practically all of the charge in regions away from $r = 0$. On the other hand, if one attempts to minimize $\bar{V}$ by localizing the charge distribution entirely at the nucleus, $\bar{T}$ becomes infinite, since localization of a particle implies infinite kinetic energy on the basis of the uncertainty principle, and consequently $\bar{H}$ becomes infinite and positive.

What actually happens in the case of the hydrogen-like system is a compromise between these opposing tendencies, and the minimum value of E is that for which $T = -\frac{1}{2}V$, and $E = T + V = \frac{1}{2}V$.

The corresponding eigenfunction for the normal state has the form

$$\psi = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\epsilon^{-\rho} \tag{7}$$

where $\rho = r/a_0$ and a_0 = radius of normal Bohr orbit. If we plot ψ^2 as a function of ρ, it is observed that while this distribution function has a maximum value at $\rho = 0$, as might be expected from the fact that in this region V approaches a minimum value (of $-\infty$), there is a considerable probability for the occurrence of the electron in the region for which $r \geqslant a_0$,—a fact which is the result of the tendency to have T as small as possible.

This display of compromise between two opposing tendencies by the wave function is characteristic of the quantum-mechanical description of atomic systems, and recurs constantly. Individual terms of the energy operator make certain demands upon the wave function in order that they may best contribute toward minimizing the integral (equation 5). The wave function does not favor any one of these demands to the limit, however, but effects a compromise between all. It is in fact just this state of affairs that makes quantitative investigations of atomic problems difficult, because too rough a treatment of any one term will lead to considerable error in the description.

THE HYDROGEN MOLECULE

The Schrödinger equation for this system (consisting of nuclei A and B and electrons 1 and 2) has the form

$$\nabla^2\psi + \alpha^2(E - V)\psi = 0 \tag{8}$$

where

$$\alpha^2 = 8\pi^2\mu/h^2$$

and

$$V = \frac{e^2}{R} + \frac{e^2}{r_{12}} - \left(\frac{e^2}{r_{A1}} + \frac{e^2}{r_{A2}} + \frac{e^2}{r_{B1}} + \frac{e^2}{r_{B2}}\right) \tag{9}$$

Thus, we find in the potential energy function (equation 9) three different types of terms corresponding to the following: (1) nuclear repulsion, represented by the first term; (2) electronic repulsion, represented by the 2nd term; and (3) electron–nucleus attraction, represented by the four terms in the bracket. It follows that V as an energy operator contains, in addition to those of the type occurring in the hydrogen atom, an electron-electron interaction term. There are two methods by which this system and all molecular systems are usually treated to a first approximation. The first is by the use of so-called *atomic orbitals*. This is the method of Heitler and London. The second, which is designated the Hund–Mulliken method, involves the use of *molecular orbitals*.

Let us first consider the Heitler–London method. In this treatment the eigenfunction which corresponds to attraction of the two atoms and molecule formation is represented by the linear sum of two eigenfunctions in the form

$$\psi_S = \frac{1}{\sqrt{2 + 2S^2}}\{u_A(1)u_B(2) + u_A(2)u_B(1)\} \tag{10}$$

where u_A (1) represents the single electron eigenfunction for the condition in which electron 1 is associated with nucleus A, and corresponding interpretations are to be given to the other three single electron functions inside the parentheses in equation 10. That is,

$$u_A(1) = \frac{1}{\sqrt{\pi a_0^3}}\,\epsilon^{-r_{A1}/a_0} \tag{11}$$

and similar expressions are to be used for $u_A(2)$, u_B (1), and u_B (2).

The quantity S^2 in equation 10 is defined by the relation

$$S^2 = \int u_A(1)u_B(1)u_A(2)u_B(2)d\tau \tag{12}$$

and it is found that when this integral is evaluated, the result is

$$S^2 = \epsilon^{-2D}\{1 + D + (1/3)D^2\}^2 \tag{13}$$

That is, S^2 is a function of $D = R/a_0$, with a value varying from 1 for $D = 0$ to 0 for $D \rightarrow \infty$.

According to Heitler and London, the *binding energy* for the formation of H_2 is given by

$$W_S = \frac{E_{11} + E_{12}}{1 + S^2} \tag{14}$$

where E_{11} and E_{12} are integrals over the configuration space.

By evaluating the integral for E_{11} it is found that this has a minimum value $E_{11} = -0.4877$ v.e. for $D = 1.90$. Since the corresponding value of S^2 is 0.3466, it follows that $E_{11}/(1 + S^2) = 0.3622$ v.e. $=$ 8.349 kg-cal. per mole. The evaluation of the integral E_{12} was carried out by Sugiura, and he deduced the value $W_S = 3.2$ v.e., so that the term $E_{11}/(1 + S^2)$ constitutes only 11.32 per cent of the total theoretical binding energy. Comparing 0.3622 v.e. with the observed value $W_S = 4.72$ v.e., it is seen that the integral E_{11} corresponds to only 7.67 per cent of the total experimental binding energy.

Now, if there were no possibility of interchange of electrons between the two atoms, the total binding energy would be given by the term E_{11} alone, which corresponds to the interaction energy of the nuclei and electron charge distributions for each electron about their respective nuclei. However, as the atoms are made to approach there is an increase in the frequency of interchange of electrons, and this is taken into account by the term E_{12}. Hence, E_{11} has been designated the *Coulomb integral* and E_{12} the *exchange integral.*

A great deal has been written about the non-classical nature of the term E_{12}, and since this term accounts, as shown above, for a large part of the energy of formation of H_2, a distinction has been drawn between the types of forces involved in the two energy terms. Evidently such a distinction is only the result of the mathematical computation, for, as a matter of fact, the quantum-mechanical treatment recognizes that the only forces involved in the binding of two hydrogen atoms are those which arise from electrostatic attraction and repulsion between the four particles which constitute the system. The exchange integral is merely an expression of the physical requirement that the electrons in H_2 cannot be regarded as localized about the nuclei with which they were associated in the separated atoms.

The fact that the Heitler-London method leads to a binding energy which is only 3.2 v.e. as compared with the observed value of 4.72 v.e., however, shows that this treatment is incomplete. In accordance with the remarks made at the end of the previous section, the existence of this discrepancy suggests at once that the effect of at least one of the energy terms has been slighted in this approximate treatment of the problem. Actually, two very important effects, which we shall now enumerate, have been neglected.

In the first place the kinetic energy term will demand that the complete function be spread smoothly throughout the entire space, while the nuclear potential terms will require localization in the line joining the two protons, since the nuclear field is strongest there. The Heitler-London treatment does not give the best distribution for the purpose of these two terms, and by altering the atomic functions used in the previous computations in such a way that there is a large amount of charge spread smoothly throughout the internuclear region, Rosen succeeded in increasing the theoretical binding energy to 4 volts. The final distribution shows the expected compromise in the two terms. This appears to be about the best that one can do with an energy that is divided into only exchange and Coulomb terms, and since three-quarters of a volt is left unaccounted for, we see that it is not at all correct to describe the valence bond as due to the action of so-called exchange and Coulomb forces. This is even more striking in cases in which the binding energy per electron is smaller than in the case of H_2.

The remaining discrepancy is to be associated, principally, with the second neglected effect, that is, the effect of the presence in the expression for V of the electron repulsion term. In order to satisfy this term alone, we would expect a charge distribution in which the two electrons are as far apart as possible. Since this implies that one electron be at $+\infty$ and the other at $-\infty$, which would not be the most suitable for the other energy terms, a compromise results. The electrons will move around in a region the size of molecular dimensions, but will do so in such a way that they are seldom near each other. A part of this effect is contained in the previous approximation and appears in the fact that the electrons spend more time near different atoms than on the same one. The exchange energy is essentially the term arising from this effect, and, as remarked previously, constitutes a large percentage of the binding energy. This is not entirely sufficient, however, and the remaining discrepancy would be almost completely removed if the repulsion effect were included in more detail.

Actually it proves very difficult to do this in an approximation scheme that is based on the Heitler-London first approximation, and has not been carried through for H_2. It has been treated in a way that bears comparison with the Hund-Mulliken scheme, however, so we shall consider this next.

In the method of molecular orbitals we start with electronic wave functions which represent the behavior of each electron in the field resulting from the presence of the two nuclei and the other electron. While molecular orbitals may be constructed out of atomic orbitals, this is not at all necessary. Having chosen some function involving one or more arbitrary parameters, we then apply the variational method to determine the energy of the system in a manner analogous to that already described.

But this method, like the Heitler–London method, also does not take adequate cognizance (7) of the fact that the electrons will tend to avoid each other. This may be illustrated by reference to figure 2 (a and b). If we use the simple Hund–Mulliken view, the probability function for *each* electron as a function of interelectronic distance (r_{12}) is given by figure 2a, and the calculation yields a value for the energy of binding which is about one-half the observed value. On the other hand, when account is taken of electronic repulsion which represents another stage of approximation, we obtain the probability function shown in figure 2b, and we find, as mentioned previously, that this gives an additional binding energy, which is sufficient to raise the total calculated binding energy to approximately the same value as that observed. This term which thus arises in the computation as a result of taking into account the correlation of the electrons more fully than the one-electron function scheme allows is known as *correlation energy*. The exchange energies in both the Heitler–London and Hund–Mulliken schemes may be regarded as correlation energies which are included in a manner that is incidental to the use of an antisymmetric function constructed of one-electron functions. It is more convenient, however, to reserve the latter expression for the additional term arising from a higher approximation.

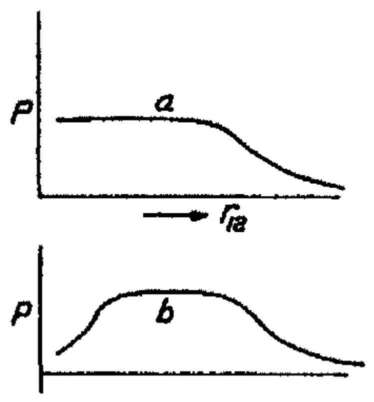

FIG. 2

It is of interest to compare the two points of view. As an illustration let us consider still further the case of the hydrogen molecule. We can express the molecular orbital for each electron in terms of atomic orbitals and thus obtain for the wave function of the system an expression of the form

$$\begin{aligned}\psi &= \{u_A(1) + u_B(1)\}\{u_A(2) + u_B(2)\}\\ &= \{u_A(1)u_B(2) + u_A(2)u_B(1)\} + \{u_A(1)u_A(2) + u_B(1)u_B(2)\} \qquad (15)\end{aligned}$$

The first two terms are the same as in the Heitler–London theory; the last two terms are *ionic* in nature, since they indicate that the two electrons are associated with *either* nucleus A or nucleus B. Thus the use of molecular orbitals implies that we regard the bonds as partly homopolar and partly heteropolar, and if necessary we can replace the right-hand side of equation 15 by an expression of the form

$$\psi = a\psi_S + \sqrt{1 - a^2}\,\psi_M \qquad (16)$$

where ψ_S corresponds to the sum of the first two terms on the right-hand side of equation 15 and ψ_M to the sum of the second two terms.

Furthermore, we may use for ψ a more general expression of the form

$$\begin{aligned}\psi &= \{au_A(1) + bu_B(1)\}\{au_A(2) + bu_B(2)\}\\ &= ab\psi_S + a^2u_A(1)u_A(2) + b^2u_B(1)u_B(2) \qquad (17)\end{aligned}$$

If $a = b$, this becomes identical with equation 15, while if a is very much less than b, so that both ab and a^2 are small compared to b^2, then we can speak of the molecule as of the polar type. The differences between the different states corresponding to these eigenfunctions may be represented symbolically thus:

Shared electron bond (pure Heitler–London eigenfunction)	A:B
Ionic bond	A: B or A^-B^+ A :B or A^+B^-
Eigenfunction in expression 15	(A:B) + (A: B) + (A :B)

The introduction of ionic terms along with Heitler–London terms in the function ψ represents an attempt to take care of electronic repulsion without having to introduce the so-called r_{12} term. This however leads in many cases to an overemphasis of ionic terms, which implies excessive simultaneous localization of the electrons at the two nuclei and therefore a smaller value for the binding energy than the true value.

It is evident from this discussion that in quantum mechanics the distinction between homopolar and ionic compounds is not nearly as sharp as chemists have usually considered it to be. As Van Vleck and Sherman point out, "There are elements of truth in the old-fashioned chemistry that HCl has the structure H^+Cl^-, as the true wave function of HCl is expressible as a linear combination of various ionized types, and certainly H^+Cl^- must be given some representation. . . . One great service of quantum mechanics is to show very explicitly that *all gradations of polarity are possible*, so that in a certain sense it is meaningless to talk of such *idealizations* as homopolar bond, heteropolar bond, covalent bond, dative bond, etc."

Pauling has presented the same ideas in an interesting paper (2) in which he uses as illustrations of such transitions from one bond type to another the alkali and hydrogen halides.

DIRECTED VALENCES

For the chemist the concept of directed valence bonds is a logical consequence of the properties and behavior of many compounds. While such ideas could not be deduced from the simple Heitler–London theory, it has been shown by both L. Pauling and J. C. Slater, working independently, that it is possible to construct on the basis of quantum mechanics single electron eigenfunctions which have directional properties and may thus be used to interpret directed valence bonds.

> "It has been found," Pauling writes, "that the strength and direction of an electron-pair bond formed by an atom are determined essentially by one *electronic eigenfunction*. The bond tends to be formed in the direction in which the eigenfunction has its maximum value, and the greater the concentration of the eigenfunction in the bond direction, the stronger the bond will be. The spherically symmetrical *s* eigenfunction can form a bond in any direction of strength 1 according to the semi-quantitative treatment, and a *p eigenfunction* a bond of strength 1.732 in either of two opposite directions. But in most atoms which form *four or more bonds* the *s and p* eigenfunctions *do not retain their identity, being instead combined to form new eigenfunctions, better suited to bond formation.* The best bond eigenfunction which can be formed from the one *s* and three *p* eigenfunctions in a given shell has the strength 2.000. Moreover, three other equivalent bond eigenfunctions can also be formed, and the *four bonds* are directed toward the corners of a regular tetrahedron. This result immediately gives the quantum-mechanical justification of the chemist's tetrahedral carbon atom, with all its properties, such as *free rotation about a single bond* (except when restricted by steric effects) and lack of it about a double bond, and shows that many other atoms direct their bonds toward tetrahedron corners."

As is evident from a plot of one of these tetrahedral eigenfunctions we must not consider that in the C—H bond the electrons are actually localized in a "cigar-like" region between the two nuclei. Rather, what we infer from Pauling's deductions is that in methane the electronic charge density will tend to be greatest along those lines which are directed from the carbon nucleus towards the corners of a regular tetrahedron. While Pauling has not carried out any computation of the binding energy by use of his suggested eigenfunctions, it is evident that such a calculation would yield too low a value of the binding energy because of the failure to take into account correlation energy. For, while a part of the binding energy undoubtedly arises from the tendency for the electrons to localize between the carbon nucleus and each of the four hydrogen nuclei, the rest of the binding energy must be ascribed to the fact that the electrons will also tend to avoid each other.

Slater has derived expressions for the energy of a system consisting of two, three, or four univalent atoms in each of which the valence electron is in the *s*-state. The resulting expression for the binding energy involves both Coulomb and exchange integrals which are similar in nature to those occurring in the Heitler–London treatment of hydrogen. Such computations must however be regarded as only a first approximation to the true values, since they omit any consideration of correlation energy terms. That the inclusion in the calculation of these latter terms offers grave mathematical difficulties is, of course, the main reason for the failure on the part of "theoreticians" to attempt this task. However, it should be realized that all calculations of binding energies, and energies of activation which are based on this artificial device of dividing the energy into Coulomb and exchange energy are liable to be only the roughest kind of approximations to the true values.[3]

The present status of this whole problem has been very well described by Van Vleck and Sherman at the beginning of their comprehensive review. We cannot do better than quote their remarks.

> "The subject of valence is really concerned with energy relations. If we knew the energies of all the possible different kinds of electron orbits in molecules, and also in the atoms out of which the molecule is formed, the rules of valence would automatically follow.
>
> "Now the principles of quantum mechanics enable one to write down an equation for any system of nuclei and electrons, the solution of which would provide us with complete information concerning the stability of the system, spatial arrangements of the nuclei, etc. . . .
>
> "The complexities of the n-body problem are, alas, so great that only for the very simplest molecule, namely H_2, has it proved possible to integrate the Schroedinger wave equation with any real quantitative accuracy. Hence to date, anyone is doomed to disappointment who is looking in Diogenes-like fashion for honest, straightforward calculations of heats of dissociation from the basic postulates of quantum mechanics. How, then, can it be said that we have a quantum theory of valence? The answer is that to be satisfied one must adopt the mental attitude and procedure of an optimist rather than a pessimist. The latter demands a rigorous postulational theory, and calculations devoid of any questionable approximations or of empirical appeals to known facts. The optimist, on the other hand, is satisfied with approximate solutions of the wave equation. If they favor, say, tetrahedral and plane hexagonal models of methane and benzene, respectively, or a certain order of sequence among activation energies, or a paramagnetic oxygen molecule he is content that these same properties will be possessed by more accurate solutions. He appeals freely to experiment to determine constants, the direct calculation of which would be too difficult. The pessimist, on the other hand, is eternally worried because the omitted terms in the approximations are usually rather large, so that any pretense of rigor should be lacking. The optimist replies that the approximate calculations do nevertheless give one an excellent 'steer' and a very good idea of 'how things go,' permitting the systematization and understanding of what would otherwise be a maze of experimental data codified by purely empirical valence rules. In particular, he finds that a mechanism is really provided by quantum mechanics for the Lewis electron pair bond, and for the stereochemistry of complicated organic compounds. It is, of course, futile to argue whether the optimist or pessimist is right. . . . One thing is clear. In the absence of rigorous computa-

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[3] See the criticism of such calculations by A. S. Coolidge and H. M. James (J. Chem. Physics **2**, 811 (1934)).

> tions, it is obviously advantageous to use as many methods of approximation as possible. If they agree in predicting some property (for instance, the tetrahedral structure of methane) we can feel some confidence that the same property would be exhibited by a more rigorous solution,—otherwise none. . . ."

IONIC COMPOUNDS

In quantum mechanics there is no rigid distinction, as already mentioned, between homopolar and ionic compounds. Even in the case of such molecules as hydrogen and methane in which the valence bonds are ordinarily regarded as of the shared electron or homopolar type, it is found that the most satisfactory electron eigenfunctions are obtained as a linear combination of Heitler–London and ionic terms.

When we consider the case of a typically ionic compound, such as sodium chloride, we find that from the point of view of quantum mechanics the electronic charge distribution is not localized to nearly the extent demanded by such a model as that of Born. According to the prevalent view the sodium atom in sodium chloride has lost an electron which the chlorine atom has gained. In terms of quantum mechanics this means that there is an excess charge distribution in the neighborhood of the chlorine nucleus which corresponds to that of one electron, and that there is corresponding deficiency around the sodium atom. However, some recent calculations have shown that even in this case the bond eigenfunction is best represented by a linear combination of an ionic function (ψ_I) and a Heitler–London function (ψ_S) of the following form

$$\psi = a\psi_I + \sqrt{1 - a^2}\psi_S \tag{18}$$

where $a >> \sqrt{1 - a^2}$.

On the whole then, we must conclude that the strictly classical picture of ionic substances is not wholly correct, and that an appreciable fraction of the binding energy arises from electronic distributions which are the same as those met with in valence compounds. This occurs as a result of the same need for compromise between competing energy terms which we have discussed in previous sections. Additional computations on solid ionic crystals, based on a Hund–Mulliken type of approximation, also confirm the significance of this point of view.

QUANTUM-MECHANICAL RESONANCE

One of the most significant deductions which has appeared as a result of the application of quantum mechanics to atomic and molecular interactions is the existence of the *resonance* effect. If we have a system consisting of three univalent atoms in which the atoms are at approximately equal distances from each other, there are three possible ways by which a bond may be established between any pair. Since only two of these three bond-structures are independent, the eigenfunction for the system is represented by a linear combination of two terms, one for each of the so-called *canonical structures*, and it is found that the energy of the complex of three atoms is lower than that for either of the independent structures by itself. This is generally described as being due to a sort of coupling action between the two possible structures. From the standpoint we have emphasized above, it may be regarded as arising from the fact that the linear combination of functions leaves room for a more intricate description of electronic motions than any single one of the functions, and hence one which is nearer the true description, so that the mean values of all energy terms are mutually lowered.

The most interesting illustration of this resonance energy is furnished by the benzene ring and similar aromatic compounds. As is well known, it was not possible by means of the classical concepts of valence to determine the correct method of assigning bonds to the carbon atoms in the benzene ring. Kekulé, Claus, Ladenburg, Dewar, and others each postulated a certain structure. Now according to L. Pauling and G. W. Wheland (3) the actual state of the molecule is apparently to be regarded as a mixture of these different possible structures. There are five independent bond structures or canonical structures. If we represent these by ψ_{I} to ψ_{V}, it is found that the eigenfunction which represents the state of the molecule most adequately is of the form

$$\psi = a(\psi_{\mathrm{I}} + \psi_{\mathrm{II}}) + b(\psi_{\mathrm{III}} + \psi_{\mathrm{IV}} + \psi_{\mathrm{V}})$$

where I and II refer to the two possible Kekulé structures and III, IV, and V refer to the Dewar structure.

Because of the constant interaction of these five structures, the binding energy is greater than that which would be obtained for any of the structures alone. The difference constitutes the so-called resonance energy, and it may be regarded as contributing towards an increased stability of the system.

VAN DER WAALS FORCES

The development of an adequate interpretation of the nature of van der Waals forces must be regarded as another important achievement of quantum mechanics. According to London there exists between any pair of atoms or molecules an attractive energy which varies inversely as R^6, where R is the intermolecular distance. In order to understand the origin of this attraction we form a model of the atom in which, owing to the motion of the electron, we may consider the system of electron and nucleus as a dipole, of which both the moment and direction of orientation are varying continuously. This fluctuating dipole gives rise to a field, and when two atoms are made to approach, there is a tendency for the electrons in each atom to move in phase owing to interaction of the two fields, thus resulting in an energy of attraction. This motion is, of course, closely connected with the motions which give rise to correlation energy.

From the fact that latent heats of evaporation are considerably smaller than molecular heats of formation, it is evident that the magnitude of the van der Waals energy must in general be of a different order from that of the energy exhibited in bond formation. However, from the point of view of quantum mechanics there must also occur cases in which the difference between the so-called physical type of cohesion and the chemical form of cohesion is not at all sharply defined, for both these forms of attraction energy are essentially electrostatic in origin. Only, in the case of bond formation the electric charges are so near each other that the inverse square law of attraction is of prime significance, while in the case of van der Waals attraction, the individual atoms are so far apart that their interaction is more suitably represented as that between dipoles, which, as already mentioned, are not stationary, but fluctuating rapidly.

Obviously, as two hydrogen atoms are made to approach each other from an infinite distance there should be a region of internuclear separation in which the energy of attraction changes gradually from the more loose form to the valence form. So far no theory has been developed to take into account such a transition in the nature of the energy. But it is possible, in the case of atomic hydrogen, to derive some idea of the extent of the region in which the energy changes over by gradual stages from the van der Waals to the valence form.

For the van der Waals attraction energy between two hydrogen atoms E_W, the most accurate calculations lead to the relation

$$\begin{aligned} E_W &= -\frac{6.5\,e^2}{a_0}\left(\frac{a_0}{R}\right)^6 \\ &= -13W_0(a_0/R)^6 \end{aligned} \tag{19}$$

where W_0 = ionization energy of H = 13.53 v.e.

This relation is valid only for values $(R/a_0)^3 >> 9$, that is, $R/a_0 >> 2.08$. Using the Morse form of potential energy function for the hydrogen molecule and the value for the dissociation energy, $D_0 = 4.72$ v.e. (which includes zero point energy), we obtain for the valence energy the relation

$$E_V = 4.723(\epsilon^{-4\rho} - 2\epsilon^{-2\rho}) \text{ v.e.}$$

where $\rho = R - 0.74$. Hence,

$$E_V = -21.23\epsilon^{-2R}(2 - 4.3936\epsilon^{-2R})$$

For $R > 4$ A.U., we have the relation

$$E_V = -42.46\epsilon^{-2R} \text{ v.e.}$$

If now we plot E_V and also E_W, each as a function of R, it is found that for $R \leq 7.0$ A.U. (approximately) $E_V > E_W$, while for $R > 7.0$ A.U., $E_V < E_W$. This value of R is undoubtedly too great, since actual observation on the equation of state for hydrogen leads to a maximum van der Waals energy of 2.5×10^{-3} v.e. at an intermolecular distance of about 3.5 A.U. Furthermore, it is probably not justifiable to extrapolate the Morse curve to much larger values of R than this. But qualitatively it is evident that for values of R greater than a certain definite value, E_W must be greater than E_V.

That van der Waals energies of cohesion may be of the same order of magnitude as bond energies is evident from the observation that a very large number of organic and some inorganic compounds decompose long before the temperature attains a value that even approaches the theoretically calculated value for boiling or sublimation at atmospheric pressure.

Even an approximate calculation shows that the total energy of evaporation of such compounds may be accounted for on the basis of the quantum mechanically deduced relations. Recently A. Müller (1) has shown that a more rigorous calculation for the case of a normal CH_2-chain molecule in a paraffin crystal actually yields values in very good agreement with those deduced from measurements of vapor pressure. For a homologous series of hydrocarbons it may be shown that the latent heat of evaporation is proportional to the total surface of the molecule. It follows that the value of the latent heat of evaporation for very large molecules must become of the same order of magnitude as the energy of some of the weaker bonds, and hence when the liquid is heated the tendency to break such bonds may exceed that for the molecules to become separated as individual systems.

METALS

While there is not ample space for a thorough discussion of the cohesive properties of metals, it is worth mentioning that these substances, which were generally omitted from chemists' classifications of bond types, may be described very satisfactorily by the methods of quantum mechanics. It turns out that the binding energy arises from almost exactly the same sources as the binding energy of valence compounds. The important difference between metals and valence compounds, from the standpoint of cohesion, lies in the fact that directional properties of the wave functions are not stressed nearly as much in metals. In the case of the alkalies, computations have been carried to an extent in which the correlation energy is included, and many of the remarks relating to this quantity, which were made in previous sections, are based upon an examination of these cases.

CONCLUSION

About twenty years ago it began to dawn upon chemists that there is no fundamental distinction between so-called physical and chemical reactions. Both may be treated by the same thermodynamical method, and such a classification is merely of historical and pedagogical interest.

Similarly, at the present time, we must realize that in all forms of cohesive energy, whether between atoms in non-polar molecules, between ions in polar compounds, between the carbon atoms in diamond or the sodium atoms in metallic and liquid sodium or between the molecules of methane in liquid methane, the cohesive energy arises from electrostatic forces. There are no other mysterious forms of forces. It is true that it is possible to calculate the magnitude of this energy in only a relatively few simple cases. This arises largely because of the difficulties in calculating correlation energies for the binding of the electrons. Whether it will be possible to overcome these difficulties is a matter that cannot be predicted at present.

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THE THEORY OF THE LIQUID STATE[1]

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During the past few years there has been a great deal of progress made in the development of a theory of liquids. A general survey of its present status was presented at the symposium[2] of the Faraday Society held in September, 1936, and the subject has been discussed by Hildebrand (7), Frenkel (11), Herzfeld and Goeppert-Mayer (12), and others. In this paper we shall treat the liquid as though it were composed of individual molecules, each moving in an average potential field due to its neighbors. The partition function for the liquid can then be written:

$$F_l = V_f \frac{(2\pi mkT)^{3/2}}{h^3} R_l \, \mathrm{Vib}_l \exp\left(\frac{\Delta E}{RT}\right) \tag{1}$$

This equation may be considered as the definition of the free volume, V_f. Here ΔE is the energy of vaporization; R_l and Vib_l are the rotational and vibrational parts of the partition function of a molecule in the liquid; and m, k, h, and T are the mass of the molecule, the Boltzmann constant, the Planck constant, and the absolute temperature, respectively. The partition function for a molecule in the gas is:

$$F_g = V_g \frac{(2\pi mkT)^{3/2}}{h^3} R_g \, \mathrm{Vib}_g \tag{2}$$

where V_g is the total volume of the gas divided by the number of molecules, R_g and Vib_g are the rotational and vibrational parts of the partition functions of a molecule in the gas. We shall consider first the molecules which are sufficiently symmetric that the partition functions for rotation and internal vibrations are the same for the liquid as for the gas.

At equilibrium between gas and liquid,

$$kT \ln \frac{F_l}{F_g} = p(V_g - V_l)$$

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[1] Presented at the Symposium on Molecular Structure, held at Princeton University, Princeton, New Jersey, December 31, 1936 to January 2, 1937, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society.

[2] The papers presented at this symposium are published in the Transactions of the Faraday Society, 1936.

so that:

$$\frac{V_g}{V_f} = \exp\left(\frac{\Delta H}{RT}\right) \tag{3}$$

We now can see what is meant by V_f. If a fluid which obeys the perfect gas law:

$$pV = RT \tag{4}$$

expands isothermally from V_f to V_g, the work done is

$$\Delta H = RT \log\left(\frac{V_g}{V_f}\right)$$

This is equation 3 and therefore V_f is the effective volume in which a particular molecule in the liquid can move and obey the perfect gas law,

$$p_f V_f = RT \tag{5}$$

Substituting $\frac{1}{V_g} = \frac{p_{\text{vap}}}{RT}$ into equation 3, we obtain the vapor pressure equation:

$$p_{\text{vap}} = \frac{RT}{V_f} \exp\left(\frac{\Delta H}{RT}\right) \tag{6}$$

The external pressure, p_{ex}, acting on the liquid may be calculated from the well-known equation

$$p_{\text{ext}} = RT \frac{\partial}{\partial V_l} \log F_l = RT \frac{\partial}{\partial V_l} \log V_f + \frac{\partial \Delta E}{\partial V_l} \tag{7}$$

Here V_l is the total volume of the liquid divided by the number of molecules in the liquid.

To go further, we require the relationship between the V_l and V_f. For simplicity we shall consider cubical packing, in which one molecule oscillates about the origin and the six nearest neighbors are imagined fixed at their mean positions along the three axes. Each molecule is thus at a distance $V_l^{1/3}$ from the origin. Now if d is the incompressible diameter of each of these molecules, then $2V_l^{1/3} - 2d$ is the distance that the central molecule is free to move along each axis. The free volume is then just this quantity cubed, i.e.

$$V_f = 8(V_l^{1/3} - d)^3 \tag{8}$$

(see figure 1). For other types of packing and for a more rigorous derivation, we still expect the relationship

$$V_f = b^3(V_l^{1/3} - d)^3 \tag{9}$$

in which b may vary somewhat with temperature and differ from 2. A critical discussion of equation 9 is given later in this paper. Using equation 9, we obtain:

$$\frac{\partial V_f}{\partial V_l} = b\left[\frac{V_f}{V_l}\right]^{2/3} \tag{10}$$

Since the kinetic energy terms in the liquid and gas are equal (see equations 1 and 2), it follows that ΔH is equal to ΔE, the difference in potential energy of a molecule in the gas and in the liquid state, plus RT, the work done against the atmosphere. Now combining equations 7 and 10 we obtain an equation of state for the liquid:

$$\left[p_{ex} - \frac{\partial \Delta E}{\partial V_l}\right] V_l^{2/3}\, V_f^{1/3} = bRT \tag{11}$$

Eliminating V_f from equation 11 by means of equation 9:

$$\left[p_{ex} - \frac{\partial \Delta E}{\partial V_l}\right] [V_l - dV_l^{2/3}] = RT \tag{12}$$

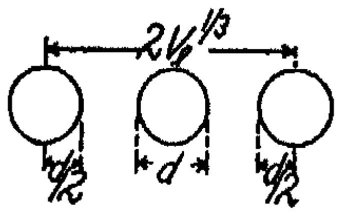

FIG. 1. The relationship between the free and total volume
$V_f = (2V_l^{1/3} - 2d)^3$

It is interesting to note that equation 12 is independent of the value of the "packing factor," b. We can solve equation 11 for the free volume:

$$V_f = \left[\frac{bRT}{p_{ex} - \dfrac{\partial \Delta E}{\partial V_l}}\right]^3 \frac{1}{V_l^2} \tag{13}$$

This value of V_f may be substituted into equation 6 to obtain the equation for vapor pressure:

$$p_{vap} = b^{-3}\left(\frac{V_l}{RT}\right)^2\left[p_{ex} - \frac{\partial \Delta E}{\partial V_l}\right]^3 \exp\left(-\frac{\Delta H}{RT}\right) \tag{14}$$

For many liquids it has been shown that, to a good approximation, ΔE is a function only of the volume of the liquid. This is shown by the fact that for normal liquids the specific heats at constant volume of liquid and gas are nearly equal (10). We shall take

$$\Delta E = \frac{a}{V_l^n} \tag{15}$$

where a and n are constants. From the work of Hildebrand and his coworkers (8) it is found that n is usually close to unity. Since $\frac{\partial \Delta E}{\partial V_l}$ is of the order of thousands of atmospheres, p_{ex} may be neglected when it is of the order of 1 atmosphere. Using equation 15:

$$-\frac{\partial \Delta E}{\partial V_l} = \frac{na}{V_l^{n+1}} = nV_l^{-1}\Delta E \tag{16}$$

Thus:

$$p_{vap} = n^3 RT b^{-3} V_l^{-1} \left(\frac{\Delta E}{RT}\right)^3 \exp\left(-\frac{\Delta E}{RT} - 1\right) \tag{17}$$

Taking $n = 1$ (corresponding to $\Delta E = aV_l^{-1}$) and $b = 2$ (cubical packing), equation 17 becomes:

$$p_{vap} = \frac{RT}{8V_l}\left[\frac{\Delta H}{RT} - 1\right]^3 \exp\left(-\frac{\Delta H}{RT}\right) \tag{17a}$$

This equation for the vapor pressure gives the Hildebrand rule when it is realized that the specific volume, V_l, is about the same for most normal liquids. Using $V_l = 82$ cc. we obtain:

$$p_{vap} = \frac{T}{8}\left[\frac{\Delta H}{RT} - 1\right]^3 \exp\left(-\frac{\Delta H}{RT}\right) \text{ atmospheres} \tag{18}$$

Thus if liquids 1 and 2 have the same concentrations in the vapor

$$\left[c_g = V_g^{-1} = \frac{p_{vap}}{RT}\right]$$

at the respective temperatures T_1 and T_2, then it follows that

$$\frac{\Delta H_1}{T_1} = \frac{\Delta H_2}{T_2}$$

Trouton's rule can be obtained if we realize that most of the liquids usually considered boil in the neighborhood of 300 to 400° Absolute. Taking $T =$ 300°K:

$$p_{vap} = \frac{300}{8}\left[\frac{\Delta H}{RT} - 1\right]^3 \exp\left(-\frac{\Delta H}{RT}\right) \text{ atm.} \tag{19}$$

At the boiling temperature, T_b, i.e., when $p_{vap} = 1$ atm., then $\frac{\Delta H}{RT_b} = 10.4$, which is the usual Trouton rule value. In this derivation of $\frac{\Delta H}{RT_b} = 10.4$

there is a certain arbitrariness in the values chosen for V_l and T, but for most normal liquids the change in these quantities will not change $\frac{\Delta H}{RT_b}$ by more than one unit. For the molten salts where T_b is around 1400°K. and V_l is as small as 40 cc., $\frac{\Delta H}{RT_b}$, may become as large as 13. For gases boiling at low temperatures equation 18 yields a low value for $\frac{\Delta H}{RT_b}$, in accord with experiment.

The thermal expansion can be investigated using the equation of state (equation 12). Taking:

$$-\frac{\partial \Delta E}{\partial V_l} = naV_l^{-(n+1)}$$

and differentiating both sides of equation 12 with respect to T one obtains:

$$[-n(n+1)aV_l^{-(n+2)}(V_l - dV_l^{\frac{1}{3}}) + [p_{ex} + anV_l^{-(n+1)}](1 - \tfrac{2}{3}dV_l^{-\frac{1}{3}})]\frac{\partial V_l}{\partial T} = R \tag{20}$$

Solving this equation for

$$\alpha \equiv V_l^{-1}\left(\frac{\partial V_l}{\partial T}\right)_{p_{ex}}$$

$$\alpha = \frac{3R[p_{ex} + nV_l^{-1}\Delta E]}{V_l[p_{ex} + nV_l^{-1}\Delta E]^2 + 2RTp_{ex} - (3n+1)nRTV_l^{-1}\Delta E} \tag{21}$$

The external pressure can be neglected when it is small compared with $nV_l^{-1}\Delta E$ and one obtains:

$$\alpha = \frac{3}{T}\,\frac{\left(\frac{RT}{n\Delta E}\right)}{1 - (3n+1)\left(\frac{RT}{n\Delta E}\right)} \tag{22}$$

Using the Trouton approximation:

$$\alpha = 3[9.4\,T_b - 4T]^{-1} \tag{23}$$

Similarly the equation for the compressibility of the liquid may be obtained by differentiating both sides of equation 12 with respect to p_{ex}. Solving for

$$\beta \equiv V_l^{-1}\left(\frac{\partial V_l}{\partial p_{ex}}\right)_T$$

we find:

$$\beta = -\alpha T[p_{ex} + nV_l^{-1}\Delta E]^{-1} \tag{24}$$

When it is justifiable to neglect the external pressure,

$$\beta = -\frac{\alpha T V_l}{n \Delta E} \qquad (25)$$

This is a special form of the general thermodynamical relationship:

$$c_p - c_v = \frac{\alpha^2 V T}{\beta}$$

To the approximation of Trouton's rule:

$$\beta = -\frac{3V_l T}{9.4\, T_b R[9.4\, T_b - 4T]} \qquad (26)$$

Therefore at the boiling point Trouton's rule leads to:

$$(\alpha)_{T_b} = 0.55 T_b^{-1}$$

$$(\beta)_{T_b} = -7.1 \times 10^{-4} V_l T_b^{-1}$$

These formulas usually give the coefficients of thermal expansion and of compressibility to within a factor of two.

In table 1, α and β are calculated for a number of liquids, all at 25°C. The experimental values of

$$\left(\frac{\partial \Delta E}{\partial V_l}\right)_T$$

and of

$$n_1 = \frac{V_l}{\Delta E}\left(\frac{\partial \Delta E}{\partial V_l}\right)_T$$

are taken from the work of Hildebrand and his coworkers (9). The values of the observed p_{vap}, α and β are obtained from the *International Critical Tables* and from the Landolt-Börnstein *Tabellen*. n_2 is the experimental value for n which is obtained by the use of equation 25, i.e.

$$n_2 = -\frac{\alpha T V_l}{\Delta E}$$

In most cases, it will be noticed that n_1 agrees quite well with n_2 and is usually close to unity. α and β are calculated from equations 22 and 24, respectively. The values of b which are given in this table are calculated from equation 17, in which the experimental values of p_{vap}, ΔE, n, and V_l are used. For most of the "normal" liquids considered, b has a value close to 2. The free volumes are calculated from equation 13, and it is to be noticed that they are of the order of 0.1 cc. The liquids considered here are of a complicated structure, and therefore it is surprising that we should obtain any agreement between the calculated and the observed properties. In methyl alcohol and in mercury there must be important deviations from the properties of normal liquids, due to causes which we have not considered in this treatment.

Newton and Eyring (10) proceeding from a different point of view, have given an equation for the vapor pressure. The free volume which they have introduced differs from that used here in two particulars. First, they chose to define it in such a way that it contains all the variations in the potential energy of the liquid with temperature, i.e., their Boltzmann factor is $\exp(-E_0R^{-1}T^{-1})$ where E_0 does not vary with the temperature, while we use $\exp\left(-\frac{\Delta E}{RT}\right)$. Secondly, they use the equation:

TABLE 1

LIQUID	V_l	t_b	p_{vap} AT 25°C.	$\left(\frac{\partial \Delta E}{\partial V_l}\right)_T$	n_1	n_2
	cc.	*°C.*	*atmospheres*	*atm. per cm.³*		
n-Heptane	147.6	98.4	0.062	2510	1.12	
Ethyl ether	104.5	34.6	0.707	2370	1.03	1.60
CCl_4	97.1	76.5	0.151	3311	1.10	1.16
$CHCl_3$	80.7	61	0.262	3660	1.11	1.15
Benzene	89.3	80	0.125	3642	1.09	1.09
CS_2	60.7	46	0.481	3670	0.89	1.16
Acetone	73.3	56.5	0.302	3331	0.89	1.29
CH_3OH	40.4	64.7	0.163	2940	0.34	0.48
Mercury	14.8	356.9	0.00184	14650	0.33	0.35

LIQUID	V_f	b	$\alpha \times 10^3$		$\beta \times 10^5$	
			Calculated	Observed	Calculated	Observed
	cc.		*deg.⁻¹*	*deg.⁻¹*	*atm.⁻¹*	*atm.⁻¹*
n-Heptane	0.174	1.60	0.94		11.2	
Ethyl ether	0.714	1.92	1.68	1.58	21.2	12.9
CCl_4	0.386	2.08	1.14	1.23	10.7	10.5
$CHCl_3$	0.667	2.44	1.31	1.27	10.3	10.0
Benzene	0.365	2.12	1.12	1.24	8.5	9.5
CS_2	0.696	2.05	1.86	1.22	15.2	7.6
Acetone	0.404	1.76	1.60	1.49	14.9	9.2
CH_3OH	0.028	0.43	3.53	1.19	35.3	8.5
Mercury	0.00019	0.21	1.46	0.18	3.3	0.39

$$\frac{1}{V_f^{\frac{1}{3}}} \frac{\partial V_f^{\frac{1}{3}}}{\partial T} = \frac{\alpha}{3}$$

while the free volume which we have used is defined in such a manner that:

$$\frac{1}{V_l^{1/3}}\,\frac{\partial V_f^{1/3}}{\partial T} = \frac{b\alpha}{3}$$

The first of these differences is purely a formal one. The second difference would be non-existent if b were taken as 1 in the present treatment.

The problem of deriving the "packing constant" b from a knowledge of the mutual potential energy between pairs of molecules is analogous to the problem of calculating the characteristic frequencies of a crystal. A rigorous treatment of the problem would require the simultaneous consideration of the oscillations of the N molecules in the liquid, to obtain the $3N$ normal modes of vibration, and from these it would be necessary to compute the mean distance which the molecules move from their respective equilibrium positions. The derivation of b given here is not strict, but it is similar to the treatment which Grüneisen (6) used for the solid and for which he obtained fairly good agreement with the properties calculated by the more accurate treatments of Debye and Born (see, for example. references 2 and 5).

Since the equations for α and for β depend only on the functional form for the relationship between V_f and V_l [not on b and d, for example], the agreement obtained between the experimental and the theoretical values is an indication that $V_f^{1/3}$ is really linearly related to $V_l^{1/3}$. If b or d were temperature dependent, α, but not β, would be affected, but the agreement which we obtained for α as well as for β and the fact that n_1 is almost equal to n_2 (see table 1) indicates that such temperature dependence is not large.

The partition function which we have obtained here can be used in calculating the viscosity of a liquid. In a previous paper by one of us (3), the viscosity of a liquid has been shown to be proportional to the partition function for the normal state, F_n, divided by that for the activated state, F_a^*, times a Boltzmann factor, $\exp\left(\frac{E_0}{RT}\right)$, where E_0 is the activation energy for the individual process. For liquids in which the slow process is for a single molecule to pass from one position of equilibrium to an adjacent one, we expect that the partition functions will only differ in an important way in this one degree of freedom. Thus the activation process may be thought of roughly as the vaporization in one degree of freedom, i.e., the activation energy will be of the order of one-third the heat of vaporization. Also, using equation 17:

$$\frac{F_n}{F_a^*} = \frac{(2\pi mkT)^{1/2}}{h}\,V_f^{1/3} = 2V_l^{1/3}\left[\frac{RT}{\Delta H - RT}\right]\frac{(2\pi mkT)^{1/2}}{h} \qquad (27)$$

If we had used equation 13 instead of equation 17 in obtaining equation 27, we would have a slightly more general relation. Andrade (1) compared the Boltzmann factor in viscosity with twice the van der Waals constant *a* divided by the volume of the liquid, i.e., $2\,\Delta H - 2\,RT$; however the Boltzmann factor which was required for the large number of liquids which he considered was slightly less than one-sixth of this value, or a little less than one-third of the heat of vaporization.

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THE PHOTOCHEMICAL BEHAVIOR OF THE ALDEHYDES[1]

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The photochemical behavior of the aldehydes has been investigated by a number of people, with the net result that fairly good agreement exists concerning the experimental facts but two markedly different viewpoints are represented in the interpretation of these facts. The American group, represented by Leighton (6), Kistiakowsky (4), Leermakers (5), and Blacet (2), has favored a mechanism in which the primary action of the light is considered to be a rupture of the molecule into an alkyl radical and a CHO radical, with the final products being produced by secondary reactions of these substances. Norrish (8) and his students have preferred a mechanism in which a molecule of carbon monoxide is ejected, leaving a hydrocarbon molecule. Recently Norrish (9) has modified his mechanism slightly so as to permit some formation of alkyl radicals and hydrogen atoms, although still maintaining the direct formation of hydrocarbon and carbon monoxide from activated molecules as the principal reaction. Each of these mechanisms will explain a great many facts, but definite objections may be raised against each of them. In this paper it will be shown that the observed facts can be accounted for if we will assume that on activation by light some of the molecules dissociate into free radicals, some decompose into hydrocarbon and carbon monoxide without passing through a free radical stage, and some may enter into polymer formation, fluoresce, or return to the lowest state through collision processes. The division between these different possibilities is assumed to be a continuous function of the wave length of the exciting light.

For simplicity let us first consider the photochemical behavior of acetaldehyde, for which the observations are most complete, and then extend the discussion to include the other aldehydes. According to Leighton and Blacet (7) the absorption spectrum of acetaldehyde begins at about 3480 A. U. and extends to about 2400 A. U. The spectrum appears to consist of a number of bands, some of them diffuse, beginning at 3480 A. U. and

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extending to 2666 A. U. with a maximum absorption at 3100 A. U. and a continuous absorption extending from 3250 A. U. (estimated from the photometer curve (6)) to 2400 A. U. with a maximum at 2750 A. U. The usual interpretation of such a spectrum assumes that any diffuse structure or continuum corresponds to a dissociation of the molecule in a time of 10^{-11} sec., or less. An abundance of evidence has been secured which supports this interpretation in the case of diatomic or very simple molecules. However, extreme caution must be observed in extending this idea to complex molecules, as a spectrum which is "experimentally continuous" may be obtained with polyatomic molecules without having any dissociation. In order to see how such a spectrum can be obtained let us compare the transitions which may occur in a simple diatomic molecule, such as bromine, with those which occur in an aldehyde molecule, RCHO. From a consideration of the Bohr frequency relation and the uncertainty principle we know that a sharp line will appear in the absorption spectrum for every transition between two definite quantized states in the molecule, provided the life of these states is of the order of 10^{-10} sec. or greater. In a diatomic molecule there is only one degree of freedom for vibration and one moment of inertia for rotation, so there are relatively few states possible and a fine structure should be observed in the spectrum unless dissociation occurs within a very short time. With a polyatomic molecule, even if we consider that we are limiting the electronic changes to a particular portion of the molecule, such as the carbonyl group in the aldehydes, we have many more vibrational and rotational states than exist in the diatomic molecule. To be specific, there are three moments of inertia corresponding to rotation about each of three axes and several degrees of freedom with respect to vibration which would have to be considered. Furthermore, owing to the various ways in which the different modes of vibration may be combined, there will be a certain amount of variation in the moments of inertia. Even if this effect amounts to only a few per cent it would be enough to reduce the rotational structure of the bands to a blur. If this blurring does not extend over too wide a range of rotational quantum numbers it will still be possible to see the structure due to vibration. However, we must also consider that the molecule may change rapidly by a process such as is assumed to explain predissociation from the electronic state produced initially by the absorption of light to various other states, with corresponding changes in the vibrational and rotational effects. With such transitions occurring within 10^{-11} sec. or less of the absorption act we must expect to find an "experimentally continuous" spectrum. In the spectrum of acetaldehyde a comparison of the separation of the maxima of the discontinuous and continuous absorptions and the separations of the long wave-length and short wave-length limits for these two types of absorption suggests that we are observing transfers from the lowest state to two higher electronic states separated by approximately 5100 cm.$^{-1}$ If we will assume that in one of these excited states the molecule does not change readily to a different electronic structure by the predissociation process but that it does from the other state, we can account for the observed spectrum without assuming any dissociation into free radicals. In order to reach a decision as to the nature of the action of the light we must consider other kinds of evidence.

Definite evidence for the formation of free radicals by the action of light on acetaldehyde was obtained by Pearson (10). He employed Rice's (11) method of the removal of metallic mirrors to demonstrate that illumination of the aldehyde vapor produced some dissociation of this type. The results are not quantitative, but a comparison of the effect obtained using acetaldehyde with that obtained with such substances as acetone indicated that the formation of radicals from the former is a rather inefficient process. Another method of attack was used by Leermakers (5), who studied the photolysis of acetaldehyde at about 300°C. and found quantum yields as high as 300. The behavior of the system under these conditions could be explained by assuming that free radicals were formed by the action of the light and these caused the decomposition of other acetaldehyde molecules in a chain mechanism of the type postulated by Rice. This mechanism receives further support from the recent observations of Fletcher and Rollefson (3) at a temperature of 440°C., which show that free radicals from the decomposition of ether or ethylene oxide can set up chains which result in the decomposition of a thousand or more aldehyde molecules for each radical introduced. The experiments of Leermakers may be considered as showing that some free radicals are formed, but supplies no information concerning the efficiency of the primary light process.

The experiments just cited show that any complete mechanism for the decomposition of acetaldehyde must include a reaction which yields free radicals. There are other experiments, however, which indicate that other processes must be considered as well. The recent work of Fletcher and Rollefson (3) and of Staveley and Hinshelwood (13) has shown that the thermal decomposition of acetaldehyde, under conditions such that the rate is measurable, proceeds to methane and carbon monoxide without passing through a free radical stage. The activation energy is 58,000 calories, which is far less than is supplied by light in the photochemical reaction, so we must consider the possibility of direct decomposition into the final products any time the molecule is activated to a higher state than that reached in the thermal reaction.

The recent careful analyses of Blacet and Roof (2) have shown that at least three equations must be written to represent the chemical changes which occur when acetaldehyde is illuminated. These are: (1) $CH_3CHO \rightarrow CH_4 + CO$; (2) $n\ CH_3CHO \rightarrow (CH_3CHO)_n$; (3) $CH_3CHO \rightarrow CO, H_2,$

and an unidentified hydrocarbon (possibly ethane or ethylene). The distribution between these three possibilities was found to vary approximately linearly with the wave length of the light absorbed, reaction 2 decreasing toward short wave lengths and the other two increasing. Blacet and Roof attribute the variation in products to the increase in the velocity of separation of the radicals as the frequency of the absorbed light is increased. This does not seem to be very probable, as a simple calculation shows that these velocities vary by only a factor of two over the range of frequencies used. Furthermore, at the pressures used in the experiments the mean free path of the separating radicals would be at least twenty or thirty diameters, which is sufficient to remove each from the field of influence of the other. Also the probability that they would be driven back toward each other is negligible, and their speeds would soon be reduced to that of ordinary thermal motion. Therefore the reactions which the radicals undergo will in no way be determined by the original velocity of separation.

TABLE 1

Fractions of the activated aldehyde molecules reacting according to the various possible paths

λ	PATH			
	1	2	3	4
3130	0.56	0.02	0.18	0.24
2804	0.37	0.094	0.43	0.11
2537	0.05	0.18	0.72	0.05

In a similar manner objections can be raised to any mechanism which assumes solely free radicals or solely activated molecules. Let us assume that we have both free radicals and activated molecules and that the relative number produced is a function of the exciting wave length. Applying this viewpoint to acetaldehyde we must consider that a molecule which has absorbed light may (1) return to the lowest state with the emission of light or by collisions with other molecules, (2) dissociate into free radicals, (3) rearrange to give methane and carbon monoxide, (4) react with another molecule or molecules to form a polymer. It is known from an extrapolation of Leermakers' work to room temperature that it is unnecessary to consider any chain mechanisms under these conditions, so we shall assume that the sum of the quantum yields of the four processes listed is unity. In addition let us consider that the hydrogen is formed only by process 2. On this basis the data of Blacet and Roof may be interpreted as shown in table 1, in which are listed the fractions of the activated molecules which react according to each of the above-mentioned paths (the path numbers listed in the table correspond to the numbering above). The values given for the polymerization are one half of the quantum yields given for that process by Leighton and Blacet (7), as Smith (12) has shown that the amount of polymer formed is a linear function of the pressure for constant light absorbed, so we may conclude that at least one molecule of aldehyde in addition to the activated one goes to form polymer. No attempt has been made to separate process 1 into deactivation by collision and fluorescence, as no quantitative data are available for that purpose. From the fact that the quantum yields of the decomposition processes do not increase as the pressure is decreased, it may be argued that process 1 is occurring primarily through fluorescence or at least that the rate-determining step in the deactivation is monomolecular.

An inspection of table 1 shows that as the dissociation processes 2 and 3 increase, the processes 1 and 4, which are associated with activated molecules, decrease. It is not surprising that the decrease is not exactly the same, as we have seen that we must consider two different electronic levels for the upper state, and it is quite possible that they will not be equally efficient in causing polymerization. The increases in processes 2 and 3 may be due to a difference in the behavior of these two states, as well as a change in the probability of decomposition with increasing vibrational energy in the upper state. The chance of these electronic levels fluorescing must be approximately the same, as the absorption coefficients corresponding to the two transitions are not markedly different. This is probably not true of the other processes, or the character of the absorption spectrum would not be so different.

The mechanism of formation of the hydrogen from free radicals must be left indefinite on account of insufficient data. It is possible for either the carbon-hydrogen bond or the carbon-carbon bond to be broken. In order to make a decision it would be desirable to know: (1) whether ethylene or ethane is formed, and (2) whether any products, such as glyoxal, which may be formed from CHO are present. Other tests would involve the determination of the effect on the hydrogen yield of various substances, such as nitric oxide, which are known to react readily with free radicals, and a determination of the percentage of hydrogen in the products obtained, using light absorbed by one of the bands observed by Leighton and Blacet as compared to the percentage obtained with light from the adjacent regions of continuous absorption.

The data for other aldehydes, except formaldehyde, are less complete than for acetaldehyde and therefore more difficult to interpret. Formaldehyde apparently separates into hydrogen and carbon monoxide without the formation of any free radicals, but this must be looked upon as a very special case as the molecule has a symmetry which does not exist in the other aldehydes. Propionaldehyde (6) reacts much the same as acetaldehyde, except that the hydrogen yield passes through a maximum at a wave length near 2700 A. U. and the polymerization passes through a minimum at 3020 A. U. From the facts that fluorescence was observed at all wave lengths down to 2654 A. U. and that the polymerization is relatively more important than with acetaldehyde, it may be concluded that the life of a molecule in the activated state is greater than in acetaldehyde. The sum of the quantum yields is somewhat greater than unity at all wave lengths, according to Leighton and Blacet, but if we divide their value for the polymerization by 2 the discrepancy disappears except for the two highest frequencies (λ = 2654 A. U. and 2537 A. U.). The high yield may be due to short chains, such as Staveley and Hinshelwood (13) have found at high temperatures in the thermal decomposition.

Crotonaldehyde is of special interest, since Blacet and Roof (1) have reported that it neither decomposes nor fluoresces and gives only a very slight amount of polymer. According to the views which have been expressed in this paper the stability of this aldehyde must be attributed to a rapid distribution of the energy absorbed into other degrees of freedom, followed by collisional deactivation and possibly some fluorescence of rather long wave length. Blacet and Roof suggest the formation of free radicals followed by recombination in preference to other possible reactions, owing to the higher heats of activation of the latter. It seems improbable that the radicals obtained from this aldehyde should differ so much from those obtained from other aldehydes. If their theory is correct the decomposition should appear at higher temperatures and increase rapidly as the temperature is raised. According to the theory presented in this paper temperature should have little or no effect.

The data on the other aldehydes are not sufficiently complete to warrant drawing any conclusions about the mechanism of decomposition. In general the views which have been expressed in this paper require that the composition of the products shall depend only on the wave length of the light absorbed and be practically independent of the temperature or pressure in the system. If the temperature is raised high enough to set up reaction chains, the composition of the products will be influenced by the nature of the chains set up. Fluorescence and polymerization will show similar changes and the decompositions will change independently of each other, but in such a way that the sum of the decompositions will increase as fluorescence and polymerization decrease.

SUMMARY

It has been shown that the photochemical behavior of the aldehydes, especially acetaldehyde, is such that it is necessary to assume that the photoactivated molecules can react in several ways at comparable rates. Part of the decomposition which occurs proceeds through free radicals. The relative importance of the different processes is discussed for acetalde-

hyde. Some experimental tests of the various theories have been suggested.

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THE REACTION BETWEEN BROMOSUCCINATE ION AND THIOSULFATE ION[1]

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About five years ago several articles appeared containing experimental data which the authors of the articles felt were at variance with the Brönsted theory of salt effects. Thus Conant and Peterson (2) stated that they were unable to correlate their data on some coupling reactions with the theory. La Mer and Kamner (10) found that although increasing the ionic strength had the theoretical effect on the reaction between α-bromopropionate ion and thiosulfate ion, it had the opposite effect on the corresponding reaction between β-bromopropionate ion and thiosulfate ion. To explain this anomalous salt effect, La Mer and Kamner advanced their theory of oriented collisions, according to which a thiosulfate ion repels the carboxyl group of the acid ion and thus produces a favorable orientation for replacement of the bromine by the thiosulfate ion. The amount of this favorable orientation is decreased by the presence of other ions, thus overshadowing the primary salt effect. Sturtevant (14) showed from theoretical grounds that such a theory could not account for the phenomenon.

The β-bromopropionate reaction showed several other anomalies. Thus the beta-substituted compound reacted faster than the alpha-substituted compound, which is contrary to a widely accepted rule of organic chemistry. La Mer (9) also reported that the heat of activation of this reaction had a temperature coefficient of over 100 calories per degree.

Bedford (1) and his colleagues, studying the reaction between thiosulfate ion and bromosuccinate ion, in which the bromine is alpha to one carboxyl group and beta to the second, not only confirmed the peculiar salt effect of La Mer and Kamner, but found a temperature coefficient of the heat of activation fully three times as large as that reported by La Mer. These results were the more surprising since Olson and Long (13) have shown that reactions between bromo- and chloro-succinic acids and chloride and

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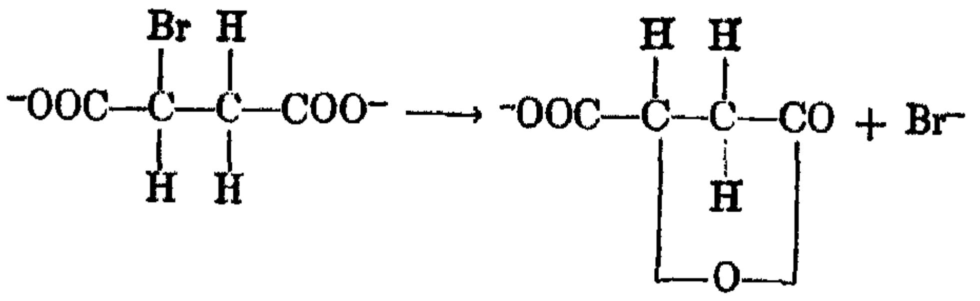
bromide ions exhibited heats of activation that in every case were independent of the temperature. Apparently the only essential difference between this latter work and the investigations of Bedford, was that Olson and Long kept their solutions distinctly acid in order to exclude side reactions.

Quite recently Nielsen (11) studied the alkaline saponifications of various ester ions in which the charge was progressively farther removed from the reaction position. No effect due to the position of the charge was observed.

Nielsen also performed a few simple experiments on the reactions of thiosulfate ion with bromosuccinate and β-bromopropionate ions. His procedure was simply to follow simultaneously both the rate of disappearance of thiosulfate and the rate of appearance of hydrogen ion for varying ratios of the reactants. He showed that the second-order constants for the bromosuccinate reaction exhibited a pronounced drift with time, as is also apparent in the original investigations of Bedford and coworkers. A few calculations given by Nielsen show that a combination of first- and second-order reactions, when treated as pure second order, could give salt effects of a sign opposite to that predicted by the Brönsted theory. He decided that an interpretation of the bromosuccinate and β-bromopropionate results necessitated an accurate restudy of these reactions, and concluded, "At present, therefore, it cannot be said that these reactions are clear-cut or a definite contradiction to the Brönsted theory."

As long ago as 1912 Holmberg (3) and Johansson (7) showed that bromosuccinate ion reacted in neutral solution to form a β-lactone,



Further work by Johansson and Hagman (8) showed that the formation of lactones is probably a common reaction for beta-substituted acids and is often concealed only by the high reactivity of such lactones. It was to avoid this lactone formation that Olson and Long, in the work mentioned above, maintained a high hydrogen-ion concentration. It therefore suggested itself to us that the anomalous results reported for the reaction of thiosulfate ion with bromosuccinate ion might be connected with this phenomenon.

This could be very simply tested by a method involving the use of optically active materials. Thus, from *l*-aspartic acid and from *l*-asparagine we can prepare *l*-bromosuccinic acid and its *l*-monoamide, $HOOCCBrHCH_2CONH_2$, respectively, by similar reactions. The properties of the amide are remarkably like those of the acid. They are both levorotatory and to about the same extent. In acid solution, they react bimolecularly with substituting agents at nearly the same rate to give optically active products having dextrorotation. When the solutions are neutralized and

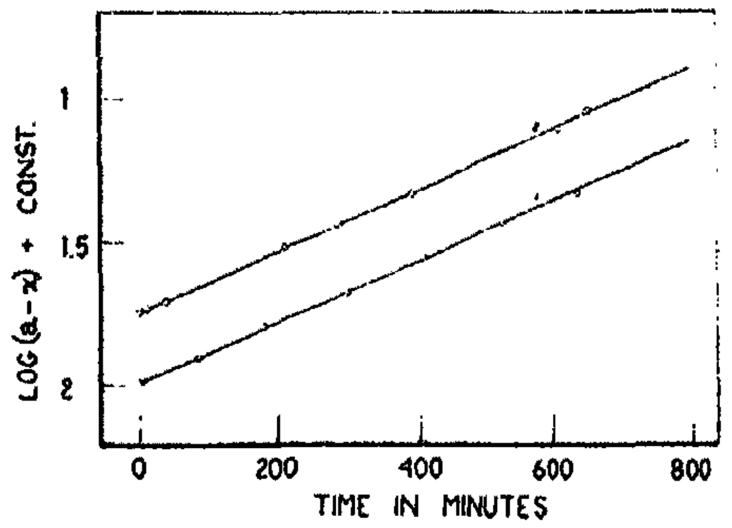


FIG. 1. Showing unimolecular character of reaction. Concentrations are 0.100 molal bromosuccinate ion and 0.1554 molal thiosulfate ion. For curve 1, which was obtained by titration of thiosulfate, logarithms of unreacted bromosuccinate have been plotted against the time. Curve 2 gives the plot of log $(\alpha_0 - \alpha)/(\alpha_0 - \alpha_\infty)$ against the time where α_0 and α_∞ are the initial and final polarimetric readings and α is the reading at time t.

TABLE 1

Reaction of l-bromosuccinamidate and thiosulfate at 40°C.

$S_2O_3^{--}$ = 0.200 molal; amide = 0.200 molal

TIME IN MINUTES	DEGREES ROTATION	BIMOLECULAR RATE CONSTANT
0	−4.80	
17	−4.58	0.0107
64	−4.01	0.0101
232	−2.80	0.0102
358	−2.17	0.0102
716	−1.10	0.0101
1312	−0.18	0.0109
1597	+0.01	0.0106
2202	+0.41	0.0115
2877	+0.66	0.0107
∞	+1.43*	0.0104 (Av.)

* Calculated.

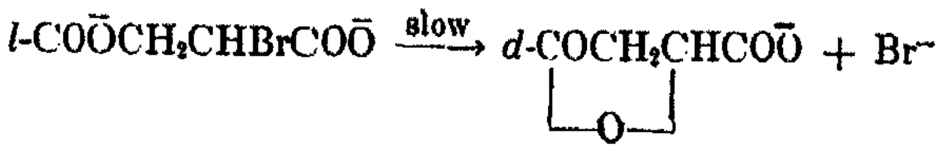
treated with thiosulfate ion, big differences appear. With the acid, the resulting thiosulfate compound shows a strong levorotation. The rate of reaction, measured either polarimetrically or by titration with iodine, is unimolecular. Figure 1 gives the results of a determination of this rate for concentrations of 0.100 molal bromosuccinate ion and 0.1554 molal thiosulfate ion. The amide, on the other hand, when reacting with thiosulfate ion, yields a dextrorotatory compound. The reaction is bimolecular as is shown in table 1, where we give the results for a polarimetric determination of the rate of this reaction at a temperature of 40°C. In addition, under comparable conditions, the reaction of the amide is many times slower than the reaction involving bromosuccinate ion.

The important distinction between the bromosuccinic acid and its beta amide that might lead to a different mechanism is the fact that, as has previously been shown by Holmberg (4), the amide is incapable of forming a lactone. Thus the reaction of this amide with thiosulfate ion is bimolecular and leads to a product whose rotation is of the opposite sign from that of the original acid, as would be expected from the ordinary process of direct substitution accompanied by inversion. The unimolecular character of the reaction involving the bromosuccinate ion and the fact that the rotation of the final product is of the same sign as that of the original bromosuccinic acid suggests very forcibly that the reaction takes place through the production of the lactonic ion as an intermediate.

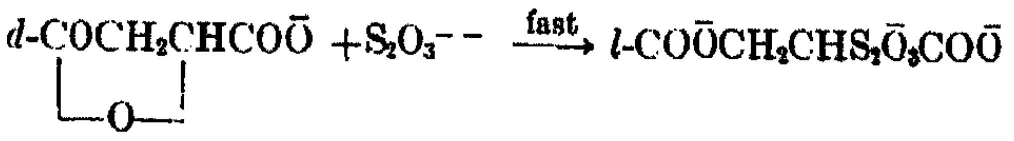
For the *l*-bromosuccinamide the reaction would then be

$$l\text{-}\mathrm{CO\bar{O}CH_2CHBrCONH_2} + \mathrm{S_2O_3}^{--} \rightarrow d\text{-}\mathrm{CO\bar{O}CH_2CHS_2\bar{O}_3CONH_2} + \mathrm{Br}^-$$

while for the *l*-bromosuccinate ion the reaction is very probably



$$l\text{-}\mathrm{CO\bar{O}CH_2CHBrCO\bar{O}} \xrightarrow{\text{slow}} d\text{-}\mathrm{COCH_2CHCO\bar{O}} + \mathrm{Br}^- \quad (1)$$



$$d\text{-}\mathrm{COCH_2CHCO\bar{O}} + \mathrm{S_2O_3}^{--} \xrightarrow{\text{fast}} l\text{-}\mathrm{CO\bar{O}CH_2CHS_2\bar{O}_3CO\bar{O}} \quad (2)$$

Here the order of the reaction would depend upon which is the rate-determining step, but the final product would always have a levorotation.

Still further evidence that the above mechanism is the correct one may be obtained by considering each of the two steps in detail. Step 1, the production of the lactone from the bromosuccinate, has been extensively investigated by Johansson (7, 8) and by Holmberg (5). Johansson followed the rate of production of the lactone by titrating the bromide ion with silver nitrate solution. For a 0.02 molal solution at 25°C. he found a unimolecular rate constant of 0.00240, a value which is in striking agreement with the rate constant given by the results shown in figure 1, which is 0.00245.

The *d*-β-propionolactonic acid which is formed from the *l*-bromosuccinate ion has never been isolated in a pure state, but in neutral or slightly acid solutions it is fairly stable. A concentrated solution of the lactone may be obtained by treating a solution of bromosuccinate ion with silver nitrate solution over a period of several hours. Precipitation with excess silver nitrate frees this solution from any malate or bromosuccinate ions. Finally, acidification, extraction with ether, and a reëxtraction with water gives an almost pure solution of the lactonic acid. An exact determination of the concentration of this somewhat unstable material is difficult, but it can be done with fair accuracy by titrating to neutrality, adding excess hydroxide ion to effect hydrolysis, and then back-titrating after the hydrolysis is complete.

If a solution of the optically active lactone is neutralized and treated with thiosulfate ion a rapid reaction takes place. Knowing, however, the initial rotation of the lactone, it is possible to follow the reaction polarimetrically. Table 2 gives the data for such a determination. The initial concentration of lactone was 0.0822 molal and that of the thiosulfate ion 0.1036 molal. It is obvious from these data that the reaction is bimolecular. Another run with the same concentration of lactone but with a thiosulfate concentration of 0.2 molal gave the slightly higher bimolecular constant of 1.12 as contrasted to 1.03. It is important to notice that the optical rotation of the product is strongly levorotatory just as was given by the mixture of bromosuccinate ion and thiosulfate ion. In addition the rate of the bimolecular reaction between the lactone and thiosulfate ion is fast enough so that step 1 in the postulated mechanism would be the rate-determining step, step 2 being simply a rapid follow reaction. Thus all the known facts are in accord with the postulated mechanism.

TABLE 2

Determination of rate for lactonate and thiosulfate ions at 25°C.

d-lactonate ion = 0.0822 molal; thiosulfate ion = 0.1036 molal

TIME IN MINUTES	DEGREES ROTATION	$\alpha_0 - \alpha$	BIMOLECULAR RATE CONSTANT
0	+1.32	0	
2.33	0.79	0.53	0.99
3.16	0.66	0.66	0.94
4.58	0.41	0.91	1.02
6.34	0.17	1.15	1.04
10.42	−0.19	1.51	1.02
14	0.40	1.72	1.02
18	0.62	1.94	1.09
26	0.85	2.17	1.07
34	1.01	2.31	1.06
∞	1.40	2.72	1.03 (Av.)

Since the qualitative investigations outlined above showed that the previously postulated bimolecular mechanism was wrong, we attempted to recalculate the rate constants assuming a unimolecular reaction, but published data were too fragmentary. We have, therefore, investigated the reaction between bromosuccinate ion and thiosulfate ion for various concentrations of the reactants and various ionic strengths at several temperatures. The reaction has been followed by a titration method and by a polarimetric method where feasible.

PREPARATION OF MATERIALS

The *l*-bromosuccinic acid was prepared from *l*-aspartic acid according to the method described by Holmberg (6). The *l*-bromosuccin monamide was made by a similar method from *l*-asparagine. Since we could prepare the optically active bromosuccinic acid in a very pure state, we used this material for the titrations as well as for the polarimetric determinations.

The standard solutions were made up with the usual precautions. Twice recrystallized potassium iodate was used as the primary standard for determining the concentration of the thiosulfate solutions.

The usual buffer solution was 1/30 molal disodium phosphate and 1/30 molal potassium dihydrogen phosphate, which had a pH of 6.8. For a few runs, however, a mixture of these two substances giving a pH of 6.4 was used.

EXPERIMENTAL METHODS

In making a run the bromosuccinic acid was weighed into a volumetric flask, dissolved in water, and enough sodium hydroxide solution pipetted in to just neutralize it. Then the proper amount of sodium thiosulfate solution was pipetted in, buffer solution, if used, was added, and the solution brought to the proper volume. For the work at 25°C. the time of addition of sodium hydroxide was taken as zero time. For runs at other temperatures, however, the solutions were allowed to come to temperature before the final volume adjustment was made, and the time of the first sample was taken as zero time. Since the reaction is unimolecular, this procedure was satisfactory. For all runs the unit of time is the minute.

When titrating thiosulfate ion, samples were removed from the mixture as the reaction progressed and pipetted onto crushed ice to stop the reaction. For the bromide ion, which was determined by the Volhard method, the samples were pipetted into known amounts of silver nitrate solution containing excess nitric acid. The reaction has been followed in all cases up to at least 65 per cent completion. Titrations were performed with calibrated volumetric burets. For all of the dilute solution titrations corrections were made for the indicator constants. The thermostat temperatures, which are accurate to ±0.01°C., were measured by thermometers that had been calibrated by the Bureau of Standards.

EXPERIMENTAL RESULTS

In table 3 and figure 2 we have collected the data for the results at 25°C. for 0.1 molal concentrations of bromosuccinate ion. The straight lines given by the logarithmic plots show immediately that the reaction is unimolecular; this is confirmed by the small changes in the slopes shown for the different concentrations of thiosulfate. The rate of disappearance of thiosulfate ion is thus determined solely by the rate of production of the lactonic ion. Fortunately the rate of reaction of the lactone with thiosulfate ion is so fast that in these concentrated solutions we can neglect the amount of lactone which disappears, either by hydrolysis of the lactone or by the re-formation of bromosuccinate ion through reaction with bromide ion. This has been confirmed by a quantitative determination of the rates of the three reactions which are competing for the lactone. The specific rate constant for the bimolecular reaction between thiosulfate and lactone

TABLE 3

Data at 25°C. for 0.1 molal bromosuccinate ion

RUN	CONCENTRATION OF THIOSULFATE	ADDED SALT	μ	UNIMOLECULAR RATE CONSTANT $\times 10^3$
	molal			
1	0.1513	—	0.754	2.471
2	0.1513	—	0.754	2.474
3	0.1513	—	0.754	2.484
4	0.1554	Buffer	0.808	2.454
5	0.1554	(Polarimetric)	0.766	2.425
6	0.400	(Polarimetric)	1.500	2.58
7	0.1513	0.9 *M* KNO_3	1.654	3.389

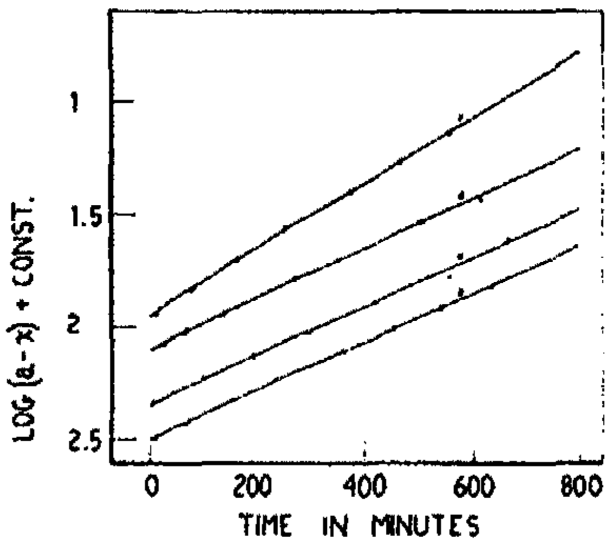


FIG. 2. Logarithmic plots for 0.1 molal bromosuccinate ion and varying concentrations of thiosulfate ion at 25°C. The numbers of the curves correspond to the numbers of the runs as given in table 3.

has previously been shown to be 1.03; for the bimolecular reaction between lactone and bromide ion the specific rate is approximately 0.001. At a pH of 6.4 the unimolecular rate of reaction of the lactone with water as determined polarimetrically in a buffered solution is 0.000413. The latter two rates are from unpublished work in this laboratory.

TABLE 4

Polarimetric determination of rate

Bromosuccinate ion = 0.1 molal; thiosulfate ion = 0.1554 molal

TIME IN MINUTES	DEGREES ROTATION	NET READING	$k = \frac{2.303}{t} \log \frac{\alpha_0 - \alpha}{\alpha_0 - \alpha_\infty}$
0	−3.00	−1.11	
11	2.97	1.08	
37	2.91	1.02	0.00238
212	2.55	0.66	0.00245
287	2.44	0.55	0.00245
390	2.32	0.43	0.00243
611	2.145	0.255	0.00241
655	2.11	0.22	0.002425 (Av.)
∞	1.89*		

* Calculated.

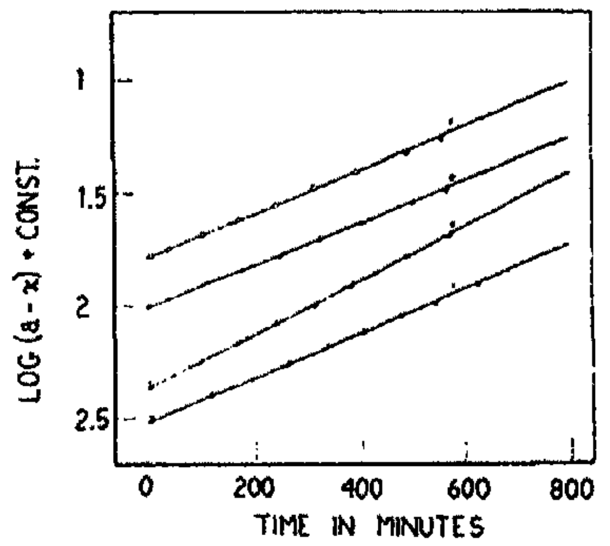


FIG. 3. Logarithmic plots for 0.04 molal bromosuccinate ion at 25°C. The numbers refer to the runs given in table 5. Curves 1, 4, and 6 show a slight induction effect which curve 7, obtained by titrating the bromide ion, does not show.

In table 4 we give detailed data for the polarimetric determination of the rate of this reaction, which is listed as run 5 in table 3. In this run we measure not only the appearance of the *l*-thiosuccinate ion but also the disappearance of the *l*-bromosuccinate ion. Nevertheless the specific rate constant which we obtain from these data agrees within the limits of experimental error with the results obtained from the titration method, which measures the disappearance of thiosulfate ion only. This agreement is shown in figure 1, which gave the logarithmic plots for two runs having the same concentrations of bromosuccinate ion and thiosulfate ion but followed polarimetrically in one case and by titration in the other. The rate constant from the polarimetric method is less accurate than that for the titration method, because of some uncertainty in the value of the molal rotation of the *l*-thiosuccinate ion.

Runs in which the bromosuccinate ion is 0.04 molal are listed in table 5 and plotted in figure 3. A discussion of the changes exhibited by the rate constants as the ionic strength is changed will be postponed until a later paragraph. The most interesting detail in these 0.04 molal runs is the induction period, which is apparent at the beginning of those runs in which thiosulfate was determined, as shown by the log plots of figure 3. Thus the bimolecular reaction between lactone and thiosulfate ion is, at this concentration, slow enough compared to the unimolecular formation of the lactone so that an appreciable concentration of it must be built up to reach a steady state.

TABLE 5

0.04 molal bromosuccinate ion at 25°C.

RUN	CONCENTRATION OF THIOSULFATE	ADDED SALT	μ	$k \times 10^{3}$
	molal			
1	0.0605		0.302	2.257
2	0.0605		0.302	2.250
3	0.0605		0.302	2.230
4	0.0605	0.45 *M* KNO_3	0.754	2.746
5	0.0605	0.45 *M* KNO_3	0.754	2.770
6	0.0605	0.113 *M* $MgSO_4$	0.754	2.150
7		(Volhard titration) Buffer	0.147	2.285

TABLE 6

0.01 molal bromosuccinate ion at 25°C.

RUN	CONCENTRATION OF THIOSULFATE	ADDED SALT	μ	$k \times 10^{3}$
	molal			
1	0.01513		0.0754	1.66
2	0.01513		0.0754	1.69
3	0.01506		0.0752	1.63
4	0.01497	Buffer	0.157	1.65
5	0.01513	0.676 *M* KNO_3	0.752	2.39

This induction period becomes quite prominent in the runs listed in table 6, where the concentration of bromosuccinate ion is 0.01 molal, indicating that the lactone now forms an appreciable fraction of the material which has not yet reacted with the thiosulfate ion. Figure 4 is a plot of these results. At these low concentrations we still can neglect the reaction of bromide ion with the lactone, but we no longer can neglect the hydrolysis of the lactone. This has been shown by titration of the hydrogen ion produced during the course of the reaction, as given in table 7. The increase in hydrogen ion is sufficient to account for the falling off in the rate towards the end of the reaction, for not only does some of the lactone disappear by hydrolysis but the hydrogen ion produced decreases the rate of production of the lactone. To check this, runs at these concentrations were repeated using buffered solutions. Curve 4 in figure 4 shows that this buffering was sufficient to correct most of this falling off.

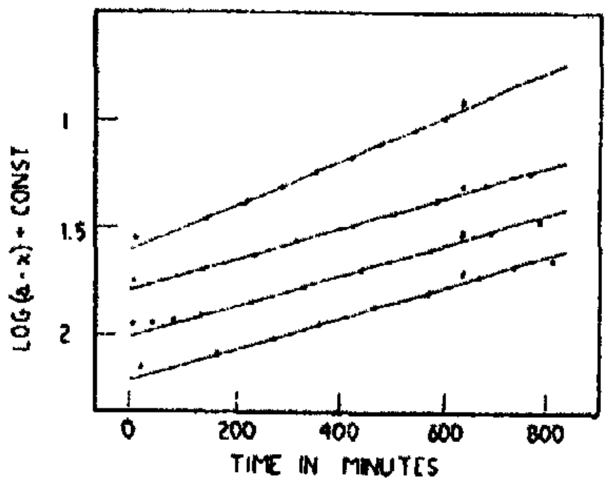


FIG. 4. Results for 0.01 molal bromosuccinate as determined by titration of the thiosulfate ion. Curve 3 shows nicely the large induction effect.

TABLE 7

Comparison of reaction and hydrogen ion production at 37.39°C.

Bromosuccinate ion = 0.01 molal; thiosulfate ion = 0.01513 molal

TIME IN MINUTES	EQUIVALENTS OF $S_2O_3^{--}$ USED × 10^3	EQUIVALENTS OF H^+ PRODUCED × 10^3
0	0.05	0.01
28	1.08	0.045
53	2.42	0.13
82	3.83	0.22
109	4.93	0.33
134	5.76	0.38
157	6.41	0.475
240		0.525

While the results in buffered solutions give a fair unimolecular rate, they nevertheless do not give the true rate of formation of the lactone. One reason is that some of the lactone is disappearing by a hydrolysis reaction.

Still more important is the fact that, even without hydrolysis, the relatively large concentration of lactone causes the amount of thiosulfate that has disappeared at any time, no longer to be equal to the amount of bromosuccinate ion that has reacted. Because of this, calculations of a unimolecular rate constant from the amount of thiosulfate ion that has disappeared are erroneous. *It is important to realize that, without a knowledge of the concentration of the lactone, the only specific rate that can be measured in this work with thiosulfate and bromosuccinate ions is the production of the lactone from the bromosuccinate.* This coincides with the disappearance of thiosulfate ion in the more concentrated solutions, but no longer even approaches it in the dilute solutions. However, as we mentioned earlier, the rate of this lactone production can be measured in a more direct fashion by titrating the bromide ion that is produced. This was the method used by Johansson and later by Ölander (12), when he studied the hydrolysis of bromosuccinic acid. In a later paragraph we give the results obtained by these investigators and show the excellent agreement between their results and those that we have obtained for the more concentrated solutions of bromosuccinate and thiosulfate ions.

TABLE 8

Rates as determined by bromide-ion titration

CONCENTRATION OF BROMOSUCCINATE	ADDED SALT	μ	$k \times 10^3$
molal			
0.01	Buffer	0.0633	2.260
0.01	Buffer	0.0633	2.278
0.004	Buffer	0.0387	2.245

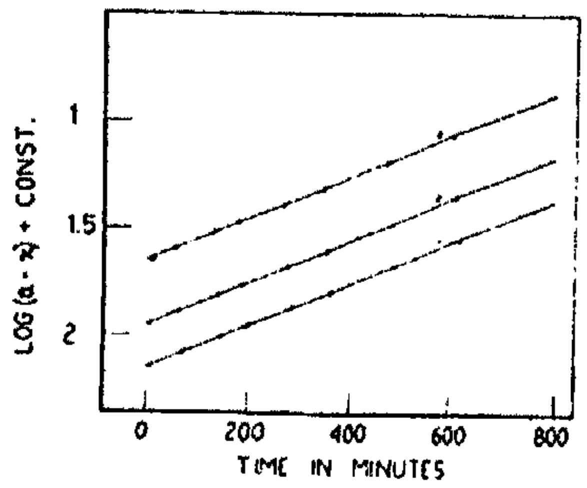


FIG. 5. Results for 0.01 and 0.004 molal bromosuccinate ion as determined by titration of the bromide ion. The numbers of the curves correspond to those of the runs listed in table 8.

In order to obtain more satisfactory data in the dilute solution region, we also made a few determinations of the rate of production of the lactone in buffered solutions by titrating the bromide ion that is formed. The results that were obtained for concentrations of 0.01 and 0.004 molal bromosuccinate ion are collected in table 8 and plotted in figure 5. An additional run was made with 0.04 molal bromosuccinate ion, but the results from it have been given in an earlier table. The most striking feature of these results is the great discrepancy between the rate constants obtained by this method and those obtained from the dilute solutions by titration of thiosulfate ion. It is interesting to note that, as would be expected, the induction effect disappears completely when the reaction is followed by titrating the bromide ion.

TABLE 9

Data for heat of activation

Bromosuccinate ion = 0.1 molal

RUN	CONCENTRATION OF THIOSULFATE	ADDED SALT	μ	$k \times 10^3$
		12.46°C.		
	molal			
1	0.1513		0.754	0.3483
2	0.1513		0.754	0.3488
3	0.1513		0.754	0.3494
4	0.1513	0.9 *M* KNO_3	1.654	0.5008
		37.39°C.		
1	0.1513		0.754	14.65
2	0.1513		0.754	14.60
3	0.1513		0.754	14.74
4	0.1513	0.9 *M* KNO_3	1.654	19.20

HEAT OF ACTIVATION

The heat of activation for the production of lactone and bromide ion in 0.02 molal solution was calculated by Ölander (12) from measurements at 25° and 50°C. to be 26,600 calories. In table 9 we give data for runs with 0.1 molal bromosuccinate ion at 12.46° and 37.39°C. The determinations were again made by titrating the thiosulfate ion. From these results and from those at 25°C., listed in table 4, we calculate the heats of activation given in table 10. The almost exact agreement between the values for the two temperature intervals is, of course, fortuitous. However, it is evident that there is no noticeable temperature coefficient of the heat of activation over this temperature range, a remarkable contrast to the results obtained by Bedford (1). In addition our value of 26,390 calories agrees within the probable experimental error with the result obtained by Ölander, who followed the reaction by a very different method.

TABLE 10

Heats of activation

Bromosuccinate ion = 0.1 molal; thiosulfate ion = 0.1513 molal

TEMPERATURE	$k \times 10^3$	ΔE
°C.		*calories*
12.46	0.3488	26,400
25.00	2.476	26,380
37.39	14.66	

0.9 *M* KNO_3 added

TEMPERATURE	$k \times 10^3$	ΔE
12.46	0.5008	25,770
25.00	3.389	25,740
37.39	19.20	

TABLE 11

Salt effects for lactone formation at 25°C.

METHOD OF INVESTIGATION	CONCENTRATION OF BROMOSUCCINATE	CONCENTRATION OF THIOSULFATE	ADDED SALT	$\sqrt{\mu}$	$k \times 10^3$
	molal	*molal*			
Polarimetric............	0.10	0.400		1.224	2.58
Thiosulfate titration....	0.10	0.1513		0.867	2.48
	0.04	0.0605		0.547	2.25
Bromide titration.......	0.04		Buffer	0.383	2.28
	0.01		Buffer	0.251	2.27
	0.004		Buffer	0.197	2.25
Thiosulfate titration....	0.10	0.1513	0.9 *M* KNO_3	1.285	3.39
	0.04	0.0605	0.425 *M* KNO_3	0.867	2.76
	0.04	0.0605	0.113 *M* $MgSO_4$	0.867	2.15
Bromide titration.......	0.02		Buffer	0.312	2.29*
Bromide titration.......	0.02			0.245	2.40†
	0.02		0.11 *M* $NaNO_3$	0.412	2.47†
	0.04		0.07 *M* $Ba(NO_3)_2$	0.608	2.47†

* Ölander, pH = 9.2.

† Johansson, pH = 7. The temperature scale may have been different here, since all Johansson's results seem slightly high.

In the presence of a large concentration of potassium nitrate, there is a lowering of the heat of activation which is greater than the experimental error.

SALT EFFECT

In table 11 we have collected data from the previous tables which are pertinent to a discussion of salt effects. We have also included some determinations of the rate of lactone production that were made by Ölander and Johansson. The data collected here represent experiments performed by three sets of investigators and obtained by three different types of observation. The changes in ionic strength have been produced by increasing the concentrations of the reactants, by adding phosphate and borate buffers, and by adding such varied salts as potassium nitrate, sodium nitrate, magnesium sulfate, and barium nitrate.

The two results given in table 11, where the ionic strength was increased by using a large amount of potassium nitrate, both show abnormally large specific rates. When, however, the magnesium sulfate was employed to obtain the same ionic strength, no such increase in rate was obtained. Seemingly in these concentrated solutions the rôle of the potassium nitrate is no longer that of an inert salt, since not only is the rate increased far beyond what would be expected, but, as was previously shown in table 10, the heat of activation is definitely lowered. If we exclude these two runs, we find that the specific rate shows a variation of only about 10 per cent under these widely different experimental conditions, a result which is definitely in accord with the Brönsted theory.

SUMMARY

It has been shown by kinetic and polarimetric methods that, in the reaction between bromosuccinate ion and thiosulfate ion in neutral solution, the initial and rate-determining step is the unimolecular production of a β-lactone.

The heat of activation for this step is 26,400 calories. The heat of activation in the temperature range from 12.5° to 50°C. is independent of the temperature.

An increase in the ionic strength, whether by an increase in the concentrations of the reactants or by the addition of neutral salt, is almost without effect, in complete accord with the predictions of the Brönsted theory.

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THE REACTIONS OF OXYGEN AND HYDROGEN AT LOW PRESSURES[1]

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The oxygen molecule is unique among the common elementary diatomic molecules. Chemists had always considered oxygen as a bivalent atom, but when they began to think in terms of the Lewis theory of valence this fact of paramagnetism naturally caused doubt as to whether the atoms in the oxygen molecule were linked by a double bond. Attempts were made to argue from the reactivity of the oxygen molecule as to the nature of the bonding. It never became necessary to point out that reactivity depends on factors which are not directly related to the strength of the bonding in a molecule, because the proponents of the argument could not agree as to the degree of reactivity to be attributed to the oxygen molecule. The reason for this difference of opinion lies, of course, in the erratic behavior of oxygen. If oxygen supported combustion with the same readiness that it supports respiration, all dry organic matter would doubtlessly be consumed in a short time. The reason for this erratic behavior is certainly to be found in the fact that the lowest energy state of the oxygen molecule is a triplet state, whereas the great majority of other molecules, including, of course, the products of combustion, exist in singlet states. The fact that the lowest energy state of the atom is also a triplet state undoubtedly adds to the peculiarities of the behavior of oxygen. Any reaction involving a change in multiplicity in the atom may be expected to proceed much more slowly than it would were the case otherwise. The factor is 10^{-3} or less, so that such reactions may be regarded in many cases as not taking place at all.

It had occurred to the author and doubtless to many others that the explanation of the activity of oxygen in supporting respiration was to be sought in the paramagnetic character of the iron in hemoglobin. Recent work by Pauling and Coryell (6) appears to confirm this idea. Hemoglobin is paramagnetic, while the oxygen compound is diamagnetic.

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Another example of a rapid reaction, involving in this case the oxygen atom, is the reaction

$$O + NO_2 = NO + O_2$$

which was studied by Spealman and Rodebush (9). Here there is presumably no change in multiplicity, and a rapid reaction is to be anticipated. Aside from these reactions with molecules known to be paramagnetic, rapid reactions involving oxygen are likely to be rare. The direct oxidation of unsaturated molecules by addition of molecular oxygen is not a probable reaction. Most oxidations, as, for example, combustion reactions, are likely to involve chain reactions. These chains will presumably produce active species such as atoms or radicals. At higher temperatures, these exothermic reactions are likely to be rapid for various reasons, one of which is that oxygen atoms are likely to be produced in the higher energy singlet states.

Since we can produce the various active species of atoms and radicals in the laboratory by photochemical activation or electronic bombardment, it becomes possible to study the separate steps of the hypothetical chain reactions. In this paper will be reported some conclusions based on the study of the various activated species of oxygen and hydrogen produced by the electrodeless discharge at low pressures. This method of study has two advantages over the method of photochemical activation at higher pressures. It is possible to produce larger quantities of atoms or other activated species, and the mechanism of a homogeneous reaction can be established with certainty because of the infrequency of triple collision. There is one serious disadvantage in that seldom, and perhaps never, can the possibility of reactions occurring on the walls be entirely eliminated. Reactions on the walls will not take place to a considerable extent, however, unless one of the reactants is strongly adsorbed. But one who works at low pressures becomes more and more convinced of the truth of the old dictum that gaseous reactions occur only at surfaces. Certainly the homogeneous mechanisms which have been established for gaseous reactions are few in number.

One may, of course, argue that a study of reactions at low pressures will not give much information about what happens at high pressures. This is true to some extent, but negative evidence cannot be disregarded. On account of the great increase in the number of triple collisions, simple mechanisms are less likely to play a rôle at higher pressures; certainly not unless they are sufficiently rapid to be observed at low pressures.

The technique employed in obtaining the results discussed here consists in dissociating a gas or mixture of gases in a bulb by means of an electrodeless discharge. The dissociation products are pumped rapidly through a series of traps cooled with dry ice or liquid air. If it is desired to prolong the time for reaction in the gaseous phase, a 5-liter flask is interposed between the discharge and traps. This does not greatly increase the surface area in contact with the gas, and does greatly increase the ratio of collisions in the gas phase to collisions with the walls. The pressure varies from 0.3 to 0.7 mm., and the time required for the gas to pass through the flask may be as much as thirty seconds.

The factors influencing dissociation are not well understood. It is known that the presence of water tends to reduce the catalytic activity of the walls in causing the recombination of hydrogen atoms, but this is not true for all atoms (8). Definite evidence has been obtained in this laboratory that impurities increase the amount of dissociation. It is well known that pure nitrogen does not give an afterglow, but if oxygen, water, or hydrogen is present in small amounts, an afterglow is obtained. A brilliant afterglow can be obtained with a small amount of hydrogen. Recent work by Rabinowitch and Wood (7) suggests the explanation of this phenomenon. When a molecule is excited by electron bombardment, it is likely to return to its normal state by radiating the acquired energy. Collision with another molecule may prevent this by transforming the molecule to a metastable or repulsive state. For reasons which may be surmised, foreign gas molecules may be more effective than molecules of the same kind. The whole subject requires further investigations.

THE REACTION OF OXYGEN ATOMS WITH HYDROGEN

Oxygen atoms do not react with molecular hydrogen at low pressures. Exhaustive experiments fail to show any trace of reaction, either in the gas phase or on the walls of the liquid-air trap. What the experiments actually prove is that the recombination of oxygen atoms is a much more rapid reaction than any reaction with hydrogen. The recombination of oxgyen atoms does not involve any change in multiplicity, but it requires triple collisions and is not particularly rapid. There is no evidence of catalytic activity by the walls under ordinary conditions.

The reaction

$$O + H_2 = H_2O$$

is not to be expected, both because of the large heat of activation and because of the change in multiplicity. The reaction

$$O + H_2 = OH + H$$

might, however, be expected to take place. It is slightly exothermic, and its failure to take place must be due to a fairly large heat of activation. If it did take place, regardless of what might happen to the hydroxyl, the hydrogen atoms so formed should react with oxygen molecules to form hydrogen peroxide and water, and no evidence for this reaction could be obtained. Oxygen atoms can undoubtedly be made to react with hydrogen at higher pressures, but it seems doubtful if a simple bimolecular mechanism will account for the results in the pressure region, where triple collisions are relatively frequent. The probability of reaction in a triple collision may, of course, be very different from that for a double collision.

Oxygen atoms will not react with hydrogen atoms in a double collision. The possibility of their reaction on the walls of a liquid-air trap will be discussed later.

THE REACTION OF HYDROGEN ATOMS WITH OXYGEN MOLECULES

Hydrogen atoms react with oxygen molecules to form hydrogen peroxide and water, the relative amounts varying widely with the experimental conditions. That there is a primary gas-phase reaction here is almost certainly demonstrated by our experiments, in which the 5-liter flask is interposed in the system. There is evidence for the rapid disappearance of hydrogen atoms. Of course, there is possibility of reaction on the walls of the flask, especially if a triple collision reaction is involved. It is difficult to decide what the initial step may be, in view of the apparent rapidity of the reaction. The bimolecular mechanism

$$H + O_2 = OH + O$$

is doubtful for various reasons, but primarily because it is probably endothermic by 10 or more large calories. While the heat of formation of hydroxyl is not known with certainty, a number of observers believe it to be about 105 cal. Evidence will be presented later which indicates that hydroxyl is not a primary product in the reaction of hydrogen atoms with molecular oxygen.

The second possible mechanism is

$$H + O_2 = HO_2$$

This mechanism should involve a triple collision. It is very difficult to prove by experimental methods that a mechanism involving triple collisions is taking place.

THE FORMATION OF HYDROGEN PEROXIDE

Hydrogen peroxide is formed in large amounts in two ways,—when water vapor is passed through the discharge or when hydrogen atoms are mixed with molecular oxygen. In order to obtain hydrogen peroxide, it is necessary to use a liquid-air trap. A dry-ice trap will condense either water or hydrogen peroxide if either is present in the vapor, but in the experiments reported here no appreciable quantity of hydrogen peroxide was ever obtained without the use of a liquid-air trap. We may, therefore, suppose that the final step in the formation of hydrogen peroxide takes place in the walls of the liquid-air trap. It is useless, therefore, to speculate as to the mechanism of these wall reactions. We can only inquire as to what the activated species may be that enter the trap.

When water vapor is passed through the electrodeless discharge, and immediately thereafter through the liquid-air trap, fairly consistent results are obtained. About 45 per cent of the water molecules are converted to hydrogen peroxide, 45 per cent are condensed as water, and the remainder escape as hydrogen and oxygen in the molecular state.

The first step in the dissociation of water is probably the formation of hydrogen atoms and hydroxyl radicals. There is reason to believe that the dissociation may be nearly complete, since, under some circumstances, very little of anything is condensed in a dry-ice trap. A corollary of this observation is that neither hydrogen atoms, oxygen atoms, nor hydroxyl radicals are condensed by a trap at −80°C. We must, of course, believe that some of the hydroxyls are further dissociated into hydrogen and oxygen by the discharge, but we shall present evidence later that this dissociation does not take place to a very great extent, and is probably about equal to the amount of oxygen passing through the trap as molecular oxygen.

If the tube leading from the discharge bulb to the trap becomes warm, or a silver foil is introduced into the tube, no peroxide is obtained, and the yield of water is increased. But if a 5-liter flask is interposed, the yield of water remains unchanged, very little peroxide is obtained, and a large amount of hydrogen and oxygen escape from the trap in the molecular form. The first two results are explained by assuming that on the surface of the warm tube or the silver foil the reactions

$$\begin{aligned} H + OH &= H_2O \\ OH + OH &= H_2O + O \\ O + O &= O_2 \\ H + H &= H_2 \end{aligned}$$

are taking place. The last phenomenon could be explained if the mechanism proposed by Bonhoeffer and Pearson (2) as a vapor-phase reaction

$$OH + OH = H_2O + O$$

occurs.

As we shall show later, there is no evidence for the presence of oxygen atoms in the flask. We shall, therefore, assume that the reaction above takes place only on the walls of the flask, and that the adsorbed atoms of oxygen recombine before desorption. This would account for the yield of water remaining substantially unchanged.

We may summarize the results of the observations on water vapor by saying that there is no evidence for any gas-phase reactions. The principal products of the discharge appear to be hydrogen atoms and hydroxyl, and there is no reason to suppose that the direct condensation of these might not yield hydrogen peroxide and water. Geib (3) has suggested other possible mechanisms, and these may very well occur, but they presuppose, in most cases at least, rapid gas-phase reactions. The condensation of oxygen atoms and hydrogen atoms in the liquid-air trap may produce hydrogen peroxide, but when one allows for the considerable loss of molecular oxygen as such, it does not appear that this reaction can account for the major part of the peroxide formation.

The evidence in regard to hydroxyl still remains wholly negative. It is the most elusive radical in inorganic chemistry, and no one who has spent much time attempting to pin down any particular rôle on this radical would be dogmatic about his conclusions. Jackson (4) has shown that carbon monoxide is oxidized by something in water vapor from a discharge that is not removed by a platinum surface. It is known, of course, that atomic oxygen is not destroyed effectively by platinum. The reaction

$$O + CO = CO_2$$

is a forbidden reaction in the vapor phase, but might, of course, take place on the walls of the vessel. On the other hand, oxygen atoms were shown not to oxidize carbon monoxide, so that Jackson's evidence falls into the same class with the other evidence reviewed here. In the absence of evidence to the contrary or an alternative explanation, one must attribute an important rôle in these reactions to hydroxyl.

THE DISCHARGE IN MIXED GASES

The primary products obtained on passing a mixture of hydrogen and oxygen through the discharge are certainly hydrogen atoms and oxygen atoms.

Since the oxygen atoms have been shown not to react with hydrogen (except possibly in the liquid-air trap), one might predict that a discharge in mixed gases would produce the same reactions as are produced by the introduction of hydrogen atoms into molecular oxygen. This prediction is, in the main, confirmed. Since hydrogen peroxide may be produced in considerable amounts in mixed gases, we have studied the reactions in this system carefully with the idea of contrasting the behavior with that of water vapor. In doing this, we reasoned that, whereas the water vapor from the discharge contained large amounts of hydroxyl and relatively few oxygen atoms, in a mixture of hydrogen and oxygen the active species must be chiefly hydrogen and oxygen with relatively small amounts of hydroxyl. The mechanism of the reactions to form hydrogen peroxide should be different in the two cases, and the behavior should, therefore, be different. The results obtained appear to substantiate this view.

Hydrogen and oxygen were mixed in the proportions in which they exist in water and passed through the discharge. The yield of peroxide is extremely variable,—in some cases very small. In these cases, however, there was evidence of catalytic activity on the walls of the vessel, as shown by a rise in temperature. A low yield of peroxide was not accompanied by a corresponding increase in water formed, but rather by an increased loss of hydrogen and oxygen in the molecular state. One may, therefore, disregard those runs in which low yields of peroxide were obtained. The runs in which relatively high yields of peroxide resulted on the other hand indicate that the catalytic activity of the walls was at a minimum, and these runs must, therefore, be taken at their face value.

The maximum conversion to peroxide obtained was about 37 per cent, calculated on the basis of the reaction

$$2H_2 + O_2 = H_2O_2 + H_2$$

in order to be comparable to the results on water vapor. This may be taken as the result when the catalytic activity was at a minimum. The loss of oxygen and hydrogen in molecular form was correspondingly larger than with water vapor running from 20 to 30 per cent. On the other hand, if a 5-liter flask is interposed in the system, the peroxide yield is not greatly reduced as in the case of water vapor, but falls to about 27 per cent, conversion being on the same basis as before. This behavior alone appears to establish a fundamental difference in the reaction mechanism in the two cases.

Another test which resulted in a markedly different behavior was made by introducing a piece of silver foil into the system. The peroxide yield dropped to zero in every case, but with water vapor, as has already been stated, the yield of water increased, while with the mixed gases, the result depended upon the location of the foil. If placed near the discharge, a large yield of water was obtained, which can probably be explained as resulting from the reactions of atoms of one or both elements on the surface of the foil. When the foil was placed at the exit of the 5-liter reaction chamber, loss of oxygen and nitrogen in the molecular form increased to 65 per cent of the total.

THE PERCENTAGE OF OXYGEN ATOMS IN THE DISCHARGE

Recently Spealman and Rodebush (9) have investigated a very sensitive test for oxygen atoms. If nitric oxide is mixed with atomic oxygen, a brilliant greenish-white luminescence is obtained, which has apparently been called by some observers the "oxygen" afterglow, as distinguished from the nitrogen afterglow, which is an entirely different phenomenon. The mechanism of this reaction is the formation of a nitrogen dioxide molecule, presumably by a triple collision in an excited state. The radiation results from the return of the molecule to its normal state.

The nitric oxide was introduced into the exit end of the 5-liter reaction chamber and allowed to diffuse back against the gas flow. With the mixed gases, a quite intense glow was obtained which extended one-third to one-half of the way across the flask. With water vapor, the glow was less intense, and did not extend very far into the reaction chamber. Since we know from previous work that not more than about 30 per cent of the oxygen is dissociated into atoms, it seems evident that not more than 10 to 15 per cent of the water is completely dissociated, and the oxygen atoms from this dissociation disappear very rapidly. The absence of oxygen atoms in the reaction chamber is evidence against the occurrence of the reaction

$$OH + OH = H_2O + O$$

in the gas phase.

THE HO_2 MOLECULE

We shall finally consider the evidence for the existence of the HO_2 molecule, which has been proposed by Marshall, Bates (1), and others. The evidence is that in the mixed gases the mechanism for the formation of peroxide is different in some step, at least, from that in the water vapor discharge. When the 5-liter reaction chamber is in the system, about thirty seconds is required for the gases to pass from the discharge to the trap. All of the atoms must have certainly recombined in this time, and according to the evidence of Oldenberg (5) any hydroxyl present will have disappeared. No peroxide is present as such. However some active species is present, having a life period of thirty seconds or more, which will form peroxide in a liquid-air trap, but which is decomposed into the original elements by silver foil. The species which behaves in this way must have a much longer life period than a hydrogen or oxygen atom, but must still be very reactive. In the absence of any other possibility, one must consider the possibility of an HO_2 complex. The formation of this complex should require a triple collision, but our results indicate that the reaction is relatively rapid as compared with the recombination of hydrogen atoms. This result is in agreement with the observations of other investigators.

One concludes from the foregoing discussion that no special emphasis should be placed on the non-occurrence of reactions of oxygen with hydrogen, involving a change in multiplicity, since it has not been possible to prove that any homogeneous bimolecular mechanism, involving oxygen and hydrogen, takes place at low pressures. The reaction between hydrogen atoms and oxygen molecules, while relatively rapid, certainly requires further study.

The discussion in this paper has been restricted to results obtained in this laboratory. This is not because the author is not aware of a large amount of significant work that has been done elsewhere. He has hesitated to include a discussion of the results from other laboratories because of the uncertainty that must always exist as to the comparability of experimental conditions.

The conclusions expressed here are based upon a very large amount of data obtained in this laboratory, chiefly by Mr. C. W. J. Wende and Dr. R. W. Campbell. The detailed report of these experiments will be published elsewhere.

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THE ABSORPTION SPECTRUM AS A TEST FOR FREE RADICALS[1]

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The purpose of a group of experiments being carried through at the Physics Laboratory of Harvard University is to apply to chemical analysis the absorption spectra of free radicals in gases. In the present paper, after a brief report of results, the advantages and the limitations of the method will be discussed.

Since no characteristic chemical test was known for free OH radicals, they were the first object of investigation. Their absorption spectrum had been observed by Bonhoeffer and Reichardt in thermally dissociated water vapor, but only with a small resolving power. In order to make the absorption spectrum as sensitive a test as possible, single lines of the band had to be observed. For this purpose practically the highest resolving power obtainable at the spectroscopic laboratory was needed. The bands had been analyzed in emission so thoroughly and their intensity rules were known so well theoretically (5) that the single lines which were expected to be most intense in absorption could be predicted quite accurately. They are not identical with the lines which are most intense in emission (7).

If the absorption spectrum is taken in snapshots of 1/100 sec., for example, a stage of a rapidly progressing reaction can be analyzed. As 1/100 sec. is an insufficient exposure for the continuous background, photographed with high dispersion, the reaction and snapshot must be repeated several thousand times.

In an electric discharge through water vapor of less than 1 mm. or a few millimeters pressure, the concentration of free OH is so high that the absorption spectrum can well be observed. During the discharge proper the chemical processes might be different from reactions studied in chemistry, since positive and negative ions are present. As it was the aim to analyze processes which would be of interest to the chemist, the spectra were taken after interrupting the discharge, when the ionization was

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[1] Presented at the Symposium on Molecular Structure, held at Princeton University, Princeton, New Jersey, December 31, 1936 to January 2, 1937, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society.

known to disappear in a comparatively short time. The OH radicals could be traced through 0.4 sec. after interrupting the discharge.

The OH radicals were consumed by a reaction which probably formed either water or hydrogen peroxide. The most probable reactions were

$$OH + H + M \rightarrow H_2O + M \qquad (1)$$
$$OH + OH + M \rightarrow H_2O_2 + M \qquad (2)$$
$$OH + OH \rightarrow H_2O + O \qquad (3)$$

In these reactions it was presupposed that the combination of two particles (reactions 1 or 2) requires a triple collision.

First, the order of the reaction consuming OH had to be determined. This was done by comparing the rate for the same concentration of OH and varying the total pressure of water or of the added helium. The experiments were largely carried through by Dr. A. A. Frost. They were based on the following consideration: each branch of a band shows rotational lines, the relative intensities of which are determined by the temperature distribution of energy over the quantized rotation of OH. One therefore computes from the constants of the molecule and the temperature that, for example, the most intense line (quantum number 3 1/2) and a distant fainter line (quantum number 7 1/2) represent concentrations of OH with the ratio 1:5. Consequently the rotational lines can be used as concentration marks. Let us suppose that the most intense absorption line (quantum number 3 1/2) of a later exposure showed the same intensity as the line 7 1/2 of the earlier exposure; it follows that the concentrations indicated by both exposures were in the ratio 1:5. (Actually interpolation is needed. Furthermore, this ratio must be corrected by intensity factors given by the theory of Hill and Van Vleck.) Experimentally only the matching of absorption lines of equal intensity is needed, a problem simpler than regular photographic photometry.

The result was that, for the same concentrations of OH, the rate of the reaction consuming OH increased with the pressure of water or of helium which was added. This result pointed to a third-order reaction; it eliminated reaction 3.

Differentiating between the third-order reactions 1 and 2, some arguments seemed to indicate a high concentration of hydrogen peroxide produced by the discharge through water. Therefore the concentration of hydrogen peroxide was investigated simultaneously with the observation of OH by a similar method,—the absorption spectrum. The result was that the concentration of hydrogen peroxide in the discharge tube immediately after interrupting the discharge was below the limit of observation. With a photoelectric cell and amplifiers this limit was pushed to 0.1 mm. of hydrogen peroxide. The absence in the discharge of any considerable amount of hydrogen peroxide agreed with arguments put forward recently by Campbell and Rodebush (2) and by Geib (3). It must be concluded that OH is largely consumed by reaction 1, that is, by combination with H in triple collisions.

The *absolute* rate of this reaction cannot be computed from the foregoing results alone, since only *relative* values of the concentration of OH are determined by the matching of absorption lines. In order to determine the absolute rate, the absorption spectrum of OH had to be calibrated with a known concentration. The experiments were carried through in collaboration with Dr. F. F. Rieke. For the calibration, the intensity of the OH absorption spectrum, that is, the "f-value" of these bands, was measured in thermally dissociated water vapor at 1200°C. The high temperature, as discovered by Bonhoeffer and Reichardt (1), partially dissociates the H_2O into OH and H. At present, the accuracy with which this f-value can be determined seems to be limited by the accuracy with which the dissociation can be computed; the difficulty was pointed out by Gordon (4). This computation has not yet been carried through.

While in water, dissociated by an electric discharge, the free OH radicals produced have the greatest chance to react with OH or H, another opportunity arises when OH radicals are produced by the dissociation of hydrogen peroxide. In such experiments they were observed to disappear at a much higher rate. (Since hydrogen peroxide is rapidly decomposed by the electric discharge, a fresh supply must be used for each brief duration discharge with following exposure of the absorption spectrum.) The most plausible rapid reaction is a bimolecular reaction of OH and H_2O_2.

The advantages of absorption spectra are evident from the example given: free radicals can be observed as well as neutral atoms. Absorption spectra are so sensitive that small concentrations can be detected. In particular they are valuable in that they can be used to analyze the gradual progress of a rapid reaction in snapshots. For saturated molecules, of course, many examples of absorption spectra and their application to chemical analysis are known,[2] in particular in solutions. The test for gaseous hydrogen peroxide is discussed above. Even *free atoms* in gases may be detected by the same methods for the purpose of chemical analysis. In this laboratory an attempt is being made to detect free hydrogen atoms by their absorption spectrum, that is, by absorption of the first line of the Lyman series at 1216 A.U. For this purpose the LiF windows transparent for wave lengths as short as that, made and tested in this laboratory by Schneider,[3] prove very valuable.

The *limitations* of the ability of absorption spectra to reveal faint con-

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[2] For example, a sensitive test for I_2 molecules is described by E. Rabinowitsch and W. C. Wood (J. Chem. Physics **4**, 497 (1936)).

[3] See reference 8; the production of large single crystals of LiF was described by D. C. Stockbarger (Phys. Rev. **49**, 200 (1936)).

centrations are as follows: First of all, the absorption spectrum of a radical must either be known or be predictable from the emission spectrum. This brings in no difficulty for diatomic radicals like OH, NH, CH, CN, the spectra of which are known as well as those of many atoms. But the spectra of more complicated radicals like HO_2 and the radicals investigated by Paneth and by F. O. Rice are not known, and there is no general method by which they may be discovered. Very possibly such spectra are largely continuous, as are the absorption spectra of the lighter halogens and of many organic compounds. This would rule out the application of this method, as a continuous absorption is not sufficiently characteristic. It can be used only in exceptionally simple cases, such as that of hydrogen peroxide, when one can make sure that no other particle present shows continuous absorption within the same spectral range.

For a quantitative test the "*f*-value" of the particle must be known. There is not much chance to determine this value except by direct calibration for stable molecules, for OH which can be produced at known concentrations, and for H which can be calibrated by another method.

A second limitation is given by the effect of another gas present at the reaction which may obscure the absorption spectrum of radicals. Oxygen, for example, would obscure the largest part of the Schumann region, although it becomes rather transparent again at shorter wave lengths near the beginning of the Lyman series (6), fortunately for the investigation of hydrogen atoms. According to a general rule put forward by H. N. Russell, radicals have absorption spectra at longer wave lengths than stable molecules, since chemical stability is in many cases correlated with a high excitation potential.

Finally, the technical difficulties must be mentioned. First, the reaction to be studied must take place in a column long enough to provide depth for the absorption experiment. The greatest technical difficulty is as follows: Faint, discrete absorption spectra—different from emission spectra—can be observed only with high resolving power as given by large gratings or other interference instruments. In order to secure sufficient intensity of the continuous background, special precautions must be taken. Actually, our experimental work on radicals had to start with the problem of how to raise the intensity of illumination in large grating spectrographs.

In spite of these difficulties it is hoped that in coöperation with chemical methods, absorption spectra will contribute to the investigation of the part played by simple radicals—and maybe atoms—in gas reactions and will thus supplement chemical methods.

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DISCUSSION OF THE PAPERS PRESENTED AT THE SYMPOSIUM ON MOLECULAR STRUCTURE[1]

Solved and Unsolved Problems in the Spectra of Diatomic Molecules (page 5). R. S. MULLIKEN (University of Chicago).

R. S. MULLIKEN (University of Chicago): In section II the number of possible diatomic molecules is of course not 92!, but only 92 × 93/2, which, however, is still rather large. There are doubtless other errors and misstatements in this paper, for which the author asks forgiveness.

The word "species" introduced in this paper in "electronic species" represents a rough translation of the German "Rasse". Possibly some other word than "species" would be better, but there seems to be a real need here for *some* word distinctive or special other than "type" or "kind" or "class". "Species" seems to fill the need fairly well.

In reply to Dr. Herzberg's criticism of the qualifying adjectives "homogeneous" and "heterogeneous", respectively, implying (between states) "of the same electronic species" or "of different electronic species" in classifying perturbations and predissociation, it seems to me that there is a definite need for some such adjectives, although I agree with Dr. Herzberg that the choice of "homogeneous" and "heterogeneous" is not as simple or unique as one might wish. On the other hand, there are objections to alternative choices, such as "electronic" and "rotational", respectively, in that they are liable to misinterpretation. Also, the words "homogeneous" and "heterogeneous" are better adapted to the more varied situations which arise in polyatomic molecues.

G. HERZBERG (University of Saskatchewan): If Professor Mulliken's suggestion is correct that maxima in potential curves are of a more common occurrence than hitherto believed, it might lead to rather serious consequences for the spectroscopically determined heats of dissociation (D). Almost all of these values have been determined on the tacit assumption that the potential curves of the electronic states which were used for the

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[1] This Symposium on Molecular Structure was the first annual symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society. It was held at Princeton University, Princeton, New Jersey, December 31, 1936 and January 1 and 2, 1937.

Only comments received in written form are included in this discussion. The officers of the Division are not responsible for any of the opinions expressed.

The page numbers given refer to Volume 41 of This Journal, unless otherwise noted.

determinations have no such maxima. If maxima were present the D values obtained would only be upper limits to the true values.

Because of the scarcity of cases where a potential maximum has been definitely established,[2] the writer feels rather confident that most of the accepted spectroscopic D values are not influenced by such potential maxima. It would of course be highly desirable if in each individual case this possibility could be definitely excluded. I should like to mention two points which will be of considerable help in doing this.

(1) If two or more different dissociation limits are observed spectroscopically and the difference between them agrees exactly with the corresponding energy difference of the separated atoms one may be practically sure that there is no maximum in the potential curves, because if there were a maximum it would have to have exactly the same height in the two (or more) states, which seems to be extremely unlikely. Thus, for example, in the case of O_2 two dissociation limits have been found whose separation is very nearly equal to the excitation energy of the ^1D state of the oxygen atom. Consequently in this case no maximum interferes with the determination of the heat of dissociation, and therefore the accepted value $D(O_2) = 5.09$ volts is correct.

(2) When predissociation is used for the determination of heats of dissociation it is important, as pointed out previously (G. Herzberg: Ann. Physik **15**, 677 (1932)), that a breaking off of the rotational levels is observed in more than one vibrational level of the upper state. Naturally this breaking off occurs at different J values and slightly different energy values for the different vibrational levels. As previously shown, from these differences in energy and J value the approximate positions (r values) of the maxima of the "*effective*" potential curves can be easily obtained.

If the zero rotation potential curve had a maximum the maxima of the corresponding effective potential curves would be at about the same r value, and this r value would be derived from the predissociation. It seems obvious that if the zero rotation maximum has an appreciable height it cannot occur at a very large nuclear distance, whereas the maxima of the effective potential curves if no maximum for zero rotation is present are at rather high r values. Thus if, from the observed breaking-off points, the maxima of the effective potential curves are calculated to be at small r values (say smaller than twice the equilibrium distance) one may conclude that there is a maximum even for zero rotation. If the maxima are at large r values (say $> 2r_0$) one may conclude that there is no appreciable potential maximum for zero rotation. Also, in the latter case the maximum of the effective potential curve should be shifted to smaller r

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[2] One of the three cases mentioned by Professor Mulliken, that of AlH, does not appear to the writer to be definitely established.

values with increasing J, whereas in the first case it should be rather independent of J, namely, nearly at the position of the maximum of the zero rotation potential curve. As an example let us consider the predissociation of N_2 in the upper state of the second positive group at 12.08 volts. The maximum of the effective potential curves of the state which causes the predissociation was found to be at about $r = 4.4$ A.U. (G. Büttenbender and G. Herzberg: Ann. Physik **21,** 577 (1935)). No appreciable maximum of the zero rotation potential curve could lie at this large distance (the equilibrium distance of the predissociating state is 1.15 A.U.). Moreover the maximum shifts appreciably to smaller r values for increasing J (see figure 8 of the reference given just above), which is not in harmony with the assumption of a potential maximum for zero rotation in this case. Therefore, as the heat of dissociation of N_2 was mainly determined from this predissociation, the accepted value (G. Herzberg and H. Sponer: Z. physik. Chem. **26,** 1 (1934)) of $D(N_2) = 7.347$ volts has to be considered as correct and is not influenced by a potential maximum.

The two examples given show that even considering the possibility of a maximum of the potential curves accurate spectroscopic values for heats of dissociation may be obtained if sufficient data are available to exclude definitely the occurrence of a maximum in the particular case.

R. S. Mulliken (University of Chicago): In suggesting that maxima in potential energy curves may be more common than we have hitherto supposed, I wished more to emphasize the desirability of keeping this hitherto underemphasized possibility in mind, than to express an opinion on the matter. However, the fact that the probable existence of maxima has *forced* itself on our attention in two or three cases tends to indicate that further examples are likely to be found relatively more frequently if we are *expecting* them. Nevertheless, the fact that the existing examples (except apparently in the nearly no-man's-land cases of IBr and ICl) have not been established quite beyond all doubt makes the matter a little uncertain.

Spectra of Diatomic Molecules of Elements of the Fifth Group (page 47).
G. M. Almy (University of Illinois).

G. M. Almy (University of Illinois): The force constant k should be defined as $4\pi^2c^2\omega_e^2\mu$ and the scale of k in figure 2 should be increased by a factor of four. The two errors are independent.

Miss Sponer has called my attention to a paper by Nakamura and Shidei (Japan. J. Physics **10,** 11 (1935)) on the absorption spectra of Sb_2, Bi_2, and SbBi. Their analyses of the first two agree in general with those discussed, but the spectrum of SbBi is new. It consists of a few bands arranged in a system with $T_e = 40{,}617$ cm.$^{-1}$, $\omega_e'' = 220$ cm.$^{-1}$, $\omega_e' = 190$ cm.$^{-1}$ They conclude that what are here called the D state of Bi_2, the

F state of Sb_2, and the upper state of SbBi are corresponding states. If, on the other hand, the arrangement in figure 1 is correct, the upper state of SbBi probably corresponds to the *D* states of Sb_2 and Bi_2. At first glance, the value of T_e for the upper state of SbBi appears to be too high for this interpretation, but it fits in smoothly if one supposes (1) that $D_0(X)$ for SbBi is intermediate (as the data indicate) between $D_0(X)$ for Sb_2 and Bi_2, and (2) that the products of dissociation of state *D* of SbBi are Bi in a $^2P_{3/2}$ state and Sb in either ^2D state. The correlation of these and other excited states cannot be settled without more work. It appears that the mixed molecules may give valuable clues as to products of dissociation and correlation of states.

MAURICE L. HUGGINS (Eastman Kodak Co.): May not many of the differences between the spectra of N_2 on the one hand and of P_2, As_2, Sb_2, and Bi_2 on the other—and especially between the constants for the ground states—be related to the generalization (Lewis: Valence and the Structure of Atoms and Molecules, p. 94. The Chemical Catalog Co., Inc., New York (1923)) that elements, such as nitrogen, in the first row of the Periodic Table can form stable double and triple bonds, whereas elements of higher atomic number rarely form multiple bonds, and then only weak ones? As I have repeatedly pointed out, this generalization agrees with a multitude of known facts of structural chemistry. With its aid, in fact, I was able to predict correctly the tetrahedral structure of the P_4 molecule, the ring structure of the S_8 molecule, and the arrangement in space of the atoms in many other molecules and crystals.

Intermolecular Forces Responsible for Pressure Broadening of Band Lines (page 61). W. W. WATSON (Yale University).

W. W. WATSON (Yale University): Recent measurements of S. D. Cornell on line widths in the absorption bands of several dipole molecules serve as added evidence for the assignment of "excess" widths to dipole interactions and as an indication of the complexity of the phenomenon in general. Using a longer absorption column (7 meters) and a narrower slit width (0.04 mm.), it is evident that for all vapor pressures from 120 mm. to 545 mm. the lines of the 1.04 μ hydrogen cyanide band have widths varying with *J* in the expected manner. The lines involving rotational states at or near the maximum of the Maxwell distribution of rotational velocities ($J \cong 8$) are definitely broader than the lines of lower or higher *J* values. This effect is merely superposed on a general broadening produced by the various van der Waals interactions. Its presence may be taken as experimental evidence for the existence of the alignment effect between the interacting dipoles.[3]

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[3] The discussion of this possibility referred to in footnote 3 (page 62) will be found in the January 1, 1937 issue of *The Physical Review*; the reference for footnote 2 (page 62) is Phys. Rev. **50**, 1186 (1936).

There is also some roughly quantitative evidence for the existence of dipole interactions between water vapor molecules in the pressure broadening of the lines of the infra-red water vapor bands. The lines of the 11,350 A.U. band as produced by the water vapor in the atmosphere of the grating room (relative humidity 60 per cent) have half-widths of 0.40 ± 0.04 cm.$^{-1}$ (average of fourteen lines, slit width 0.04 mm.). With an absorption tube 1 meter long containing water vapor only at 100°C. in the path, these same lines have an average half-width of 0.63 ± 0.06 cm.$^{-1}$ The comparison of these two values for the half-width is subject to the criticism that in the second case there is still some absorption from the water vapor in the air in the room, the temperature is not the same, etc. However, there is surely a greater pressure broadening when water vapor molecules are the perturbers than when air molecules produce the broadening. The ratio of the μ^4 values for hydrogen cyanide and water vapor is about 3.5:1. Taking the "excess" line width for hydrogen cyanide at atmospheric pressure again as 1.00 cm.$^{-1}$, that for water vapor might be expected then to be about 0.3 cm.$^{-1}$, close to the observed value of 0.23 cm.$^{-1}$

Finally, it has been found that with the same slit width of 0.04 mm. the average half-width of several of the narrowest lines of the 7920 A.U. ammonia band is 1.04 cm.$^{-1}$, the ammonia gas being at atmospheric pressure in the 7-meter absorption tube. This width is slightly greater than Chao's (page 64, reference 4) estimated value. From the relative values of the dipole moments of ammonia, water vapor, and hydrogen cyanide, one would not expect such a large half-width for the ammonia lines. The explanation is possibly that since these are not single lines, but have unresolved fine-structure components of different K values ($K \leqq J$), the usual theory does not hold. The dipole forces may perhaps perturb more violently these levels because of the greater possibility of equal energy level spacing with nearly equal angular momenta in the interacting molecules. It should be noted that London's formula (page 65, reference 14) holds only for larger distances between dipoles, i.e., interaction energy less than rotational energy level spacing. With multiple energy levels the situation is much more complex. The very large pressure broadening of the lines of the methyl alcohol bands (page 64, reference 1) and the lack of fine structure in the bands of the other alcohols (R. M. Badger and S. H. Bauer: J. Chem. Physics **4**, 711 (1936)) is understandable then, since these molecules all have the multiple rotational energy level spacing of symmetrical or asymmetrical tops and all have large permanent dipole moments.

[4] The statement by Dr. Burg was made in reply to a question from the floor concerning the work of Stock and his collaborators on the conductance and ion transference of diborane in solution in liquid ammonia, which showed two protons to be dissociated from the B_2H_6 molecule.

The Puzzle of Rare-earth Spectra in Solids (page 67). J. H. Van Vleck (Harvard University).

F. H. Spedding (*Cornell University*): I was very pleased when I learned that Professor Van Vleck had decided to devote part of his time to this subject. I should like to re-emphasize the importance of understanding the nature of the levels in solids theoretically. We could then not only make all of the correlations between physical and chemical properties and energy states that have been made for gases, but in addition we could learn a great deal about the fields which are active in the condensed state. As Professor Van Vleck has pointed out, the electric fields which we study are mainly determined by the first row of atoms about a given atom. Thus, a study of spectra should prove a powerful tool in the investigation of short range order in crystals, solutions, and glasses.

Professor Van Vleck, naturally, has presented this subject from the viewpoint of the theorist and I, therefore, should like to make one or two comments from the experimental point of view. First I should like to correct a misapprehension in the paper with regard to my views as to the nature of the excited states. I never have maintained that all of the excited states arose from the $4f^{n-1}\,5x$ configuration, but only that some of them did. As far as I know, there is no experimental evidence whatever which rules out the type of transition which Professor Van Vleck discusses. On the other hand, if one makes the assumption that they are all of that type, one immediately encounters difficulties when one attempts to account for the observed spectra. The Zeeman splitting of the excited states of gadolinium is one example of such difficulties, as the splittings are not at all what theory as at present developed would indicate, but are exactly the same as for Cr^{+++} in chrome alum, where all states must arise from electron configurations which are not shielded by completed shells of electrons. A second difficulty is that there are too many multiplets and too many lines in the multiplets to be accounted for adequately by present theory. Professor Van Vleck's suggestion that perhaps in a solid the eigenfunctions of the vibrational levels and crystal-splitting levels may scramble so as to give rise to new levels, all of which have some of the properties of the crystal-splitting levels, looks promising and when developed may overcome these difficulties. Until they are accounted for, however, I prefer to believe that both types of transition occur.

On page 75 Professor Van Vleck reports me as giving levels in gadolinium at 0, 37, 53 and 79 cm.$^{-1}$ He has evidently overlooked the fact that these levels were tentatively put forward in an early paper on the basis of constant energy differences and were almost immediately retracted (Phys. Rev. **37**, 777 (1931)) when the spectra were investigated with instruments of higher dispersion. All subsequent papers have emphasized the fact that the basic state of gadolinium is single and has no other states occurring near it (J. Am. Chem. Soc. **55,** 496 (1933); J. Chem. Physics **1,** 143 (1933); ibid.: in press, January, 1937).

A Comparison of Some Ultra-violet Absorption Spectra of Polyatomic Molecules with Those of Diatomic Molecules (page 81). W. ALBERT NOYES, JR. (Brown University).

ROBERT S. MULLIKEN (University of Chicago): In agreement with Dr. Noyes, I am extremely skeptical in regard to all conclusions drawn, on the basis of approximate equality of vibration frequencies, as to close similarities of electronic structure between the carbon monoxide molecule and carbonyl group, or between other pairs of this sort. Rough agreements in vibration frequencies are to be expected in many such cases because of rough agreements in bond strength and in the masses of vibrating parts. In regard, however, to the *close* agreements which one can often find by exploring among excited states of molecules, I see no reason at all for supposing that the closeness of agreement is, in general, more than accidental in cause.

In regard to the question whether C_2 in its normal state contains a double bond, I would be inclined to say that it does, but at the same time to insist that this double bond differs considerably in electronic constitution from those in ethylene and its derivatives. In general, it would be quite possible to have two or more considerably different electronic structures all meriting a name such as "double bond" or "triple bond"; it is even not unlikely that such differing structures might be nearly alike in bond strength and vibration frequency.

Ultra-violet Absorption Spectrum of Diborane (page 91). E. BLUM AND G. HERZBERG (University of Saskatchewan).

ROBERT S. MULLIKEN (University of Chicago): Before commenting on the paper by Blum and Herzberg, perhaps I ought to emphasize that the theoretical account I have given of the electronic structure and some of the properties of diborane is more tentative than similar accounts of other better known molecules. Its validity is based on the assumption that the diborane molecule has the same symmetry as the ethane molecule, as is strongly indicated by x-ray data. The recent work of Jahn and Teller, however, according to which degenerate electronic states of most symmetrical polyatomic molecules are unstable in such a way that the molecule tends to become less symmetrical accompanied by splitting up of such states into non-degenerate states, suggests that some, or perhaps all, of the low-energy states of diborane have a lower symmetry than that of ethane. This would be in line with Wiberg's idea that diborane is plane, although it seems hardly likely that the distortion would go so far as that. In any case, it is difficult to see how there can help being a large number of low-lying electronic energy levels not very far above the normal level. However, if this is the case, it would seem probable that there should be infra-red absorption of appreciable intensity corresponding to one or more electronic transitions. I should like to report at this time that Mr. H. J. Plumley, at Chicago, has made absorption spectrograms of diborane and has detected no absorption whatever out to 12,000 A.U. (pressure about 1/5 atm., tube length 1 meter). The diborane was kindly supplied by Dr. A. Burg. In the ultra-violet also down to 2500 A.U. there was no noticeable absorption. In some other work in which diborane at atmospheric pressure was exposed to the radiation from a quartz mercury arc, Mr. Plumley observed some interesting photochemical decomposition. This last result is in agreement with that of Blum and Herzberg.

In regard to the excited states of diborane corresponding to the two regions of continuous absorption, observed by Blum and Herzberg, the suggestions of the latter seem reasonable, but should, I think, be regarded as very decidedly tentative. In general, it is a very slow and difficult matter, requiring a great deal of caution, to reach definite conclusions as to the electronic structures of polyatomic molecules in excited states. For the normal states, to be sure, and in *favorable cases* also for excited states, one can often obtain fairly definite, reliable, conclusions as to electronic structures. I think it is desirable to make these remarks here in order to dispel possible false impressions and also especially to discourage possible false hopes of arriving at correct electron configurations for excited states of molecules.

ANTON B. BURG (University of Chicago):[4] Having studied the ammoniation products of diborane very carefully for a long time, I feel sure that the experiments here mentioned have been interpreted in a manner not completely justified by the facts as we now know them. In some unpublished experiments, performed in collaboration with Professor Schlesinger at the University of Chicago, it was found that a freshly prepared solution of the diammoniate of diborane in liquid ammonia reacts with sodium at −75°C. to produce the quantity of gaseous hydrogen (0.50 cc. per cubic centimeter of diborane) corresponding to one ammonium ion per molecule of diborane. But it proved to be altogether impossible to demonstrate the presence of a second ammonium ion in this salt. The study was complicated by the occurrence of a slow secondary reaction which very gradually raised the total hydrogen to 0.65 cc. per cubic centimeter of diborane. The slow excess production of hydrogen could not be attributed to some slight secondary ionization of the salt, for another experiment, in which a liquid ammonia solution of the diammoniate of diborane was allowed to stand for ten hours at −40°C. before the reaction with sodium was carried out at −75°C., yielded 0.65 cc. of hydrogen (per cubic centimeter of diborane) immediately. The rapid production of the excess hydrogen in this case showed that some unexplained secondary reaction of the diammoniate of diborane with the solvent ammonia had produced the 30 per cent excess of ammonium ions, beyond the quantity to be expected from a monobasic acid-former.

The occurrence of this reaction was also clearly indicated by the results of a study of the pressure-composition isotherm of the system diborane-ammonia at −50°C.: of the 1.4 molecules of ammonia taken up by the diammoniate at that temperature, 0.35 molecule could not be removed by pumping, even at temperatures as high as −40°C. This result is quite in contrast to the easy removal of excess ammonia from the freshly prepared diammoniate at temperatures below −80°C.

In addition to these remarks, I wish to point out that the experiments of Stock and his collaborators did not include any measurements of ion transference. The conclusions which have been drawn from their experiments appear to have been based solely upon the variation in the conductivity of the solution with the total quantities of hydrogen and nitrogen produced by the electrolysis.

It is hardly necessary to mention that the homogeneous reaction of sodium with the dissolved ammoniates of diborane should be expected to give results more easily interpretable than the results of the essentially heterogeneous process of electrolysis. In fact, a careful study of the details of Stock's experiments (Ber. **65B**, 1715 (1932)) shows that secondary reactions, involving the formation of nitrogen, actually occurred before the primary process was complete.

To sum up the matter, I would say that diborane clearly shows a tendency to give up one proton easily, but the tendency to lose a second proton is not indicated by these experiments, nor by any others within my knowledge. On the contrary, we find a very plausible explanation of the facts on the subject, if we assume only the dissociation

$$B_2H_6 \rightarrow H^+ + B_2H_5^-$$

and note that the electron octet of one boron atom in the negative ion is incomplete by a pair of electrons. Thus with ammonia, we seem to obtain the complex salt $NH_4^+ \bar{B}_2H_5NH_3$, whose negative ion has an electronic structure appearing like that of the ethylammonium ion.

We expect to publish the details of our experiments on the subject very soon.

Photochemistry of Polyatomic Molecules (page 97). JAMES FRANCK (The Johns Hopkins University) AND KARL F. HERZFELD (The Catholic University of America).

FARRINGTON DANIELS (University of Wisconsin): This paper gives an excellent account of the application of chemical kinetics to the problem of the photochemistry of complex molecules, but the application to photosynthesis by chlorophyll depends on the generally accepted belief that four quanta are involved for each molecule of carbon dioxide reacting. We find after an investigation of several years that the process is much less efficient. Actually about twenty quanta are required for each molecule of carbon dioxide. Dr. W. M. Manning (Duggar, Stauffer, and Daniels: Science **79**, 2054 (1934). Preliminary report) has extended the investigation and carried it to a fresh water lake where the algae, under normal living conditions, were found again to require about twenty quanta per molecule.

It is evident that hypotheses for explaining photosynthesis by chlorophyll need no longer be handicapped by this requirement of "the four photons." In fact several new hypotheses can now be considered. Photochemical and kinetic theory demand only a *minimum* of about four photons and there is no theoretical objection to a requirement of more than four.

If a very complex molecule absorbs twenty quanta, perhaps it can deliver the energy equivalent of four at a particular part of the molecule without violating any energy principles, but it seems unlikely that a single molecule can absorb twenty quanta in a short enough period of time to effect this result. The existence of several intermediate steps or a series of molecular rearrangements of low quantum efficiency may well be involved in the photosynthesis by chlorophyll.

J. Franck (The Johns Hopkins University) and K. F. Herzfeld (The Catholic University of America): The belief "that four quanta are involved for each molecule of carbon dioxide reacting" is based on W. Warburg's experimental results. He used algae cultivated so that no ineffective chlorophyll was present. Moreover there was an excess of carbon dioxide. Under natural conditions, under which Dr. Daniels and his coworkers made their observations, some inactive chlorophyll will always be present, and the amount of carbon dioxide is so small that it acts as a limiting factor. The low yield obtained by Daniels is therefore not in contradiction with Warburg's results and agrees with other observations.

G. Richard Burns (Vermont Agricultural Experiment Station and Hunter College): In regard to the particular reaction which has been chosen as an illustration in this article, the remarks of the authors at the top of page 102 should be emphasized, since from the viewpoint of plant physiologists the use of the wave length 680 $m\mu$ as the long wave length limit within which the absorption of chlorophyll still gives photosynthesis seems incorrect. This is the longest wave length at which the quantum yield has been determined, but photosynthesis, and also absorption by pigments in the plant, is found at longer wave lengths,—possibly at much reduced quantum yield. (In a personal discussion, J. Franck agreed that

680 mμ is the limit for photosynthesis only in very thin layers of chlorophyll, but that for thick layers the few thermally excited molecules would account for the photosynthesis beyond 680 mμ.)

O. K. RICE (University of North Carolina): There may be excitation of vibrational energy coincident to the electronic excitation when light is absorbed by a polyatomic molecule. The reason for this is the same as in the case of a diatomic molecule, namely, change in equilibrium position for the vibrators and operation of the Franck–Condon principle. In polyatomic molecules, however, the amount of vibrational energy may be greater, for a number of oscillators may be affected. This vibrational energy excited in the light absorption is available to cause decomposition of the molecule by flowing into the bond which breaks, *provided that the reaction takes place in the gas phase*, so that it cannot be dissipated to other molecules. In the case of azomethane an increase in pressure causes decrease in quantum efficiency, indicating dissipation of this vibrational energy on collision with the azomethane molecules. Work is being started to investigate the effect of inert gas molecules.

J. FRANCK (The Johns Hopkins University) AND K. F. HERZFELD (The Catholic University of America): We agree with the viewpoint of Dr. Rice. As observations on fluorescence have shown, a molecule, brought by light absorption into an excited state in which part of the energy is electronic and part vibrational, can lose the latter part through collisions. This is particularly so in liquids. The collisions are here so numerous that the vibrations and rotations in an excited molecule will reach thermal equilibrium with the surroundings before an appreciable number of molecules have lost their energy by emission or chemical reaction. Our remarks on the accumulation of energy in one bond by fluctuation refer to molecules with electronic excitation whose vibrations and rotations are in thermal equilibrium with the surroundings.

The Nature of the Hydrogen Bond (page 117). ALBERT SHERMAN (University of Wisconsin).

MAURICE L. HUGGINS (Eastman Kodak Co.): Comparison of the heats of combustion of *o*-, *m*-, and *p*-derivatives *in the vapor state* might be used as a criterion for the presence or absence of strong intramolecular hydrogen bridges, but not the heats of combustion *in the solid state*. In the solid, an *inter*molecular hydrogen bridge affects the heat of combustion to the same degree as an *intra*molecular bridge and analogy with other known structures makes it practically certain that a mole of solid *m*- or *p*-nitrophenol, for instance, contains as many such bridges *between* the molecules as exist *within* the molecules in a mole of *o*-nitrophenol.

The possibility and advisability of setting up a rigorous criterion for the presence or absence of hydrogen bridges are at least questionable. Bridges of all degrees of strength, up to a certain maximum, probably exist and the problem resembles that of determining or defining rigorously a "size" or "sphere of influence" of a molecule. The result necessarily depends on the method. For most practical purposes it is perhaps best to speak of hydrogen bridges only when the bridge strength is such that the three atoms concerned maintain approximately (in spite of molecular vibrations and collisions) their relative positions for appreciable periods of time. A discussion of the strengths of hydrogen bridges with energy data for a number of examples is included in an article of mine now in process of publication (J. Org. Chem., in press).

The strength of a hydrogen bridge in a ring such as that in the enol form of acetylacetone is undoubtedly due in considerable measure to electron resonance between two Lewis structures. An additional factor, which has been previously neglected, is the increased stability resulting from an oscillatory motion of the valence electron system in the ring synchronized with the vibrational motion of the bridge hydrogen. It can be shown also that in a ring such as that in the formic or acetic acid dimer the oscillations of the two bridge hydrogens tend to be synchronized, the structure being more stable with such synchronism than without it. Similarly the hydrogen oscillations in the chains of hydrogen bridges existing in many hydroxyl compounds, in proteins, etc., also tend to be synchronized. (Huggins: Letter submitted to Nature, December, 1936.)

Incidentally, the term "hydrogen bridge," which I have been using, seems to me much preferable to "hydrogen bond," because of possible confusion with an ordinary electron pair bond joining a hydrogen atom to another atom. A hydrogen *bridge* consists of a hydrogen atom joined to two electronegative atoms by *two* (quite polar) electron pair *bonds*.

On the Photographic Infra-Red Spectrum of Methylacetylene (Allylene) and the C—C Single Bond Distance (page 123). G. Herzberg (University of Saskatchewan), F. Patat (University of Göttingen), and H. Verleger (Technische Hochschule, Darmstadt).

G. Herzberg (University of Saskatchewan): The following point was mentioned in the oral presentation of the paper but not in the written manuscript: The difference between the C—C single bond distance as given in our paper and that determined by electron diffraction is in all probability due to the fact that the assumed constancy of interatomic distances only holds if the particular group of two atoms considered is situated *in similar surroundings.* That a constancy of interatomic distances irrespective of the surroundings does not hold in general can already be seen from the difference of the C—H distance in C_2H_2 and CH_4 (in one case $\equiv$C—H), in the other (—$\overset{|}{\underset{|}{C}}$—H), whereas when there are similar surroundings as in C_2H_2 and HCN (in both cases the CH group is bound to the rest of the molecule by a triple bond) the distances actually do turn out to be the same within ±0.003 A.U. (cf. reference 10 of our paper). Most of the electron diffraction values for the C—C single bond distance refer to cases where both carbon atoms are bound to the rest of the molecule by three single bonds $(-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-)$, whereas our value refers to the case where there are three single bonds on one side and a triple bond on the other $(-\overset{|}{\underset{|}{C}}-C\equiv)$. Considering the observed difference between $r(-\overset{|}{\underset{|}{C}}-H)$ and $r(\equiv C-H)$ a similar difference between $r(-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-)$ and $r(-\overset{|}{\underset{|}{C}}-C\equiv)$ seems to be rather probable, so that the observed difference between our C—C bond distance and the electron diffraction value may indeed be real.

D. M. DENNISON (University of Michigan): This paper represents a very beautiful investigation of the molecular structure of methylacetylene as revealed by its near infra-red spectrum. Although the band lines are so close together, being separated by only a little more than 0.5 cm.$^{-1}$, they seem to have been sufficiently well resolved to permit a unique analysis and an accurate determination of the moment of inertia. The simplicity of the band proves without doubt that the molecule possesses a linear, symmetrical form. The calculation given by the authors of the single bond C—C distance is in my opinion very convincing, but it would be desirable if some check on it could be made. They suggest a study of CD_3C_2H. It seems probable however that any small errors in measuring the line separation would be greatly magnified in the calculation of the C—C distance. An independent method of obtaining this distance would be through a study of the ethane spectrum. Using the constants derived by Herzberg, Patat, and Verleger one may calculate the line spacing to be about 2.38 cm.$^{-1}$ These lines could be separated in the region of the fundamental bands as well as in the photographic infra-red. The work of Levin and Meyer (A. Levin and C. F. Meyer: J. Optical Soc. Am. **16,** 137 (1928)) shows that this might be difficult because of overlapping bands. However, in the case of the band at 2954.8 cm.$^{-1}$ they appear to have partially resolved a few lines and find a spacing of this order of magnitude.

Raman Spectra of Amino Acids and Related Compounds. II. Guanidine and Urea Derivatives (page 133). JOHN T. EDSALL (Harvard University Medical School).

D. M. Dennison (University of Michigan): Dr. Edsall has approached the problem of analyzing the Raman spectra of these rather complicated molecules in a very careful manner which attempts to explain the essential features of the spectrum and not to be confused by the less important details. His deduction that the guanidonium ion possesses trigonal symmetry is convincing. The lessening of the symmetry in the cases of the urea derivatives shows itself in a richer spectrum, as might be expected. Dr. Edsall's calculation of the frequencies of the carbonate, nitrate, and guanidonium ions leaves me with the impression that here, as in the case of other molecules composed of atoms other than carbon and hydrogen, it is quite impossible to use valence forces. This was shown clearly by Dr. Rosenthal for the tetrahedral molecules (J. E. Rosenthal: Phys. Rev. **46**, 730 (1934)). For the molecules with which Dr. Edsall is dealing it might be more appropriate to use central forces and employ the equations of Menzies (A. C. Menzies: Proc. Roy. Soc. London **134A**, 265 (1931)). The central force model required three potential constants. However the molecule YX_3 possesses four frequencies, and so Menzies in applying his equations to the nitrate and carbonate ions has one independent check. While this check is not rigorously satisfied, the discrepancy is much smaller than that found by Dr. Edsall using valence forces. Incidentally it would be very interesting to look in the infra-red spectrum for the fourth frequency to be expected for the guanidonium ion. It would probably lie slightly below ν_4 and is inactive in the Raman spectrum.

Entropy and Symmetry of the Benzene Molecule (page 149). R. C. Lord, Jr., and D. H. Andrews (The Johns Hopkins University).

G. B. Kistiakowsky (Harvard University): The evidence which Drs. Lord and Andrews adduce to show that the lowest vibrational frequency of the normal benzene molecule is in the neighborhood of 400 cm.$^{-1}$ is very strong. But strong evidence exists also in favor of one frequency being only 162 cm.$^{-1}$ The ultra-violet absorption spectrum consists, as is well known, of band groups separated by ca. 920 cm.$^{-1}$ (further towards the short wave lengths this structure becomes obscured by many other bands which need not concern us here). Each band group can be regarded as a superposition of two v'' progressions displaced by 83 cm.$^{-1}$, starting with the strongest band on the short side and fading towards the red. As was shown by Shapiro and others (Phys. Rev. **38**, 1170 (1931)) some time ago the relative intensity within each band progression changes with temperature, higher members (situated towards the red) increasing in intensity with rising temperature. The spectrum has now been photographed in the Harvard Chemical Laboratory at temperatures ranging from −20° to 200°C., and while quantitative measurements are not completed, a simple inspection of the plates is sufficient to confirm the finding of Shapiro.

All but the first member of the shorter wave length progression increase in intensity with rising temperature; all members of the other progression show the same but more pronounced behavior. The effect is greater for the higher members in both progressions. Further observations to be considered are: (1) At the temperature of liquid air benzene in solution shows a spectrum in which practically only the first member of the strong progression (which is temperature independent in the vapor spectrum) can be observed. (2) Even at 200°C. the intensity of this band is greater than that of any other one in the progressions. (3) In fluorescence quenched by benzene or by foreign gases, in which transitions occur from the non-vibrating state of the molecule, as made probable by several observations, the intensities of the different members of the two progressions which coincide with those in absorption are nearly the same.

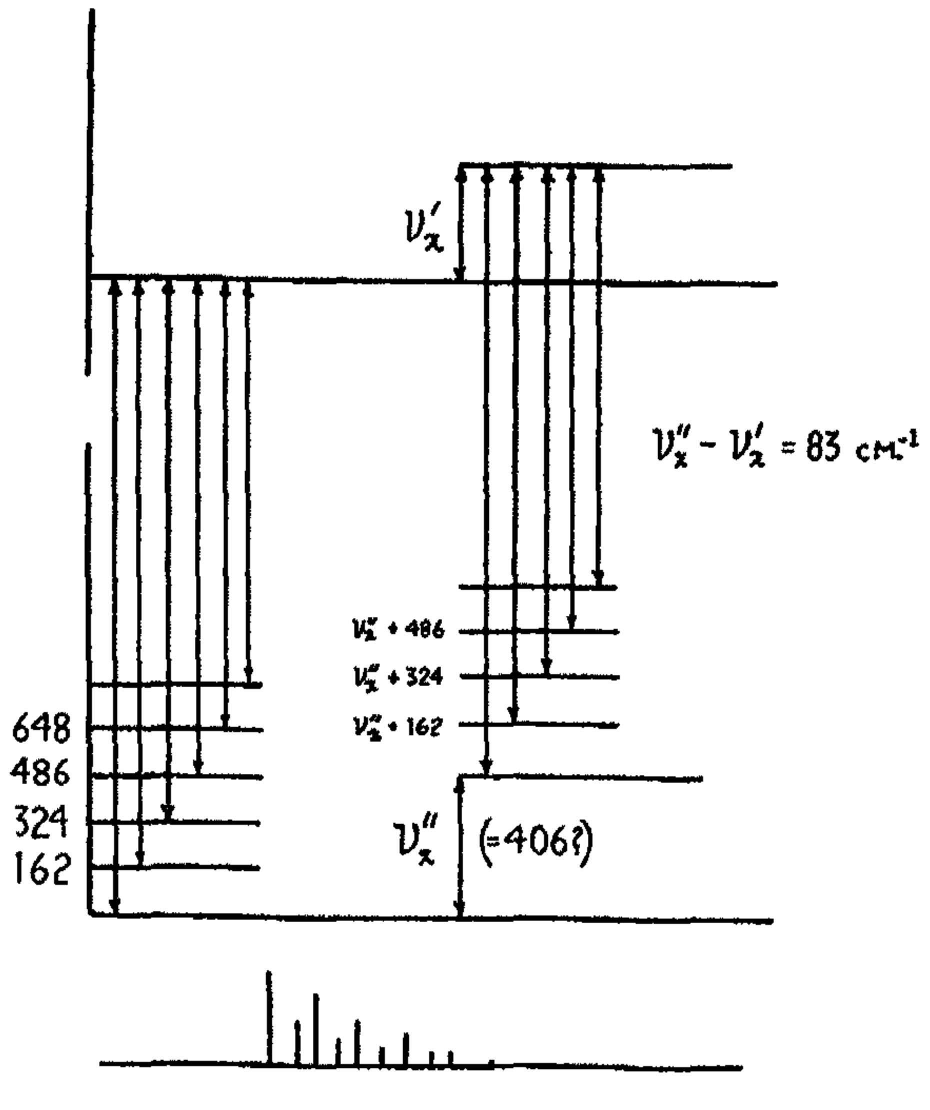

FIG. 1

The last observation suggests that transition probabilities leading to the different member bands are the same, and that their intensities in absorption are determined mainly by the Boltzmann factor in the distribution of normal molecules among the several vibrational states causing the spectrum; this is supported by the second observation. The first observation shows that absorption from the non-vibrating state leads to only one level of the excited state. If one now compares the relative intensities of the successive members of a progression at, say, room temperature and compares them with the Boltzmann factors, one finds readily that energy spacing of the vibrational levels of the normal molecule cannot be much greater than 160 cm.$^{-1}$ In view of all this, and of other facts which will be discussed in a forthcoming publication after quantitative measurements of the plates have been completed, the following diagram seems to represent the vibrational levels of benzene in a most satisfactory manner (see figure 1).

The question of the low frequencies in the benzene molecule is therefore by no means as definitely settled as Drs. Lord and Andrews now believe.

E. TELLER (George Washington University): The measurements of specific heat as interpreted by Lord and Andrews and also analogy with the vibration spectrum of other molecules make a frequency of 162 cm.$^{-1}$ in the fundamental state of benzene most improbable. Though I cannot give a satisfactory interpretation of the benzene spectrum as described in the remark of Dr. Kistiakowsky I should like to point out that even the spectroscopic evidence itself is not completely explained by the assumption of a frequency of 162 cm.$^{-1}$ in the fundamental state. In particular the benzene absorption measurements by Kronenberger (Adam Kronenberger: Z. Physik **63**, 449 (1930)) at liquid hydrogen temperature show lines with separations of 160 wave numbers. At such low temperatures the corresponding energy levels in the fundamental state could not be excited. Therefore some other interpretation must be found at least for these lines in solid benzene. Moreover benzene fluorescence at low pressures does not show frequency differences of 162 wave numbers, though according to the Franck-Condon principle it is difficult to see why there should not be transition probabilities to several quantum states of the 162 cm.$^{-1}$ vibration if this vibration belongs to the fundamental state.

Some Proposals Concerning Nomenclature and Symbols for Polyatomic Molecules (page 159). R. S. MULLIKEN (University of Chicago).

E. BRIGHT WILSON, JR. (Harvard University): Perhaps in many applications it would be more convenient to use ν_1, ν_2, etc., in place of the symbols νa_1, etc., and to give in each paper a small table showing the significance of the numbering and the symmetries involved. The configuration would thus be written $(\nu_1)^2$ $(\nu_2)^3$ (ν_3) etc. In cases where the symmetry of the vibration was of special importance it could be added as $\nu_6 b_1$, but ordinarily I feel that this will not be necessary as long as a table is given somewhere. It would be a great help, of course, if all writers dealing with a given type of molecule would use the same numbering as the first investigator, and it is a particularly disagreeable habit to require the reader to refer to other papers for the significance of the numbering.

R. S. MULLIKEN (University of Chicago): In connection with the idea of "vibrational configurations", I should have given partial credit to Dr. A. Henrici, who in a letter some time ago proposed the use of exponents to indicate the number of quanta with which any given mode of vibration is excited, also the use of numerical values (cm.$^{-1}$) to denote particular modes of vibration.

In regard to the nomenclature discussed in this paper, I agree with the comment made to me in a letter by Dr. Wilson that much of it, especially the vibrational symbols, would probably not be used in everyday work. Whenever a symbol is to be used repeatedly in a paper or discussion, it is of course inevitable and proper, as Dr. Wilson suggests, that a simpler "nickname" symbol should be used instead of the full and usually cumbersome official symbol. But it seems to me that back of these simplified and rather lawless names and symbols there ought to be a set of officially recognized and rigorously established names and symbols, and that at the beginning of any discussion the author should consider the possibility of making the discussion more readily intelligible by stating or tabulating systematic official designations corresponding to his unofficial ones.

In regard to the possible use of the terms "homogeneous" and "heterogeneous" I have commented in the discussion following my paper on diatomic molecules.

Some Aspects of Investigations of Molecular Structure of Organic Compounds (page 175). G. B. KISTIAKOWSKY (Harvard University).

H. S. TAYLOR (Princeton University): In the Princeton laboratory we have found evidence in support of a higher value for the C—C bond based on some recent determinations by Morikawa and Trenner on the activation energies of the reactions

$$CH_4 + D = CH_3 + HD$$

and

$$CH_3 + D_2 = CH_3D + D$$

Our best values for these at present are 15.6 and 11.1 kg-cal., respectively. Hence we deduce

$$CH_4 + D \underset{11.1}{\overset{15.6}{\rightleftarrows}} CH_3 + HD - 4.5 \text{ kg-cal.}$$

Now

$$HD = H + D - 103.5 \text{ kg-cal.}$$

Hence

$$CH_4 = CH_3 + H - 108 \text{ kg-cal.}$$

According to Bischowsky and Rossini

$$2C_{(s)} + 3H_2 = C_2H_6; \quad \Delta H_{291} = -20.96 \text{ kg-cal.}$$
$$2C_{(s)} + 4H_2 = 2CH_4; \quad 2\Delta H_{291} = -36.48 \text{ kg-cal.}$$

whence

$$2CH_4 = C_2H_6 + H_2; \quad \Delta H_{291} = 15.5 \text{ kg-cal.}$$

since

$$2CH_3 + 2H = 2CH_4; \quad \Delta H = -216.0 \text{ kg-cal.}$$

and

$$H_2 = 2H; \quad \Delta H = 102.9 \text{ kg-cal.}$$

We derive

$$2CH_3 = C_2H_6; \quad \Delta H = -97.6 \text{ kg-cal.}$$

Louis S. Kassel (Universal Oil Products Co., Riverside, Illinois): Professor Taylor has stated that his value of 98 kg-cal. for the C—C bond is a source of difficulty for reaction kinetics. There are at least some instances, however, in addition to the kinetic method by which that value was determined, where such a bond strength is welcome. In particular, recent experiments by Dr. H. H. Storch and myself seem to us to prove that the dominant reactions in ethane pyrolysis do not have a chain mechanism. If the C—C bond were as weak as 75 kg-cal., it would be hard to understand how the rate of the chain reaction could be as low as this result requires. A strength of 98 kg-cal. is sufficient to suppress the chain reaction.

Our experiments also indicate that the equilibrium constant for ethane dehydrogenation is lower than previously supposed. Our value agrees with that calculated from statistical mechanics on the assumption of free rotation about the C—C bond, and is seriously less than the value calculated using the retarding potential of 2–3 kg-cal. suggested by recent work based on the third law of thermodynamics and on the appearance of the absorption spectrum.

The Heat of Sublimation of Graphite. G. Herzberg (University of Saskatchewan), K. F. Herzfeld (Catholic University of America), and Edward Teller (George Washington University).

This paper follows the discussion of the symposium papers (see page 325).

The Structure of the Fluorochloromethanes and the Effect of Bond Type on Chemical Reactivity (page 185). L. O. BROCKWAY (California Institute of Technology).

R. A. OGG, JR. (Stanford University): I wish to take exception to certain statements and interpretations in the communication of Dr. Brockway. On page 192 it is stated that the higher monofluorides lose hydrogen fluoride spontaneously, and that all of the monofluorides are hydrolyzed readily by acids and bases. These assertions are in contradiction to experimental results recorded in the literature (Chemical Abstracts **16,** 3062; **28,** 5805), where it is found that the straight chain amyl and hexyl fluorides are stable, and that the decomposition of secondary and tertiary fluorides is no more rapid than is that of corresponding chlorides. Further, alkyl fluorides are actually extremely inert toward alkali metal hydroxides. Aside from these errors of fact, criticism is to be leveled at the facile interpretation of chemical reactivity in terms of highly simplified concepts regarding molecular structure. One cannot but draw the inference from this communication that the author considers the reactivity of a carbon-halogen bond toward ionic reagents to increase with the ionic character of the bond. Were this true, reactivity would progressively increase in the series of alkyl halides from iodides to fluorides. Actually, exactly the reverse situation obtains, and alkyl fluorides, considered by Pauling and coworkers to be the most nearly ionic, are characterized by remarkable inertness to negative ion substitution. It appears probable that the complicated problem of chemical reactivity is not to be solved in an offhand fashion by "zeroth order approximations".

MAURICE L. HUGGINS (Eastman Kodak Co.): I want to congratulate Dr. Brockway on the magnificent and important research results which he and his coworkers have recently been obtaining. Many of the interatomic distances reported agree well with the sums of atomic radii obtained by me over fifteen years ago from a very meager amount of crystal structure and band spectrum data (Phys. Rev. **18,** 333 (1921); **21,** 205 (1923); **28,** 1086 (1926)). (The revised radii published in 1934 by Pauling and myself (Z. Krist. **87A,** 205 (1934)) were computed in the same manner as the earlier values and differ but slightly from them.)

The possibility of B=F and C=F double bonds was discussed by G. N. Lewis and myself in 1919. I concluded that they might be capable of existence, the latter, however, only in a suitable positive ion ($R_2C=F^+$). So far as I am aware, no ions of this sort are known, and yet, as Dr. Brockway has shown, the addition of the resonance idea to this conception affords a satisfactory explanation for the short interatomic distances and certain other properties of the difluoro derivatives of methane.

Bond Moment and Electronegativity (page 209). CHARLES P. SMYTH (Princeton University).

Robert S. Mulliken (University of Chicago): From Dr. Smyth's paper it appears that the subject of dipole moments in relation to molecular structure is still in a stage which might be described as speculative. While I am glad that the equations I have proposed have been found useful, and while I believe that they are qualitatively well founded, I should hesitate to rely on them at present for more than very rough calculations or estimates. It seems probable, however, that they could be considerably improved by further study.

In any case, it appears from Dr. Smyth's paper that molecules containing carbon often show unaccountably large discrepancies. In particular, the carbon-iodine bond seems to have a large C^+I^- moment, whereas according to Pauling's electronegativity scale there should be a small C^-I^+ moment, which should, moreover, be enhanced by the homopolar dipole term.

Before making any suggestions concerning this, I should like to recall the fact that the presence of a fairly large dipole moment in CH_3I, with its negative end toward or on the iodine atom, is confirmed by a study of ionization potential data on CH_3I, as Price and I have pointed out (J. Chem. Physics **3**, 515 (1935)). The observed ionization potential for removal of a non-bonding electron from the iodine atom is considerably less than the value predicted assuming a neutral free iodine atom. This deficit between observed and predicted potential indicates that there is an accumulation of negative charge on or near the iodine atom in methyl iodide. Similar but increasing deficits are found in methyl bromide and methyl chloride, the effect being about twice as large for methyl chloride as for methyl iodide. It is also of interest here to note that, as Price has shown, the deficits are somewhat larger for the ethyl halides than for the methyl halides, paralleling the dipole moment evidence. Data on other molecules are also in harmony with dipole moment evidence. For instance, in H_2O there is a very considerable deficit between observed and calculated ionization potential for a non-bonding oxygen atom electron, indicating a considerable negative charge on or near the oxygen atom, in harmony with the observed rather large O—H bond moment (R. S. Mulliken: J. Chem. Physics **3**, 515 (1935)). Further, it is very interesting to note (R. S. Mulliken: J. Chem. Physics **3**, 565 (1935)) that in aldehydes and ketones the deficit in oxygen atom potential is about twice as large as in H_2O, in good agreement with the large dipole moment assigned by Smyth to the C═O bond.

Returning now to the problem of the anomalous moments observed in methyl iodide and some other carbon compounds, may it not be significant that it is just, or especially, for the carbon atom that these large discrepancies arise? One is tempted to connect this with the fact that the carbon valence electrons are of two kinds, *s* and *p*. As I have pointed out elsewhere (J. Chem. Physics **2**, 782 (1934)), the carbon electronegativity ought to be very different for *s* and *p* valence, the ordinary electronegativity on Pauling's scale being presumably a sort of weighted mean of these two. If one could have pure *p* valence alone, carbon should be strongly electropositive to iodine, while with *s* valence it should be powerfully electronegative. If one should postulate that in methyl iodide the carbon–iodine bond involves a somewhat larger fraction of *p* valence and correspondingly less of *s* valence than in the average case, one might account for a considerable C^+I^- polarity. At the same time, the C—H bonds would have to accept a larger fraction of *s* valence and less of *p* valence than usual, and this should enhance the usual H^+C^- polarity. The H^+C^- and C^+I^- dipoles would thus coöperate to make a large resultant moment. Thus on this postulate of partial *s*, *p* selectivity between the C—I and C—H bonds, one could expect a great increase in the CH_3I dipole moment as compared with what one would expect by assuming a single effective electronegativity for the carbon atom, or by subtracting C—H and H—I dipole moments.

The same postulate would permit an explanation of the surprisingly slow increase in dipole moment from methyl iodide to methyl chloride, and the decrease for methyl fluoride. In going from iodine to fluorine, one would expect the preference for *p* valence to decrease, and one might assume that in chlorine or at any rate in fluorine it is replaced by preference for *s* valence. This would have the effect of making the C^+F^- dipole, and at the same time the H^+C^- dipole, unexpectedly small.

Now it may be asked, is our postulate tenable? It must be admitted at once to be rather surprising that, as between hydrogen and iodine in methyl iodide, the more electronegative atom iodine should show a preference for the less electronegative *p* valence, and the less electronegative hydrogen a preference for the more electronegative *s* valence. It is still more surprising that in methyl bromide (and perhaps even in methyl chloride and methyl fluoride), the halogen atom apparently still has some preference for the *p* valence of carbon, if we are to explain the dipole moments in this way. However, several factors should be involved in a quantum-mechanical consideration of the problem. Possibly the fact that the halogen atom valence electron is of *p* type, the hydrogen electron of *s* type, may be partially or largely responsible for the postulated *s*, *p* selectivity effect in the carbon valence.

The foregoing *s*, *p* selectivity postulate should be regarded for the present as merely a hastily made suggestion, since time has not yet permitted the critical analysis without which its chances of being correct must, on general principles, be considered small. However, it seems possible that it may at least contain the germ of an idea.

A few remarks on the nature of the quantity μ_s, another topic coming under the subject of Dr. Smyth's paper, may now be in order. Let us consider the molecules HI, AgI, and NaI. In each of these there are six outer electrons, two σ and four π. The σ electrons are bonding in HI, but may be taken in first approximation in NaI as belonging to the iodine atom, making it I^-. The π electrons are always non-bonding iodine electrons. In the weakly polar molecule HI there should be a large homopolar dipole term of polarity H^-I^+, due to the bonding pair of σ electrons centered nearer to the hydrogen than to the iodine nucleus. As a result of the accumulation of negative charge in the homopolar bond, the readily polarized iodine electrons will tend to be displaced away from the hydrogen atom, thus giving a μ_i opposing the homopolar dipole and assisting the ordinary H^+I^- dipole. The results of the last sentence hold, however, only if the ordinary H^+I^- dipole charges are sufficiently small; but this is almost certainly true.

If now we turn to the extreme heteropolar case of Na^+I^-, where the σ electrons may at first be assigned to the I^-, there should be very little homopolar dipole effect. In second approximation the π (and the σ) electrons of the I^- are polarized in the direction of the Na^+ ion. In this case μ_i due to the π electrons, as well as the polarization of the σ electrons, opposes the primary Na^+I^- dipole and so aids any homopolar dipole term which may be present. From these examples one sees that μ_i may either assist or oppose the primary dipole, and likewise the homopolar dipole, depending on circumstances.

Finally, it may be appropriate here to point out (Phys. Rev. **50**, 1028 (1936); **51**, (1937)) that in certain molecules containing an atom of low ionization potential (MH and probably MX, where M = alkali metal atom, X = halogen atom), the basic suppositions underlying Pauling's electronegativity scale apparently fail completely, while the writer's scale also loses all but qualitative significance. It appears not unlikely that the concept of electronegativity may some day outlive its usefulness.

Maurice L. Huggins (Eastman Kodak Co.): It is of interest to compare the relative electronegativities computed from bond energies, ionization energies, and dipole moments with those obtained by Hixon and others (Hixon and Johns: J. Am. Chem. Soc. **49**, 1786 (1927); Goodhue and Hixon: ibid. **56**, 1329 (1934); **57**, 1688 (1935)) from ionization constants of acids and bases in water solution. In general, the order of negativities is the same, but with carbon and hydrogen the order is apparently reversed. This reversal is readily explainable by means of the hydrogen bridge theory. A hydrogen bridging to a water oxygen atom is more negative than a carbon (of an aliphatic radical); whereas a non-bridging hydrogen seems to be less negative than such a carbon. This matter is more fully discussed in my paper on "Hydrogen Bridges in Organic Compounds" (J. Org. Chem., in press).

Remarks on Molecular Structure and Van der Waals Forces (page 221). E. MACK, JR. (University of North Carolina).

MAURICE L. HUGGINS (Eastman Kodak Co.): Dr. Mack's work in this field has been very interesting and suggestive; with most of it I am heartily in agreement. Instead of using a relatively small ball for the carbon atom, with a special dome structure for the benzene ring, it seems more logical to me, however, to represent carbon atoms (as he does hydrogen atoms) by balls, of radius proportional to the "*non-bonding*" radius, which are cut off on the side toward each *bonded* atom. The essential point is that the equilibrium interatomic distance for two non-bonded atoms is much larger than that for two bonded atoms. I believe that the evidence Dr. Mack has presented in favor of his dome model for benzene will apply equally well to the model arrived at in the above way.

It should be emphasized that equilibrium distances are not strictly additive functions of constant atomic radii, deviations from constancy and additivity being especially large for non-bonded atoms. Contact between a carbon sphere of the proper size for C...C contacts and a hydrogen sphere of the size appropriate to H...H contacts does not give correctly the C...H equilibrium distance. In spite of such limitations, models of this sort are very useful.

The Theory of the Liquid State (page 249). HENRY EYRING AND JOSEPH HIRSCHFELDER (Princeton University).

H. EYRING AND J. HIRSCHFELDER (Princeton University): In our treatment, we introduced the free volume V_f in such a way that it appears in the partition function for the whole liquid $(F_l)^N$, as $(V_f)^N$. On the other hand, Guggenheim (E. A. Guggenheim: Proc. Roy. Soc. London **135A**, 181 (1932). Also R. H. Fowler: Statistical Mechanics, 2nd edition, p. 522. Macmillan and Co., New York (1936)) suggests another definition for effective volume, which he calls v, and this is related to our V_f by the following equation: $(V_f)^N = N!\,v^N$ and therefore very nearly, $V_f = Nv/e$. In Guggenheim's argument, v is the volume in which a molecule can move about its equilibrium position treating the liquid as a quasi-crystal. In our quasi-gaseous treatment, we suppose that the molecules move about as in the gas and can share the total free volume of the system, V_f, between them. We calculate from our model the average volume in which the center of a simple molecule in the liquid can move, v_f, and take $V_f = Nv_f$. The quasi-solid theory leads to a vapor pressure greater by a factor of e (and a free volume less by this factor) than that given in our paper. These two treatments are applicable to different cases depending on the nature of the potential field in which the molecules are moving. If it requires a considerable amount of energy compared with kT to displace a molecule from its mean position the quasi-solid theory can be used, otherwise the quasi-gaseous theory is indicated. Near the melting point the quasi-solid is probably realized, whereas at high temperatures the liquid will approach the quasi-gas. The specific heat at constant volume, C_v, is a useful criterion. If the value of C_v for the liquid approximates that for the solid, the quasi-solid theory should be used, while if it approaches that for a gas the present treatment is preferable. Two obvious refinements of our theory are the introduction of the proper temperature dependence to our temperature independent free volumes and a consideration of holes at least at the higher temperatures. We are indebted to Dr. G. E. Kimball for calling our attention to the Guggenheim treatment. That our treatment is in accord with the usual quasi-gaseous theory for the liquid may be seen by a slight extension of the argument of Nernst (W. Nernst: Theoretical Chemistry, p. 250. Macmillan and Co., New York (1923)) which may be used to obtain our equation 3, as Dr. O. K. Rice has pointed out to us. We also wish to thank Dr. Samuel Levine for helpful discussions.

In the article, the symbol V_f has been used for the free volume per molecule, v_f, as well as for the free volume per mole in the liquid state. The same ambiguity occurs for V_l and V_g. Because of the great difference in magnitude of these quantities, i.e., a factor of Avogadro's number, it is hoped that there will be no confusion. Unfortunately it was not feasible to make the necessary changes in proof.

One of us (J. O. H.) would like to express his appreciation to the American Philosophical Society for a research grant which provided some financial assistance throughout the course of this work.

The Photochemical Behavior of the Aldehydes (page 259). G. K. ROLLEFSON (University of California).

MILTON BURTON (New York University): Professor Rollefson indicated the possibility that hydrogen atoms might be formed during the photolysis of acetaldehyde in one primary act. In the discussion of this report some work (Burton: J. Am. Chem. Soc. **58**, 1655 (1936)) of the writer, using a guard mirror method (Burton: J. Am. Chem. Soc. **58**, 1645 (1936)), leading to a contrary conclusion was cited. It was the writer's contention, in agreement with the proposal advanced by Blacet and Roof (J. Am. Chem. Soc. **58**, 278 (1936)), that the photolysis yields hydrogen molecules probably by the mechanism

$$2HCO \rightarrow 2CO + H_2 \qquad (1)^*$$

An additional source of molecular hydrogen might lie in the disproportionation reaction

$$2CH_3 \rightarrow C_2H_4 + H_2$$

Dr. Bates pointed out that in reactions producing HCO radicals glyoxal is detected among the products (cf. Farkas and Sachsse: Z. physik. Chem. **27B,** 111 (1934) and Frankenburger and coworkers: Z. Elektrochem. **36,** 757 (1930)). In a subsequent private discussion he also suggested the possibility that hydrogen atoms were formed and disappeared by reaction with acetaldehyde molecules on the first collision. In that event the writer's failure to detect hydrogen atoms would not be traceable to any supposed stability of HCO, although evidence for that conclusion is supported by the work of Farkas and Sachsse.

It is interesting to examine the consequences of the hypothesis suggested by Bates. There are two possible displacement reactions,

$$CH_3CHO + H \rightarrow CH_4 + HCO \qquad (2)$$

$$CH_3CHO + H \rightarrow H_2 + CH_3CO \qquad (3)$$

as well as reactions involving the addition of hydrogen atoms to acetaldehyde with the formation of stable radicals (Rice and Rice: The Aliphatic Free Radicals, p. 189. Johns Hopkins University Press, Baltimore (1935)). The latter may be neglected unless it be assumed that they enter into further chains, in which case the results will be the substantial equivalent of reactions 2 and 3 and their subsequent reactions.

It may be expected that the C—C bond in acetaldehyde is weaker than the C—H bond (cf. Kistiakowsky: J. Phys. Chem. **41,** 175 (1937)) and consequently that the initial step in the production of free radicals is

$$CH_3CHO + h\nu \rightarrow CH_3 + HCO \qquad (4)$$

and that the hydrogen atom present in reaction 2 results from the presumable instability of HCO. Consequently, the HCO formed in reaction 2 would likewise decompose

$$HCO \rightarrow H + CO \qquad (5)$$

thus producing long chains. The extrapolation of Leermakers' data (Leermakers: J. Am. Chem. Soc. **56,** 1537 (1934)) to room temperatures indicates the improbability of any chains. Consequently, reaction 2 most probably does not occur. On the basis of bond strengths, apart from steric considerations, reaction 3 would be considered less probable than reaction 2. However, if it does take place on the first collision, and even if, according to Norrish (Acta Physicochimica U. R. S. S. **3,** 171 (1935)), the reaction

$$CH_3CO \rightarrow CH_3 + CO \qquad (6)$$

follows immediately, the CH_3 formed would not enter into chains. There would be a slight increase of quantum yield, nevertheless, for each hydrogen atom produced would be responsible for the decomposition of a second molecule of acetaldehyde according to reactions 3 and 6. Now, if we assume that the mechanism of the photolysis of acetaldehyde is by the primary reaction

$$CH_3CHO + h\nu \rightarrow CH_4 + CO \tag{7}$$

or reaction 4 followed by reactions 5, 3, and 6 and

$$2CH_3 + M \rightarrow C_2H_6 + M \tag{8}$$

it is clear that the table assembled by Rollefson will have to be modified in respect to the quantum yields of the primary reactions as indicated in table 1.[5]

TABLE 1

Quantum yields of primary reactions

λ	PATH			
	1. Energy lost	2. Reaction 4	3. Reaction 7	4. Polymerization
A.U.				
3130	0.57	0.01	0.18	0.24
2804	0.42	0.05	0.42	0.11
2537	0.16	0.14	0.65	0.05

In Rollefson's table column 1, which represents the fraction of molecules which lose absorbed energy by collision or fluorescence without reacting, was obtained independently of any considerations as to the path of decomposition. According to Leighton and Blacet (J. Am. Chem. Soc. **55**, 1766 (1933)) fluorescence is detectable in acetaldehyde vapor at all wave lengths between 3130 and 2804 A.U. but not at 2654 or 2537 A.U. This is quite understandable on the basis of that column, but not on the basis of the similar column in table 1. When the amount of energy lost at 2537 A.U. is 16 per cent of the amount absorbed, it would be expected that fluorescence would be observed. Table 1 takes into account the consequence of the entrance of hydrogen atoms into the reaction, whereas Rollefson's does not. Consequently, we must conclude that if hydrogen atoms are formed during the photolysis they have no effect on the further course of the reaction or, which is more probable, that hydrogen atoms are not formed.

In this argument the only assumption has been that in acetaldehyde the C—C and C—H bonds have their usual order of strength and that the molecule decomposes in accordance with that order.

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[5] The figures in table 1 have been calculated directly from the data of Leighton and Blacet (J. Am. Chem. Soc. **55**, 1766 (1933)) and of Blacet and Roof (J. Am. Chem. Soc. **58**, 278 (1936)), except that the figures for the polymerization are those assumed by Rollefson. The latter estimates may be shown to be *practically* unaffected by the path assumed for the production of molecular hydrogen.

THE HEAT OF SUBLIMATION OF GRAPHITE

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Recent spectroscopic determinations of the heat of dissociation of carbon monoxide[1] lead to values of the heat of sublimation of graphite which are in serious disagreement with the thermal measurements of Marshall and Norton (4) (cf. 1, 2). Though there is a slight possibility that the predissociation of carbon monoxide observed at 9.5 volts is spurious, all indications are that the value of 9.10 volts for the dissociation energy of carbon monoxide and as a consequence the value of 124 kg-cal. for the heat of sublimation of carbon are correct.

The value of 177 kg-cal. given by Marshall was obtained by measuring the velocity of sublimation of graphite in a vacuum. He has obtained this from both the absolute rate and the temperature coefficient of this velocity. We are going to show, however, that Marshall's measurements can be reconciled with the heat of sublimation of 124 kg-cal. obtained from spectroscopic data.

The sublimation of graphite in a vacuum proceeds in such a way that atoms with a high "heat of sublimation" and atoms "with low heat of sublimation" evaporate alternately. The mean value is the true heat of sublimation. On the other hand the velocity of sublimation in a vacuum is determined by the slower one of the two alternating reactions and therefore yields an apparent heat of sublimation which is higher than the real one.

We consider, as usual, graphite as consisting of planes, the structure of which is shown in figure 1. We assume all the bonds in the plane to be equal and call the energy necessary to break one bond ϵ. We neglect the interaction between planes. As there are three bonds originating in every carbon atom and as each bond connects two carbon atoms, the average heat of sublimation, Q, is $\frac{3}{2}\epsilon$.

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[1] A full discussion of the spectroscopic data leading to a value of $D(\mathrm{CO}) = 9.10$ volts is given in reference 1.

If one tries to remove an atom out of an inner point of the plane (e.g., the atom A in figure 1), one has to break three bonds and an energy $3\epsilon = 2Q$ is necessary.

If, however, one removes an atom B from the edge of the plane, two bonds are broken with an energy $2\epsilon = \frac{4}{3}Q$. After this process, the atom D remains, attached with only one bond to the crystal plane. The energy necessary to remove it is therefore $\epsilon = \frac{2}{3}Q$. Thus the evaporation of the crystal takes place by alternately breaking two bonds and one bond, giving an average heat of sublimation of $1.5\epsilon = Q$.

We find the same result if we start on the other edge of the plane. To remove atom E, two bonds must be broken; to remove F, the breaking of two bonds is again necessary, but then G is left with one bond only linking it to the crystal, and from then on there is again an alternation between the breaking of two bonds and of one bond (see atoms H and I).

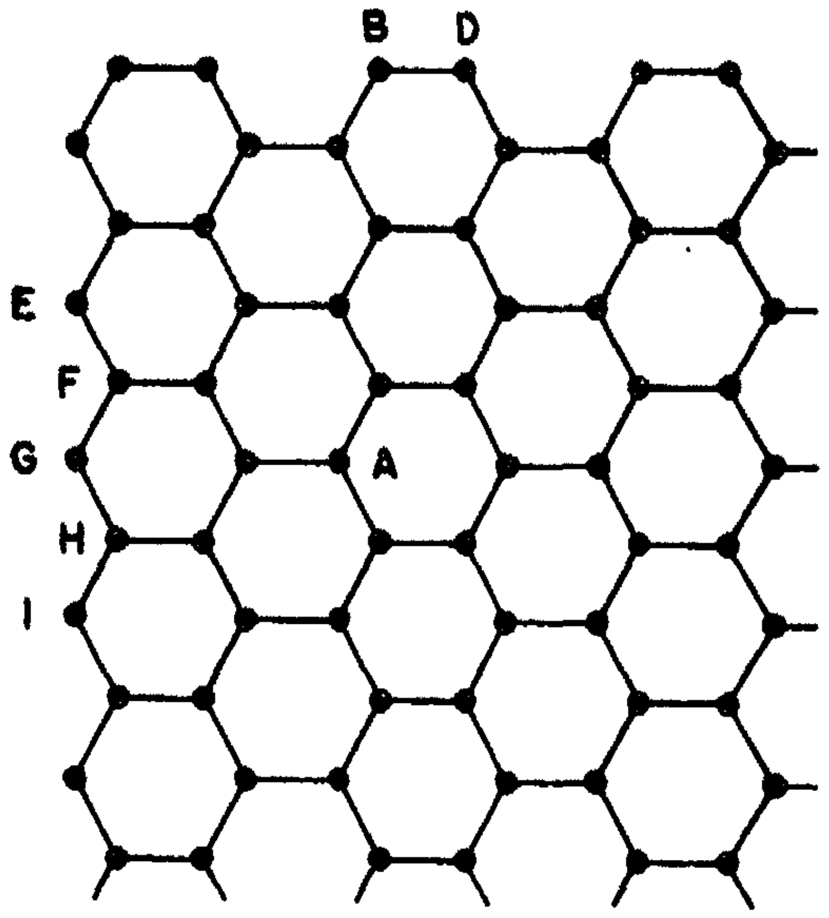

FIG. 1. The structure of graphite

The average time it takes for an atom bound by two bonds to the plane to escape is given by

$$t_1 = a_1 \exp \frac{4}{3} \frac{Q}{kT} \tag{1}$$

where a_1 has the dimension of time, is of the order of magnitude 10^{-13} sec., and does not depend strongly on the temperature.

The time for atoms bound only with one bond is

$$t_2 = a_2 \exp \frac{2}{3} \frac{Q}{kT}$$

where a_2 is of the same order of magnitude as a_1.

As t_1 is much larger than t_2, and as the second reaction can only take place after the first has occurred, the rate-determining step is the first reaction. Hence, both the absolute rate and the temperature dependence of the evaporation in a vacuum are governed by the factor $\exp - \frac{4}{3} \frac{Q}{kT}$.

Assuming[3] for QN the spectroscopic value 125 kg-cal., we obtain for this factor $\exp - \frac{167 \text{ kg-cal.}}{RT}$. Marshall's data fit the expression $\exp - \frac{177 \text{ kg-cal.}}{RT}$. We do not wish to discuss the remaining discrepancy of only 10 kg-cal., because it would be difficult to take into consideration the interaction of different layers, which we have neglected. Moreover the picture of valence bonds is perhaps not quite correct and might have to be supplemented by the effects of free electrons, graphite being a conductor. Free electrons would invalidate the proportionality between energy content and the number of C—C bonds.

We must discuss an alternative mechanism of evaporation. If the dissociation energy of C_2 is sufficiently large, the evaporation of a C_2 molecule will require less energy than $\frac{4}{3}Q$ and will then be the most rapid process.

In order to remove two carbon atoms simultaneously, three bonds have to be broken, but on the other hand the dissociation energy of C_2 is gained. The energy of three bonds, $3\epsilon N = 2QN$, is 250 kg-cal., according to the spectroscopic value which we have accepted. The dissociation energy of C_2 is known only from a rather uncertain extrapolation of vibrational levels (5). A linear extrapolation leads to 140 kg-cal. Linear extrapolation, however, gives frequently too high values. Any value between 90 and 150 kg-cal. therefore seems quite compatible with the spectroscopic data on C_2. These extreme values would give a rate of evaporation proportional to $\exp - \frac{160 \text{ kg-cal.}}{RT}$ and $\exp - \frac{100 \text{ kg-cal.}}{RT}$. Marshall's results are only compatible with the former. We must therefore conclude that the dissociation energy of C_2 cannot be much higher than 90 kg-cal.

The question arises for which other lattices the distinction between the true heat of sublimation and the energy as determined by a kinetic formula from the rate of evaporation into a vacuum is important. A short con-

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[3] N signifies the number of molecules per mole.

sideration shows that in lattices in which each atom (or molecule) has an even number of neighbors the rate of sublimation will correspond to the true heat. At the beginning a few loosely bound particles are removed (e.g., in a simple cubic lattice atoms sitting on an otherwise flat crystal plane). From then on the evaporation proceeds in such a manner that atoms are taken off which have half as many neighbors as an atom in the interior (3, 6, 7).[3] The energy necessary to tear them off will be equal to the average binding energy of an atom in the lattice. If, however, the atoms possess an odd number of neighbors in the interior of the crystal, an atom leaving the surface cannot have half as many neighbors as an atom in the interior. The atoms which are most difficult to tear off will then govern the rate of evaporation. It will be noticed that whereas graphite gives thus a too slow rate of sublimation the velocity for diamond—could it be measured—would correspond to the true heat of sublimation.

We have to show next that we get the correct formula for the vapor pressure in equilibrium, in spite of equation 1. We call n_1 the number of carbon atoms (per 1 cm. length of the edge) attached by two bonds and n_2 the number attached by one bond, both in the state of equilibrium. The numbers evaporating per second and per centimeter are n_1/t_1, n_2/t_2. In equilibrium the number of atoms of each kind which evaporate must be replaced by an equal number of atoms condensing from the vapor. We assume that every atom sticks which hits any one of the n places per centimeter of the edge. If p is the pressure of the vapor, the number of these atoms (per second and per centimeter) is

$$nZp$$

where Z is only slightly dependent on the temperature and is of the order 10^9 if p is measured in atmospheres. But if an atom coming from the vapor hits one of the n_2 atoms attached to the surface with only one bond, the incoming atom itself forms two new bonds, becoming one of the group of n_1 strongly bound atoms. If, on the other hand, it hits one of the n_1 atoms already bound with two bonds, it can only form one new bond and belongs now to the group of n_2 weakly bound atoms.

Therefore the equilibrium conditions are

$$n_1 a_1^{-1} \exp - \frac{4}{3}\frac{Q}{kT} = n_2 Z p \qquad (3)$$

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[3] In a perfect cube of the sodium chloride type a corner atom is the one most easily removed. It has to be torn away from three neighbors, corresponding to the fact that in the interior each atom has six neighbors. Sublimation will progress in breaking the cube down from the corner and generating more and more atoms with exactly three neighbors.

$$n_2 a_2^{-1} \exp - \frac{2}{3}\frac{Q}{kT} = n_1 Z p \qquad (4)$$

Multiplying equations 3 and 4, one gets

$$n_1 n_2 (a_1 d_2)^{-1} \exp - \frac{2Q}{kT} = n_1 n_2 Z^2 p^2$$

or

$$p = Z^{-1}(a_1 a_2)^{-\frac{1}{2}} \exp - \frac{Q}{kT} \qquad (5)$$

We have therefore here the true heat of sublimation, Q, in the exponent, as it must be thermodynamically.

Dividing equations 3 and 4 one finds

$$\frac{n_1}{n_2}\frac{a_2}{a_1} \exp - \frac{2}{3}\frac{Q}{kT} = \frac{n_2}{n_1}$$

or

$$\frac{n_2}{n_1} = (a_2/a_1)^{\frac{1}{2}} \exp - \frac{Q}{3kT}$$

As the right side is small compared to 1 even for $T = 4000°$, one can put

$$n_1 \sim n$$

and

$$n_2 = n \left(\frac{a_2}{a_1}\right)^{\frac{1}{2}} \exp - \frac{Q}{3kT}$$

The correct vapor pressure formula comes out, because in equilibrium there are mainly singly bound atoms evaporating, the number of which increases with $\exp - Q/3kT$, while the rate per atom increases proportional to $\exp - 2Q/3kT$. These atoms are mostly supplied by condensation from the vapor.

On the other hand, in the case of sublimation in a vacuum, we have

$$n_1' : n_2' = t_1 : t_2$$

or

$$n_1' \sim n \qquad n_2' = n \frac{a_2}{a_1} \exp - \frac{2Q}{3kT}$$

The loosely bound atoms are much scarcer here ($\exp - 2Q/3kT$) and supply an amount of evaporation equal to that of the strongly bound ones and therefore much smaller than in equilibrium. Therefore the total number of atoms leaving the surface increases rapidly if one approaches the equilibrium condition. We have here one of the rare cases in which the reaction velocity in one direction (rate of sublimation) near equilibrium is quite different from the value it has far away from it.

Another consequence is that the accommodation coefficient, measured by the number of atoms condensing, can be 1, and nevertheless the rate of evaporation in a vacuum be much smaller than the one calculated in the usual way from the equilibrium and the assumption of an accommodation coefficient of 1, as Marshall did. Therefore our conclusions do not contradict an old experiment of E. Thomson (8), in which he observed that in a carbon filament lamp obstacles throw shadows on the blackening wall of the bulb. This observation proves that the carbon atoms evaporating from the filament are not reflected from the wall (which after some time is covered by carbon), so that the accommodation coefficient cannot be far from unity. However, it is not certain that the carbon is present as graphite; it might be active carbon which may have a different accommodation coefficient.

In a certain sense the viewpoint presented here resembles the assumption of a potential hill which the evaporating molecules have to overcome (1). But while, in the usual picture of such a hill, the molecules passing over it would emerge with a considerable kinetic energy, the theory developed here requires both the tightly and the loosely bound atoms to leave the surface with thermal energies according to the Maxwell distribution law only. In the case of a potential barrier, the excess energy necessary to overcome this barrier is converted into kinetic energy, while here the excess energy of the first atom reduces the energy necessary for the second atom. Moreover the idea of a potential hill is incompatible with an accommodation coefficient of 1.

Even though the considerations given above do not explain the rate of evaporation of graphite in a quantitative and complete way, they show that no actual disagreement exists between the spectroscopic value of the dissociation energy of carbon monoxide and the rate of sublimation of graphite.

SUMMARY

The difference between Marshall and Norton's value, 177 kg-cal., for the heat of sublimation of graphite and the value 124 kg-cal., which follows from the spectroscopic value for the heat of dissociation of carbon monoxide, is explained by the consideration that in the process of evaporation in a vacuum as used by Marshall and Norton for every alternate

carbon atom two C—C bonds have to be broken instead of the average 3/2 bond. The spectroscopic value is the average value, and should accordingly be roughly 25 per cent smaller than the value for evaporation in a vacuum.

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NEW BOOKS

The Thermochemistry of the Chemical Substances. By F. Russell Bichowsky and Frederick D. Rossini. 460 pp. New York: Reinhold Publishing Corp., 1936. Price: $7.00.

The sub-title, "The assembly of a self-consistent table of 'best' values for the heats of formation of the chemical substances (except carbon compounds containing more than two carbon atoms), including heats of transition, fusion and vaporization," indicates very well the scope of this volume, which is a "complete revision and extension" of the section on thermochemistry prepared by Bichowsky for Volume V of *International Critical Tables.*

In the original compilation, all "values were recorded in joules, in the hope that thermochemists might come to use this fundamental unit in their calculations and writings. But the attempt to break away from the calorie as a unit in thermochemical and thermodynamical calculations proved to be unpopular and apparently hopeless of accomplishment." Therefore the data in the present work are given in calories, the calorie being defined as 4.1833 international joules.

The introduction (pp. 9–16) explains the method of using the tables and gives the necessary information concerning the units, symbols, abbreviations, methods of calculation, etc.

The first section (pp. 17–170) consists of a tabular presentation of the data, and contains 5840 values of heats of formation, also 350 values of heats of transition, fusion, vaporization, or reactions for substances for which the heat of formation is not known. As far as possible, there are given for each compound the physical state, a description of its crystalline form or electronic configuration, the heat of formation, and the heats of dissociation, etc., depending upon the value known for the compound in question. Every value is given as the heat evolved when the reaction takes place at a constant pressure, or a fugacity, of 1 atmosphere and at a temperature of 18°C.

The second section (pp. 171–405) comprises the text of the volume and contains a discussion of all the published thermochemical data on reactions which can be utilized in computing the heat of formation of a given substance. These are arranged in the same order as the compounds in the tables. It would have added to the usefulness of the book if page references to the text had been given in the tables; it is realized, however, that this would have increased very much the mechanical difficulties of producing the volume, possibly increasing the cost out of proportion to the added value.

Section three is devoted to the bibliography; there are 3730 references, which include all the publications covered by *Chemical Abstracts* up to January 1, 1931 and nearly all of the important and significant contributions published from that time to the end of 1933.

The reviewer's connection with *International Critical Tables* gives him a very clear idea of the tremendous amount of laborious calculation and of checking and rechecking of values involved in the preparation of this book. The worth of the tables is greatly enhanced by the text. There can be no question but that the work will be of real value to all interested in this field, as well as to those who make only infrequent use of such data.

Clarence J. West.

International Table of Stable Isotopes. First report of the Committee on Atoms of the International Union of Chemistry. General Secretariat, 28 rue Saint-Dominique, Paris. F. W. Aston, *Chairman*, N. Bohr, O. Hahn, W. D. Harkins, G. Urbain.

The table of stable isotopes published in English, French and German contains the atomic numbers, the mass numbers (in whole numbers only), and the relative abundance of each isotope for all the elements except numbers 43, 61, 85, and 87 and the radioactive ones 84, 86, 88, 89, and 91.

Although no discussion by the Commission accompanies the table, one must be struck, not only by the number of individual isotopes and the diversity of their distribution, but also by the evident fact that as means for detection or fractionation are refined, a much larger number of those of rare occurrence is certain to be disclosed.

S. C. Lind.

Fundamentals of Qualitative Chemical Analysis. By Roy K. McAlpine and Byron A. Soule. 5¼ x 8¾ in.; ix + 325 pp. New York: D. Van Nostrand Co., Inc., 1936. Price: $2.40.

This brief text can be used to excellent advantage in a course in qualitative analysis. This is not a mere condensation of the author's classic, Prescott and Johnson's *Qualitative Chemical Analysis*, but as the authors state in their preface, "An attempt has been made to provide more specific assistance than usual for the teacher and the student." Anyone who has had much experience teaching this subject will acknowledge that their aim has been attained.

Among the meritorious new features of this text, particularly from the pedagogic point of view, are two that are outstanding: (1) A chapter devoted to study aids. Material is given here to show the student how and what to study. Fourteen questions of the usual type on group I are given, with brief but comprehensive answers. The student may follow a similar plan with the other groups. (2) A splendid summary and review at the end of each group separation.

An interesting and probably reasonable departure from the usual procedure, to quote from the preface, is: "placing the arsenic division of group II in a chapter by itself and postponing its introduction until the other groups have been presented in detail. In a scheme arbitrarily limited in scope, there is a definite advantage in using the arsenic division to illustrate the increase in complexity of procedure that will normally be required when the list of metals is expanded."

The first four chapters are devoted to (1) review material, which is essential for an understanding of qualitative analysis, (2) chemical arithmetic, (3) formulas and equations, (4) ionization theory, including common-ion effect, solubility product, hydrolysis, etc. The remaining chapters include the usual ones,—one on laboratory technic, a separate chapter on each group or division, including common compounds, reactions of the ions, separations, relation to other groups, equations, in the case of metals a summary and review, problems and laboratory exercises; an excellent appendix with useful reference tables is provided.

The authors do not employ the more modern meanings of acid and base as proposed by Brönsted and by Lowry.

The physical make-up of the book is in keeping with the contents. The book is to be recommended.

Lillian Cohen.

Introduction to Theoretical Chemistry. By W. B. Meldrum and F. T. Gucker, Jr. 614 pp. New York: American Book Company, 1936. Price: $3.50.

In the preface to this book the authors state that their purpose is "to outline a course of study which will amplify the too thinly disseminated knowledge of important generalizations already possessed by the student" who has completed his first year of college chemistry. The information on the fundamentals of physical chemistry, which is contained in the first 436 pages of the book, is comparable to that usually included in a good introductory text of general chemistry. In addition to the description of an unusually large number of experiments illustrating the various chemical principles, a great deal of historical material is included in this part of the book. It is interesting to compare the discussion of atomic properties, chapters 17 to 22, from which the earlier historic material has been largely omitted and in which the illustrative experiments are taken largely from present-day work.

In the reviewer's opinion the authors deserve especial praise for choosing, as illustrations, a number of inorganic reactions which are not commonly included in an elementary text, and thereby suggesting to the thoughtful student that inorganic chemistry is a complex subject which may be worthy of his further attention. On the other hand, it is regrettable that the modern theory of acids and bases is not presented, if not to the exclusion of, at least as an alternate to, the more clumsy classical theory. The unqualified acceptance (p. 4) of the validity of the Allison magneto-optic method and of the evidence for the existence of alabamine and virginium is not justified by the present status of the subject, and is particularly unfortunate in an elementary text. The authors' bias (p. 341) against representing the total chemical reaction which occurs in a galvanic cell when the circuit is closed is not only unjustifiable, but is also definitely inconsistent with the equations written for complete cell reactions on pp. 374, 375, 376, 377, 384, 390, 411, and 413. The reviewer believes that the book would be improved if this chapter (Chapter 13) were omitted and the descriptive material which it contains incorporated in Chapters 14 and 15.

The book is marred by a number of minor errors, of which the following are typical. Figure 15, p. 83, appears to be incorrectly labeled and is entirely misleading; it might well be omitted. On p. 92, the definition of the triple point is given instead of that of the freezing point; this same confusion of the triple and freezing point is implied on p. 151. The two equations given on p. 165 do not represent the detailed mechanism of the reduction of iodic acid by sulfurous acid, and the statement that these "two consecutive reactions take place" is misleading. While the statement, on p. 168, that "a rise of 10°C. in temperature approximately doubles the rate of a chemical reaction" is roughly true for many reactions occurring at room temperature, it is obviously incorrect to conclude from this that the rate at 100°C. will be 256-fold greater than that at 20°C. (this factor being about threefold too large). On the upper half of p. 181, "Influence of Concentration" appears to be a misprint for "Influence of Pressure." The statement, on p. 209, that "dry liquid hydrogen chloride is not a conductor of electricity" might be an acceptable approximation for a high-school text, but it is an oversimplification for a book intended for college sophomores. On p. 347, it is implied, incorrectly, that sodium in an amalgam will not react with water, in a sodium chloride solution, if a positive current is flowing from the solution to the amalgam, but will react if the current is discontinued. It is doubtful if the increase of reactivity of water toward metals with increasing temperature is due chiefly to the increase in ionization of water, as is stated on p. 404. The peroxide ion is erroneously indicated with a single charge on p. 589.

On the whole the book is well written and contains a great deal of interesting information. Some subjects, as in Chapter 9, are particularly well presented. However, whether a book of this character will prove to be of real value to the student of chemistry remains an open question.

ROBERT LIVINGSTON.

The Chemistry of the Colloidal State. By John C. Ware. Second edition. 9 x 6 in.; 334 pp. New York: John Wiley and Sons, 1936. Price: bound, $3.75.

In the preface the author says: "The text has been largely rewritten and, wherever possible, the practical applications of the colloidal state have been interwoven with the theoretical material. The space given to adsorption has been doubled, and the subject now occupies an entire chapter. A section on electrokinetic potential has been added to the chapter on the electrical character of interfacial phenomena. The chapter on the precipitation of colloids has been revised and extended to include the recently developed material on the subject. A new chapter has been added on intermediate cases and soaps."

There are a few obvious errors of facts. When discussing gas and vapor (p. 19), the author has confused boiling temperature with critical temperature. Perrin did not work with gutta-percha (p. 37). The German word "Gummigutt" has bothered other people. The rise of liquids in a capillary tube is certainly not necessarily due to the presence of an air film on the liquid and the capillary tube (p. 76). It is unwise not to differentiate between a semipermeable membrane and a dialysis membrane (p. 132). It is not possible (p. 112) for transition colors to change quite generally yellow → red → blue → purple → green → brown. The purple must come between red and blue. Body color is not due to reflected light (p. 109).

This book presents colloid chemistry through a slight haze. The outlines of any topic are blurred. It is probable that the author does not consider the interference colors of uniform oil films as garish. The book possibly appeals to people holding a certain point of view, but it equally obviously does not appeal to those who look at things differently. The book can only be recommended to those to whom it will be helpful and the reviewer cannot write specifications as to them.

Wilder D. Bancroft.

The Renaissance of Physics. By Karl K. Darrow. 306 pp. New York: The MacMillan Co., 1936. Price: $3.00.

Although this outline of physics is apparently intended for the lay reader, the spectacular results of modern physics are presented not as isolated achievements, nor as revolutionary supplanters of classical physics, but rather as the culmination of years of progress which began with the first studies of those phenomena which are produced when amber is rubbed with cloth. Of the twelve chapters which make up the book, the first seven deal with classical physics; nuclear physics and closely related topics are discussed only in the last three. It is noteworthy that the author has produced a sound outline of physics without the use of any mathematics whatever. While a few equations occur in the text, these (with the exception of the "chemical" transmutation equations of Chapter X) seem to be included, not because they are needed in the argument, but rather because they, like the photographs of apparatus, serve to "decorate the book." The author has not hesitated to lighten his style by the introduction of a number of vigorous figures of speech. For example, an alpha-particle which is neutralized when it loses its velocity is compared to "a man who gets tired of a fast free life and settles down with a family," and a neutron which unhindered passes the electrostatic barrier of a nucleus and then brings about its disintegration is compared to "the Trojan horse of legend."

Robert Livingston.

Kernphysik. Edited by E. Bretscher. 24 x 16 cm.; 141 pp. Berlin: Julius Springer, 1936. Price: in paper covers, 12 RM.

From time to time a discussion extending over a week is held in the Institute of

Physics of the Technische Hochschule at Zürich, for which some theme from modern physics is selected. Last year the chosen subject was the physics of the nucleus, and the volume before us is made up of the various contributions. Dr. Bretscher, the editor, has provided an introduction, in which he briefly explains the essence of the nuclear problems of today.

The book is divided into three sections: Nuclear Physics; the Compton Effect; and Cosmic Radiation. It is not possible in the short space at our disposal to summarize the different papers; it must suffice to give the authors, whose names will vouch for the authoritative nature of their contributions. From England come Oliphant, Cockcroft, and E. J. Williams, discussing, respectively, conservation problems in the transformation of light elements, the emission of electrons and positrons in transmutations, and nuclear disintegration by cosmic radiations, as well as certain other aspects of the problem. Dunning, from America, writes of the interaction of neutrons with matter. From Germany Meitner treats of the artificial radioactivity of uranium isotopes; Bothe of coincidence measurements on the Compton effect, among other things; Geiger of cosmic showers; Fleischmann of energy relations in the capture of neutrons. From France, Halban and Preiswerk discuss the absorption and diffraction of neutrons, and Auger the analysis of the cosmic radiation into hard and soft components. Bernadini and Franchetti, from Italy, give a very short account of experiments on coincidences bearing on the Compton effect. Clay, from Holland, contributes a brief systematic treatment of the properties of the primary cosmic rays. The languages used are English, French, and German.

The book gives a very good picture of the present intense activity in the field of nuclear research, although, needless to say, there are many branches which are not represented. The treatment is, in general, simple, although a pretty good acquaintance with previous work is assumed on the part of the reader. For the man who wants to know the kind of work that is being done on nuclear transmutations and cosmic radiation the book possesses great value.

E. N. DA C. ANDRADE.

Simplified Structure Factor and Electron Density Formulae for the 230 Space Groups of Mathematical Crystallography. By KATHLEEN LONSDALE. 28 x 22 cm.; iv + 181 pp. London: G. Bell and Sons, Ltd., 1936. Price: 10/- net.

All workers on the determination of crystal structures will be grateful to Mrs. Lonsdale for this set of tables. It contains, for every one of the 230 space groups, the coördinates of the general equivalent points, and the corresponding general form of the geometrical factor, together with the simplified forms that the factor assumes when some of the indices become zero. The relationships between $F(hkl)$ and its values obtained by permutation of sign among the indices are clearly set out, and in those cases in which the origin of coördinates is not a center of symmetry of the structure the same information is given for the phase angle $\alpha(hkl)$ which then occurs in the formulae. Finally, the electron density function, expressed as a Fourier series, is given for each space-group, in that useful form in which the summation extends only over the positive range of the indices. The worker will in fact find here, in a readily accessible form, all that information which, at the cost of much labor, he would otherwise have had to derive from first principles for himself. The tables are, however, intended to be used in conjunction with the excellent introduction, in which the symbols and conventions used in them are clearly explained.

The whole book, with the exception of the preface, is in manuscript, reproduced by a photographic process. This has made it possible to produce the book at the very moderate price of 10/-; but it is in itself far from being a disadvantage. Mrs. Lonsdale's beautifully neat manuscript and mathematical formulae are a pleasure to read, and give a personal touch to this work that is lacking in most scientific treatises.

R. W. James.

Aluminium-Legierungen Patentsammlung geordnet nach Legierungssystemen. 2 Teil (Zugleich Anhang zu Aluminium Teil A in Gmelins Handbuch der anorganischen Chemie, 8 Auflage). By A. Grützner and G. Apel. *Nebst einem Markenverzeichnis bekannter Aluminium-Legierungen.* By A. von Zeerleder. 25 x 17 cm.; 344–868 pp. Berlin: Verlag Chemie, 1936. Price: 40.50 RM.

The second part of this work deals with alloys of aluminum with titanium to zirconium, the first part having dealt with silver to thorium. The arrangement is in three columns, the first giving the composition, the second the properties and uses, and the third the author and literature (patent numbers). The supplement on trade designations gives the name of the alloy, the manufacturer or inventor, and the percentage composition. The preface states that the work is now complete. In view of the increasing importance of aluminum alloys the collection of information in these two volumes cannot fail to be of considerable service.

J. R. Partington.

Das Ausblühen der Salze. By Karl Schultze, Hygien. Staatsinstitut Hamburg. Sonderausgabe aus den Kolloid-Beiheften Bd. 44. 23.5 x 15.5 cm.; 99 pp.; 36 fig. Leipzig: Th. Steinkopff, 1936. Price: 4 RM.

Although "Ausblühen" is usually translated as "efflorescence" the author interprets this term very liberally and includes in his very interesting book a range of phenomena which normally would not be classified under this heading. One naturally expects to find an account of the loss of water from salt hydrates and the effects obtained in the evaporation of solutions, e.g., the creeping of salts and the formation of crusts. There are, however, interesting accounts of the formation of alkalis, nitrates, gypsum and other substances on the surface of soil and desert land, and valuable comments on the causes of bloom of sulfur on vulcanized rubber, patina formation, the rise of sap in plants, and the appearance of efflorescent substances on building materials. Many will also read with advantage the references to those curious thread-like growths such as hair silver, copper hair, and alumina threads. Careful consideration is given to the theories which have been advanced to explain these various phenomena; the author expresses his preference for the capillary theory, as it can be usefully applied in very diverse fields. There is much within the scope of this book to interest the chemist, the physicist, and the biologist, including those directly engaged with soil problems.

W. Wardlaw.

Principles of Biochemistry. By Albert P. Mathews, Andrew Carnegie Professor of Biochemistry, University of Cincinnati. x + 512 pp.; 4 fig. Baltimore, Maryland: William Wood and Company, 1936. Price: $4.50.

This is not a revision of the well-known *Textbook of Physiological Chemistry* by the same author, but rather an entirely new book designed for use in colleges and medical schools where the course offerings preclude the use of the larger and more detailed text.

The text is written in a flowing and very readable style and there are interspersed between the discussions of facts and scientific findings those thoroughly enjoyable and apt philosophical comments of the author which characterize most of his publications. To Mathews, science, and especially physiology and physiological chemistry, is a living, dynamic thing, and he tells its story with an infectious enthusiasm.

The text is subdivided into forty chapters under the six major headings as follows: "The Chemistry and Metabolism of the Glucides"; "The Chemistry and Metabolism of the Lipides"; "The Chemistry and Metabolism of the Proteins"; "The Special Chemistry of Important Tissues. Blood and Connective Tissues"; "The Catalytic Agents of Growth and Development. Vitamins and Hormones"; and "The Income of Energy." As might be anticipated from these major headings, the applications of physics and physical chemistry to problems of biochemistry and physiology have been almost wholly ignored, only casual mention of physicochemical principles appearing here and there (ten pages are devoted to "the physical chemistry of the blood and tissues").

The reviewer believes that it is unfortunate that Mathews seems to prefer the term "glucides" as a substitute for the generally used English term "carbohydrates," although actually he uses the two terms more or less interchangeably. It appears to be extremely doubtful if this particular series of nomenclature changes will be officially adopted by English-speaking chemists, and its introduction into a textbook intended largely for the instruction of future physicians cannot but bring with it a certain element of unnecessary confusion.

However, any minor faults are insignificant when contrasted with the real accomplishments. It is a most admirable and accurate textbook of physiological chemistry and deserves a wide adoption in colleges and medical schools where the emphasis of the course is placed upon the physiology and biochemistry of the human. It is not a general biochemistry text but specifically one directed at the human organism, and as such ranks with the best in that field.

Ross Aiken Gortner.

Applied Radiochemistry. By Otto Hahn. 278 pp. Ithaca, New York: Cornell University Press, 1936. Price: $2.50.

Scientists are indebted to Cornell University for making available in the form of monographs the lectures given by their Non-Resident Lecturers in Chemistry. The present volume by the well-known director of the Kaiser Wilhelm Institute for Chemistry in Berlin-Dahlem constitutes a welcome summary of the valuable work done in the writer's laboratory and elsewhere in applied radiochemistry, and comprises the lectures delivered by Hahn at Cornell University in 1933. Since that time our knowledge of certain subjects covered in the text has increased and the interpretation of various phenomena has changed. For this reason it is to be regretted that the book has not been kept up to date.

After the introductory lecture, "From the Ponderable to the Imponderable" (published in Science 77, 397 (1933)), the book is divided into four parts. The first part gives a condensed account of the chemistry of radioactive elements. In order to avoid duplication of more extensive reviews found in monographs of previous lecturers (Paneth, Fajans), Hahn discusses particularly the selection of radioactive atomic types suitable for applied radiochemistry. The main bulk of the book is devoted to the latter subject and gives a clear exposé of the brilliant researches carried out in Hahn's laboratory, with due reference to the literature on radiocolloids, distribution of minute amounts of solid material in gases, and of radioactive elements between solids and solutions, adsorption, coprecipitation (formation of mixed crystals and anomalous mixed crystals), indicator methods (with application to biological problems), and emanation methods. The latter are finding more and more recognition in studies of the behavior of solids on heating.

The author not only gives a description of the phenomena, but has also attempted to interpret them. Certainly, with regard to the interpretations, the last word has not yet been said and in this respect the book is stimulating to further research. For example, it is hard to assume that bismuth (ThC) is mainly present in the form of anions at a pH of 4 (p. 58–9). If this were true the effect of ammonia upon the formation of radiocolloids (p. 60) is hard to account for. Hahn's "precipitation law" (p. 67) is stated in too general a way because even in the case of the formation of true mixed crystals the distribution of the micro-component depends upon the manner of formation of the precipitate. This is evident from Hahn's own discussion further on in the book (p. 73ff).

In conclusion, it should be said that full credit is given to other workers in the fields covered and that their views are discussed in an impartial way, even if they happen not to be in complete agreement with those of the author. Print and appearance of the book are excellent.

I. M. KOLTHOFF.

Enzymologia. Carl Oppenheimer, Editor-in-chief. Published by W. Junk, The Hague, Holland. Each volume to contain approximately 400 pages and to appear in 6 parts. The parts will appear at irregular intervals. Priced at 15 fl. (Dutch) per volume.

This is a new scientific journal devoted exclusively to the broad field of enzyme chemistry, enzyme kinetics, and enzyme behavior in its biological and technological aspects. An imposing array of collaborating editors, including practically all of the outstanding leaders in enzyme research, is listed on the cover page and assures the subscriber that the new journal will be truly international in scope. Articles are acceptable for publication in either English, French, or German.

Volume I, Part 1 was published June 30, 1936, and Part 2 appeared August 1, 1936. These two parts contain twenty original papers including contributions from such well-known authorities as C. Neuberg, K. Linderstrom-Lang, A. Fischer, J. H. Quastel, H. D. Kay, J. B. Sumner, and others of equal standing. Among those papers which have appeared there are several which should be of interest to the physicist and physical chemist, especially the one "On the Luminescence of Bacteria," which includes a quantitative study of the spectrum of the light emitted by *Photobacterium phosphoreum* and the influence of various environmental factors on the light emission of this organism.

If the two parts before the reviewer are representative of what we may expect in future issues, this journal will rapidly become an indispensable tool to all workers in biochemistry and physiology, for more and more students of life processes are coming to realize that the reactions of living matter are largely governed by enzymatic phenomena.

ROSS AIKEN GORTNER.

Industrial Chemical Calculations. By O. A. HOUGEN AND K. M. WATSON. Second edition. 487 pp. New York: John Wiley and Sons, Inc., 1936. Price: $4.50.

Those of us who found valuable material in the first edition of this book on the application of physical and chemical principles to industrial problems will welcome this new edition with its considerable rearrangement of the old material and the addition of some that is new.

For the benefit of those who are not familiar with the first edition, the following partial list of subjects treated will be of interest: *P–V–T* relationships of both ideal and actual gases; vapor pressure relationships; vaporization processes; humidity and wet- and dry-bulb thermometry; specific heat of gases, liquids, and solids; heat content; thermochemistry, including heats of reaction, of solution, of wetting etc.; weight and material balances in combustion processes and in miscellaneous chemical and metallurgical processes; calculations of crystallization, adsorption, and related processes; elementary treatment of entropy, free energy and fugacity and chemical equilibrium in both ideal and non-ideal systems. The treatment is quantitative in all cases, and methods of calculation are well illustrated by many numerical examples. A collection of additional problems is given at the end of each of the fourteen chapters.

Several of the chapters are practically unchanged from corresponding ones in the previous edition. Others have been reorganized to give a more logical sequence. New material added includes a treatment of the Merkel enthalpy-concentration diagrams for binary solutions; a section on conversion of units, symbols, and equation; a treatment of the thermochemistry of petroleum; and the introduction of chapters on *free energy, entropy, and fugacity* as a basis for the subsequent treatment of chemical equilibrium which has been broadened to include the calculation of equilibrium constants from free energy data and application to non-ideal gas equilibria. Room for the new material has been provided by omitting the chapter in the previous edition which treated distillation equilibria.

Anyone concerned with the quantitative application of physicochemical principles to industrial problems could not fail to find this a valuable source-book for problem data.

BARNETT F. DODGE.

Protoplasm. By WILLIAM SEIFRIZ. First edition. 584 pp.; 27 chapters; 179 illustrations. New York: McGraw-Hill Book Co., Inc., 1936. Price: $6.00. A McGraw-Hill Publication in the Agricultural and Botanical Sciences.

Professor Seifriz is a versatile scientist. His work on emulsions, gels, and other colloid topics is well known among chemists and physicists, but they may not be aware that Professor Seifriz is a member of a botany department and is an active investigator in botany and biology. Professor Seifriz's general attitude toward science, and, in particular, his point of view in his book is typified by the quotation from Descartes with which he introduces his preface: "If, therefore, anyone wishes to search out the truth of things in serious earnest, he ought not to select one special science; for all the sciences are conjoined with each other and interdependent."

The extent to which Professor Seifriz lives up to his principles is well illustrated by the titles of the chapters in his book: namely, The Living Substance; The Cell; Model Making; Micrurgy; Tissue Culture; The Colloidal State; Emulsions; Hydrophilic Sols and Gels; Surface Tension; Adsorption; Osmosis; Imbibition; Viscosity; Elasticity; The Structure of Protoplasm and Organic Colloidal Matter; Permeability; Acidity; Electrophysiology; Electrokinetics; Radiant Energy; The Rôle of Water; Salts; Carbohydrates; Fats; Proteins; Regulatory Substances; The Origin of Living Matter. As indicated by these chapters, the scope of the book is by no means as restricted as its title might suggest. In fact, a considerable number of the chapters cover the same ground, admittedly in a novel way, as is covered in the average elementary book on applications of physical chemistry to biology. The book abounds in literary quotations, bits of philosophy, and personal and historical items.

In his preface, Professor Seifriz states that his book was written for students in biology and medicine, and is not intended for his colleagues. It is evident that the author has striven to make the book easy and entertaining to read. Being free of footnotes and references, the pages have a "clean" appearance, and, with the many illustrations, make the book as readable as a novel. Very little knowledge of chemistry and physics and no knowledge of college mathematics is required of the reader.

In fact, the reviewer feels that the author has gone to extremes in simplifying his presentation and in avoiding numerical data, curves, and mathematical equations. It does not speak well for the scientific ability of the biologist if he is awed by graphs and simple equations. However, since most of the graphs and equations that could have been used would concern physicochemical matters with which the average chemist would be familiar, their omission should not prevent the chemist or physicist from gaining a stimulating and comprehensible view of many basic biological problems. The book presents an interesting expression of how a broad-minded botanist looks at his world.

The spirit of the book may be illustrated by a few quotations from the section on vitalism and mechanism: In considering the vitalism and mechanism points of view, the author states: "The experimental scientist is often loath to turn to the philosopher for a suggestion on the solution of his problems, but this would appear to be the best way out of the present situation. Let us rather not deny mechanism or vitalism, but ask the philosopher to tentatively interpret life for us. Philosophically inclined biologists see in *emergent evolution* an escape . . . from the mechanistic-vitalistic dilemma. . . . No matter how much knowledge we may have of carbon, hydrogen, and oxygen . . . , it will avail us nothing in an understanding of glucose. A whole is more than the sum of its parts, not merely because of complexity, but because in the functional whole we have another type of system. . . . Living matter is a mechanism obeying all natural laws, but it is incapable of definition or explanation; everything that goes to make up a living system is mechanical, and the individual parts of it are definable, but the collective all is indefinable. . . . A philosophy wherein living matter is interpreted as an organized functional system is not only an escape from a too rigid acceptance of either the mechanistic or vitalistic concepts, but it is also an escape from the fatalistic attitude of those who bemoan the harsh severity of experimental science."

Unfortunately, the book is somewhat marred by rather numerous errors, and the unwary biological student is apt to gain rather unusual ideas about various physicochemical matters. To mention a few noticed in the section on Brownian motion, for instance: It is said that Brown noticed the trembling motion of particles about 0.004-0.005 in. in size, and on the next page, it is said that particles larger than $4\ \mu$ (0.00016 in.) show no motion in water. Brownian motion does not cease at a "definite maximum size", and density is not a factor in Brownian motion. Figure 77 does not show the complete path of a particle in Brownian motion, but only the positions of the particle at fixed intervals of time. Larger particles do not exhibit a motion of greater amplitude than smaller particles. These and similar errors in other sections, the author will undoubtedly correct in a second edition.

E. O. KRAEMER.

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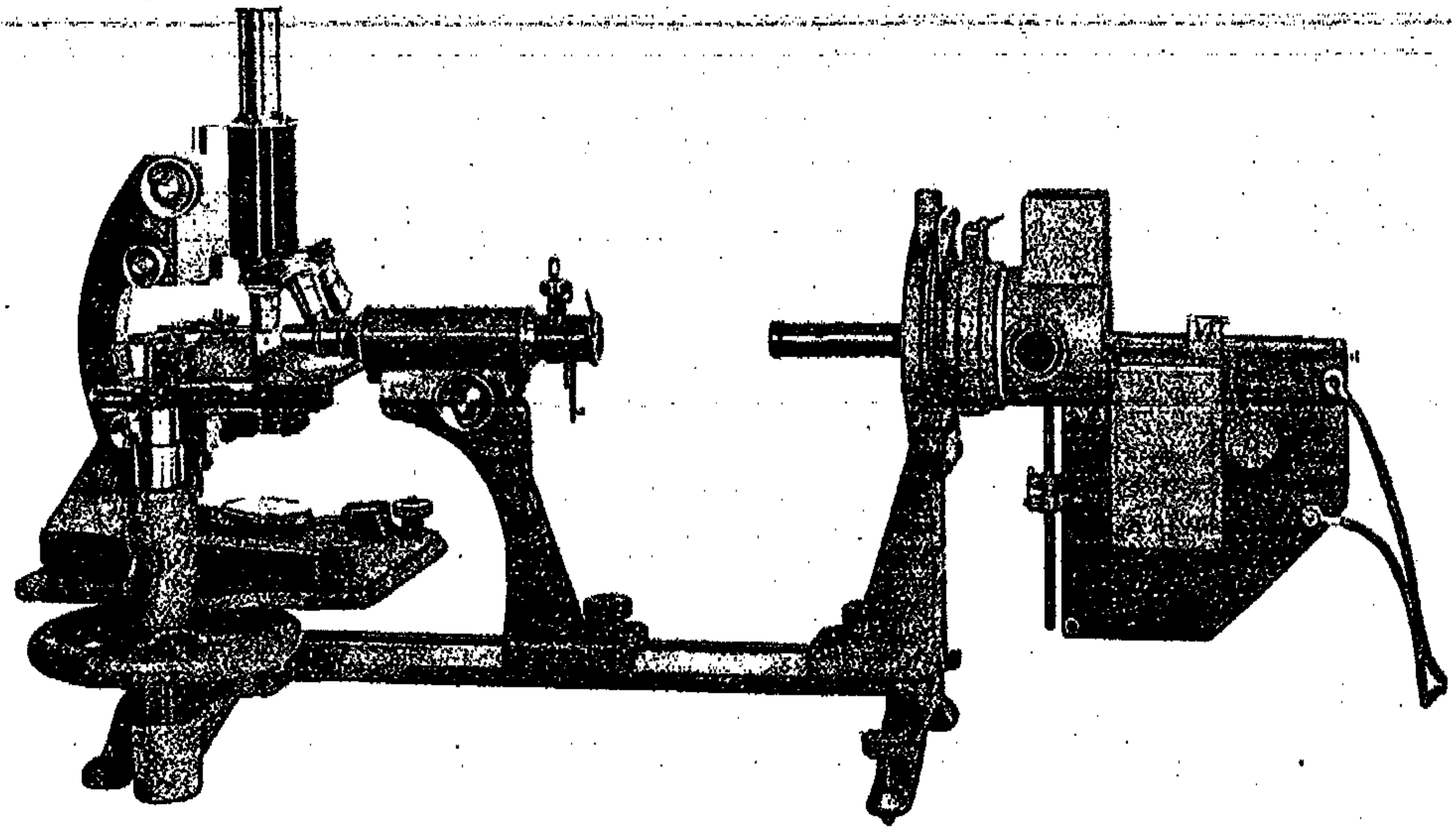

THE SOLUBILITY OF INDIUM IN MERCURY FROM 0° TO 50°C.[1]

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1513-59

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INTRODUCTION

Continuing an investigation begun in this laboratory on the solubility of metals in mercury (16, 17) we have studied the solubility of indium over the temperature range 0° to 50°C. The only work involving indium amalgams to be found in the literature is that of Richards and Wilson (21), Hildebrand (6), Williams (24), Davies and Keeping (2), and Narayan (15). These investigations covered a variety of subjects. However, they all employed dilute liquid amalgams and no data were obtained on the solubility of the metal in mercury.

The purpose of this investigation was to supply this solubility data over a convenient temperature range and to observe the general properties of indium amalgams. This information is desirable before attempting to employ amalgams of indium in reversible galvanic cells for free-energy measurements. If indium, which forms a trivalent ion in aqueous solution, can be used successfully for E.M.F. work it will provide an excellent means for testing the extension of the Debye-Hückel (3) theory as given by Gronwall, LaMer, and Greiff (5) for unsymmetrical valence type electrolytes. It is our purpose to extend this work on indium to include an investigation of electrochemical cells involving indium trichloride and indium sulfate.

PREPARATION OF MATERIALS

The indium used in preparing the amalgams was a commercial product claimed to be 99.99 per cent pure. Baxter and Alter (1), using a Féry spectrograph, examined a sample of indium from the same source and found only traces of lead, tin, zinc, cadmium, and copper. These impurities are negligible in this investigation.

Mercury-redistilled mercury was stirred under a molar solution of nitric acid and mercurous nitrate for three days and then redistilled three times

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[1] This article is abstracted from a thesis submitted by Walter G. Moran to the Faculty of Rhode Island State College in partial fulfillment of the requirements for the degree of Master of Science in Chemistry, June, 1935.

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in a slow current of air as recommended by Hulett (9). In addition the mercury was finally distilled under high vacuum to remove any possible non-volatile oxides which might have been carried over by the air current used in the previous distillation.

C.P. solutions of nitric and hydrochloric acids and ammonium hydroxide were used and diluted to the desired concentrations.

EXPERIMENTAL PROCEDURE

Since indium dissolves very readily in mercury, the amalgams were all prepared by the addition of a weighed quantity of the pure metal directly to a weighed quantity of the purified mercury. In this manner amalgams varying from 0.5 to 5 per cent indium were prepared and placed in a constant-temperature oil bath for from thirty-six to forty-eight hours in order to reach equilibrium. The equilibrium point was approached from both sides of the temperature being studied. The amalgams were frequently shaken during this period.

The constant-temperature bath was equipped with a brine coil, tap-water coil, and two heating coils. One heating coil was a permanent heater operated by a switch, while the other was operated by thermostatic control. The brine, which was pumped through the brine coil when operating below room temperature, was kept at −15°C. by means of a large refrigerating machine. The temperatures studied were 0°, 12.5°, 25°, 37.5°, and 50°C., and were easily maintained to within ±0.01°C. The Beckmann thermometers were checked periodically against the laboratory standard, which was certified by the Bureau of Standards. After the amalgam had reached equilibrium at the desired temperature, samples for analysis were removed, using the filter pipet method described in detail previously (16).

A method for the quantitative determination of indium in the presence of mercury could not be found in the literature. Mellor (12) gives detailed directions for analysis of the ores which are composed mainly of zinc, lead, and iron. It was found that the indium compounds formed in these methods were soluble or insoluble along with the corresponding mercury compounds. Jukkola, Audrieth, and Hopkins (10) decomposed rare-earth amalgams by distilling off the mercury in a vacuum furnace. They worked with lanthanum, neodymium, and cerium. This method of separation was attempted in the case of indium. A special distilling apparatus was constructed, but it was definitely unsuccessful. The mirror formation previously mentioned by several investigators (10, 18) appeared. In the earlier investigations it was removed by heating to a temperature of 1000°C. Our apparatus was not able to withstand this temperature. However, even at a temperature around 300°C. the distillate was found to have a dirty grey appearance, which indicates an imperfect separation due either to the mechanical carrying over of indium by the mercury vapor and air current or to volatilization of indium. The latter cause would indicate a rather high vapor pressure for indium. The greyish-black indium monoxide was probably formed in the receiver.

The following procedure was finally adopted. A weighed sample of the amalgam was dissolved in concentrated nitric acid. This solution was evaporated to dryness three times with concentrated hydrochloric acid to drive off as much of the nitrate ion as possible. The residue was taken up in 0.3 normal hydrochloric acid, which gives a hydrogen-ion concentration above that at which indium sulfide will precipitate (25). The solution was saturated with hydrogen sulfide gas to precipitate the mercury. Owing to the large precipitate formed it was advisable to do the precipitation and filtration in two steps. This procedure saves time and facilitates washing. All washing was done with 0.3 normal hydrochloric acid to maintain a constant pH as long as any hydrogen sulfide was in the solution. After evaporation to approximately 100 cc., ammonium hydroxide was added until the solution was definitely basic. The precipitated indium hydroxide was digested for several hours to facilitate filtering. The filtrate in all cases was tested for complete precipitation. An electric furnace operating at 800°C. was employed to convert the hydroxide to the oxide. According to Meyer (13) volatilization of In_2O_3 does not take place until approximately 900°C. The method was tested by analyzing several amalgams containing a weighed quantity of pure indium. As a further check several additional amalgams were analyzed.[2] The precision obtained was approximately 0.1 per cent. The determined weight tended to be lower than the actual weight taken, indicating possible adsorption of indium during the precipitation of the mercuric sulfide.

In some instances the oxide showed a brown color, rather than the characteristic canary-yellow of the sesquioxide. In these cases large discrepancies were found in the results. The phenomenon is probably due to the formation of other oxides, perhaps In_3O_4. No explanation as to why this occasionally occurred is offered at this time.

RESULTS AND DISCUSSION

The solubility of indium in mercury is summarized in table 1 for the various temperatures studied. The results tabulated represent the average of at least three separate determinations on individual amalgams. From a consideration of all the errors involved in the method the precision is indicated to be ±0.2 per cent. All values showing a variation greater than ±0.2 per cent have not been included in the table.

The results in table 1 are shown graphically in figure 1, where the log of the weight fraction is plotted against the reciprocal of the absolute

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[2] These analyses were performed by Mr. Bertram Brown, a senior student in chemistry.

temperature. The solubility curve was drawn in such a manner that the most reliable results were given the greater weight. The slope of the line was determined from a large scale plot and the line corresponds to the equation

$$\log N_2 = \frac{53.57}{T} + 1.714$$

where $\log N_2$ represents the weight fraction of indium in the saturated amalgam. The straight line indicates an ideal system conforming to Raoult's law. The specific heats of the crystals and liquid must be nearly identical, and the composition of the solid phase separating out must be constant over the temperature range 0° to 50°C.

TABLE 1

The solubility of indium in mercury

t	WEIGHT PER CENT INDIUM	AVERAGE	ATOMIC PER CENT INDIUM
°C.			
0	1.20		
	1.26		
	1.23	1.23 ± 0.02	2.14
12.5	1.29		
	1.25		
	1.27	1.27 ± 0.01	2.20
25	1.25		
	1.26		
	1.26	1.26 ± 0.00	2.18
37.5	1.29		
	1.27		
	1.28	1.28 ± 0.01	2.22
50	1.33		
	1.29		
	1.31	1.31 ± 0.01	2.27

In the light of the relationship between the melting point of a metal and its solubility in mercury, established by Tammann and Hinnüber (22), our results are not unreasonable. They find that for metals melting at from 300° to 400°C. more than 1 per cent of the metal is soluble in mercury. The solubility decreases with increasing melting point. Indium melts at 155°C., consequently one would expect it to be soluble to the extent of 1 per cent or greater.

These data may be interpreted in terms of internal pressures and the metallic solution theory of Hildebrand (7). The solubility of indium and mercury in each other should follow from their position in the table of internal pressures, providing no compound formation takes place. From coefficient of compressibility and expansion data (20) indium is placed between lead and thallium in the table given by Hildebrand, Hogness, and Taylor (8). A similar position is indicated by the method of Gilfillan and Bent (4), that is, by dividing the boiling point (14) by the atomic volume (20). The solubility of lead in mercury has been determined by Thompson (23) and found to be 1.60 atomic per cent at 25°C. However, thallium is extraordinarily soluble in mercury. At 20°C. a liquid amalgam may contain as much as 43.3 per cent of thallium. In this case compound formation has been definitely proved (19). Therefore our results, together with those of other investigators, indicate the correct position of indium in the table of internal pressures. The predicted mutual solubility of indium in lead and thallium has not been investigated, although the results of Kurnakoff and Puschin (11) indicate that solubility does take place.

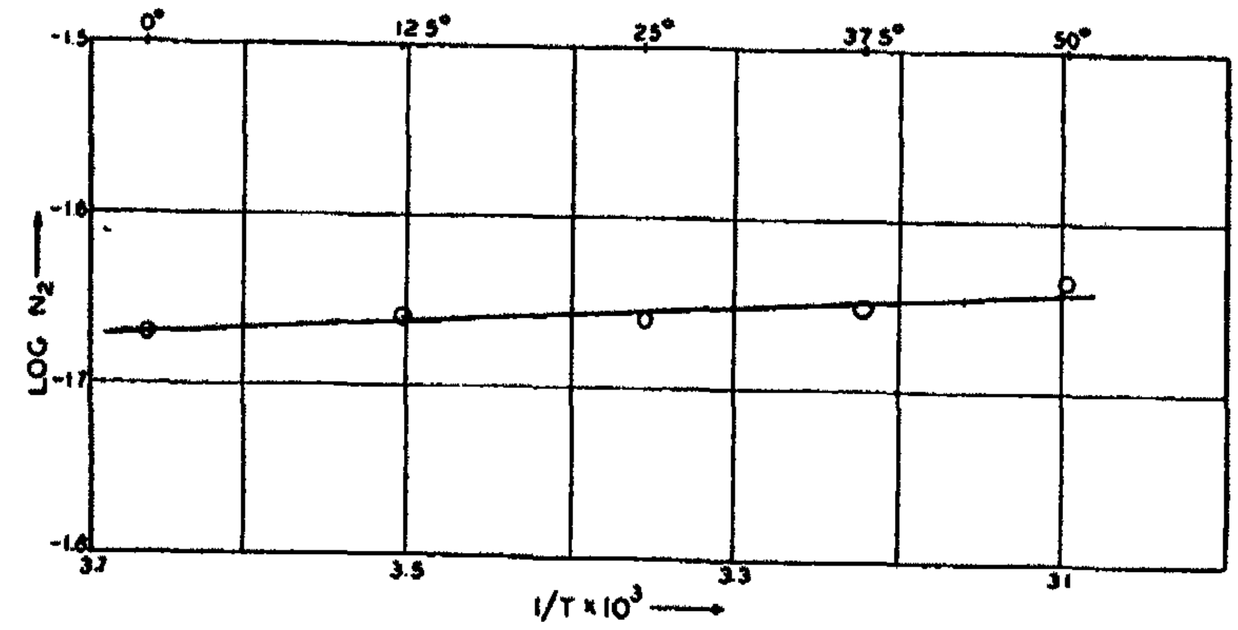

FIG. 1. The solubility of indium in mercury

The solubility of a sparingly soluble metal in mercury is not likely to be a definite quantity as long as filtration is the only method for determining a homogeneous phase. The wide variation in particle size and the diameter of the filter pores, together with the conditions of filtration (i.e., pressure), will control the meaning of the term "solubility." However, we believe that our data at least fix the upper limit of the solubility and that greatest credence should be given to the lowest results. A more detailed discussion of this problem has been given previously (16).

The properties of indium amalgams as observed during this investigation lead us to believe that precise E.M.F. measurements could be made using an amalgam electrode. The customary technique for excluding oxygen from the cell should be employed.

SUMMARY

1. Indium amalgams were prepared by the direct addition of a weighed quantity of the metal to a weighed quantity of mercury.
2. The solubility of indium in mercury is reported at 0°, 12.5°, 25°, 37.5°, and 50°C.
3. In the temperature range from 0° to 50°C. the solubility is represented by the equation:

$$\log N_2 = \frac{53.57}{T} + 1.714$$

where N_2 is the weight fraction of indium in the saturated amalgam.

4. The difficulties involved in the determination of a homogeneous phase by filtration are pointed out.
5. The solubility of indium in mercury indicates that indium has a rather high internal pressure, approximately the same as that of lead.
6. From the general behavior of indium amalgam we believe it to be suited for precise E.M.F. measurements.

We wish to express our thanks to the National Research Council for a grant-in-aid which in part made possible the construction of the apparatus used in this investigation.

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THE REACTION OF HYDROGEN CYANIDE WITH SULFURIC AND PHOSPHORIC ACIDS[1]

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INTRODUCTION

The interaction of concentrated sulfuric acid with cyanides of the metals is known to give quantitative yields of carbon monoxide (9). It was of interest to compare this decomposition of hydrogen cyanide by sulfuric acid with that observed when organic acids such as formic (8), malic (12), oxalic (1), and triphenylacetic (3) acids are decomposed by sulfuric or phosphoric acids. The decomposition of the organic acids probably occurs through the formation of an intermediate complex between the acid and the decomposing solvent, although no such intermediate has been isolated. The existence of an intermediate complex between hydrogen cyanide and sulfuric acid was postulated by Krieble and Peiker (6) to explain the catalytic hydrolysis of hydrogen cyanide in dilute sulfuric acid solutions. Compound formation between the halogen acids and hydrogen cyanide is well known and has been rather completely investigated (2). It is probable, therefore, that other strong mineral acids, such as sulfuric or phosphoric acid, form compounds with hydrogen cyanide. Such a compound of hydrogen cyanide and sulfuric acid may well act as an intermediate in the decomposition of a simple cyanide by sulfuric acid.

REACTIVITY OF VARIOUS ACIDS TOWARD HYDROGEN CYANIDE

Hydrogen cyanide was mixed with the acid to be tested and allowed to stand at room temperature for several weeks. Evidence of reaction was indicated by the disappearance of hydrogen cyanide or by a change in appearance of the acid. Those acids showing no reactivity were acetic (and acetic anhydride), formic, metaphosphoric, oxalic, perchloric (60 per cent), and selenous. Those acids showing a reaction were sulfuric, selenic, and phosphoric. Concentrated sulfuric and selenic acids to which several drops of hydrogen cyanide were added became warm a minute or so after mixing. A diluted sample of the mixture after standing a few minutes

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[1] This article is a portion of a thesis to be submitted by Alan W. Cobb to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

showed a complete absence of the cyanide ion. A sample diluted immediately after mixing always showed the presence of cyanide ion. Phosphoric acid (100 per cent), which had been supercooled, reacted similarly with hydrogen cyanide but very much more slowly.

PREPARATION OF THE REAGENTS

Hydrogen cyanide was prepared by the action of dilute sulfuric acid on sodium cyanide (14). The purified product was water-white, showed no decomposition over a period of nearly a year, and gave a freezing point of −14.85°C., which is in agreement with the accepted value (7). The 100 per cent sulfuric acid was prepared by adding "reagent quality" fuming sulfuric acid (20 per cent excess sulfur trioxide) to 96 per cent C.P. acid until the maximum freezing point (10.45°C.) was reached. Analysis gave the hydrogen sulfate content as 99.96 per cent.

The crystalline 100 per cent phosphoric acid was prepared by the vacuum dehydration of 85 per cent acid (11) of analytical reagent quality. A current of dry air was passed through the acid at 100°C. under the vacuum of a water pump for thirty-six hours. The crystals, which slowly formed upon cooling, were drained from the mother liquor in a vacuum desiccator. The recrystallized acid melted at 42.3°C., which agrees well with the value reported by other investigators. The product on analysis showed 100.00 per cent hydrogen phosphate.

COMPOUND FORMATION BETWEEN HYDROGEN CYANIDE AND SULFURIC ACID

When approximately equimolecular quantities of hydrogen cyanide and 100 per cent sulfuric acid were mixed at 0°C., a white and very hygroscopic solid was formed after several days. If the reacting mixture was not made up cold and kept cold by immersion in ice water, a vigorous frothing occurred with almost explosive violence. When a known excess of hydrogen cyanide was allowed to react with 100 per cent sulfuric acid for two days, an analysis of the excess cyanide showed that exactly one molecular weight of hydrogen cyanide had combined with each molecular weight of sulfuric acid. The analysis was carried out by diluting the mixture with water and titrating the excess cyanide with silver nitrate in the presence of potassium iodide and ammonia (5). The results of two such experiments showed that: (a) 0.00371 mole of hydrogen cyanide combined with 0.00372 mole of acid, and (b) 0.00384 mole of hydrogen cyanide combined with 0.00382 mole of acid. The white solid may be represented by the formula, $HCN \cdot H_2SO_4$.

The important properties of the compound were found to be its instability, insolubility in inert solvents, extreme deliquescence in moist air, and reaction with water and alcohol. The compound slowly decomposed even at 0°C. to yield carbon dioxide and sulfur dioxide. It was completely insoluble in all the common organic solvents. With alcohol it formed insoluble ammonium sulfate and ethyl formate. When exposed to air for a short time sufficient water was taken up to dissolve the substance completely, with hydrolysis to ammonium formate and sulfuric acid. The water solution was analyzed by making it basic with sodium hydroxide and distilling the ammonia into standard acid. The residue was then acidified with dilute sulfuric acid and the volatile formic acid distilled off. When the compound formation occurred in the presence of a large excess of 96 per cent sulfuric acid, the hydrolysis products gave a quantitative yield of ammonium formate. The following data were obtained with 9.680 g. of hydrogen cyanide and 25 cc. of sulfuric acid:

	Moles NH_3 found	*Moles HCOOH found*	*Moles HCN used*
Run I	0.0253	0.0252	0.0251
Run II	0.0248	0.0255	0.0251

When the compound was hydrolyzed in the absence of sulfuric acid the agreement was not as close as above. These results gave conclusive evidence that the complex formed in excess sulfuric acid hydrolyzed quantitatively to ammonium formate according to the following equation:

$$H_2O + HCN \cdot H_2SO_4 \rightarrow HCOONH_4 + H_2SO_4$$

The thermal decomposition of the complex in sulfuric acid solution will be discussed later in this paper.

RATE STUDIES ON COMPOUND FORMATION WITH SULFURIC ACID

Since it was impossible to find an inert solvent in which the reaction could be studied, measurements of rate formation were carried out in the presence of hydrogen cyanide and sulfuric acid mixtures of differing proportions, ranging from a molecular ratio of 1:1 up to 1:7.05 (H_2SO_4). The reactants were immersed in a constant-temperature bath at 0°or 10° C., and the free hydrogen cyanide determined by titration at definite time intervals. The results of this rate study are shown in table 1.

In the presence of a large excess of sulfuric acid the rate behavior is strictly of the first order, but as the proportion of hydrogen cyanide is increased the rate behavior becomes more nearly that of a zero-order reaction. When the ratio of reactants was 1:2 or 1:4, the reaction began as one of the zero order but during the last half became almost of the first order. The zero-order behavior which occurs in the absence of a large excess of sulfuric acid can be satisfactorily explained as due to autocatalysis by the products of the reaction. The reaction products would be present in the largest concentration when the molecular ratio of reactants was equal, and it was only a coincidence that the catalytic effect in this case is just great enough to give a zero-order behavior to the reaction. The reaction was unaffected by either glass or light.

The effect of 3.8 per cent of water is to decrease the rate of reaction to one-third in the presence of excess sulfuric acid. In the presence of equimolecular quantities of reactants, 1.9 per cent of water decreases the rate to one-third and 3.8 per cent of water decreases it to one-fifth. This is a very small effect compared to other reactions that occur in concentrated sulfuric acid. For example, in the decomposition of citric acid by 100 per cent sulfuric acid 3.93 per cent of water decreases the rate to one-sixtieth. The effect of sulfur trioxide is not great, for in 103 per cent sulfuric acid the rate is increased by only 12 per cent over that in 100 per cent sulfuric acid.

TABLE 1

Summarized results of rate study

TEMPERATURE	PER CENT H_2SO_4	MOLE RATIO $HCN:H_2SO_4$	ORDER	RATE CONSTANT*
°C.				
0	100	1:1	0	34.0 × 10^{-6}
10	100	1:1	0	115.0 × 10^{-6}
0	96.2	1:1	0	5.4 × 10^{-6}
10	96.2	1:1	0	21.1 × 10^{-6}
10	98.1	1:1	0	39.7 × 10^{-6}
0	103	1:1	0	39.2 × 10^{-6}
0	100	1:2	0–1	25.8 × 10^{-6}
10	100	1:2	0–1	114.0 × 10^{-6}
0	100	1:4	0–1	17.5 × 10^{-6}
10	100	1:4	0–1	65.1 × 10^{-6}
0	100	1:7.05	1	71.5 mins.
10	100	1:7.05	1	27.2 mins.
0	96.2	1:7.05	1	224.0 mins.
10	96.2	1:7.05	1	62.3 mins.

* The zero-order rate constant is expressed as the number of moles of hydrogen cyanide reacting per minute per cubic centimeter of the reacting solution. The first-order rate constant is expressed in terms of the half-life period.

TABLE 2

Critical increments between 0° and 10°C.

E	PER CENT H_2SO_4	MOLE RATIO
15,850	100	1:7.05
19,300	100	1:4
22,800	100	1:2
18,600	100	1:1
19,500	96.2	1:7.05
20,800	96.2	1:1

The effect of temperature on the reaction is shown in table 2.

The critical increment is lower in the presence of a large excess of sulfuric acid. Since these reactions were carried out in the absence of an inert solvent, the value of the critical increment varied with the proportion of reactants used. In general, the presence of water raises the critical increment.

The effect of ether and certain salts on the reaction rate was not large. The presence of 5 per cent of ethyl ether in the 100 per cent sulfuric acid at 0°C. increased the time of half-life from 71.5 mins. to 136 mins.; 10 per cent of ether increased the value to 163 mins. Ammonium sulfate and sodium sulfate showed a slight retardation of the rate, whereas silver sulfate increased the time of half-life from 71.5 to 256 mins. In all probability the formation of $Ag(CN)_2$ ions decreased the effective concentration of hydrogen cyanide.

COMPOUND FORMATION IN PHOSPHORIC ACID

An excess of hydrogen cyanide was added to a weighed amount of 100 per cent phosphoric acid in a sealed tube and kept at room temperature for five months, after which time the tube was opened and the excess cyanide titrated, giving the exact amount of hydrogen cyanide that had reacted. Table 3 shows the results of two of these experiments. As a consequence the complex between hydrogen cyanide and phosphoric acid is represented by the formula $HCN \cdot H_3PO_4$.

TABLE 3

Compound formation in phosphoric acid

	A	B
Weight H_3PO_4	0.346 g.	0.1782 g.
Weight HCN found	0.312 g.	0.230 g.
Excess HCN found	0.00314 mole	0.00540 mole
Amount H_3PO_4 reacted	0.00353 mole	0.00318 mole
Amount HCN reacted	0.00346 mole	0.00311 mole

To determine the rate of compound formation a number of sealed tubes, each containing a known amount of phosphoric acid and a known excess of hydrogen cyanide, were prepared and kept at 37°C. At definite time intervals (every two or three days) a tube was opened and the cyanide content determined, with the following results:

Time (days)	0	2.0	5.1	8.1	10.9	(weeks later)
H_3PO_4 used up (per cent)	0	29.4	61.9	79.4	87.2	97.0

From these data the reaction can be shown to be of the first order with a half-life period of 3.6 days.

Hydrogen cyanide is but partially soluble in phosphoric acid, and phosphoric acid is practically insoluble in hydrogen cyanide, so that a two-phase system is present. Since the reaction occurs in the phosphoric acid phase, the first-order character of the reaction can be explained by assuming that the concentration of hydrogen cyanide in phosphoric acid solution is constant, so that the rate will be directly proportional to the amount of phosphoric acid present.

The complex $HCN\cdot H_3PO_4$ separated from phosphoric acid and hydrogen cyanide during the reaction as a viscous liquid, which toward the end of the reaction crystallized as a white, amorphous appearing solid. The solid was insoluble in the ordinary solvents except water, in which hydrolysis to ammonium formate and phosphoric acid occurred. It is much more stable than the complex with sulfuric acid; upon warming, however, it evolves carbon monoxide.

THERMAL DECOMPOSITION OF THE COMPLEXES $HCN\cdot H_2SO_4$ AND $HCN\cdot H_3PO_4$

When the sulfuric acid complex is warmed, carbon dioxide and sulfur dioxide are evolved in large quantities. The simplest equation to represent this would be

$$HCN\cdot H_2SO_4 \rightarrow SO_2 + CO_2 + NH_3$$

But no ammonia was found in the gases evolved, so that either supplementary reactions occurred between ammonia, sulfur dioxide, and carbon dioxide, or the decomposition gave some nitrogenous compounds as solid products. It is known (4) that ammonia and sulfur dioxide react to give a number of products, depending upon the temperature. Carbon dioxide reacts with dry ammonia to give ammonium carbamate, $NH_2CO_2NH_4$. The residue probably contains some of these products, either as a result of direct decomposition or as a result of secondary reactions. The amount of carbon monoxide evolved is very small, except when decomposition takes place in the presence of sulfuric acid.

In the presence of a large amount of sulfuric acid the gaseous products are sulfur dioxide, carbon dioxide, and carbon monoxide. When the acid concentration was below 90 per cent and above 70 per cent, it was observed that a quantitative yield of carbon monoxide was obtained. Above 90 per cent, carbon dioxide and sulfur dioxide were also evolved. In 96.7 per cent sulfuric acid 92 per cent of the gaseous product was carbon monoxide and the rest was a mixture of carbon dioxide and sulfur dioxide.

The gaseous product resulting from the thermal decomposition of $HCN\cdot H_3PO_4$ was pure carbon monoxide. In the presence of a large amount of 100 per cent phosphoric acid the yield of carbon monoxide was quantitative, but in a less concentrated acid the yield was slightly less.

RATE OF THERMAL DECOMPOSITION OF THE COMPLEXES IN CONCENTRATED ACID SOLUTION

The thermal decomposition of hydrogen cyanide in the presence of concentrated sulfuric and phosphoric acid solutions was studied by observing the volume of carbon monoxide evolved at definite times during an experiment. A mixture of 0.05 cc. of hydrogen cyanide and 25 cc. of acid was shaken in a device similar to that designed by Walton (10). The evolved carbon monoxide was conducted by capillary tubing to water-jacketed burets which were maintained at 25°C. An oil thermostat with a temperature control of ±0.1°C. served as a constant-temperature bath for the flasks. The concentration of the complex at any given time was based on the total gas volume at infinite time minus that at the desired time. The reaction was strictly of the first order and was not catalyzed by the glass wall of the container.

TABLE 4

Summary: decomposition rates in sulfuric acid

TEMPERATURE	PER CENT ACID	HALF-LIFE	$k \times 10^3$	TEMPERATURE	PER CENT ACID	HALF-LIFE	$k \times 10^3$
°C.		*minutes*		*°C.*		*minutes*	
70	79.7	74.4	9.32	90	73.1	39.0	17.8
70	79.0	74.1	9.36	90	69.5	146.	4.75
70	78.1	82.4	8.41	90	64.8	340.	2.04
70	77.2	99.5	6.97	100	95.9	217.	3.19
80	82.5	50.8	13.6	100	90.6	58.4	11.9
80	80.3	35.0	19.8	100	88.2	33.9	20.4
80	79.7	30.1	23.0	100	84.9	15.9	43.6
80	79.0	29.3	23.7	100	82.5	9.94	69.7
80	78.1	31.7	21.8	100	80.3	6.49	117.
80	77.2	35.8	19.4	100	79.7	5.70	122.
80	75.6	56.0	12.4	100	79.0	5.24	132.
80	73.1	127.	5.48	100	78.1	4.90	142.
85	95.9	810.	0.856	100	77.2	5.17	134.
90	91.3	138.	5.02	100	75.6	7.00	99.1
90	88.2	65.6	10.6	100	73.1	13.9	49.8
90	84.9	36.1	19.2	100	69.5	42.4	16.4
90	82.5	22.1	31.4	100	64.8	98.0	7.08
90	80.3	15.1	45.9	110	95.9	95.0	7.30
90	79.0	13.1	52.9	119	95.9	45.7	15.2
90	77.2	13.8	50.2	119	90.6	13.0	53.3
90	75.6	19.1	36.3				

Tables 4 and 5 summarize the results obtained in the study of the rate of decomposition of the complex $HCN \cdot H_2SO_4$ by sulfuric acid and $HCN \cdot H_3PO_4$ by phosphoric acid. In most cases duplicate experiments agreed within 2 per cent. The reaction was unaffected by glass.

The influence of temperature on the rate of decomposition is shown in tables 6 and 7. The results show that within the limits of experimental error the critical increment is independent of temperature. At high sulfuric acid concentrations (95.9 per cent) the critical increment tends to increase slightly, and at low acid concentration there is a noticeable increase in the critical increment as the concentration is decreased. In

TABLE 5

Summary: decomposition rates in phosphoric acid

TEMPERATURE	PER CENT ACID	HALF-LIFE	$k \times 10^3$	TEMPERATURE	PER CENT ACID	HALF-LIFE	$k \times 10^3$
°C.		*minutes*		*°C.*		*minutes*	
100	100.0	80.1	8.65	130	93.3	21.7	31.9
110	100.0	33.6	20.6	130	90.7	34.7	20.0
110	93.3	125.	5.55	130	88.0	55.0	12.6
110	88.0	335.	2.07	140	93.3	11.0	63.0
115	100.0	29.2	23.7	140	88.0	25.4	27.3
115	88.0	268.	2.58				
120	100.0	15.6	44.4	110*	100.0	28.7	24.1
120	93.3	51.9	13.4	115*	100.0	21.2	32.7
120	88.0	130.	5.32	115*	88.0	92.5	7.50
130	100.0	7.25	95.7	120*	100.0	12.6	55.0
130	96.7	14.5	47.8	130*	100.0	5.8	119.

* These runs were conducted by decomposing 1 cc. of a 5 per cent solution of $HCN \cdot H_2SO_4$ in sulfuric acid in the presence of phosphoric acid of the desired concentration.

TABLE 6

Critical increment of the thermal decomposition by sulfuric acid

PER CENT H_2SO_4	70-80°C.	80-90°C.	90-100°C.	110-119°C.	AVERAGE
64.8			33,300		33,300
69.5			33,200		33,200
73.1		29,800	27,700		28,800
75.6		27,300	26,800		27,000
77.2	24,500	24,100	26,000		24,600
79.0	22,300	20,300	24,400		22,300
82.5		21,100	21,300		21,200
84.9			21,900		21,900
88.2			17,700		17,700
90.6				22,900‡	22,900
95.9		23,300*	23,200†	24,100	23,500

* From 100° to 110°C.
† From 85° to 100°C.
‡ From 100° to 119°C.

phosphoric acid solutions the critical increment is higher in more dilute solutions. The value of the critical increment obtained, whether in sulfuric or phosphoric acid solutions, is essentially the same. This is an indication that the general mechanism of decomposition is probably the same in both cases.

TABLE 7

Critical increment for the thermal decomposition by phosphoric acid

PER CENT ACID	110-120°C.	120-130°C.	130-140°C.	AVERAGE
100.0	23,100	23,500	24,400†	23,500
93.3	26,200	27,100	22,350	25,800
88.0	28,200	27,050	25,450	26,900
100.0*	24,350	24,300		24,300

* See note at the end of table 5.
† From 100° to 110°C.

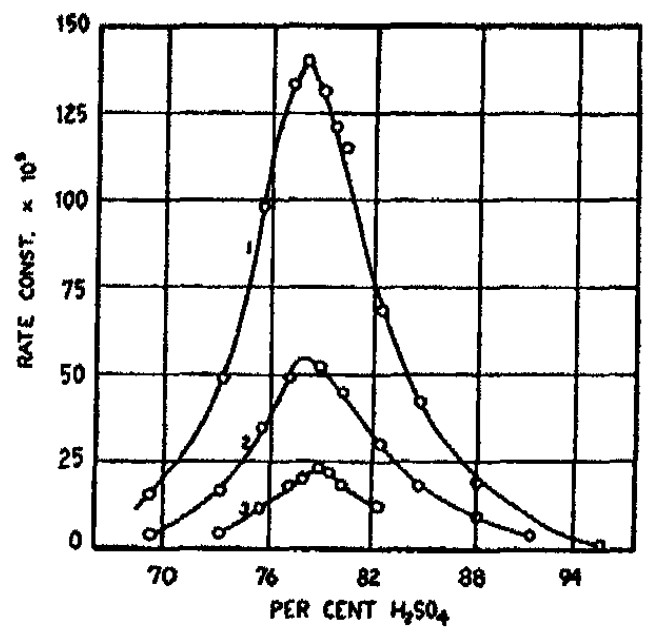


Fig. 1

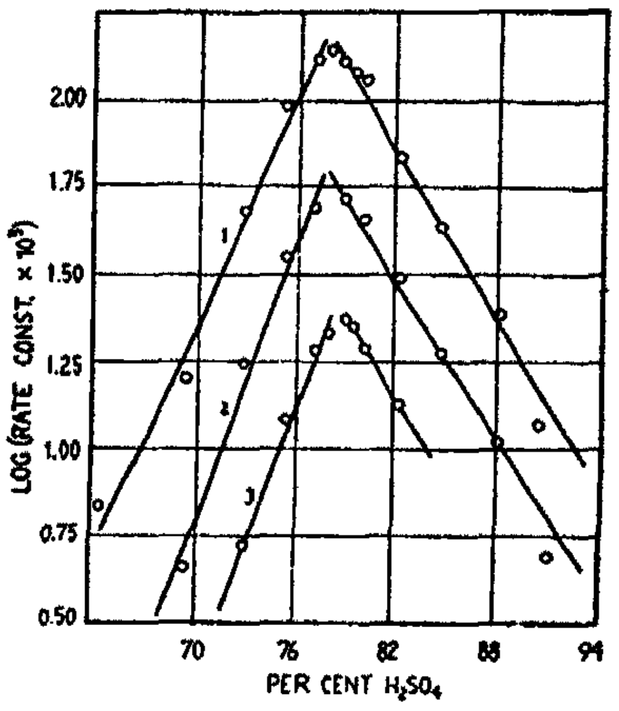


Fig. 2

Fig. 1. The effect of acid concentration on the rate. Curve 1 at 100°C.; curve 2 at 90°C.; curve 3 at 80°C.

Fig. 2. The effect of acid concentration on the logarithm of the rate constant Curve 1 at 100°C.; curve 2 at 90°C.; curve 3 at 80°C.

The influence of a number of metallic sulfates and oxides on the rate of decomposition was studied. The substance (10 mg. in all cases) was dissolved in 79.0 per cent sulfuric acid and the decomposition was carried out in the usual manner at 90°C. The sulfates of silver, aluminum, bismuth, calcium, cobalt, chromium, copper, iron, mercury (ous), mercury (ic), magnesium, manganese, sodium, ammonium, and nickel were tried, also zinc oxide, stannic oxide, and sodium phosphate. There was no appreciable affect on the reaction rate in any case.

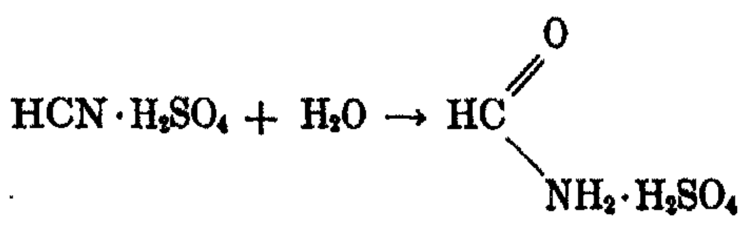
The effect of acid concentration on the rate of decomposition in sulfuric acid is important. The results recorded in table 4 show that for each temperature there is an acid concentration of about 78 to 79 per cent which corresponds to a point of maximum rate of decomposition. On either side of this point the rate falls off rapidly (figure 1). When the logarithm of k, the rate constant, is plotted against concentration of acid (figure 2), the result is two straight lines intersecting at a peak which corresponds to the point of maximum rate. The manner in which the rate is influenced by acid concentration suggests that a type of inhibition may take place in accordance with the observation of Wiig (13), who pointed out that in all cases of the decomposition of organic acids by sulfuric acid the molarity of the inhibitor is a linear function of the logarithm of the rate constant. It is also true that for the decomposition by means of phosphoric acid the logarithm of the rate constant is a linear function of the concentration. However, the decomposition of organic acids by sulfuric acid is much more affected by water, for instance, with triphenylacetic acid (3), where 1 per cent of water in the sulfuric acid reduced the rate of decomposition to one-half, or gave a total effect of over three times that observed in the decomposition of hydrogen cyanide by sulfuric or phosphoric acids.

MECHANISM OF DECOMPOSITION

As an explanation of the foregoing experiments the following mechanism is suggested. The decomposition of hydrogen cyanide involves three principal steps. The first is the combination of hydrogen cyanide with the acid to give the compound $HCN\cdot H_2SO_4$ or $HCN\cdot H_3PO_4$. The second step is the hydration of the complex to the formamide sulfate or phosphate. The third step is the thermal decomposition of the formamide sulfate or phosphate. The equations to represent the three steps are as follows:

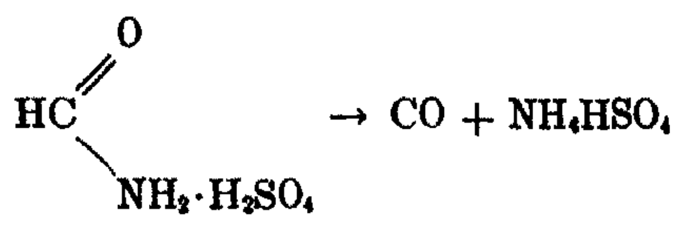
$$\text{I.}\quad HCN + H_2SO_4 \rightarrow HCN\cdot H_2SO_4$$

II.



$$\text{II.}\quad HCN\cdot H_2SO_4 + H_2O \rightarrow HC\begin{matrix}{/\!\!/}O\\ \diagdown NH_2\cdot H_2SO_4\end{matrix}$$

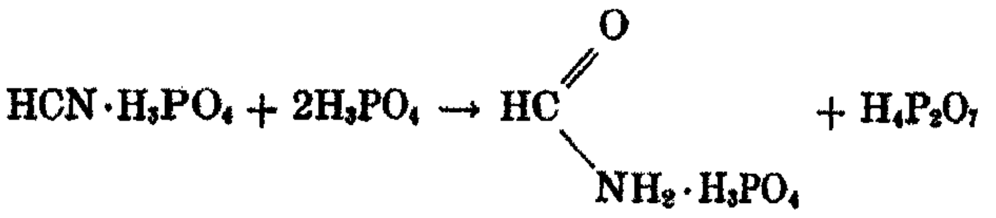
III.



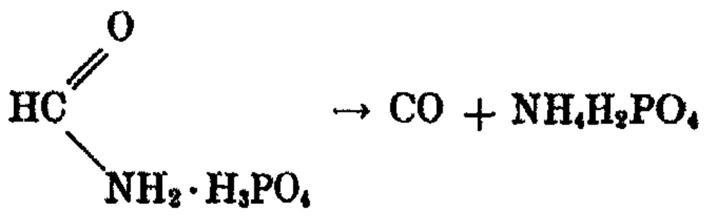
$$\text{III.}\quad HC\begin{matrix}{/\!\!/}O\\ \diagdown NH_2\cdot H_2SO_4\end{matrix} \rightarrow CO + NH_4HSO_4$$

In the case of phosphoric acid the equations are:

I. $HCN + H_3PO_4 \rightarrow HCN\cdot H_3PO_4$

II. 

$$HCN\cdot H_3PO_4 + 2H_3PO_4 \rightarrow HC\begin{array}{l} {/\!\!/} O \\ \diagdown NH_2\cdot H_3PO_4 \end{array} + H_4P_2O_7$$

III. 

$$HC\begin{array}{l} {/\!\!/} O \\ \diagdown NH_2\cdot H_3PO_4 \end{array} \rightarrow CO + NH_4H_2PO_4$$

The last step has been shown to be the rate-determining reaction, since when formamide replaced hydrogen cyanide the same rate was observed in all cases. The agreement is within the limits of experimental error. If step II is reversible, it would explain why formamide reacts similarly to $HCN\cdot H_2SO_4$ in sulfuric acid of the same concentration. Whether formamide or $HCN\cdot H_2SO_4$ is added to sulfuric acid, the same point of equilibrium will be reached and consequently the decomposition will behave similarly. The results obtained with the concentration (78 to 79 per cent) giving the maximum effect depend upon having the sulfuric acid dilute enough to allow hydration to take place and yet concentrated enough to allow an appreciable amount of decomposition to occur. It is interesting to note that the point of highest rate of decomposition corresponds in acid concentration to a solution composed of equimolecular quantities of $H_2SO_4\cdot H_2O$ and $H_2SO_4\cdot 2H_2O$.

TABLE 8

Decomposition of formamide at 90°C.

PER CENT H_2SO_4	HALF-LIFE OF FORMAMIDE	HALF-LIFE OF HYDROGEN CYANIDE
88.2	62.5	65.6
82.5	22.4	22.1
79.0	13.0	13.0
73.1	35.0	39.0
100.0*	7.5	7.25

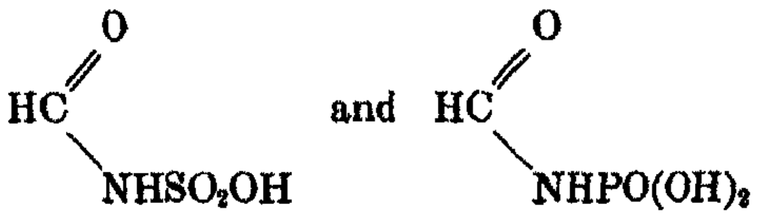
* Decomposition using 100 per cent H_3PO_4 at 130°C.

Step II for the decomposition by means of phosphoric acid is essentially a hydration in which phosphoric acid gives up water to become pyrophosphoric acid. The process may be thought of as reversible, just as in the case of the decomposition in sulfuric acid. Since the reaction proceeded most rapidly in 100 per cent acid, the amount of complex which is hydrolyzed must be quite appreciable even in 100 per cent phosphoric acid.

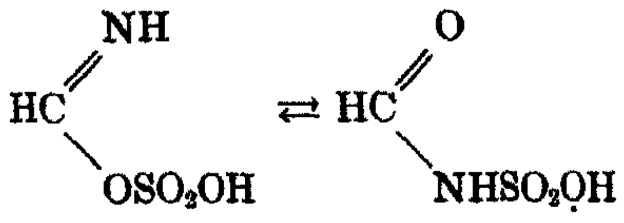
The decomposition of formic acid (8) under the same conditions is more rapid than that of hydrogen cyanide, which, together with evidence here presented, would eliminate it as an intermediate in the decomposition.

STRUCTURE OF THE COMPLEXES

The mechanism for the decomposition gives some clue to the structure of the compounds $HCN \cdot H_2SO_4$ and $HCN \cdot H_3PO_4$. Since they are easily hydrolyzed, the structures



seem most probable. These compounds upon hydrolysis would yield the amide salts. They may be thought of as existing in tautomeric equilibrium such as:



I II

The first structure would be that expected whether sulfuric acid added directly across the triple bond of hydrogen cyanide or whether it added to the divalent carbon in HN=C.

The decomposition of hydrogen cyanide by sulfuric and phosphoric acids is similar to the decomposition of the organic acids in certain respects. The decomposition in both cases occurs through the formation of an intermediate complex, and carbon monoxide is yielded as a gaseous product. However, the effect of foreign substances and water as negative catalysts is very much greater in the case of the organic acids. Also, the organic acids all decompose without involving a hydration process, and the organic acids decompose most rapidly in approximately 100 per cent sulfuric acid or greater.

SUMMARY

1. Hydrocyanic acid forms complexes with sulfuric, phosphoric, and selenic acids. The formulas of the first two complexes are $HCN \cdot H_2SO_4$ and $HCN \cdot H_3PO_4$.

2. The rates of formation and properties of these compounds have been studied.

3. The thermal decomposition of the complexes $HCN \cdot H_2SO_4$ and $HCN \cdot H_3PO_4$ in sulfuric and phosphoric acids has been investigated. The former was found to decompose most rapidly in 78 to 79 per cent sulfuric acid and the latter in 100 per cent phosphoric acid.

4. A mechanism has been presented to explain the thermal decomposition of hydrogen cyanide in sulfuric and phosphoric acids. The rate-determining process was shown to be the thermal decomposition of the formamide salt formed as an intermediate.

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CONTRIBUTIONS TO THE DETERMINATION OF THE EXACT AGE OF A CANADIAN URANINITE[1]

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Determinations of the ages of minerals based on atomic disintegration give results more precise than any other method. Kovarik (11) has stated the conditions sufficient for the exact determination of the age of a mineral by the lead method.

Since the discovery of radioactive minerals in the northern part of Canada,[2] much attention has been turned to these ores as a means of determining the age of the mineralization of that section (8, 10).

Through A. C. Lane, Chairman of the Committee on the Measurement of Geologic Time of the National Research Council, a 2-kg. sample of ore was obtained from R. J. Traill, investigator in the Ore Dressing Laboratory of the Canadian Bureau of Mines. This sample came from pit (vein) No. 2 opened up in May, 1934, on the Tatie No. 5 Claim, which is on the north side of the east arm of Beaver Lodge Lake, latitude 64°44′ N, longitude 118°12′. It was developed by Mr. Hargreaves, and at one time this Arden Bay arm of Beaver Lodge Lake was referred to as the Hottah Lake explorations. Later, however, other deposits were found further east, and these deposits are now referred to as being in the Hottah Lake region. Pit No. 2 is only about 100 ft. from pit No. 1, which yielded more of the pitchblende (about 2 tons of mixed pitchblende and hematite), and has been referred to by Joliffe (20). Pit No. 2 is near the top and pit No. 1 is farther down the slope of the south side of a big quartz ridge which separates Beaver Lodge Lake to the south from Hottah Lake on the north. The Hottah Lake and Beaver Lodge Lake deposits of pitchblende ore are located about 60 miles south of the well-known Eldorado deposits at LaBine Point, Great Bear Lake. All of these sections are in the central part of the MacKenzie District of the Northwest Territory.

The author undertook to determine the masses of uranium, thorium, and

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[1] This paper is an extract of a dissertation submitted by Frank H. Bruner to the Graduate Faculty of the University of Missouri in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1936.

[2] The original discovery of pitchblende and silver in this region was made in May, 1930, by Mr. Gilbert LaBine on the west side of Echo Bay, Great Bear Lake.

lead per given mass of mineral, to determine the parental lineage of the various isotopes of lead by investigating the actinium series in this ore, and to establish that only such changes have taken place as can be ascribed to radioactive disintegration.

The sample received by the author consisted of (a) about 2 kg. of coarsely ground, reddish-brown ore, (b) several small hand specimens having the uniform black appearance of a rather high grade ore, and (c) a polished section prepared by Dr. L. C. Graton, Professor of Mining Geology at Harvard University. The polished section showed a gradation from uniformly black compact pitchblende in the interior to brilliantly colored oxidation products of uranium on the exterior and as veinlets cutting through the interior.

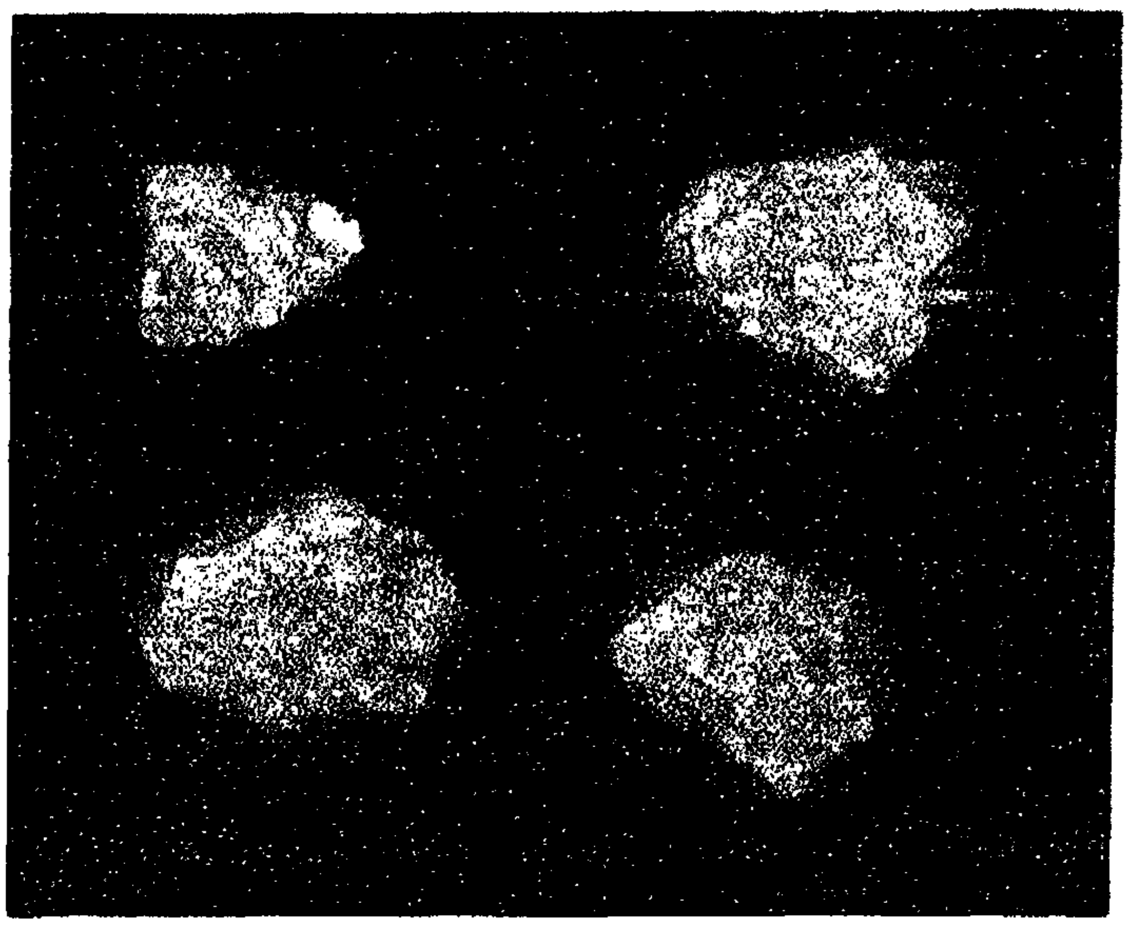

FIG. 1. Results of exposure of the ore for four days. Dr. Graton's polished specimen is in the upper left-hand corner

The microscopic character of this ore has been discussed by Dr. M. H. Haycock (19), mineragrapher of the Canadian Bureau of Mines. He points out that from a microscopic standpoint, the pitchblende deposits at Beaver Lodge and Hottah Lakes are unique in the intimate association of pitchblende with large amounts of hematite. The hematite usually predominates, and the pitchblende occurs within it as tiny grains which are commonly less than 1 micron in size. He also states that brilliantly colored oxidation products of uranium mineral are present as the fillings of small fissures and cavities, and that a younger and rather coarsely crystalline variety of hematite occurs in veinlets which cut the above assemblage.

In order to discover the distribution of the radioactive components of the ore, three of the hand specimens were ground down to a smooth flat surface. These surfaces, along with the polished surface prepared by Dr. Graton, were placed in a light-proof box in contact with a photographic plate. The radioactive rays continuously emitted from their surfaces gave a definite exposure of the film in four to six days.

The results of an exposure of four days can be seen in figure 1. The three hand specimens had a uniformly black appearance to the eye. Since the radioactive rays from the surfaces caused an exposure over the entire contact area on the film, we must conclude that all parts of the surfaces are radioactive to some extent. However, the radiographs show a distinct difference in the intensity of radiation from various portions of the surfaces. This would indicate that the radioactive component is concentrated in veins and pockets in the specimens.

TABLE 1

Analysis of the ore

INGREDIENT	PER CENT	INGREDIENT	PER CENT
U_3O_8	51.45	MgO	Trace
Fe_2O_3	41.51	Mn	Present
Pb	2.31	S	0.14
SiO_2	2.75	CO_2	0.42
Al_2O_3	1.12		
CaO	1.01	Total	100.72

The larger part of the 2-kg. sample of the coarsely ground ore was first subjected to grinding in a Braun disc pulverizer to a 40-mesh fineness. Extreme care was taken during this and all subsequent handling of the ore that no contamination be introduced.

The ore was subjected to a complete chemical analysis, the results of which are given in table 1.

The ore was tested carefully, both chemically and electroscopically, for the presence of thorium; neither determination gave the slightest indication of its presence. The determinations of lead and uranium were made with special care—the uranium by Randall's method in pitchblende with slight modifications (14), and the lead by the method described by Scott (15).

The study of polished sections under the microscope by others (19) has pointed out the fact that hematite of two different periods is contained in this ore; the first as an intimate admixture, and the second as a younger and rather coarsely crystalline variety occurring in veinlets.

If the ore had undergone admixture from the outside the lead in all probability would have been added by influx with the younger hematite, which the author proposed to remove by mechanical means. The composition of the ore indicated that it could be mechanically separated either by gravity or by magnetic means. In case this younger hematite could be removed by mechanical means, it should remove any ordinary lead that was introduced by influx with it, and the material remaining should have a lower lead-uranium ratio than the original ore.

Since pure uraninite has a specific gravity greater than 9 and that of hematite is less than 5, a gravity separation is possible if a liquid is used that will float the hematite. At 100°C. thallium formate (16) is molten and has a specific gravity slightly greater than 5; it was therefore chosen as the most suitable heavy liquid for a gravity separation of the ore. Although a fair separation was obtained in the case of the 40-mesh material, it was noticed that most of the finer brown portion could be washed out with water by differential sedimentation.

Using a sample of 50 g. of the ore, 7 g. of it was removed by washing with distilled water, leaving a black, granular residue. The lead and uranium were determined in this black residue by the methods used on the original ore.

The 40-mesh material was pulverized to a fine powder in a pebble mill. This finer material gave a poorer separation than the coarser material, both with the gravity separation and in the differential sedimentation separation.

A magnetic separation of the ore was accomplished with the use of the magnetic equipment in the Bureau of Mines Laboratory at the Missouri School of Mines, Rolla, Missouri. The magnetic separator used consists of a long buret on a jig arrangement placed between the poles of a strong electromagnet. The buret may be inclined at any desired angle. The sample is placed in the top of the buret, which is full of water and sealed so that a column of water is maintained in it throughout the separation. A small flow of water is allowed to pass through the buret while it is jigged longitudinally between the poles of the magnet. The magnetic portion is retained in the magnetic field, and the non-magnetic portion is washed out of the bottom of the buret into a vessel. As the process nears completion the flow of water and the angle of inclination are both increased. When there is no further visible separation, the magnet is turned off and the magnetic portion washed out into a separate vessel. The concentrates are recovered by decanting and drying.

Since the magnetic properties of the components of the raw ore did not differ sufficiently to obtain a magnetic separation, the ore was roasted in an atmosphere of natural gas at a temperature of 500°C. to convert the hematite to magnetite. This roasted ore was then ground to a fine powder and subjected to a magnetic separation. A sample of 65 g. of the roasted ore yielded 38 g. of the non-magnetic concentrate. This non-magnetic material was analyzed for lead and uranium by the methods employed on the original ore.

Table 2 gives the results of the lead and uranium determinations, the lead-uranium ratios, and the calculated ages for the original ore and the two concentrates.

TABLE 2

Lead-uranium ratios, with the corresponding ages

	ORIGINAL ORE	DIFFERENTIAL SEDIMENTATION CONCENTRATE	NON-MAGNETIC CONCENTRATE
Lead (per cent)	2.309	2.655	3.042
Uranium (per cent)	43.63	45.45	47.98
Lead-uranium ratio	0.0529	0.0584	0.0634
Age* (million years)	390	430	465

* By formula due to A. V. Holmes (11):

$$t = \frac{\log (U + 0.36Th + 1.155Pb) - \log (U + 0.36Th)}{6.6 \times 10^{-5}} \text{ million years}$$

RELATION OF THE ACTINIUM SERIES TO THE RADIUM SERIES IN THE ORE

Using the actinon method (13) as modified by the author (3), the constancy of the actinium-uranium ratio was determined. The actinon continuously produced in a solution of this uraninite was compared with that of a standard solution of the Great Bear Lake uraninite by means of the active deposits of actinon.

The actinon-uranium ratio for this sample of Beaver Lodge Lake uraninite was found to be the same as that of the Great Bear Lake uraninite, which had previously been shown to give an actinon-uranium ratio constant with the ratios of six other minerals (3).

In order to establish an absolute relation between the uranium-radium series and the actinium series, the protoactinium-uranium ratio was determined. The protoactinium was coprecipitated with tantalum, using a slight modification of the method outlined by Tcheng Da-Tchang (4). The protoactinium-tantalum oxide was gound in acetone, and the resulting suspension painted upon aluminum discs 60 mm. in diameter. These films were compared electroscopically with standard films of uranium oxide, whose average activity was 0.501 division per minute per milligram. Table 3 gives the results for determinations on three individual samples.

The actinium-ionium ratio was determined by the method of Gleditsch and Foyn (7), which allowed for the determination of the activities of actinium and ionium in the same film, thereby eliminating all errors due to weighing the small quantities necessary. The actinium and ionium and their isotopes were coprecipitated with thorium and lanthanum as fluorides. The isotopes of radium were removed by the repeated precipitation and solution of the earths as hydroxides. Finally the hydroxides were calcined, the resulting oxides were ground under acetone, and the suspension thus obtained was painted on aluminum discs. The initial activity and the increase of activity with the time were measured in a Wulf (18) bifilar, quartz-fiber electroscope.

The initial activity is due to ionium, thorium, radiothorium, and radioactinium; the increase of the activity is due to the active products of radiothorium and radioactinium. The increase of activity in any interval of time, *t*, after the final precipitation, is given by the equation,

TABLE 3

Protoactinium-uranium ratio

	TRIALS		
	I	II	III
Weight of sample	6.0000 g.	3.0000 g.	3.0000 g.
Weight of $(Pa\text{-}Ta)_2O_5$	0.21825 g.	0.22682 g.	0.23039 g.
Activity (divisions/minute/mg.)	0.1700	0.0815	0.0805
Total activity (divisions/minute)	37.10	18.49	18.55
Total activity (grams U_3O_8)	0.07406 g.	0.03689 g.	0.03702 g.
Activity (grams U_3O_8 per gram of U)	0.0283 g.	0.0282 g.	0.0283 g.
Number of atoms of Pa disintegrating for every 100 atoms of UI	4.06	4.05	4.06

$$\text{Increase} = (1 - e^{-\lambda_{AcX} t})x + (1 - e^{-\lambda_{ThX} t})y$$

where x is the equilibrium activity due to actinium X and its products and y is the equilibrium activity due to thorium X and its products. If the increase of activity of a film is found for two different times, the solution of the two resulting equations gives values for x and y.

From these values of x and y, the values for the activities of the radioactinium, radiothorium, and thorium can be deduced. Subtracting these values from the initial activity gives the activity of the ionium. The activity of the radioactinium is of course controlled by the quantity of actinium in the sample, and the actinium-ionium ratios can be calculated.

Figure 2 shows an analysis of an experimental curve. Curve a is the accumulation curve for both the actinium X and thorium X and their short-life products. Curves b and c are the calculated curves for actinium X, etc., and thorium X, etc., respectively, obtained from the analysis of the experimental curve a. The linear curve d represents the activity curve of the ionium, thorium, radiothorium, and radioactinium.

It was found that values calculated from the increase in activity were far more uniform if the sample was allowed to stand two to three weeks after the initial activity had been taken, in order to allow the thorium X to reach approximate equilibrium.

The four samples of ore carried through this experimental procedure allowed for the calculation of an average value of 0.0412 ± 0.020 for the actinium–ionium ratio. This value checks very closely the value of 0.0406 obtained for the protoactinium–uranium ratio.

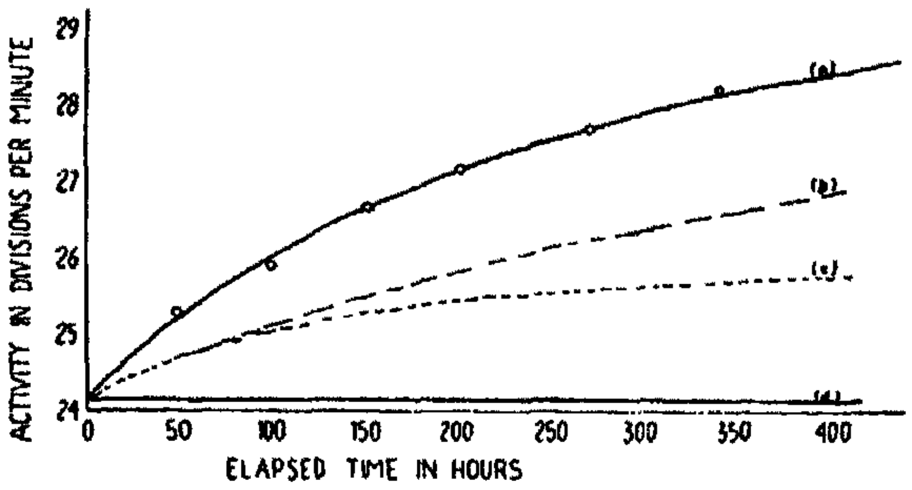

FIG. 2. Experimental curve: the accumulation of activity in an actinium–ionium sample

DISCUSSION AND SUMMARY

From the analysis of the ore it is interesting to note that uranium oxide, iron oxide, and lead account for over 95 per cent of the components of the ore, and silica, calcium oxide, and aluminum oxide account for practically all of the remaining portion. The ore is very unique in the fact that hematite is the major impurity, with extremely small amounts of other metallic constituents.

The radiographs of the hand specimens show that the ore as a whole has a quite uniform distribution of active component. However, pockets in the ore contain a component that is richer in activity than the remainder of the ore.

The mechanical separations of the ore produced concentrates that had a higher content of both uranium and lead than the original ore, but the lead is enriched to a greater extent than the uranium. Alter and Kipp (1) have noted previously that weathering is more selective toward uranium than toward lead.

If lead had been brought into the ore as ordinary lead probably it would have occurred with the influx of the younger hematite, and the removal of this younger hematite by mechanical separations should remove the ordinary lead. However, the lead-uranium ratio in the concentrates is higher instead of lower, as would be expected if an influx of lead with the hematite did occur. Therefore, it seems reasonable to assume that the lead in the ore is of radiogenic origin.

It is concluded that the weathering of uraninite is selective in the removal of uranium. This partition between uranium and lead in weathering processes of primary uranium ores could explain the existence of secondary uranium ores with very small lead-uranium ratios.

The value of 0.0529 for the lead-uranium ratio checks very well the value of 0.0530 for the lead-uranium ratio for uraninite from pit No. 1 obtained previously at the Ore Dressing Laboratory of the Canadian Bureau of Mines. However, the corrected value of 0.193 for the lead-uranium ratio for the Great Bear Lake uraninite obtained by J. P. Marble (12) is very different from those of the Beaver Lodge Lake region. It is therefore concluded that at least two distinct periods of uranium mineralization took place in this region.

The value of 0.04 for both the protoactinium-uranium I ratio and the actinium-ionium ratio is in accord with the values reported by von Grosse (17), Gleditsch and coworkers (6, 7), Da-Tchang (4), and Francis and Da-Tchang (5).

The value of 0.04 for the ratio between the actinium and radium series shows that the lead being formed at present in the ore is at the rate of 4 atoms of actinium D to 100 atoms of radium G. However, since "actinouranium", the isotope from which the actinium series is descended, decays more rapidly, the ratio of actinium D to radium G in the radiogenic lead of the ore will be greater than 0.04.

From von Grosse's (17) table giving the change of the radium G to uranium I ratio with the time and with the uranium-lead to uranium ratio, we find that there are approximately 5.3 atoms of actinium D to every 100 atoms of radium G for a mineral of a uranium-lead to uranium ratio of 0.0529. According to von Grosse (17) Aston's (1) value for the atomic weights of actinium D and radium G when transferred to the chemical scale are 206.96 and 205.95, respectively. The equation gives

$$\frac{205.96 \times 100 + 206.96 \times 5.3}{105.3} = 206.01$$

for the atomic weight of the radiogenic lead in this uraninite, assuming the absence of common lead.

Since the experimental atomic weight and the isotopic composition of the lead were not determined by the author, the exact age cannot be calculated until the absence of common lead is verified.

Incidentally, the absolute value of 0.04 for the ratio between the actinium series and the radium series was established in the same sample used to determine the constancy of the actinon-uranium ratio. The actinon method is thereby standardized for the measurement of absolute ratios. From this it is concluded that the seven minerals previously examined by the author (3) have a value of 0.04 for the ratio between the actinium and the radium series.

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CRYSTAL TRANSFER MECHANISM. II

Iodine–Iodide Crystal Exchange Reactions in Silica Gel

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INTRODUCTION

In a recent paper (4) the author has pointed out that a satisfactory system for the study of the mechanism of so-called "crystal transfer" in gel media was supplied by the formation of crystalline iodine in silica gel. Preliminary studies yielded information relative to dissolution of deposited iodine and its subsequent reprecipitation. It was pointed out that a growing crystal of iodine in silica gel displayed "stress-planes" continuous with the crystal faces. It was thought advisable to investigate this phenomenon further with the use of other crystals, as well as to interrelate the process with crystal replacement reactions in silica gel.

PREPARATION OF REACTION SYSTEMS

A series of sols, prepared by mixing equal quantities of 1.06 density water glass and N acetic acid (1), were made $N/10$ with respect to potassium iodide and poured into flat optical-glass reaction cells, whose inside dimensions were 10 x 5 x 0.5 cm. After solidification, one series of these gels was covered with $N/2$ mercuric chloride solution, a second series with $N/2$ lead acetate solution, and a third series with saturated bromine water.

After the various reactions had proceeded for some time, the series of reaction cells contained crystals of red tetragonal mercuric iodide, yellow hexagonal lead iodide, and black rhombohedral iodine, respectively.

GROWTH AND MOVEMENT OF CRYSTALS

Mercuric iodide crystals, in the general case an elongated form of the tetragonal crystals, grew at a very rapid rate, with the formation of a soluble complex (2) in the rear of the crystal band, and deposition of mercuric iodide at the crystal front. No stress-planes were noted.

Lead iodide crystals grew and moved, *en masse*, in a manner similar to that described for the rhombohedral masses of iodine crystals (4). In this

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case, however, the form of the crystals was decidedly dendritic, several thin hexagonals being joined together at a common point. The formation of the soluble complex, responsible for the apparent movement, has been described in detail (3). It is interesting to note that lead iodide crystals showed stress-planes, continuous with the major crystal faces, along which growth took place. These stress-planes always appeared prior to dendritic formation, and were most pronounced in the direction of predominant growth.

The deposition, growth, dissolution, and movement of iodine crystals in silica gel have already been described by the author (4).

REPLACEMENT REACTIONS[2]

Each of several reaction cells containing mercuric iodide crystals was covered with saturated bromine water in such a manner as to insure constant saturation. After the bromine had penetrated to the crystals, several distinct reactions resulted. Microscopic sections, along the characteristic minute depressions parallel to the crystal faces, were dissolved from a given crystal surface and iodine deposited in the place of the mercuric iodide. After some time, clear spaces were observed surrounding each minute iodine crystal, and the mercuric iodide gradually disappeared. The resulting structure was a series of rows of small iodine crystals parallel to each of the original crystal faces. Upon further diffusion of bromine, long white needles of mercuric bromide were deposited about the group of iodine crystals as a center. The iodine was then gradually dissolved. These reactions were considerably modified if dilute bromine water was used. Under these circumstances, a number of cases were observed where the replacement was so slow that half of a crystal was iodine and half mercuric iodide. In such an event, the final iodine crystal was a slightly distorted tetragonal, instead of the normal rhombohedral form.

Some of the reaction cells containing lead iodide were covered with saturated bromine water, and others with dilute bromine water. In the former case the reaction was somewhat similar to that observed for the action of saturated bromine water on mercuric iodide crystals, except that in this case the shrinkage of crystal volume was very great. After continued reactions colorless lead bromide gradually replaced the deposited iodine crystals. With dilute bromine water a very interesting reaction took place. Some distance above a given lead iodide crystal (or fused mass of crystals) several rhombohedral masses of iodine were deposited with the large front rhombohedra (4) pointed toward the lead iodide. This was the case even though the iodine group was an appreciable distance on either side. As the lead iodide crystal gradually disappeared,

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[2] The presence of free bromine in the gels clouded all of the photographs of these various processes; the reactions were easily followed microscopically, however.

exhibiting the effect of evenly distributed shrinkage, the rhombohedral iodine mass continued to grow toward it. Evidently the mutual effect of the crystals was active through a distance of several millimeters.

Some of the gels containing iodine crystals were covered with $N/2$ mercuric nitrate solution, and others with $N/2$ mercuric chloride solution. The reactions were sensibly identical. In each case, minute crystals of mercuric iodide deposited on the fused rhombohedral iodine crystals and the iodine gradually disappeared. The final structure was an intimately packed mass of discrete, red, tetragonal mercuric iodide crystals.

If the iodine crystals were made by the reaction of nitric acid on potassium iodide in silica gel (4), replacement by mercuric iodide could be so regulated that the mercuric iodide gradually replaced the iodine. Several crystals, part of which was iodine and part mercuric iodide, were obtained in this way. In the extreme, slightly distorted rhombs of almost pure mercuric iodide were obtained.

DISCUSSION OF RESULTS

In order to explain the apparent movement of deposited crystals in gel media, various soluble complexes must be considered. These have been discussed by various writers (2, 3, 4), and their existence may be taken as fact. That preferential dissolution of certain sections of deposited crystals under the influence of excess entering reagent takes place must be accounted for by the presence of adsorbed material (4, 6), perhaps in conjunction with specific peptization effects (5).

Slow diffusion processes overcome the difference in rate of dissolution in various parts of a dissolving crystal, and hence will tend to result in "perfect crystal replacement," with little or no lattice distortion. Several of the crystals which were composed of two materials, as, for instance, iodine and mercuric iodide, were carefully removed from the gel. It was found that the interface between iodine and mercuric iodide was more apparent than real, for such crystals displayed a high coherence. Several slightly distorted pseudomorphs of mercuric iodide (rhombic) and of iodine (tetragonal) were likewise shown to be essential single crystals.

The existence of stress-planes, whether the cause or the effect of crystal growth, is important from the standpoint of directional growth, particularly dendritic formation. It would appear reasonable to suppose that grain growth of intermetallic constituents in alloys, for instance, would follow a process quite similar to that presented above. In view of the importance of nucleation in alloys, studies of crystal deposition and growth in transparent media are of high importance.

SUMMARY

The formation, movement, and replacement of crystalline iodine and insoluble crystalline iodides in silica gel have been examined. The appar-

ent iodide crystal transfer has been observed to be identical in its mechanism with that previously described for crystalline iodine.

The replacement of crystalline iodine by insoluble crystalline iodide, and *vice versa*, has been studied, and it has been shown that under certain diffusion conditions pseudomorphic crystals are possible. These appear to possess excellent coherence.

It seems apparent that such studies are of value in the interpretation of crystal growth, migration, and replacement in metallic structures, wherein opacity prevents visual observation.

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PHOTOELECTRIC SPECTROPHOTOMETRY

AN APPARATUS FOR THE ULTRA-VIOLET AND VISIBLE SPECTRAL REGIONS: ITS CONSTRUCTION, CALIBRATION, AND APPLICATION TO CHEMICAL PROBLEMS

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For quantitative analytical purposes, the photographic method of determining absorption spectra is inordinately slow and usually of insufficient precision. A need for accurate and precise data in the determination of absorption spectra of chemical substances in solution instigated the construction of an accurate and sensitive instrument which would avoid the errors and inconvenience of the photographic methods. Our first effort in this direction was reported by Zscheile, Hogness, and Young (11). This first method, which was confined to the visible region, employed as its essential parts a Mazda lamp, a monochromator, a photocell, an electrometer, and absorption cells placed in front of the first slit of the monochromator.

Recently an improved instrument has been built, the current and voltage sensitivities of which are, respectively, forty and one hundred forty times those of the former instrument when convenient conditions for absorption spectra measurements are compared. Narrower slits and consequently narrower regions of the spectrum may therefore be used. In addition, the new assembly has an extended spectral range to 2200 A. U. in the ultraviolet. Each determination now requires only one-seventh the time formerly necessary, and the accuracy has been greatly improved. The absorption cells have been placed behind the second slit of the monochromator, so that solutions are now exposed to only about 10^{-5} lumens, whereas formerly they were exposed to an enormously greater intensity. Photochemical decomposition is no longer an appreciable factor. In extending the accuracy by the use of narrower isolated portions of the spectrum and consequently lower light intensities, unforeseen difficulties mount rapidly. These difficulties have been overcome in our present apparatus.

The purpose of this paper is to present a detailed description of this improved apparatus, together with a discussion of its calibration and its application to spectrophotometry. Particular consideration will be given to errors of absorption measurements, and sample absorption spectra will be presented as standards. In conclusion, some applications of the method will be briefly discussed.

DESCRIPTION OF EXPERIMENTAL EQUIPMENT

The apparatus is shown in the photograph (figure 1); figure 2 is a diagrammatic sketch of the apparatus, with accurate dimensions of the optical paths. This arrangement of parts has been designed primarily for rapid interchange between the ultra-violet and visible systems.

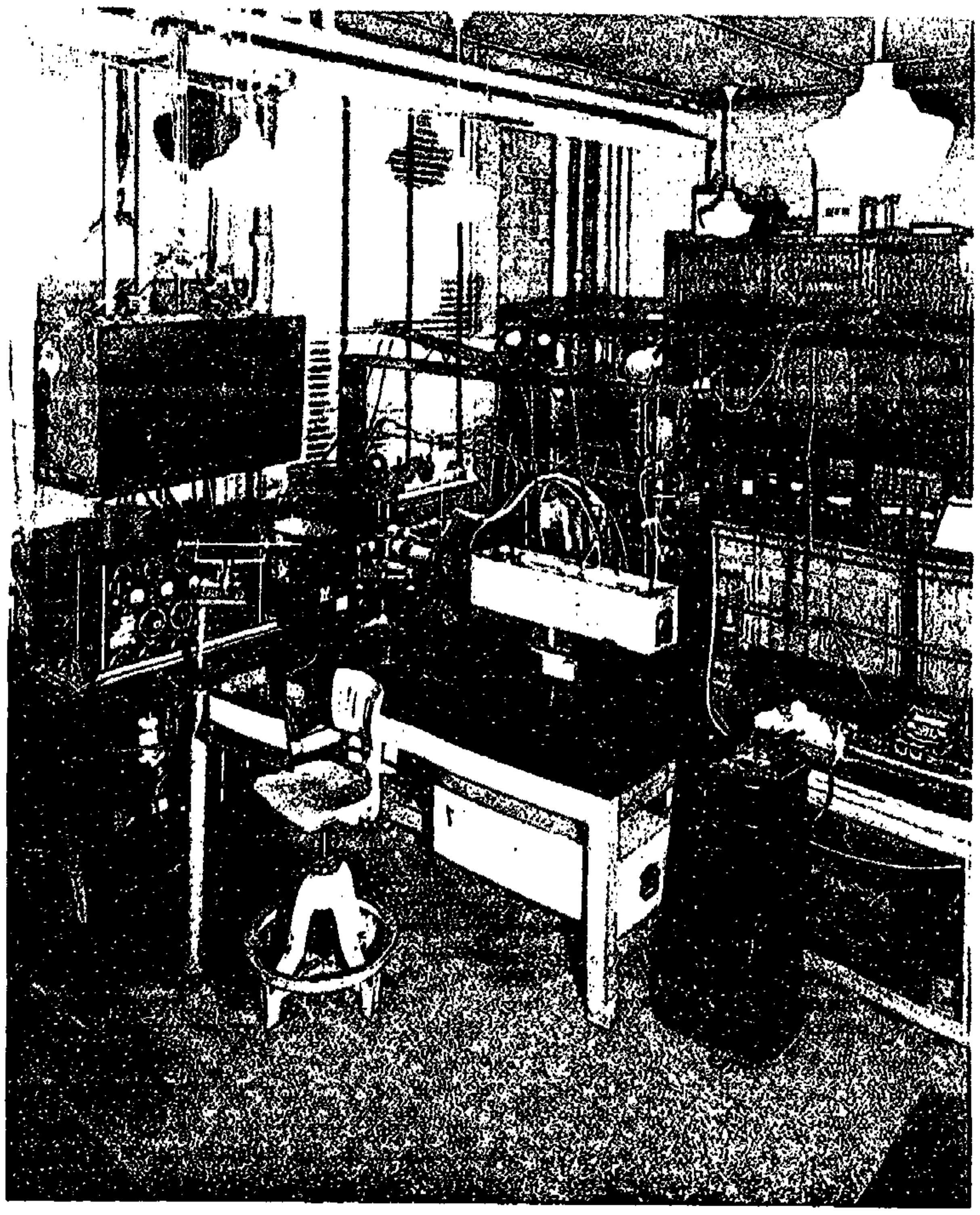

FIG. 1. Photoelectric spectrophotometer. The shielding is raised to show the amplifying set

Monochromator and optical system

A narrow spectral region is isolated from the continuous spectrum of the source by a Zeiss fixed-arm spectroscope (with deviation of 90°) used as a monochromator. Its lenses have an aperture ratio of F/5. The effective aperture ratio of the entire instrument is F/6.4, referred to λ 4861 A. U. The glass and crystal quartz prisms are interchangeable, as are also the achromatic glass and rock salt-crystal quartz collimator and telescope lenses which have diameters of 5.0 cm. and focal lengths of 24.8 cm. The

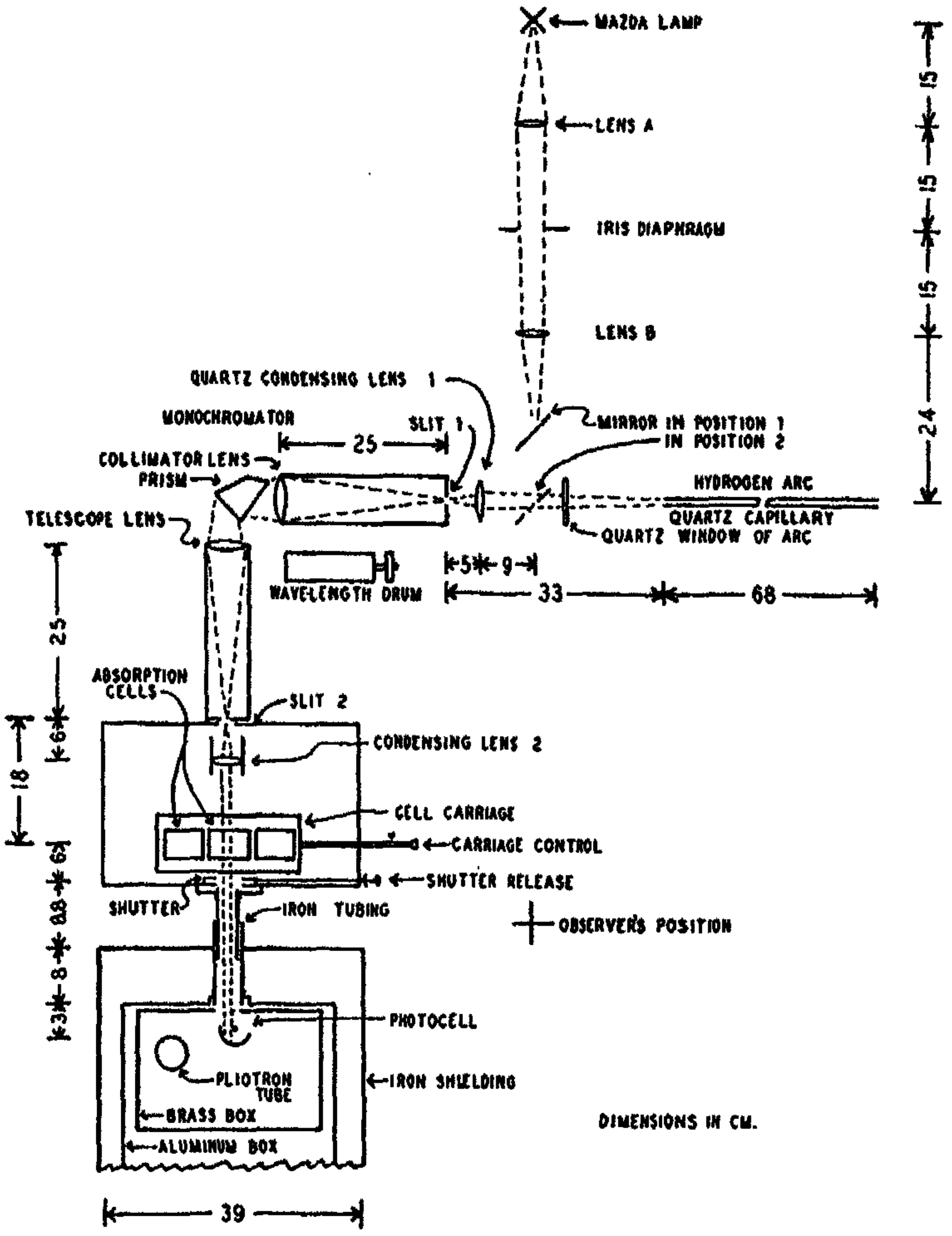

Fig. 2. Diagrammatic sketch of photometer

wave-length drum, which rotates the prism, has scales for λ 2200 to 4050 and 3850 to 7800 A. U. for the quartz and glass optical parts, respectively.

Radiation from the source is focused onto slit 1 by the crystal quartz condensing lens 1. The beam is rendered parallel by the collimator lens, dispersed by the prism, and focused as a spectrum on the plane of slit 2. Slit 2 isolates a narrow spectral region, the radiation of which is collected by condensing lens 2, a four-element, uncemented, fluorite–crystal quartz achromat, with an effective diameter of 22 mm. and a focal length of 5.2 cm. It is highly achromatic between 2200 and 7000 A. U. This lens is securely mounted in a metal holder that permits easy and fine adjustment in every direction. After leaving this lens the beam is practically parallel, and the entire beam strikes the photocell cathode and completely misses the anode and shielding pipe. The cross section of the radiation beam, as seen in visible light with slits 0.25 mm. or less in width, is 1 cm. high x 5 mm. wide at the center of the absorption cell. The small photoelectric current is amplified about 400,000 times by the General Electric F P-54 Pliotron tube, and is registered by a galvanometer.

For the purpose of stability, the monochromator is bolted securely to an iron casting equipped with leveling screws. A projection of this casting supports condensing lens 2, the absorption cell carriage, the shutter, and the light-tight sheet-iron box holding the cells. A second projection supports a 15-cm. optical bench, for condensing lens 1, and one end of a 100-cm. bench for the glass condensing system and Mazda lamp. Good mechanical stability for all optical parts is very essential for high accuracy. These supports are shown in the photograph.

Amplification circuit and galvanometer system

The amplification circuit (figure 3) is essentially that of Du Bridge and Brown (1), with minor alterations of resistance values to permit greater flexibility. It was found that the variability of different Pliotron tubes is so great that the resistances in the circuit as originally given by Du Bridge and Brown will not permit the general run of tubes to be properly balanced. The filament current is supplied by a large 12-volt battery. The Pliotron is operated continuously, inasmuch as thermal equilibrium and steady conditions are not reached until several hours after turning on the filament current. One charge of the battery lasts five weeks under continuous operation. The resistances of the main circuit are variable Type 314-A General Radio rheostat-potentiometers. The inner spring contact of this type gives the best results, as very small fluctuations in resistance, due to poor contacts, produce objectionable galvanometer fluctuations. R_6 and R_6' permit delicate balancing of the circuit. The series of resistances R_0, R_0', R_0'', R_0''' permit complete control of the galvanometer. R_g and R_e are variable box resistances that operate as a shunt and damping resistance for the galvanometer. The 1.5-volt dry cell and R_c, R_d, and R_b constitute a potentiometer system for voltage calibration of the circuit. R is a high resistance, consisting of a solution of iodine in benzene, similar to one previously described (11). The solution is contained in soft glass, with lead glass seals for the platinum leads, and has a resistance of 4.5×10^{10} ohms. This resistance has now operated very satisfactorily for two years. The galvanometer is a Leeds & Northrup Type R No. 2500-b with a sensitivity of 0.0005 microampere per millimeter at 1 meter. The scale-to-telescope distance is 10 meters, and all sensitivities given here for the amplification system are for this scale distance. Two scales are used, one above the other. One is graduated in centimeters and the other in decadic logarithms.

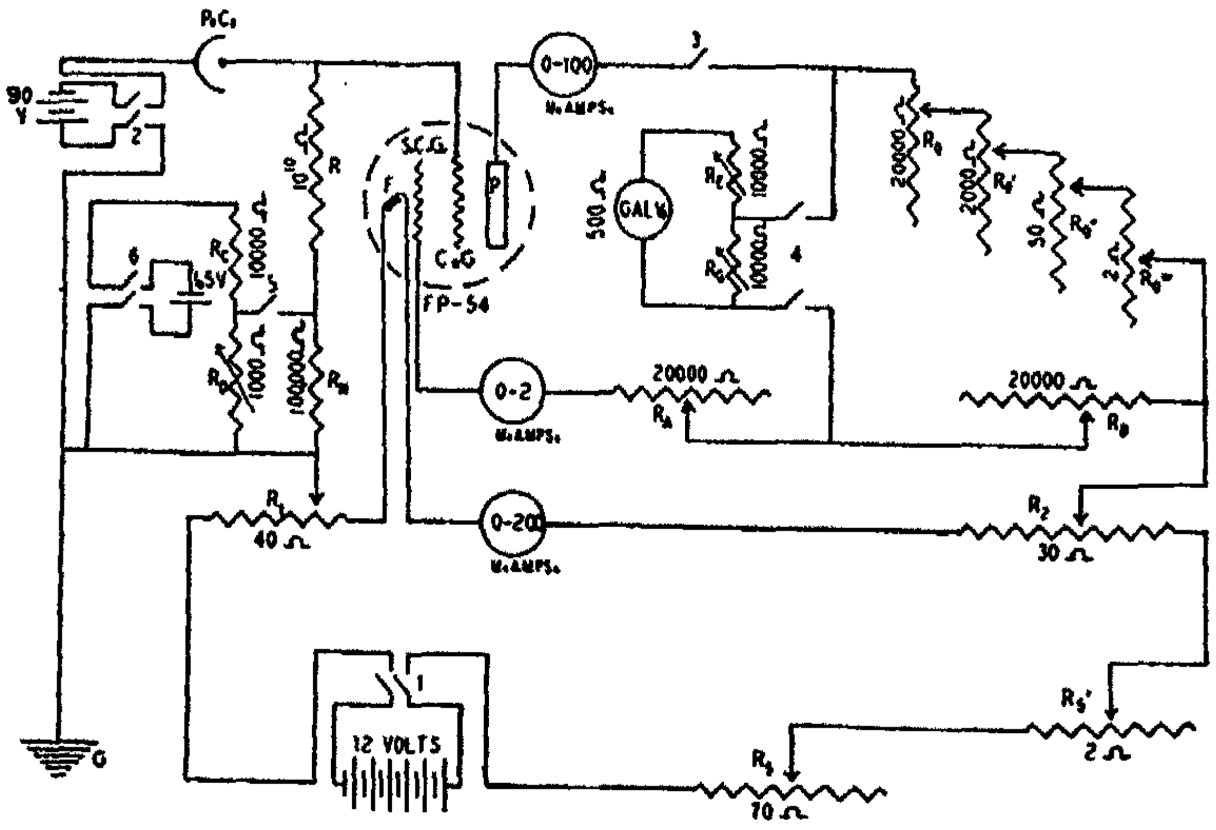

FIG. 3. Amplification circuit

The use of the logarithmic scale simplifies calculation of absorption coefficients, and the centimeter scale is useful for calibration.

The specially made cesium–cesium oxide photoelectric cell[1] with a plane fused quartz window is sensitive throughout the ultra-violet and visible regions; with grounded metal guard rings outside and inside, the "dark current" is negligible.

A typical set of resistance and current values for the circuit is as follows: R_1, 25 ohms, filament to contact; R_2, 17.5 ohms, R_5' to contact; R_a, 5000 ohms; R_b, 13,000 ohms; R_θ, 14,000 ohms; filament current, I_f, 101 milliamperes; plate current, I_p, 32 microamperes; space charge grid current, 280 microamperes.

[1] Constructed by the G-M Laboratories, Chicago, Illinois.

Within our experience I_f varies with different tubes from 88 to 103 milliamperes. The settings of R_g and R_a vary somewhat according to the value of R_0.

Shielding of the electric system against electrostatic and magnetic influences is extremely important, especially since the hydrogen discharge tube is so close to the amplifier. The Pliotron tube, photocell, and the resistance R are enclosed in a tight brass box, 6 in. x 6 in. x 15½ in. Electrical leads enter this box through amber insulators. The photocell is painted black and wrapped with heavy black felt, except for the window and a small area around the collector wire. The resistances and meters of the circuit, with the 45-volt "B" batteries, 1.5-volt dry cell, and brass box, are enclosed in an aluminum box 26 in. long, 16 in. high, and 6½ in. wide. One side of this box supports the potentiometers, switches, and meters. The aluminum box is fastened at the bottom to an iron-shielded base. The upper iron shielding (raised in the photograph) consists of ten layers of 26-gauge black sheet iron, separated by wrapping paper, and fits telescopically into its base. It is raised above the aluminum box by means of a block and tackle suspended from the ceiling. A 1-in. layer of hair felt in the shielding case provides thermal insulation for the circuit. The 12-volt battery and galvanometer shunt are contained in separate grounded shielding boxes of the same construction. R_d is outside the shield, within convenient reach of the operator. All leads between shielding boxes and the galvanometer are enclosed in iron pipes. The galvanometer is mounted on a Julius suspension and has no extra shielding. The telescopic iron tubing (inside diameter, 25 mm.) shown in figure 2, through which the

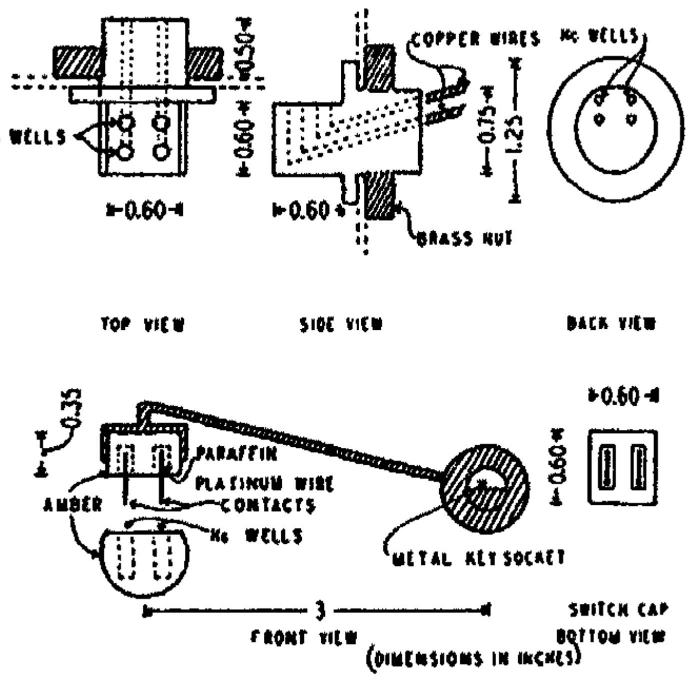

FIG. 4. Amber switch construction

radiation enters the shielding boxes, screws into sockets on either end, and shields the circuit at that point.

The switches are constructed as illustrated in figure 4. Copper leads enter mercury wells, set in transparent amber. Contact is made by amalgamated copper U-shaped wires held in an amber block by paraffin. It is very important that these switches be well insulated, and that they make good and reproducible contacts. The galvanometer switch No. 4 is the most critical. The copper wires from the circuit cannot be tinned, for mercury will then diffuse along the wire to soldered joints, giving rise to poor contacts. All junctions except the Pliotron and shunt connections are soldered. An isolantite socket supports the Pliotron. All permanent contacts are protected with optical black paint, and the surfaces between the resistance leads are coated with paraffin. R is connected with the circuit by means of mercury wells set in paraffined Bakelite. R_1, R_2, R_a, and R_b are locked to avoid accidental change. Anhydrous magnesium perchlorate is kept in both the brass and aluminum shielding boxes as a drying agent.

All switches and resistances R_6, R'_6, R_0, R'_0, R''_0, and R'''_0 are operated by means of keys which pass through ¼-in. holes in the iron shield and fit sockets mounted on the aluminum case. Friction drive dials are desirable in R_0, R'_0, and R''_0 for fine control.

Absorption cells

Absorption cells were constructed as shown in figure 5. The two ends of the Pyrex glass part are ground parallel to give the desired length and are sufficiently plane so that the cells may be used for solutions of all solvents without the use of any sealing compound to prevent appreciable leakage. Polished crystal quartz windows, protected against breakage by cork or rubber rings, are pressed against the glass ends by brass caps and brass rings (6, figure 5). The filling tubes are covered by small inverted test tubes to prevent the rapid evaporation of solvent. The diameter of each cell is much greater than necessary for the passage of the light beam. Consequently the cell may be moved 9 mm. to either side of its stop position before the passage of the light beam is obstructed. The heavy construction of the cell is advantageous in keeping the temperature of the solution constant whenever that factor is of importance, as in the case of equilibrium studies. These cells are held rigidly by the bottom pin in the cell holder. The glass and quartz parts may be readily separated and cleaned.

In figure 5 the light path distance, l, between the windows, has the following values for different cells: 0.5, 1.0, 2.0, 3.0, 4.5, 6.0, and 7.0 cm. These lengths are accurate to ± 0.25 per cent or better. A 3-mm. cell is made without the filling tubes or by replacing the glass part by metal as an integral part of the central brass section. This series of cells permits a twenty-three-fold variation in cell thickness. The windows are 3 mm. thick and 4 cm. in diameter, all cut perpendicular to the optic axis, from the same crystal of Brazilian quartz. These windows transmit from 86.6 to 89.0 per cent of perpendicularly incident radiation of λ 2200 A. U. in air. After their individual transmissions are known, they are paired so that the cells will transmit equally (within 0.5 per cent) at all wave lengths employed. In general, good crystal quartz will transmit more ultra-violet than good fused quartz and is therefore more desirable in as many of the optical parts as possible.

For solutions that are strongly acid or strongly alkaline Hilger Type D fused quartz one-piece cells are more convenient. These are mounted in individually fitted brass holders. The lengths of these cells are accurate to ± 0.15 per cent. It is very much more difficult to obtain cells of equal transmissivity in the ultra-violet region when fused quartz windows are employed. Furthermore, the transmissivity of fused quartz windows varies considerably with use. The chief difficulty in the use of fused quartz cells with attached windows is that of cleaning the inside surface of the windows. Decrease of transmissivity of fused quartz windows because of adsorption of material to the surfaces often occurs. We found that in many cases it was not possible to remove these adsorbed substances by organic solvents, acid potassium dichromate solution, aqua regia, or even by baking at a red heat. Several of these cells were ruined for ultra-violet work before we were aware of this difficulty. To date, nothing has adsorbed to the crystal quartz windows that could not be wiped off with cotton or dissolved in hot aqua regia.

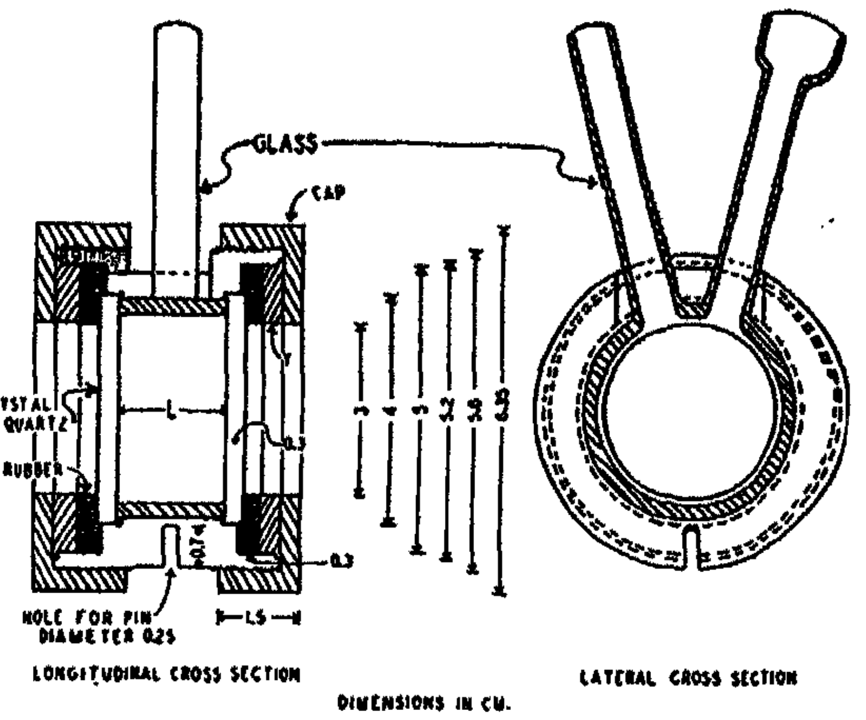

Fig. 5. Absorption cell construction

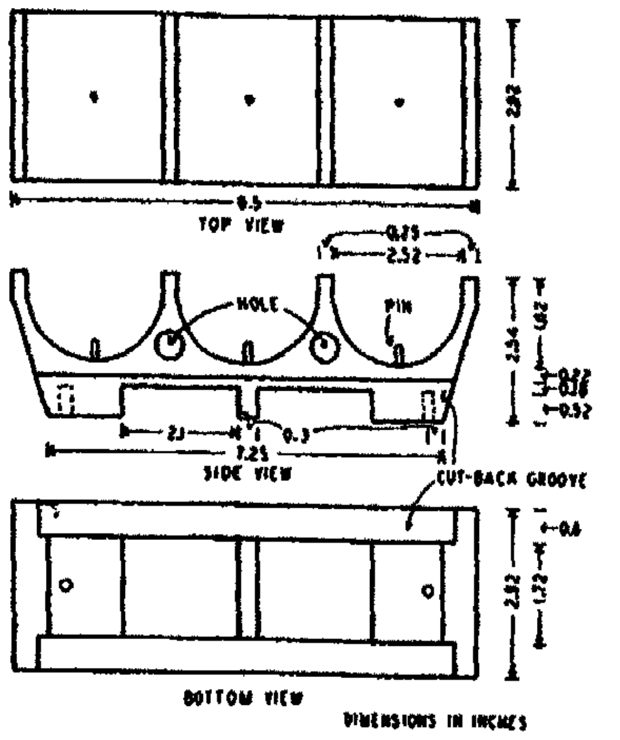

Fig. 6. Cell holder construction

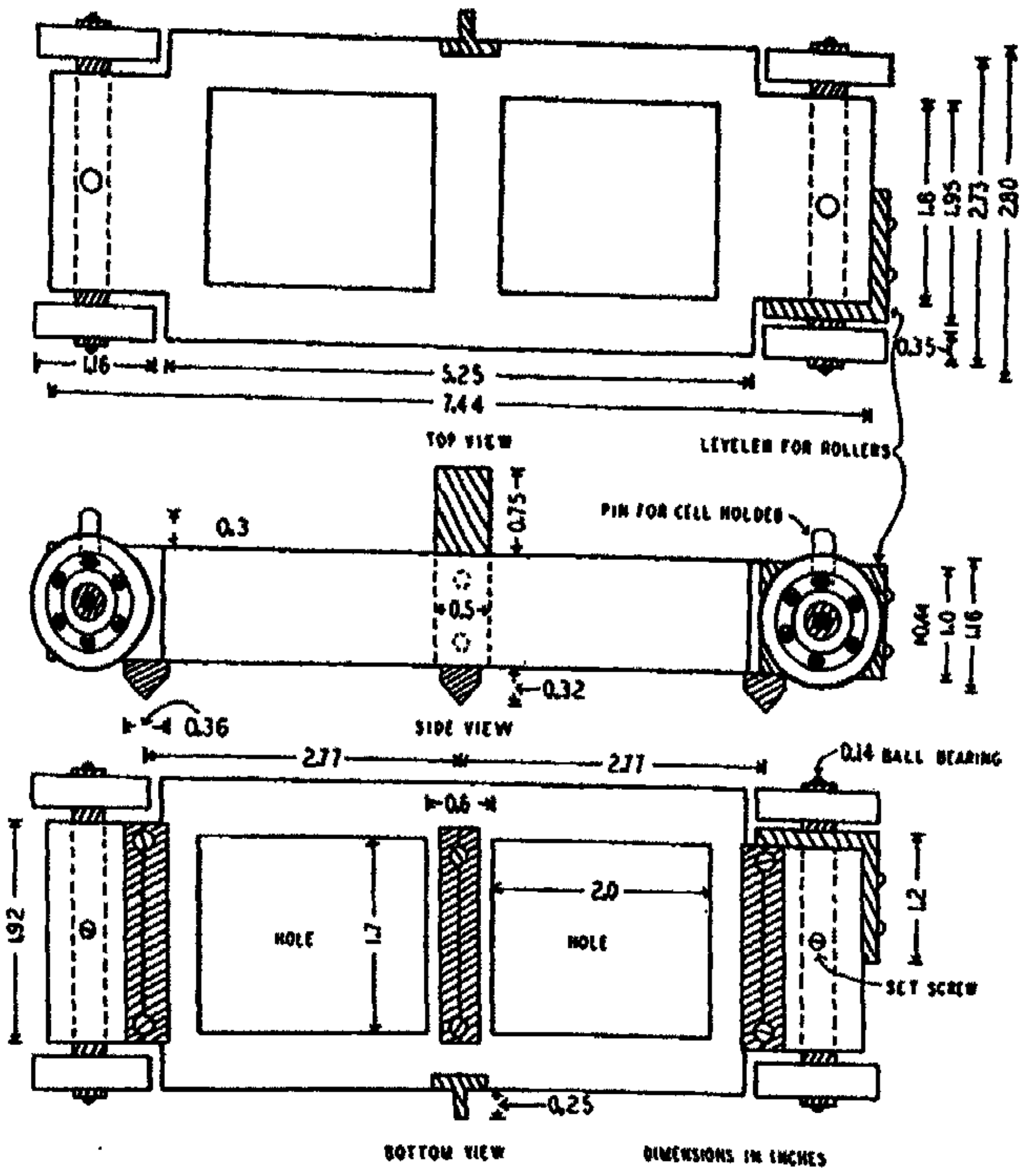

Fig. 7. Construction of carriage for cell holder

The absorption cells are held in the holder illustrated in figure 6, which accommodates three cells. By using one for solvent and two for solutions, the absorption spectra of two substances in the same solvent may be measured at the same time. The cell holder, designed for lightness, is constructed of an aluminum alloy.

The cell holder rests on a rolling carriage made of the same material with two pins to hold it in place (figure 7). The rollers are ball bearing, and operate in a groove of a heavy iron casting which in turn is bolted to the cast-iron base supporting the optical system. Ball bearings at the ends of the axles guide the carriage evenly as it moves in the groove. Three iron bars of triangular cross section across the carriage bottom complete the magnetic current of the electro-magnet when the respective absorption cells are directly in the light path and over the magnet, which is mounted below the carriage. If the magnet current is not constant, the Pliotron will be affected. A mercury contact device shown by the cross-hatched uprights at the center of one side of the carriage (figure 7) turns on one of three flashlight bulbs in front of the operator when a cell is in position for measurement. This arrangement insures reproducible stops for the cells, and is a convenience for the rapid shift of the cells in and out of the light path. The iron box containing the absorption cells, carriage, and lens 2 is air-thermostated to ± 0.5°C. The thermostat consists of a fan, a heating element, a water coil, and a relay control.

Radiation sources

The source of ultra-violet radiation is a modified hydrogen arc of the Urey type (7). Its construction and dimensions are shown in figure 8. The principal modification is a transparent fused quartz lining (5 mm. inside diameter) in the Pyrex central tube (8 mm. inside diameter). This lining is rather tightly fitted into the Pyrex tube to insure no discharge between the quartz and the Pyrex. Arcs operate quite well without this quartz lining, but are not durable enough. The ballast bulb helps to maintain a steady discharge. This arc operates best on a starting voltage of about 6000 volts, which decreases to 3000 volts after the arc is started. The maximum current capacity has not been determined, but one has operated daily at 1 ampere for six months without breaking.

Commercial electrolytic hydrogen is admitted to the arc and storage bulb through an electrically heated palladium tube. It is advisable to remove the last traces of oxygen or water vapor by pumping, in order to obtain a steady discharge. After flushing the arc several times with hydrogen, alternately running the arc and pumping to a pressure of 10^{-5} mm. of mercury, the impurities are sufficiently cleaned up and the electrodes have an evenly distributed blue discharge on the surface. The arc operates steadily without sparking provided the hydrogen pressure is within the proper range.

The ultimate steadiness of the arc also depends upon the constancy of the supply voltage. To effect a constant voltage, a synchronous motor generator set, the generator double wound for 110 or 220 volts, has been installed. Convenient flexibility is provided by a remotely controlled, manually operated rheostat by which the exciting field current of the generator may be varied by small degrees. With such an arrangement transformer primary voltages of 65 to 300 volts may be obtained. The pressure within the arc changes slowly over a period of weeks, and eventually the arc will not strike when voltage is applied. Often considerable time is saved by raising the primary voltage a few volts instead of readjusting the hydrogen pressure. The power factor of the arc circuit under good operating conditions is about 0.85; that of the arc alone is probably less than 0.7.

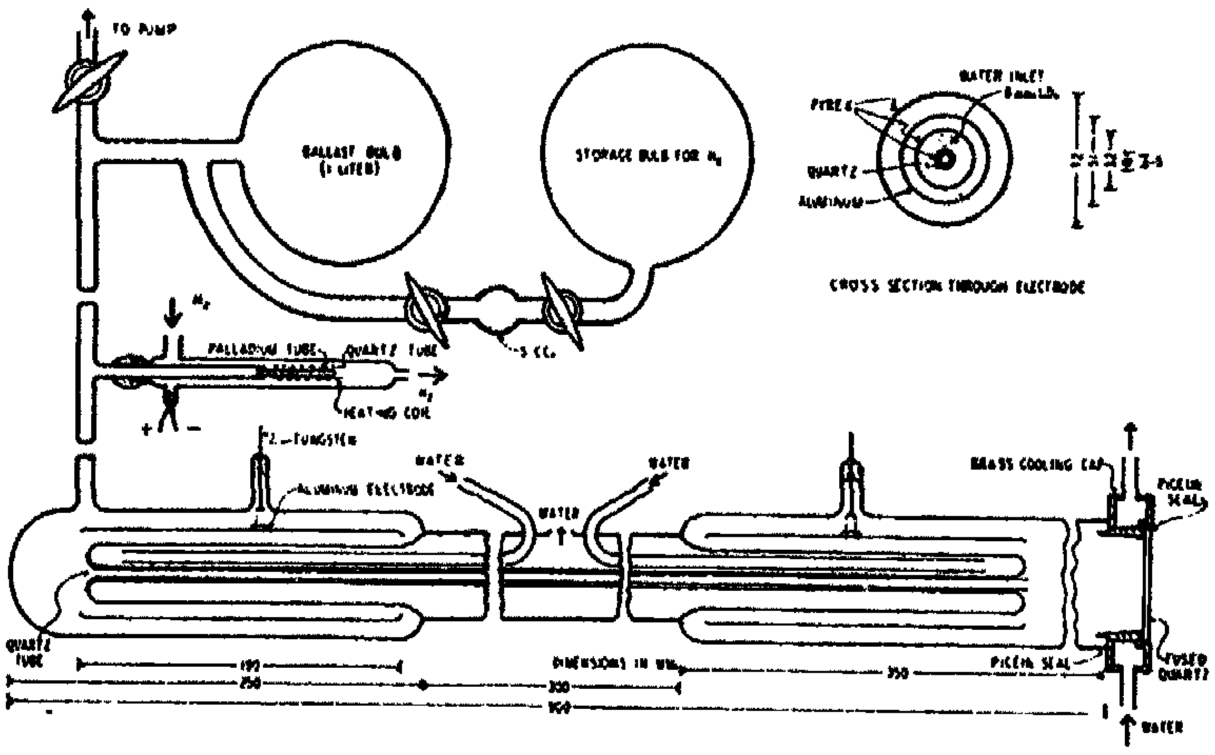

FIG. 8. Hydrogen discharge tube assembly

The source of steady visible radiation is a 50 c.p., 6–8 volt, 50-watt Mazda automobile headlight bulb, operated on six 6-volt storage batteries arranged in series-parallel to supply a voltage of 12 volts. A rheostat controls the voltage on the lamp.

Critical focusing of the radiation on slit 1 is very necessary for efficient use of energy and minimum slit widths. The crystal quartz condensing lens No. 1 is 5 cm. in diameter and has a focal length of approximately 5 cm. It is focused for the maximum deflection at 2200 A. U. from the hydrogen arc, for this wave length requires the widest slit. This lens is mounted on a hinged post which provides easy lateral adjustment. When the visible spectrum is used, the mirror is moved from position 1 to position 2. Glass lenses A and B, 3.5 cm. in diameter, and having focal lengths of 10 and 5 cm., respectively, are critically focused by the deflection method at 4000

A. U., using the Mazda lamp as a source. The iris diaphragm serves to control the intensity at the longer wave lengths when the slits are extremely narrow.

CALIBRATION OF APPARATUS

Amplifier calibration

The response of the amplification circuit and galvanometer to voltages applied on the control grid (easily tested by means of the calibration potentiometer circuit) is linear, as shown in figure 9. A stable voltage sensitivity of 175,000 mm. per volt and a current sensitivity of 1.25×10^{-10} amperes per millimeter at 10 meters scale-to-telescope distance are the usual working sensitivities. Under these conditions R_g is 10,000 ohms and R_o is 6000 ohms. The period is 7 to 8 seconds. To obtain still greater stability, at a sacrifice of sensitivity, R_g is made 5000 ohms and R_o 8000 ohms. The period remains the same, but the sensitivity is then 110,000 mm. per volt.

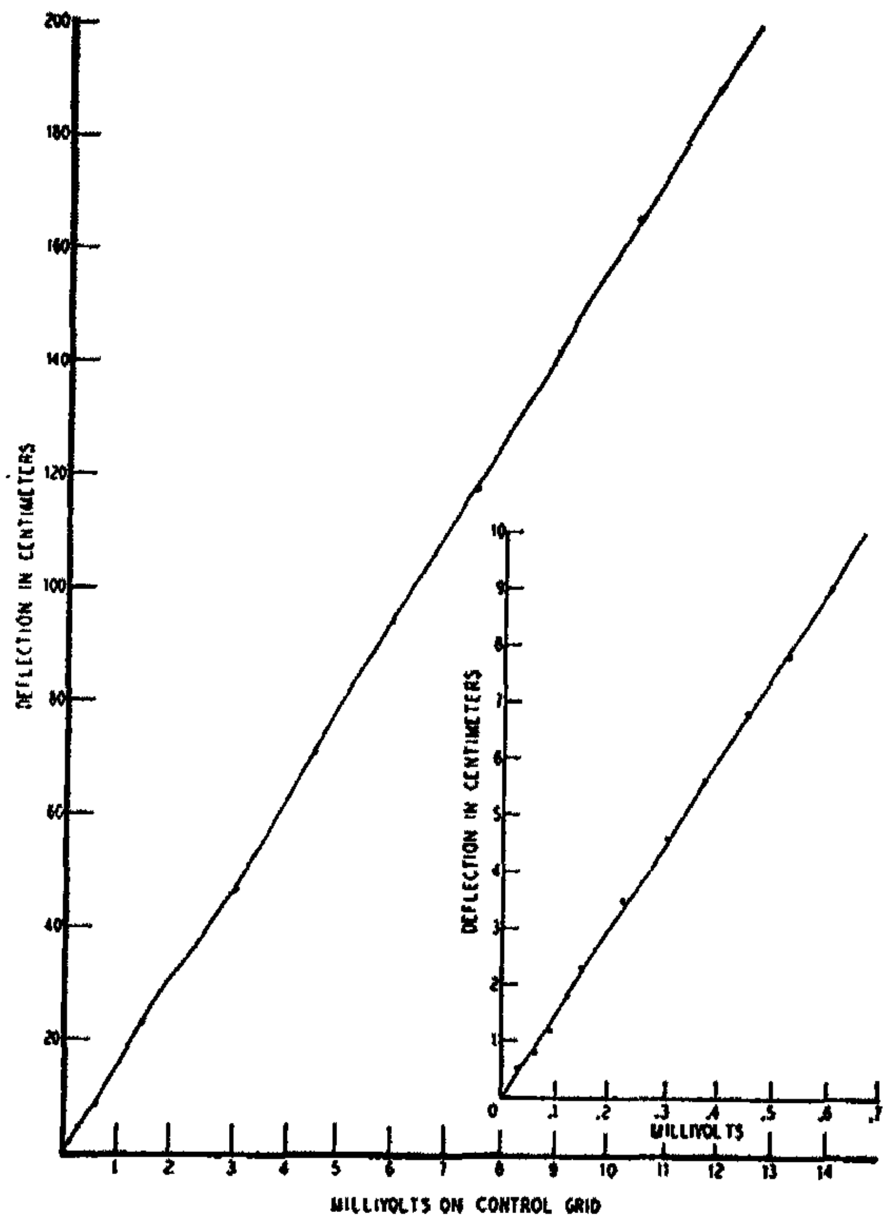

FIG. 9. Linearity of amplifier response

Photocell calibration

The wave length sensitivity curve of the photocell is probably similar to that of a cell described by Young and Pierce (9). Its sensitivity in the visible region at 90 volts is about 4.41×10^{-5} amperes per lumen per square centimeter. Its dark resistance is estimated to be about 10^{15} ohms.

The linearity of response of the photocell to radiation of low intensities such as are used for absorption spectrum measurements, was demonstrated by means of light screens. These screens, made of black silk stretched over a hoop, or of black oxidized iron or copper, were calibrated by means of a Mazda lamp, thermopile, and galvanometer. The screens were held perpendicular to a beam of light 3 cm. in diameter which covered the slit of the thermopile. The galvanometer response to an impressed voltage was linear. After calibration, the screens were held in the light path in front of the hydrogen arc or near the iris diaphragm to measure their transmissions at specific wave lengths with the photocell–amplifier system. In table 1 are given the transmission values of five filters at various wave lengths. Each value is an average of two or three determinations. When it is considered that the position of the screens was not very reproducible, the agreement between the values for the same screen is satisfactory. These data show that the photocell's response to radiation of the wave lengths and intensities employed is linear.

TABLE 1

Photocell calibration for linearity of response

FILTER TYPE	TRANSMISSION (PHOTOCELL)						AVERAGE TRANSMISSION BY PHOTOCELL	TRANSMISSION (THERMOPILE)
	2200 A.U.	2300 A.U.	4000 A.U.	5000 A.U.	6000 A.U.	7000 A.U.		
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
No. 1 cloth			11.6	11.5	12.0	12.0	11.8	12.3
No. 2 cloth	23.8	24.3	22.2	22.5	22.9	22.7	23.1	23.3
No. 12 copper			31.9	32.2	32.5	31.9	32.1	32.3
No. 9 iron	43.8	41.6	43.0	43.7	44.1	43.8	43.3	42.4
No. 8 iron			61.8	61.2	62.4	62.0	61.8	60.3

Monochromator calibration

For a given prism table position, the wave-length drum must be calibrated for both the quartz and glass prisms. This is done with a mercury-arc source, the radiation of which is focused on slit 1, either through the quartz condensing lens or through the small reflecting comparison prism that is placed in front of slit 1. The latter method is very convenient when the continuous light sources are in position and in focus. Although the collimator and telescope lenses are achromatic, there remains a small residual chromatic error which may be corrected by means of the focusing dial on the collimator lens.

Curvature of the image of slit 1 focused on slit 2 is made negligible by decreasing the height of slit No. 1 to 2 mm. Narrow slits are employed and preliminary observation is made visually by means of a small lens such as is used in the examination of photographic plates, placed on slit 2. The prism table is first so set that the lines of the mercury arc are focused as nearly as possible on slit 2 when the wave-length drum reading corresponds to their respective wave lengths. Then the more intense and isolated mercury lines are critically focused by alternate adjustment of collimator lens and wave-length drum for maximum galvanometer deflection. For each line focused in this way the collimator lens reading and the wave-length drum reading are recorded. Slits 1 and 2 are always maintained equal in width for our photoelectric measurements. With slits sufficiently wide (0.05 to 0.20 mm.) so that their widths can be more accurately measured, readings are taken at small intervals as the image of slit 1 is moved across slit 2 by rotation of the prism. Galvanometer deflections are then plotted against wave lengths. Figure 10 presents the curves

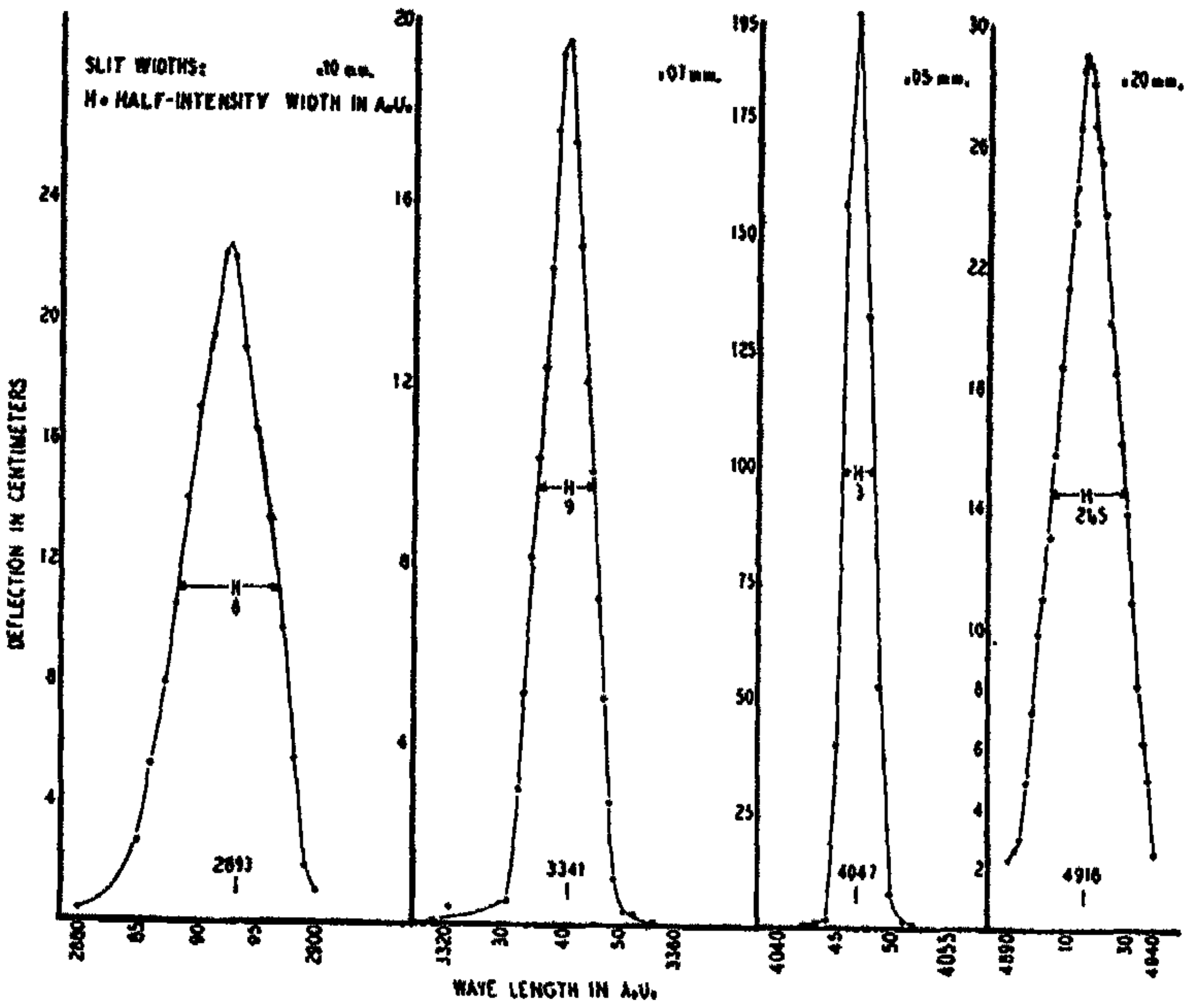

Fig. 10. Representative mercury lines for photoelectric calibration

obtained for four representative mercury lines. When the line is well focused, the curve is symmetrical in shape. From such data the calibration curves for the monochromator are then drawn.

The collimator lens settings are plotted against wave length as shown in figure 11. A smooth curve is drawn for each lens system, glass and rock salt-quartz. From these curves a table of lens settings is made which gives the correct setting in degrees for each 100 A. U. in the ultra-violet and visible regions. From 4000 to 4400 A. U. the lens setting is changed each 50 A.U. In the systematic recording of absorption spectra, the collimator lens setting is changed at these intervals only to insure that each wave length is critically and consistently focused. The maximum change of this setting in the turning of the adjustment screw is 10° in the ultra-violet and 5° in the visible region.

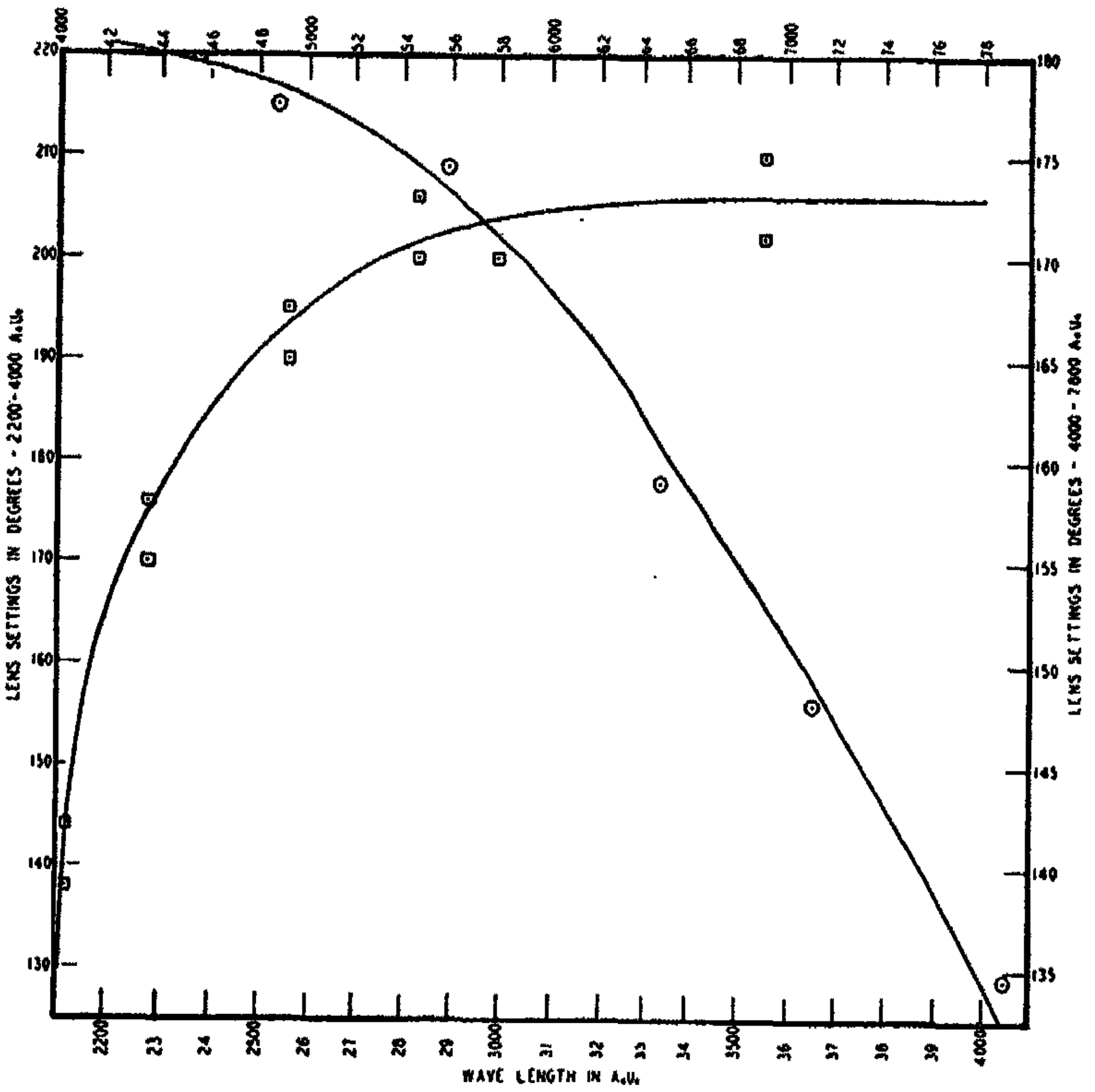

FIG. 11. Calibration of collimator lenses. ⊙, quartz-rock salt lens; ⊡, glass lens

From the maxima of the mercury line curves as indicated by the wave-length drum readings, the wave-length correction of the drum is calculated. A smooth curve is drawn through these points for as many mercury lines as possible. This curve provides the basis for the correct drum settings. For the particular instrument and prism table position in use here, the drum correction is 0 at 2200 A. U. and rises to 21 A. U. at 4000 A. U. with the quartz prism. With the glass prism, at 4000 A. U. the correction is 9 A. U. and at 7000 A. U. it is 81 A. U. Settings can be made accurately within ±1 A. U. at 2200 A. U. and ± 2 A. U. at 4000 A. U. on the ultraviolet scale. The accuracy of the drum setting on the scale for the glass prism is within ± 1 A. U. for blue and within ± 3 A. U. for red light.

There is much confusion in the literature regarding purity of light and effective widths of bands transmitted by a monochromator. The optics of the spectroscope has been discussed by Schuster (4), but the slits employed by him were too narrow for the present considerations. We consider slits of sufficient width that diffraction is not appreciable. Smith (5) obtained the effective width of the bands transmitted by taking the difference between the two wave lengths at which the galvanometer deflections were half of the maximum deflection caused by monochromatic radiation from a mercury arc. It has seemed desirable that this problem be analyzed from the point of view of practical photoelectric spectrophotometry, and that the factors entering into the calculation of the spectral region isolated be clearly explained. It is hoped that the following discussion will serve this purpose and that a more uniform convention will be adopted in different laboratories.

We shall define the spectral region isolated as the width of the second slit of the monochromator plus the width of the image of slit 1 on the plane of slit 2, translated into terms of wave-length units from the dispersion of the instrument. We shall show that this definition is applicable to all types of monochromators. "Spectral region isolated" refers to the wave-length limits of the radiation passing through the second slit of the monochromator. This region is not completely isolated from the continuous spectrum. For instance, with the widths of slit 2 and image of slit 1 equal to each other (in A. U.) only one wave length will be completely transmitted by slit 2 at any one drum setting. The intensities of other wave lengths transmitted by slit 2 decrease linearly and become zero at the two extremes of the region isolated.

Let us consider the situation at the plane of slit 2 when a line source producing *monochromatic* radiation is employed. In case 1, figure 12, let *BEDG* be slit 2 and equal to *ABCD* and *EFGH*, the images of slit 1 in the plane of slit 2 when the drum reading in A. U. is *O* and *P*, respectively. Assume the radiation to be of equal intensity throughout the image. Such is the case except when *AB* is very small. At drum reading *O*, no radiation passes slit 2. As the prism is rotated and the drum reading approaches

P, an increasing amount of radiation passes slit 2, as *ABCD* encroaches on *BEDG* until the edge of the image which was *BD* coincides with *EG* at drum reading *L*. Then all the radiation is emitted by slit 2. As the original *BD* edge of the image moves on toward *FH*, the intensity of transmitted radiation decreases to zero at drum reading *P*. At drum readings *W* and *X* the image half covers slit 2 and the intensity is one-half its maximum value, *I*. This change of intensity of radiation passing slit 2 with change of wave length is plotted in the right-hand illustrations of figure 11.

Case 1 is a special case and is presented first because of its greater simplicity. It illustrates the slit situation in the instrument described here. The width *X*-*W* in Ångström units is equal to the *H* of figure 10, the half-intensity line width obtained spectrophotoelectrically. As the drum reading passes from *W* to *X*, one edge of the image moves from *L* to *P* and the other from *0* to *L*, or the image moves one image width. Therefore *H* is equal to the image width and in this case to the slit width expressed in Ångström units. The spectral region isolated from a continuous spectrum, by our definition, is equal to 2*H*. The width *H*, divided by the slit width in millimeters, is the dispersion in Ångström units per millimeter at the wave length considered. The data shown in figure 10 are used to determine the dispersion of the prisms by the photoelectric method.

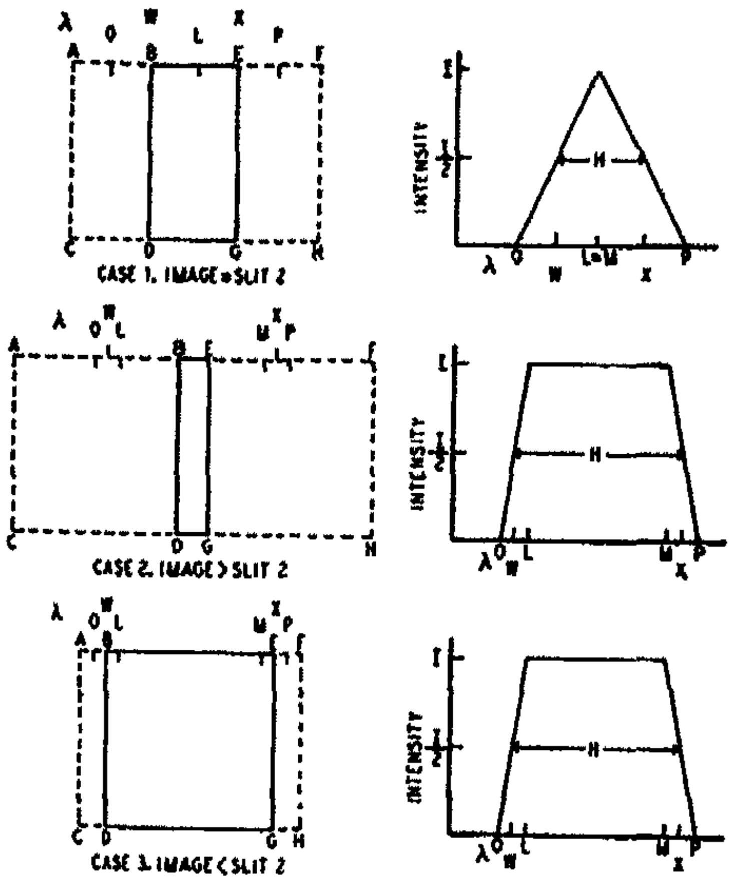

FIG. 12. Determination of spectral region isolated

Cases 2 and 3, figure 12, illustrate the more general situation when slit 2 and the image of slit 1 are of unequal widths. In these cases, the intensity–

wave length curve has a flat maximum, for now at no time do both edges of the image coincide with both edges of the slit. X-W in Ångström units is also equal to H in these cases and to the width of either the image or slit 2, case 2 or case 3, respectively.

In case 2,

$$
\begin{aligned}
OP \text{ (region isolated)} &= CD + DG \\
LM &= CD - DG \\
OP &= 2DG + LM
\end{aligned}
$$

In case 3,

$$
\begin{aligned}
OP &= CD + DG \\
LM &= DG - CD \\
OP &= 2DG - LM
\end{aligned}
$$

When $DG = CD$, $LM = 0$, as in case 1.

The spectral region isolated in both cases is

$$
\begin{aligned}
OP &= 2(H - LM) + LM \\
&= 2H - LM
\end{aligned}
$$

This region isolated from a continuous spectrum is twice the half-intensity width (using monochromatic radiation) minus the width of constant intensity translated in terms of Ångström units from the dispersion of the instrument. It is apparent that H, the half-intensity width, cannot be used generally as a definition of the spectral region isolated. When the focal lengths of the collimator and telescopic lenses are the same and slit 1 is equal to slit 2, the width of the image of slit 1 equals that of slit 2 and LM equals zero. For the reasons given here we believe it more desirable to define the region isolated as twice[2] the half-intensity width when the width of slit 1 equals that of slit 2 and LM equals zero.

Figures 13 and 14 show the dispersion curves of the quartz and glass prisms, respectively. The photographic method is, of course, the most accurate for determination of dispersion, and in these figures the dispersion curve is drawn through the points given by Zeiss, which are the most accurate of the three sets of data presented. The photoelectric data are given for a few regions to show that such data agree with the photographic. Our photographic data, indicated by squares in figures 13 and 14, were taken from very approximate measurements on plates taken with our instrument using the mercury arc as a source. These follow the data of

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[2] This factor of 2 was previously incorrectly stated as 3 (reference 10, page 110), making the regions isolated (reference 10, tables 1 and 2) too wide by one-third the value given.

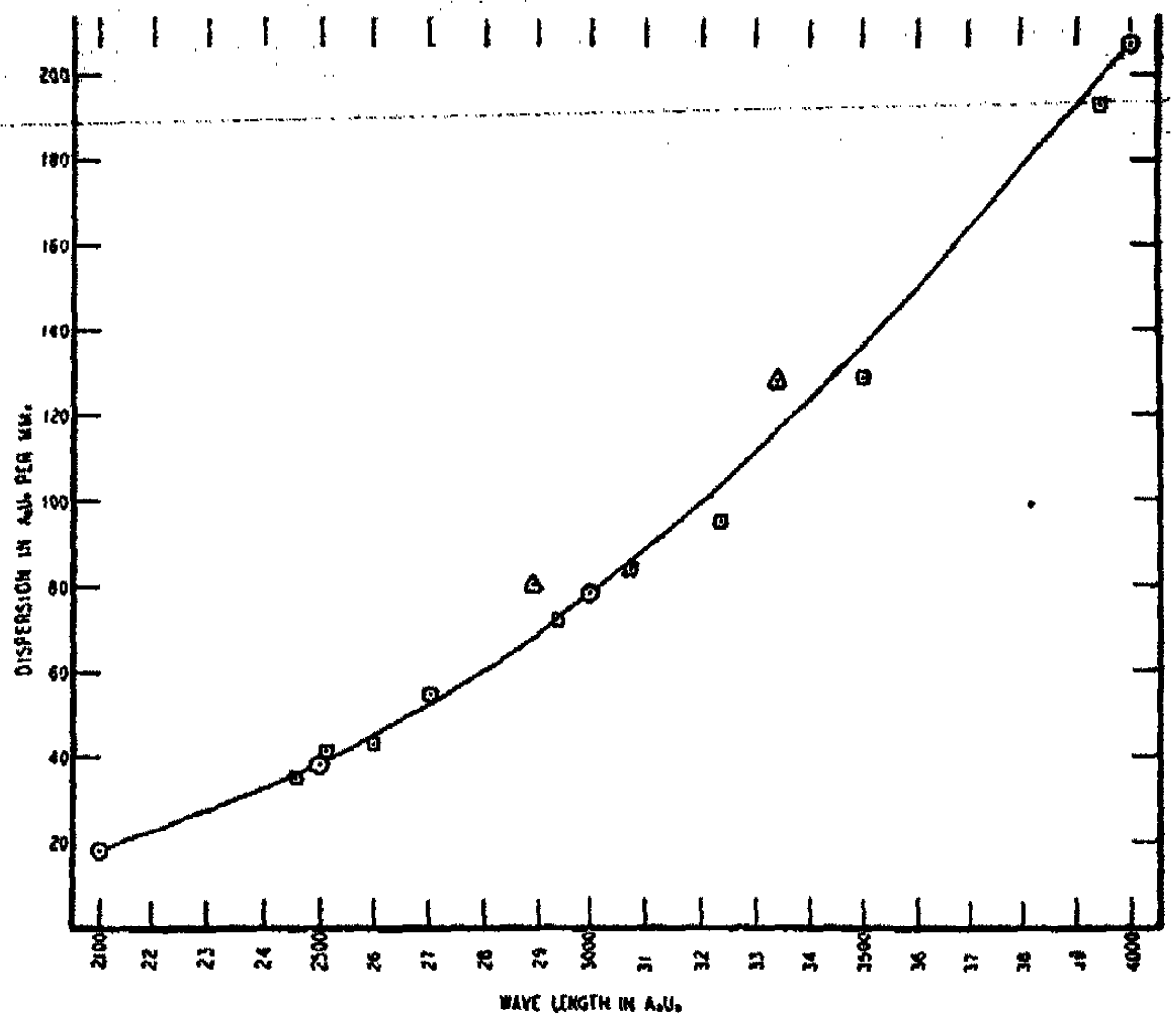

FIG. 13. Dispersion curve for quartz prism. ⊙, photographic data by Zeiss; ⊡, photographic data; △, photoelectric data

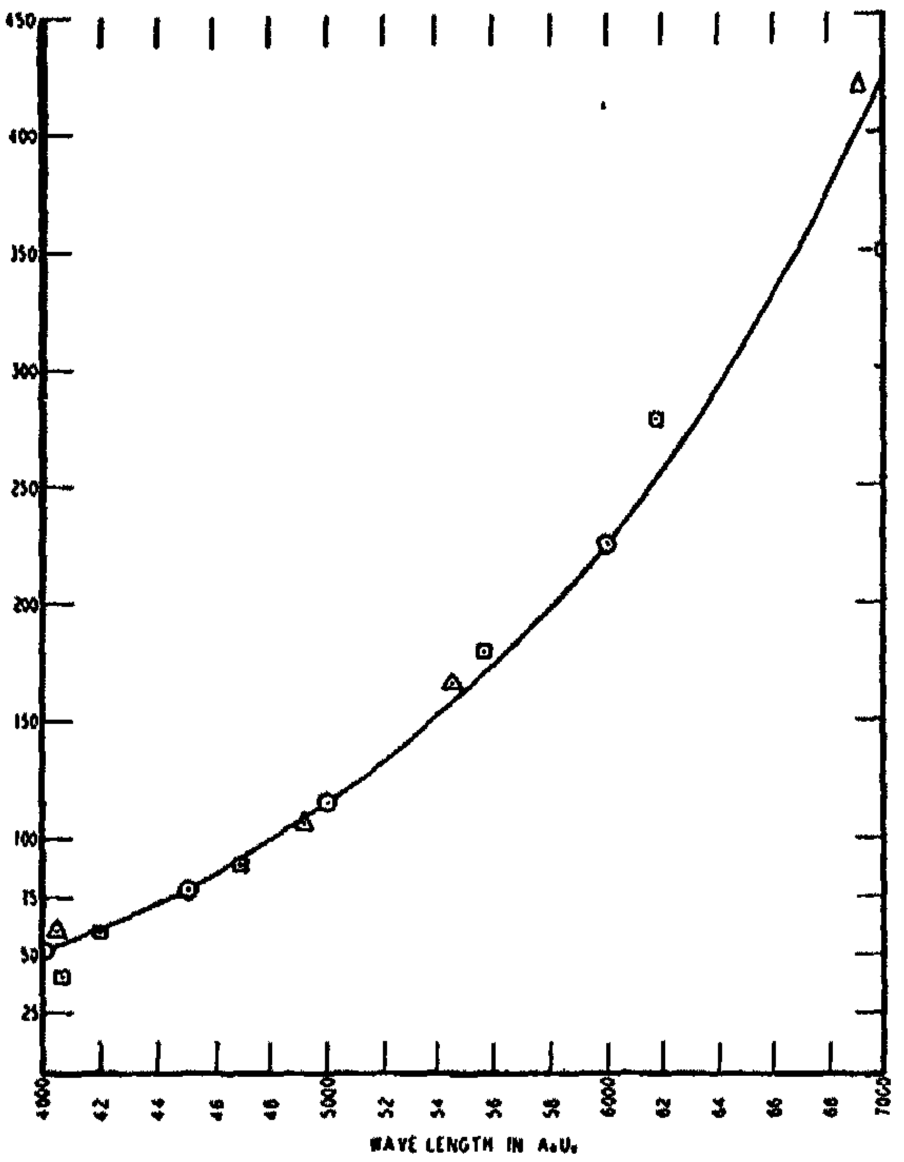

FIG. 14. Dispersion curve for glass prism. ⊙, photographic data by Zeiss; ⊡, photographic data; △, photoelectric data

Zeiss very closely. These plates also serve to confirm our collimator lens settings, previously determined by the photoelectric method, to show how very critical is this focus and to demonstrate the necessity for a good achromatic adjustment in the monochromator lens system.

TABLE 2

Slit data for the ultra-violet region with high-voltage hydrogen arc

Solvent, H_2O; cell length, 2 cm.; crystal quartz-rock salt optics

λ	DISPERSION	REGION ISOLATED	PRACTICAL SLIT WIDTHS FOR ABSORPTION MEASUREMENTS	CALCULATED REGIONS ISOLATED	I_0 DEFLECTION
A.U.	*A.U. per mm.*	*A.U. per mm. slit*	*mm.*	*A.U.*	*cm.*
2200	22	44	0.25	11.0	70
2300	26	52	0.10	5.2	50
2400	33	66	0.10	6.6	90
2450	34	68	0.08	5.5	70
2600	44	88	0.05	4.4	45
2750	55	110	0.05	5.5	60
2900	68	136	0.05	6.8	80
3200	100	200	0.04	8.0	60
3400	124	248	0.03	7.5	70
3700	162	324	0.03	9.8	60
4000	207	414	0.03	12.5	60

TABLE 3

Slit data for visible region with 50 c.p. mazda lamp

Glass optics

λ	DISPERSION	REGION ISOLATED	PRACTICAL SLIT WIDTHS FOR ABSORPTION MEASUREMENTS	CALCULATED REGIONS ISOLATED	I_0 DEFLECTION
A.U.	*A.U. per mm.*	*A.U. per mm. slit*	*mm.*	*A.U.*	*cm.*
4000	52	104	0.03	3.1	65
4150	60	120	0.02	2.4	80
4300	67	134	0.02	2.7	90
4500	78	156	0.012	1.9	75
5000	116	232	0.004	0.93	100
6000	225	450	0.002	0.90	100
7000	420	840	0.002	1.7	100

From the dispersion curve and the slit widths in millimeters, a simple calculation gives the spectral region isolated from a continuous spectrum by the monochromator, expressed in Ångström units. Tables 2 and 3 present dispersion data at various wave lengths with spectral regions isolated by slit widths practical for absorption studies on aqueous solutions. Practical slit widths for other solvents will depend upon their transmission at various wave lengths. Sample I_0 deflections with 2-cm. cells and sensitivity of 175,000 mm. per volt are included.

SAMPLE ABSORPTON CURVES

In reports of measurements made with this assembly, the molecular absorption coefficient, α, of Beer's law, will be used in most cases for which the molecular weight is known and the samples are pure. The concentration, c, is then expressed in moles per liter. The length, l, is given in centimeters. I_0 is the radiation intensity transmitted by the solvent, and I that transmitted by the solution. The molecular α is expressed in liters mole^{-1} cm.$^{-1}$, and the specific α in liters gram^{-1} cm.$^{-1}$.

Beer's law is used by us in the following form:

$$\log_{10} I_0/I = \alpha cl$$

There appears to be no uniform use of the terms "absorption coefficient" and "extinction coefficient," nor of the symbols used to designate these terms. Some authors make a distinction between these two terms on the basis of the use of either decadic or natural logarithms. It is to be emphasized that the terms used should always be clearly defined. Unfortunately this has not been done in many cases. Values of log I_0/I used in calculating the following data were restricted to the working range as given in a later part of this paper.

Benzene absorption spectrum

The ultra-violet absorption spectrum of benzene in isoöctane (2,2,4-trimethylpentane) is presented in figure 15 to demonstrate the resolution of the apparatus and its accuracy for a compound whose absorption spectrum contains many very sharp bands. This spectrum was measured accurately in all regions by varying both cell thickness and concentration. Determinations of α were made at intervals of 2 A. U. over most of the curve. The points given on the graph were experimentally determined (not averages), and their accuracy as well as the experimental conditions are given in table 4. The bands and the shoulders on the sides of the bands are all reproducible.

The benzene was purified as follows: it was kept over alkaline potassium permanganate, washed, dried over solid potassium hydroxide, distilled over phosphorus pentoxide, recrystallized four and five times by freezing, treated with phosphorus pentoxide for two days, and was finally distilled from phosphorus pentoxide immediately before use.

This spectrum of benzene may be compared with that obtained by Henri (2) in pentane solution and that given by Adam Hilger Ltd. (reference 6, p. 74) in hexane. Although the solvents are slightly different, they are sufficiently similar so that comparison of principal characteristics is valid.

Henri found that the wave-length change of the maximum did not vary by more than 4 A. U. when the solvent was changed from pentane to ethyl alcohol, and that the wave lengths of maximum absorption were the same in hexane and pentane. Hilger's spectrum does not extend below 2330 A. U., the band at 2677 A. U. is missing, and the shoulders on the bands are not as prominent as in Henri's spectrum.

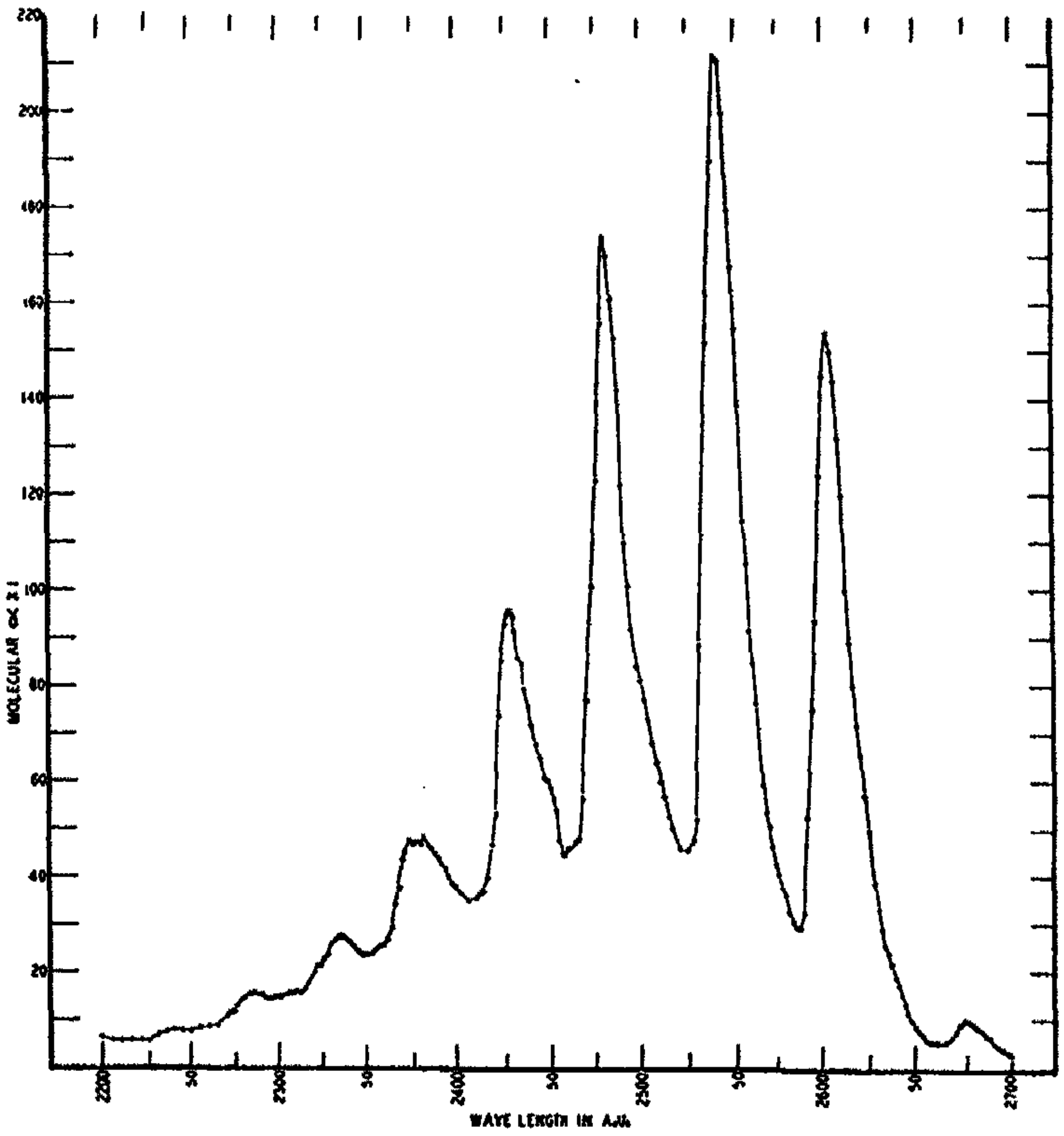

FIG. 15. Absorption spectrum of benzene in isoöctane

The curve presented in figure 15 shows greater resolution than the two curves obtained by the photographic method, as measured by the relative heights of maxima and adjacent minima. For instance, the ratio of the molecular α at 2602 A. U. to that at 2588 A. U. is 1.75 times that obtained by Hilger and 1.2 times that obtained by Henri. The shape of the more intense bands is more like that given by the Hilger curve. The small band given by Henri at 2525 A. U. was not found.

The higher maxima of benzene may be used to check the prism table setting, for their wave lengths are easily reproducible to ±2 A. U. Benzene, though a good standard substance for wave-length calibration, is not a good standard for absolute magnitude of α, owing to the extreme sharpness of the bands.

TABLE 4

Absorption spectrum of benzene in isoöctane (experimental data)

Sample weight = 2.6 g.

λ	MAXIMUM DEVIATION (3 RUNS)	MOLECULAR α	MAXIMUM DEVIATION IN α (3 RUNS)	CONCENTRATION	CELL THICKNESS	SLITS	SPECTRAL RANGE ISOLATED
A.U.	*A.U.*			*grams per liter*	*cm.*	*mm.*	
Maxima							
2540	±2	212.0	±2.0	0.105	1.00	0.08	6.4
2480	2	174.0	1.2	0.063	2.00	0.08	5.8
2602	2	154.0	3.0	0.077	2.00	0.10	8.8
2427	2	95.9	0.6	0.19	1.00	0.06	4.0
2448	3	60.0	1.0	0.30	1.00	0.08	5.6
2381	2	48.1	1.0	0.26	2.00	0.10	6.2
2373	2	47.3	1.0	0.26	2.00	0.10	6.0
2334	2	27.3	0.3	0.5	2.00	0.15	8.4
2322	2	21.2	0.3	0.5	2.00	0.15	8.4
2286	5	15.5	1.0	3.0	0.496	0.10	5.2
2677	3	10.0	0.1	2.4	1.00	0.06	5.9
Minima							
2660	5	5.49	0.1	9.6	0.496	0.06	5.8
2210	5	5.6	0.2	7.0	0.496	0.15	6.8
2348	2	23.4	0.5	0.5	2.00	0.15	8.7
2588	3	29.2	0.5	1.6	0.496	0.08	6.9
2405	3	34.9	0.4	0.7	1.00	0.08	5.1
2460	2	44.3	1.0	0.26	1.00	0.08	5.6
2525	3	45.3	1.0	0.26	2.00	0.06	4.7

Potassium chromate absorption spectrum

The spectrum of potassium chromate in 0.05 *N* potassium hydroxide as originally used by von Halban (8) is an excellent standard for absolute magnitude of α, owing to the broadness of its bands. This spectrum is presented in figure 16. The potassium chromate was recrystallized four and five times from 0.005 *N* potassium hydroxide (to prevent formation of potassium dichromate). It was dried by pumping at a pressure of 10^{-5} mm. of mercury for several hours. The dots through which the curve is drawn are taken from several series of determinations at 25 A. U. intervals, and the points on the maxima at wave lengths 2700 to 2750 and 3675 to

3750 A. U. are averages of three such series. The error in the maxima and minima and experimental conditions are given in table 5.

This curve is compared in figure 16 with the data obtained by von Halban. He used nine mercury lines in the ultra-violet and a complicated photoelectric method requiring the balance of two photocells, and the use of an electrometer, neutral wedge, and rotating sector. It is noted that seven of his points (triangles) fall very close to the curve, and that three differ from the curve by about 10 per cent. Though the reproducibility of his measurements was good and his points represent averages of a number of successive determinations, these three points of von Halban are considered to be in error. It should be remembered that his method required many corrections and calibrations for each wave length, which are not involved in the method reported here. To demonstrate that Beer's

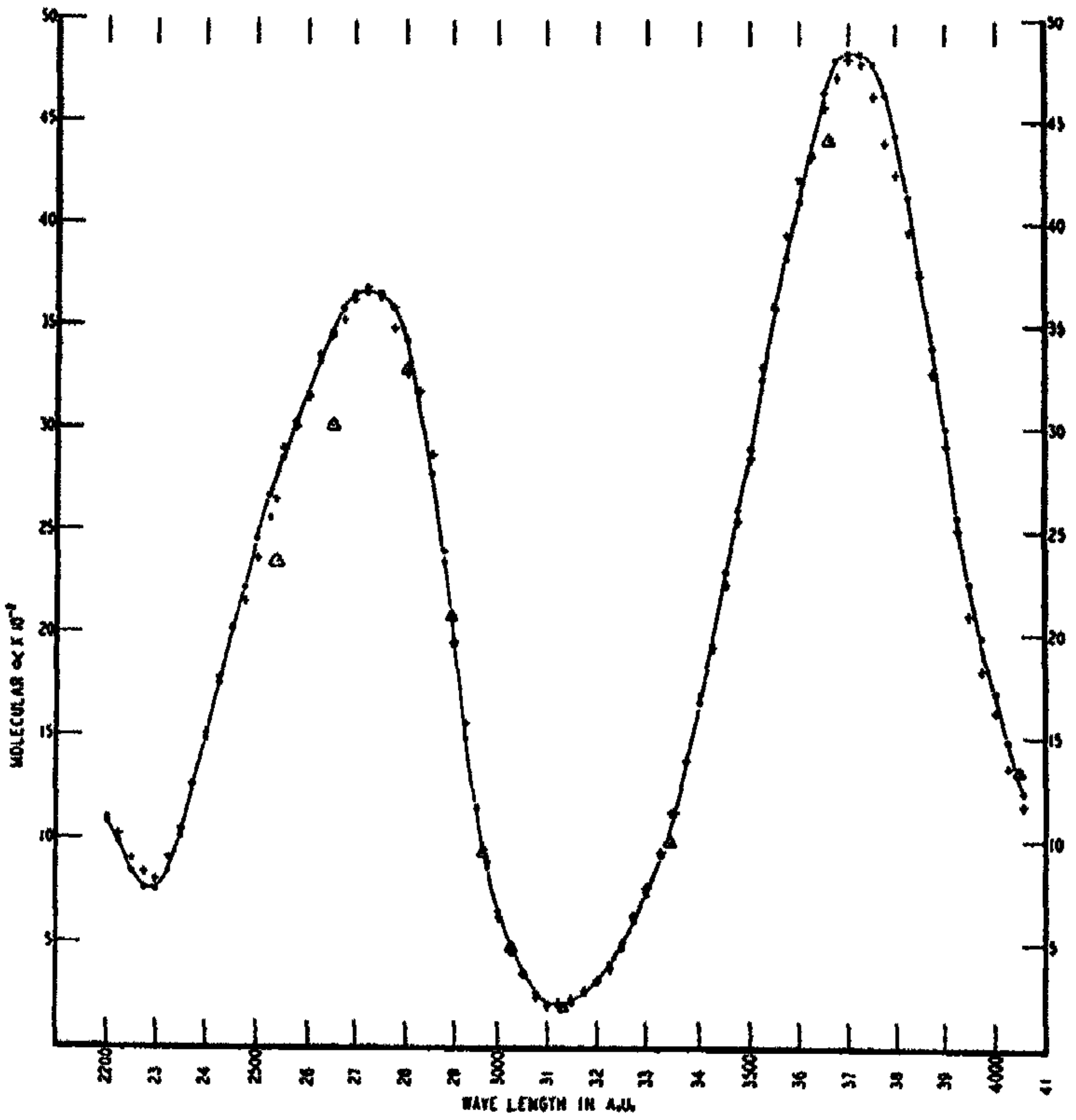

FIG. 16. Absorption spectrum of potassium chromate in 0.05 N potassium hydroxide solution. +, data on van Halban's concentration; △, data of von Halban; ●, data on optimum concentration.

TABLE 5

Absorption spectrum of potassium chromate in 0.05 N potassium hydroxide (experimental data)

Sample weight = 0.047 g.

λ	MOLECULAR α	MAXIMUM DEVIATION (3 RUNS)	CONCENTRATION	CELL THICKNESS	SLITS	SPECTRAL REGION ISOLATED
A.U.			*grams per liter*	*cm.*	*mm.*	
Maxima						
2725	3660	±40	0.00860	2	0.07	7.4
3710	4830	30	0.00650	2	0.04	13.2
Minima						
2290	752	15	0.0400	2	0.14	7.2
3125	203	6	0.0400	7	0.06	11.0

TABLE 6

Instrumental precision

Potassium chromate in 0.05 N potassium hydroxide; 2-cm. cell

CONCENTRATION = 0.0000394 M λ = 2650 A.U.		CONCENTRATION = 0.0000296 M λ = 3660 A.U.	
log I_0/I	Molecular α	log I_0/I	Molecular α
0.273	3470	0.279	4720
0.271	3440	0.281	4750
0.269	3420	0.280	4730
0.275	3490	0.279	4720
0.277	3520	0.279	4720
0.272	3460	0.280	4730
0.271	3440	0.277	4680
0.270	3430	0.279	4720
0.270	3430	0.278	4700
0.270	3430	0.277	4680
0.270	3430	0.279	4720
0.271	3440	0.279	4720
0.276	3500	0.279	4720
0.275	3490	0.279	4720
0.276	3500	0.282	4760
0.270	3430	0.279	4720
0.270	3430	0.279	4720
0.272	3460	0.279	4720
0.277	3520	0.280	4730
0.271	3440	0.280	4730
Average.........	3460 ±30	Average..........	4720 ±10

law was not involved, a run was made on exactly the same concentration used by von Halban ($0.07403 \times 10^{-3} N$ potassium chromate in 0.05 N potassium hydroxide). These data are represented as crosses and were obtained with cells of 1, 2, and 7 cm. lengths in an effort to keep log I_0/I values as near optimum as possible. These points follow the curve very closely. The points on the curve were run in both the fused quartz Hilger 2-cm. cells and the chromium-plated metal cells of different lengths, and no difference was obtained under these conditions.

The precision of our method is shown by the figures of table 6, for which twenty successive determinations of the absorption coefficient were made at wave lengths 2650 and 3660 A. U., wave lengths at which von Halban's points differ from our curve. These may be compared with his series (reference 8, table 2, page 220).

The differences between the errors at the two different wave lengths is due to differences in the stability either of the arc or of the amplifier circuit at the different times of observation.

DISCUSSION OF ERRORS

Wave length

Errors in wave length are usually negligible for absorption spectra showing broad continuous bands. The wave-length error for the sharp peaks of the benzene spectrum is only ± 2 A. U., and the wave length of the absorption peak can be repeated within this limit after removing and replacing the prism and lenses and resetting the wave-length drum. For most reproducible results, the prism must be held the same way and pressure applied at the same place to rotate the prism table slightly while the clamping screw is tightened. If this operation is not performed in the same way each time, the wave-length error may amount to ± 5 A. U. at 2540 A. U. The value of α for potassium chromate in 0.05 N potassium hydroxide at 3660 A. U. was reproduced with an error of ± 0.4 per cent after resetting the wave-length drum or removing and resetting of the prism followed by the resetting of the drum.

Precision of measurement

The error in determining the value of the absorption coefficient, or the concentration of absorbing material (when the absorption coefficient is known), is a function of $\Delta I/I$ and $\Delta I_0/I_0$, where I_0 and I are the intensities of the light transmitted by solvent and solution, respectively, and ΔI and ΔI_0 the absolute errors in the determination of the light intensities. The absorption coefficient is defined by the equation:

$$\log I_0/I = \alpha cl \tag{1}$$

and

$$\log \frac{I_0(1 \pm \Delta I_0/I_0)}{I(1 \mp \Delta I/I)} = \alpha cl \pm \Delta'(\alpha cl) \tag{2}$$

From equations 2 and 1

$$\log \frac{(1 \pm \Delta I_0/I_0)}{(1 \mp \Delta I/I)} = \pm \Delta'(\alpha cl) \tag{3}$$

When $\Delta I/I$ and $\Delta I_0/I_0$ are considered as average deviations from a mean, the deviation in $\Delta\alpha cl$ will be the average of the two combinations of signs in the left-hand member of equation 3 which produce positive deviations in αcl. I is always smaller than I_0, and in this work $\Delta I_0 = \Delta I$.

$$\log \frac{(1 + \Delta I_0/I_0)}{(1 - \Delta I/I)} + \log \frac{(1 - \Delta I_0/I_0)}{(1 - \Delta I/I)} = 2\Delta(\alpha cl)$$

$$\log [1 - (\Delta I/I_0)^2] - 2 \log (1 - \Delta I/I) = 2\Delta(\alpha cl) \tag{4}$$

Expanding the two left-hand members of equation 4 and neglecting all terms higher than the first order, we have

$$\frac{1}{2.3}\, \Delta I/I_0 \cdot I_0/I = \Delta(\alpha cl) \tag{5}$$

Dividing equation 5 by equation 1 we obtain:

$$\frac{(\Delta I/I_0)\cdot(I_0/I)}{2.3 \log I_0/I} = \frac{\Delta(\alpha cl)}{\alpha cl} \tag{6}$$

This equation is identical with that obtained by Twyman and Allsopp (6), who obtained this function by merely differentiating equation 1, keeping I_0 constant.

The value of I_0/I, or of the $\log I_0/I$, which gives the minimum error in $\Delta(\alpha cl)/\alpha cl$ is given by the condition:

$$\frac{d\left[\dfrac{\Delta(\alpha cl)}{\alpha cl}\right]}{d(I_0/I)} = 0 \tag{7}$$

For this condition $\log I_0/I = 0.4343$ or $I_0/I = 2.719$.

The values of the function

$$\frac{I_0/I}{2.3 \log I_0/I}$$

for different values of I_0/I are given in the lowest curve in figure 17. The value of this function for any given value of $\log I_0/I$ when multiplied by the fractional error in determining I_0, i.e., $\Delta I/I_0$, gives the error $\Delta(\alpha cl)/\alpha cl$. This lowest curve applies only when $\Delta I/I_0$ is small. Instances may arise when an investigator may not be able to obtain sufficient intensity of radiation to keep $\Delta I/I_0$ small (in the more extreme ultra-violet region). If in such a case a large value of the log I_0/I is obtained (sometimes unavoidably), the curves other than the lowest in figure 17 become applicable.

For a complete analysis we have determined the value of $F(I_0/I)$ for different values of $\Delta I/I_0$, using equations 4 divided by equation 1, rather than equation 6. These values are given as the upper curves in figure 17; each is labeled with the value of $\Delta I_0/I_0$ used in equation 4.

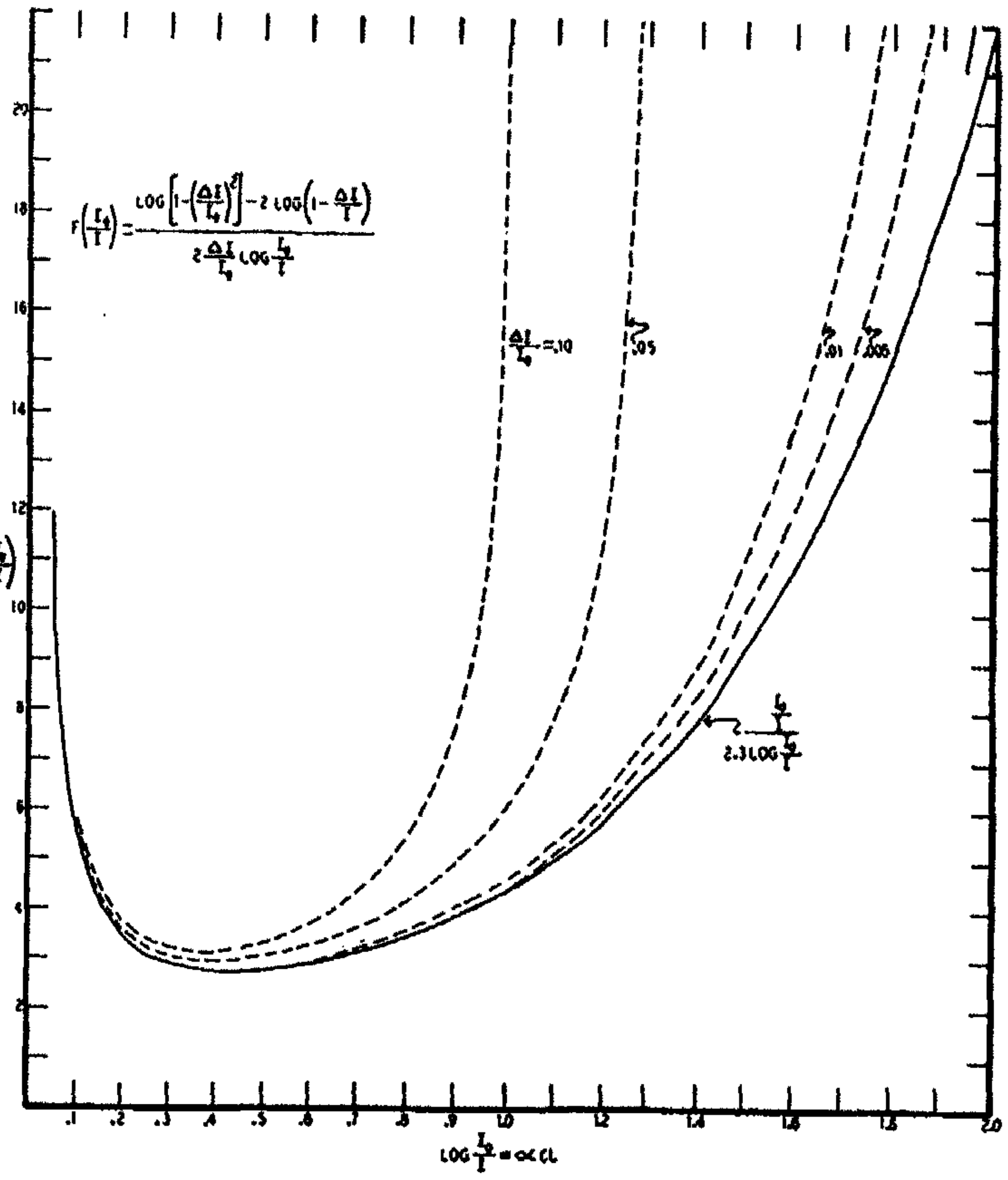

FIG. 17. Error curves

As in the case of the lowest curve, the fractional error in determining αcl, e.g., $\Delta\alpha cl/\alpha cl$, is obtained by multiplying the value of $F(I_0/I)$ (for the given value of log I_0/I and for the proper $\Delta I/I_0$ curve) by $\Delta I/I_0$.

The working range of log I_0/I for the greatest precision will depend upon the value of $\Delta I/I_0$, and may be determined from the curves of figure 17, provided that the amount of scattered radiation is negligibly small (see next section). For very small values of $\Delta I/I_0$ (0.005 or less) the working range of log I_0/I lies between the values 0.2 to 0.9. For our system $\Delta I/I_0$ under favorable working conditions is about 0.002,—an error of 0.006 in $\Delta(\alpha cl)/\alpha cl$. As will be shown in the following discussion on scattered radiation, the upper limit of 0.9 will not be applicable in many cases and will be determined by the purity of the light used in any particular measurement.

The accuracy of α depends directly on the accuracy of the sample weight and the dilution technique. In the preparation of crystalline substances for weighing, the solutions from which they are recrystallized should be filtered through a fine sintered-glass filter to remove any dust particles or filter paper shreds. An almost imperceptible amount of dust gives rise to undue scattering of light and may cause a serious error in any determinations. All volatile matter, including the solvent, should whenever possible be removed from the sample by drying *in vacuo*. It is our usual practice to dry samples in an all-glass vacuum system until the vapor pressure is less than 10^{-6} mm. of mercury. During these operations great care must be exercised to keep out dust particles and stopcock grease. The weighed sample should be dissolved in glass-stoppered containers just before the absorption measurements are made. Heat and illumination are to be avoided as much as possible in preparation of the dry sample and solution. Measurements should be checked on at least two different purification fractions before a reliable value of α can be obtained. If the substance is available from more than one source or can be purified by more than one method, such additional checks are desirable.

Scattered radiation

The amount of scattered radiation with which the experimenter must contend will depend entirely upon the construction of the monochromator used, the cleanness of the optical surfaces, the nature of the light source, and upon the arrangement of the whole optical system in general. The extent to which scattered light may interfere with accurate measurement cannot be estimated from data from calibration with a line source if continuous radiation is to be used in making the absorption measurements. For example, we found that when the 4047 A. U. mercury line was in sharp focus, with 0.01-mm. slits, a maximum galvanometer deflection of 85 cm. was obtained, and when the wave-length drum was rotated 3 A. U. the deflection was certainly less than 0.5 mm.; it could not be detected. Determinations made in the same way in the ultra-violet region showed that for the 2536 A. U. line (slits 0.04 mm.) deflections of 25 cm. decreased to 0.0 cm. when the drum was turned 5 A. U. From these observations it might be inferred that the scattered radiation is negligibly small, inasmuch as the intensity drops abruptly to a negligibly small value on each side of the line in question. It must be borne in mind that scattered radiation from a continuous source is a composite of radiation of all possible wave lengths and the scattered radiation from this source will in general be greater than that from a line source such as a mercury-vapor lamp. In the following discussion we shall present a simple method of determining the effective scattered radiation and the resulting error, when continuous radiation is employed.

In all cases the scattered radiation will be partially absorbed by the substance in question, and the amount of this scattered radiation absorbed will depend upon the region isolated and upon the absorbing substance. To make an exact calculation of the fraction of interfering scattered radiation would require integration over all wave lengths for some function involving the distribution of light intensity and absorption coefficient with wave length. Such a procedure would be practically impossible. However, we may simplify the problem by imagining the scattered radiation to be divided into two components, one of which is absorbed by the substance in question to the same extent as the region isolated and the other, not absorbed at all. This portion which is not at all absorbed we shall refer to as the effective scattered radiation and designate it by S.

Then

$$\log \frac{I_0(1 + S/I_0)}{I(1 + S/I)} = \alpha cl - \Delta(\alpha cl)^* \qquad (8)$$

Both I and α in equation 8 are "true" values which would be obtained if S were equal to zero.

Since $\log I_0/I = \alpha cl$,

$$\log \frac{(1 + S/I_0)}{(1 + S/I)} = -\Delta(\alpha cl) \qquad (9)$$

Dividing equation 9 by equation 1 we obtain

$$\frac{\log(1 + S/I_0) - \log(1 + S/I_0 \cdot I_0/I)}{\log I_0/I} = \frac{\Delta(\alpha cl)}{\alpha cl} \qquad (10)$$

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* It is possible that S have a negative value, but such a condition would rarely, if ever, be of any significance, since it means that the absorption coefficient for the region isolated would be less than the average absorption coefficient for all wave lengths.

Values of $\Delta(\alpha cl)/\alpha cl$ calculated for given values of S/I_0, the effective scattered fraction, from equation 10 are plotted against

$$\log \frac{I_0(1 + S/I_0)}{I(1 + S/I)}^*$$

in figure 18. It is to be emphasized that this curve applies to a case for which Beer's law is valid if *c*, the concentration, is varied. If *c* is kept constant the $\log I_0'/I'$ is varied by changing the length of the cell.

The following procedure is suggested for determining the fractional effective scattered radiation for any given wave length and absorbing substance. As a reference standard to be used for the purposes of comparing monochromators and judging the accuracy of experimental data, we suggest the use of potassium chromate dissolved in a 0.05 *N* solution of potassium hydroxide and wave lengths 2725 and 3700 A. U. The chromate solution is made up to such a concentration that the value of $\log I_0'/I'$ is equal to about 0.3 for a cell of 1 cm. length. With this same concentration of solution the values of $\log I_0'/I'$ are determined for cells having as widely different lengths as is convenient. To prevent the error of measurement becoming too large the maximum and minimum values of $\log I_0'/I'$ should be determined from the error curve given in the previous section. The larger values of $\log I_0'/I'$ should be weighted accordingly. From this data a curve such as that illustrated by figure 19 can be constructed. The value of $\Delta(\alpha c)$ for any value of $\log I_0'/I'$ is the difference between the dotted line and the solid curve. $\Delta\alpha cl/\alpha cl$ may thus be determined and from the rate of change of $\Delta(\alpha cl)$ with change in $\log I_0'/I'$ the value of S/I_0 can easily be determined by interpolation in figure 18.

In discussing accuracy of measurement we suggest that experimenters use this standard of scattered radiation. Instrument makers might also well use such a standard in describing their monochromators. For the quartz–rock salt and hydrogen arc system used by us the value of S/I_0 was 0.011, 0.005, and 0.004 for the wave lengths 2200, 2725, and 3700 A. U., respectively (potassium chromate solution). With glass optics and Mazda lamp the value of S/I_0 at 4047 A. U. is 0.004.

It is obvious that in most cases the working range is not determined by the curves in figure 17 but rather by a consideration of both these curves and the curves for the error introduced by scattered radiation. To keep within an accuracy of 1 per cent in determining an absorption coefficient ($S/I_0 = 0.004$) we confine the values of $\log I_0/I$ within 0.2 to 0.6. The

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* $\log \frac{I_0(1 + S/I_0)}{I(1 + S/I)}$ is the same as $\log I'_0/I'$, where I'_0 and I' are the experimentally observed intensities transmitted by solvent and solution, respectively.

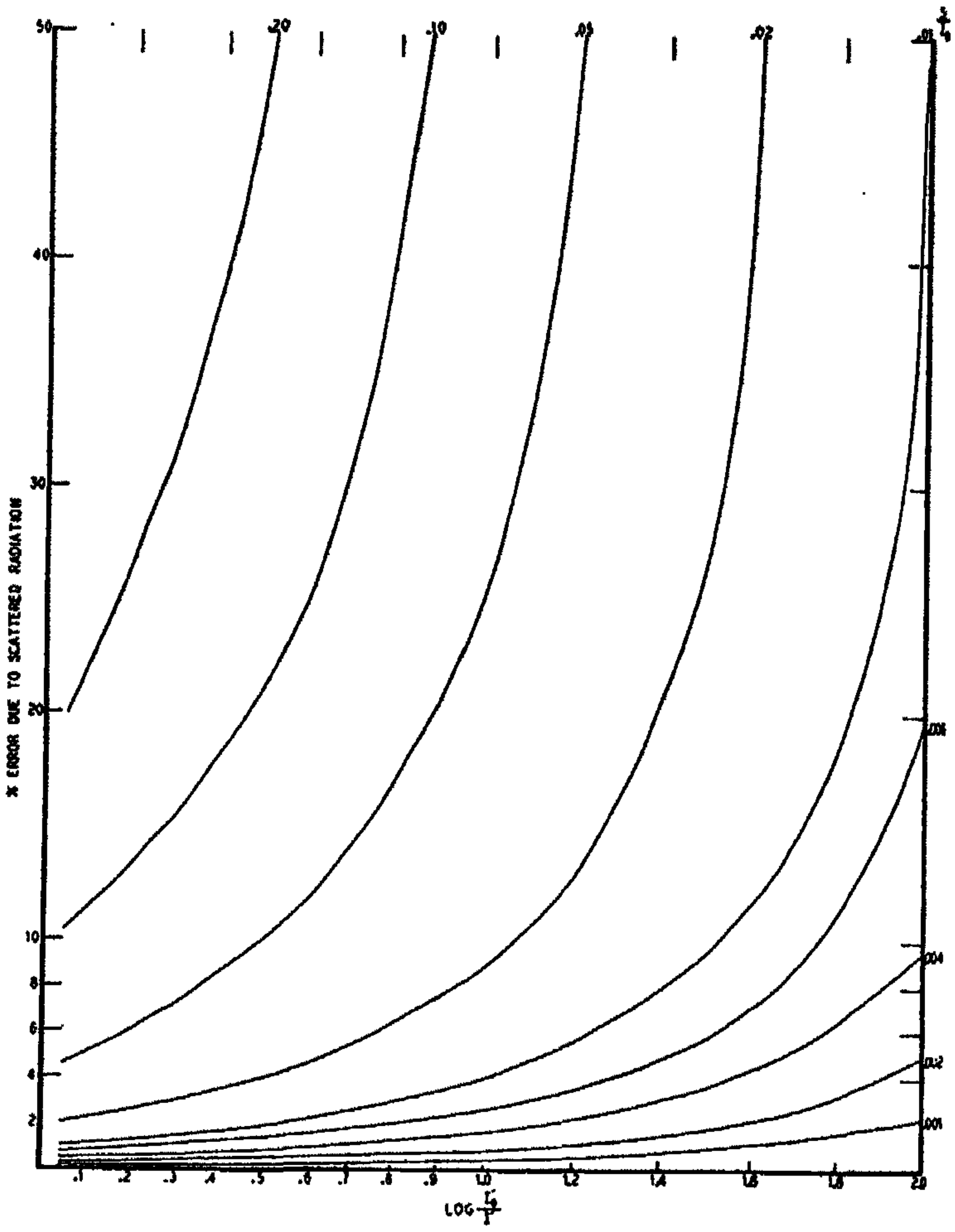

Fig. 18. Error curves for scattered radiation

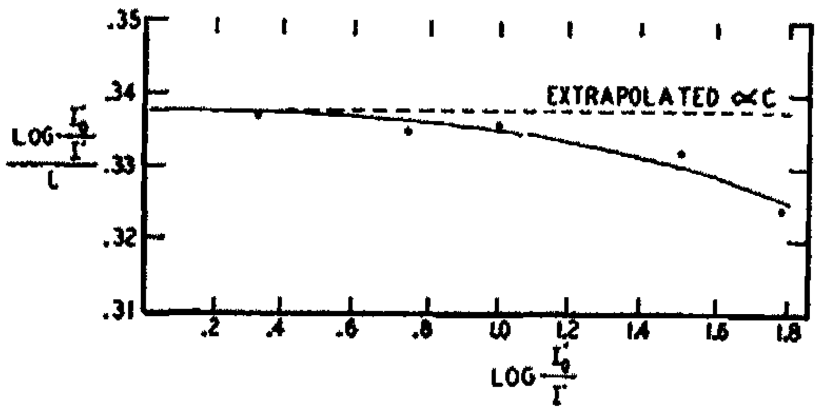

Fig. 19. Determination of effective scattered radiation with potassium chromate solution. 2725 A. U.; concentration constant

error due to scattered radiation unless corrected can, under some circumstances, become very large. If, for example, the amount of effective scattered light is 1 per cent and the value of log I_0/I is 1.6 (as might be the case in determining a maximum if proper dilution were not made) the error in determining the absorption coefficient would be 12 per cent.[3] If, however, the apparatus is used for analysis this error would be greatly diminished, inasmuch as the values of log I_0/I are relative and the error in each determination would in most part be cancelled by the error made with the standard.

It is also apparent that the ideal instrument for making absorption spectra measurements is a fast double monochromator such as the large Müller Hilger. Unfortunately, no definite scattered radiation data are given for any of the monochromators on the market.

Correction for reflection

The reflection at the surfaces between the windows of the cells and the solution is a function of the refractive index of the solution or solvent. If the refractive index of the solution were appreciably different from that of the solvent, it would be necessary to employ a procedure somewhat similar to that used in infra-red work. For the very dilute solutions used in the visible and ultra-violet spectral regions, the refractive indexes of the solution and solvent do not differ sufficiently to make any appreciable error from this source. This conclusion has been verified experimentally.

Solvents

For ultra-violet spectrophotometry below 2800 A. U., choice of proper solvents is very important. It is necessary that these solvents be highly purified. Figure 20 presents the ultra-violet transmission spectra of a number of the more common organic solvents (in most cases not purified) compared with that of distilled water. Of this group, isoöctane (2,2,4-trimethylpentane) and ethyl alcohol are best suited for use at the lower wave lengths. The 95 per cent ethyl alcohol is purified by redistillation of alkaline U. S. Industrial commercial 190 proof alcohol over a 4½-foot, 17-ball, Snyder fractionating column. Absolute ethyl alcohol is distilled in the same way after standing three days over calcium oxide (lime). Highly transmissive isoöctane is distilled over solid sodium hydroxide from Röhm and Haas' best grade of isoöctane tested by the Bureau of Standards, and has given better results than other purified hydrocarbons available on the market. Although hexane is often used by other investigators, we have found that all the commercial samples we have tested have required an undue amount of purification.

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[3] The anomalous results of Keve pertaining to Lambert's law (Biochem. Z. **224**, 347 (1930)) can be accounted for by an undue amount of scattered radiation.

Each fraction of a distilled lot of solvent should be tested for transmission at 2200 A. U. The first and last fractions are usually low in comparison with the middle one, and are therefore discarded or redistilled. Different samples of good solvent are mixed in a large bottle, and provide the stock solvent for a series of absorption spectrum measurements. In this way the solvent cell for determination of I_0 always contains the same solvent from which the solution was made. Serious disagreements will arise if this precaution is not strictly followed.

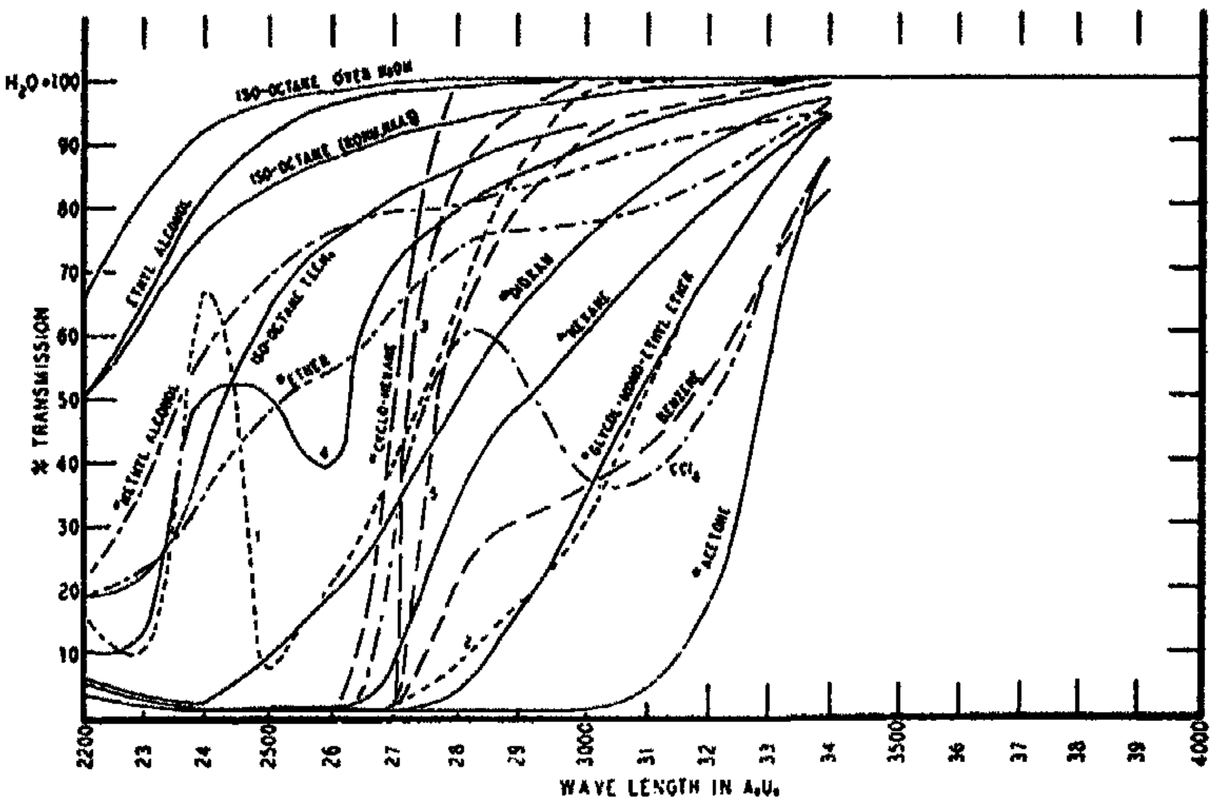

Fig. 20. Absorption spectra of common solvents. * indicates solvent not especially purified. △, student preparation. 1, isoöctane (Röhm and Haas) treated with fuming sulfuric acid; 2, *ethylene chloride; 3, heptane (Eastman), b.p. 80–95°C.; 4, *ligroin, b.p. 30–35°C.; 5, △ heptane, b.p. 93–99°C.

Comparison of absorption coefficients

Before an accurate comparison can be made between the absolute values of α obtained by photoelectric methods, the errors and experimental conditions of measurement must be known. These are determined by a comprehensive calibration of the entire apparatus as outlined above. The most important factors are the spectral region isolated by the monochromator and the effective scattered fraction, S/I_0. Experimentalists often state the dispersion, with no mention of slit width employed, and lack of this data prohibits strict comparison of their spectra with others obtained by the same general method.

The spectral region isolated must often be the same in two cases before differences in measuring systems and sensitivities may be dismissed and before other problems of chemical purity, source, constitution, etc., of the samples can be considered. This is strikingly shown by table 7, which gives data obtained on benzene with various slit widths.

For these determinations at 2540 and 2525 A. U., only the slit widths were varied (slits 1 and 2 always equal). The intensity of the source was varied as needed by means of an iris diaphragm or a small change of voltage on the arc to keep the galvanometer deflections below 100 cm. Slits varied more than twentyfold, and the value for the 2540 A. U. maximum decreased to 35 per cent of its maximum value over this slit range, while the value of the 2525 A. U. minimum increased to 160 per cent of its minimum value. Both maxima and minima approached the same value with increasing slits, demonstrating the decrease of resolution as the slits are widened. The maximum α changes more rapidly than the minimum α, as expected by the shape of the absorption curve. We consider the 2540 A. U. maximum α given in the spectrum of benzene is the true value, because it remains unchanged with slits increasing up to 0.09 mm., a width greater than was used for the determination.

TABLE 7

Decrease of dispersion with increase of slit width

SLIT	SPECTRAL REGION ISOLATED	MOLECULAR α	
		0.0064 *M* solution of benzene in isoöctane; 1-cm. cell; wave length minimum = 2525 A.U.	0.0016 *M* solution of benzene in isoöctane; 1-cm. cell; wave length maximum = 2540 A.U.
mm.	*A.U.*		
0.07	5.6	45.3	212
0.09	7.2	45.1	212
0.11	8.8	45.3	204
0.13	10.4	45.2	202
0.16	12.8	45.2	199
0.20	16.0	45.5	190
0.30	24.0	47.0	170
0.40	32	50.8	154
0.50	40	52.0	136
0.70	56	57.2	118
1.00	80	62.5	104
1.50	120	69.0	89
2.0	160	72.2	77

It is apparent from this great variation of α with slit width that investigators using the photoelectric method of spectrophotometry for a study of the same compound might obtain very different results if they used spectral regions of different widths, as determined by the use of different slit widths in millimeters with the same instrument, or with instruments of different dispersion and the same slit widths. Benzene is admittedly an extreme case, owing to the great sharpness of its principal bands, but with the increasing use of this method for the study of more complex spectra, it seems desirable to emphasize the necessity for publication of more complete instrumental data with spectra reported. In several cases of agreement in the literature, it has been fortunate that the spectra reported contained comparatively broad bands, tending to minimize any discrepancies due to differences of slit widths or dispersion.

It is suggested to the investigators in this field that each quantitative absorption curve obtained by the photoelectric method be accompanied by data such as given in tables 4 and 5, which include the spectral region isolated, cell length, concentration, and estimates of errors of maxima and minima in both wave length and α, as a minimum of experimental information. Only then can accurate comparison be made and many misunderstandings avoided.

The use of narrow slits is especially important for analytical purposes, because greater resolution permits better definition of bands and easier detection of differences. Since variation of the radiation intensity with wave length is different with different sources and operating conditions, the use of narrow slits makes determinations more reproducible.

APPLICATION

The apparatus we have just described is being used for the spectroscopic study of biologically potent substances, both for identification and analytical purposes. Since most substances absorb light only in the ultra-violet, the working wave length limits are 2200 and 4000 A.U., and since many substances may have absorption bands in the same region of the spectrum, it is imperative that the absolute value of α be determined with a high degree of accuracy to be able to distinguish one substance from another.

From the data already available there is evidence that substances which have similar structures show similar absorption bands. Androstenedione and cholestenone, for example, have like structures (like conjugation) in the 3, 4, and 5 carbon atoms, and these two have the same value of α within the limits of experimental error for all wave lengths, in spite of the appreciable difference in molecular weight. Also, the cresols and theelin, which have similar structures in their conjugated systems, have strikingly similar absorption spectra. Spectroscopic data may very probably be of great significance in determining chemical structure (3).

The usefulness of this assembly will probably be greatest when it is used as an analytical instrument. We have already successfully determined the equilibrium between ferriheme hydroxide and the cyanide ion by this method (to appear in an early publication). Studies of equilibria involving the hemochromogens are to be made in the near future. Solutions of solutes having molecular absorption coefficients of 10,000 or greater can be analyzed when the concentrations of the solutes are as low as $10^{-6}M$.

The question as to the advisability of constructing an automatic recording instrument has naturally been given consideration. For preliminary surveys of spectra such an apparatus would no doubt have advantages, but when one considers the complicating factors which might decrease the accuracy and that in analytical work only one wave length is employed, it becomes very doubtful that the advantages of automatic recording would outweigh the disadvantages. With our present system an analysis of a binary mixture can be made in about one minute. While the calculations involving Beer's law for complete absorption spectra may become tedious, they can be made easily by an untrained worker. We are of the opinion that the construction of an automatic recording apparatus of sufficient accuracy would not be worth the necessary experimentation and expense involved.

Work with the apparatus described in this article is supported by a grant from the Rockefeller Foundation for the Application of Spectroscopic Methods to Biological Problems. We wish to express our gratitude to the Foundation for the support which is making this work possible. We wish also to express our appreciation to Dr. E. S. Miller and Dr. R. H. Munch for assistance in some phases of the work.

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THE SOLUBILITY OF SILVER ACETATE IN MIXED SOLVENTS AND THE INCOMPLETE DISSOCIATION OF TERNARY ELECTROLYTES[1]

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INTRODUCTION

The experimental work described in the present paper is a continuation of studies (7, 8, 9, 10) designed to test the applicability of the theory of Debye and Hückel to solutions of electrolytes in water and in mixed solvents. For this purpose, we determined the solubility of silver acetate in mixtures of water and acetone containing 10, 20, and 30 per cent of acetone. In addition the solubility was determined when these solvents contained various amounts of the nitrates of sodium, potassium, calcium, or strontium.

In previous investigations as well as in the present one, somewhat abnormal results were obtained when the solvent contained calcium or strontium nitrate. We hoped to find out if this abnormal behavior could be accounted for by assuming that the second-stage ionization of calcium acetate or strontium acetate is incomplete.

By studying the variation of certain equilibrium constants with the dielectric constant of the medium, we planned to test Born's (2) electrostatic theory.

For a summary of previous determinations of the solubility of silver acetate in water at 25°C., reference may be made to the paper by MacDougall and Bartsch (8).

EXPERIMENTAL PART

Materials used

The silver acetate, obtained from Mallinckrodt, was 64.61 per cent silver (theoretical value, 64.64 per cent), and was used without further purification. The potassium and sodium nitrates were of Mallinckrodt's "analytical reagent" grade. They were dried at 150°C. for twenty hours and used without any further treatment. The calcium and strontium nitrates were

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[1] This paper gives the essential portions of the dissertation presented by William D. Larson to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, March, 1936.

recrystallized twice from conductivity water and dried at 175°C. until no further loss in weight was shown. A sample of the calcium nitrate, analyzed by the method of Willard and Furman (11), gave 24.40, 24.31, and 24.26 per cent calcium, as compared with the theoretical value of 24.42 per cent.

The acetone used was a commercial acetone of unknown source. It was purified by the method of Conant and Kirner (3). To check the purity of the acetone, a sample was dried over calcium oxide and fractionated with a 30-in. column packed with 5-mm. lengths of glass tubing having an outside diameter of 6 mm. The fraction that came over between 56.0°C. and 56.1°C. at 746 mm. was used. The density of this acetone at 25°C., determined by means of a Weld precision-type pycnometer, was 0.7844 ± 0.0002. The value given in the International Critical Tables (4) is 0.7844. The acetone was also analyzed by the iodometric method of Messinger (6). Two analyses gave 99.99 and 99.85 per cent acetone.

The water used was conductivity water, prepared by distillation from alkaline permanganate with a block tin condenser.

Experimental procedure

Acetone solutions, prepared by thorough mixing of appropriate amounts of acetone and water, were stored in glass-stoppered bottles, sealed with paraffin. The density of a given mixture at 25°C. was determined with the Weld pycnometer. The composition was calculated by means of the equation (5)

$$d = d_w + Ap + Bp^2 + Cp^3$$

where d is the density of the mixture, p is the per cent by weight of acetone, and $d_w = 0.99707$, $A = -1.171 \times 10^{-3}$, $B = -9.04 \times 10^{-6}$, and $C = -5.6 \times 10^{-9}$.

The nitrate solutions were prepared by weighing out the acetone–water mixture into brown glass-stoppered bottles and adding a previously weighed amount of the nitrate. Buoyancy corrections were applied to all weighings. An excess of silver acetate was then added, and the glass stoppers were heavily coated with paraffin. The bottles were rotated for at least twenty-four hours in a constant-temperature bath at 25.00° ± 0.05°C. Preliminary experiments showed that agitation for fifteen hours was sufficient to insure saturation.

The solutions saturated with silver acetate were sampled and analyzed as follows: With the bottle clamped upright in the bath, the glass stopper was removed and a two-hole rubber stopper carrying a delivery tube was put in its place. The end of the tube was loosely plugged with absorbent cotton. Somewhat more than 100 cc. of the solution (which had a total volume of nearly 200 cc.) was forced by compressed air into a graduated

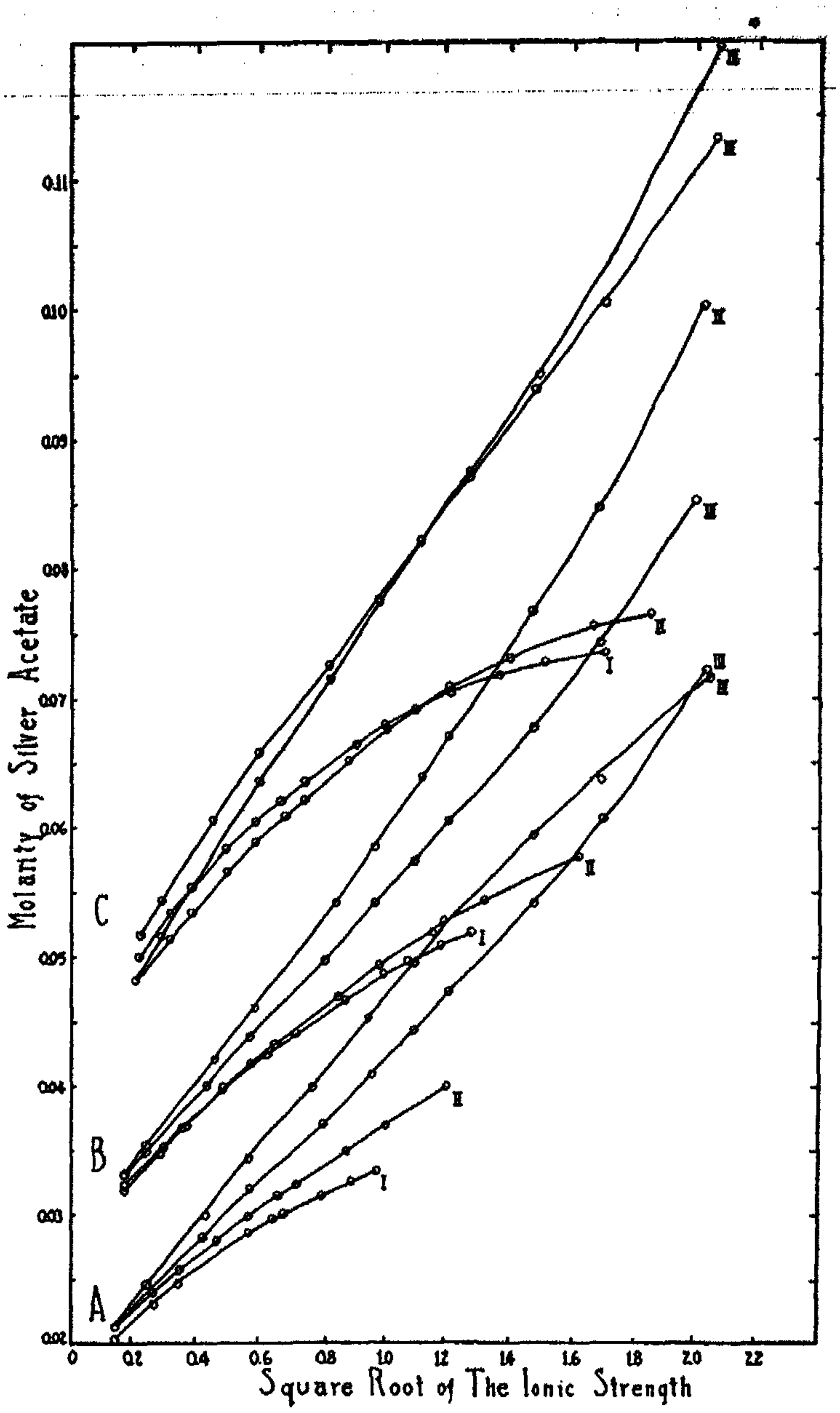

FIG. 1. Solubility of silver acetate in mixed solvents

		Per cent acetone		
		A	*B*	*C*
I.	KNO_3	30.95	18.83	9.81
II.	$NaNO_3$	28.25	20.50	10.35
III.	$Sr(NO_3)_2$	29.23	19.48	9.27
IV.	$Ca(NO_3)_2$	30.02	20.03	10.35

TABLE 1

Solubility at 25°C. of silver acetate in mixtures of acetone and water

PER CENT ACETONE	DENSITY OF SATURATED SOLUTION	C SILVER ACETATE	PER CENT ACETONE	DENSITY OF SATURATED SOLUTION	C SILVER ACETATE
9.27	0.9920	0.05100	20.03	0.9740	0.03217
9.81	0.9910	0.04990	20.50	0.9724	0.03189
10.35	0.9900	0.04815	28.25	0.9592	0.02140
18.83	0.9758	0.03237	29.23	0.9584	0.02134
19.48	0.9748	0.03228	30.02	0.9564	0.02131

TABLE 2

Solubility at 25°C. of silver acetate in mixtures of acetone and water containing sodium nitrate

10.35 PER CENT ACETONE $D = 72.8$; $d = 0.9840$			20.50 PER CENT ACETONE $D = 66.7$; $d = 0.9692$			28.25 PER CENT ACETONE $D = 62.1$; $d = 0.9566$		
m $NaNO_3$	d Satd. soln.	10^3X Ag^+	m $NaNO_3$	d Satd. soln.	10^3X Ag^+	m $NaNO_3$	d Satd. soln.	10^3X Ag^+
0.0	0.9900	0.9494	0.0	0.9724	0.6908	0.0	0.9592	0.5006
0.05228	0.9943	1.014	0.04951	0.9756	0.7569	0.0494	0.9620	0.5625
0.09728	0.9976	1.053	0.1006	0.9792	0.8003	0.1002	0.9648	0.6011
0.2010	1.0028	1.114	0.2097	0.9856	0.8665	0.1999	0.9704	0.6524
0.3052	1.0088	1.159	0.3067	0.9908	0.8993	0.3191	0.9760	0.6970
0.3997	1.0132	1.198	0.4020	0.9956	0.9400	0.4288	0.9820	0.7312
0.5005	1.0184	1.220	0.4371	0.9980	0.9416	0.5229	0.9872	0.7519
0.7434	1.0316	1.277	0.7170	1.0116	1.003	0.7908	1.0004	0.8077
1.0010	1.0448	1.321	0.9818	1.0252	1.050	1.054	1.0132	0.8526
1.521	1.0704	1.381	1.429	1.0460	1.103	1.569	1.0372	0.9215
2.082	1.0940	1.423	1.905	1.0688	1.154	2.089	1.0603	0.9698
3.072	1.1380	1.466	2.936	1.1116	1.216			
3.908	1.1711	1.480						

TABLE 3

Solubility of silver acetate at 25°C. in mixtures of acetone and water containing potassium nitrate

9.81 PER CENT ACETONE $D = 73.1$; $d = 0.9848$			18.83 PER CENT ACETONE $D = 67.7$; $d = 0.9718$			30.95 PER CENT ACETONE $D = 60.4$; $d = 0.9520$		
m KNO_3	d Satd. soln.	10^3X Ag^+	m KNO_3	d Satd. soln.	10^3X Ag^+	m KNO_3	d Satd. soln.	10^3X Ag^+
0.0	0.9910	0.9790	0.0	0.9758	0.6906	0.5125	0.9582	0.5532
0.05986	0.9952	1.048	0.05193	0.9768	0.7587	0.1048	0.9616	0.5892
0.09878	0.9979	1.089	0.1023	0.9800	0.8022	0.2088	0.9672	0.6681
0.2007	1.0051	1.147	0.2055	0.9872	0.8544	0.3159	0.9744	0.6720
0.3001	1.0108	1.186	0.2898	0.9926	0.8871	0.4110	0.9804	0.7109
0.4002	1.0162	1.218	0.3773	0.9980	0.9135	0.4599	0.9824	0.7245
0.5001	1.0223	1.249	0.4948	1.0044	0.9433	0.6395	0.9928	0.7495
0.7913	1.0398	1.308	0.7453	1.0190	0.9934	0.8133	1.002	0.7806
1.000	1.0512	1.332	1.028	1.0340	1.038	0.9671	1.010	0.8058
1.250	1.0641	1.360	1.230	1.0432	1.063			
1.500	1.0767	1.382	1.522	1.0592	1.097			
2.000	1.1021	1.419	1.772	1.0722	1.107			
2.500	1.1267	1.435						

cylinder supported in the bath. Four 25-cc. samples were withdrawn with an accurately calibrated pipet and transferred to weighing bottles. After they had been weighed, the samples were washed into Erlenmeyer flasks and analyzed for silver by means of a potassium thiocyanate solution with ferric nitrate as indicator. The thiocyanate solution was standardized against pure silver acetate.

TABLE 4

Solubility of silver acetate at 25°C. in mixtures of acetone and water containing calcium nitrate

10.35 PER CENT ACETONE $D = 72.8$; $d = 0.9840$			20.03 PER CENT ACETONE $D = 67.0$; $d = 0.9700$			30.02 PER CENT ACETONE $D = 61.0$; $d = 0.9630$		
m $Ca(NO_3)_2$	d Satd. soln.	10^3X Ag^+	m $Ca(NO_3)_2$	d Satd. soln.	10^3X Ag^+	m $Ca(NO_3)_2$	d Satd. soln.	10^3X Ag^+
0.0	0.9900	0.9494	0.0	0.9740	0.6934	0.0	0.9564	0.5076
0.01227	0.9928	1.0159	0.009057	0.9752	0.7633	0.01262	0.9584	0.5854
0.06436	0.9972	1.1349	0.06103	0.9808	0.9057	0.05617	0.9636	0.7126
0.1049	1.0044	1.2516	0.1068	0.9860	0.9927	0.1073	0.9696	0.8138
0.2052	1.0172	1.4026	0.2283	1.0004	1.1656	0.2009	0.9804	0.9529
0.3090	1.0288	1.523	0.3120	1.0100	1.259	0.3048	0.9923	1.064
0.4133	1.0400	1.613	0.4303	1.0232	1.373	0.4224	1.0052	1.173
0.5102	1.0508	1.698	0.5051	1.0312	1.439	0.5033	1.0136	1.247
0.7552	1.0776	1.862	0.7560	1.0580	1.643	0.7862	1.0432	1.348
1.014	1.1036	2.069	0.9865	1.1074	1.761	1.046	1.0680	1.471
1.542	1.1556	2.307	1.494	1.1292	2.168	1.578	1.1192	1.630
2.057	1.2015	2.687	1.874	1.1655	2.453	2.093	1.1632	1.974

TABLE 5

Solubility of silver acetate at 25°C. in mixtures of acetone and water containing strontium nitrate

9.27 PER CENT ACETONE $D = 73.4$; $d = 0.9854$			19.48 PER CENT ACETONE $D = 67.3$; $d = 0.9708$			29.23 PER CENT ACETONE $D = 61.5$; $d = 0.9550$		
m $Sr(NO_3)_2$	d Satd. soln.	10^3X Ag^+	m $Sr(NO_3)_2$	d Satd. soln.	10^3X Ag^+	m $Sr(NO_3)_2$	d Satd. soln.	10^3X Ag^+
0.0	0.9920	1.0076	0.0	0.9748	0.6920	0.0	0.9584	0.5038
0.01100	0.9936	1.0638	0.01078	0.9768	0.7484	0.00987	0.9604	0.5579
0.05130	1.0012	1.1845	0.05149	0.9840	0.8591	0.05223	0.9672	0.6705
0.1019	1.0096	1.315	0.09963	0.9915	0.9396	0.1044	0.9760	0.7596
0.2051	1.0272	1.421	0.2051	1.0092	1.064	0.2099	0.9924	0.9749
0.3055	1.0432	1.517	0.3084	1.0252	1.163	0.3134	1.0084	0.9619
0.4060	1.0592	1.592	0.4122	1.0420	1.222	0.4183	1.0282	1.059
0.5061	1.0732	1.661	0.5096	1.0564	1.268	0.5222	1.0391	1.108
0.7608	1.1131	1.819	0.7727	1.0967	1.438	0.7852	1.0763	1.263
1.019	1.1491	1.965	1.031	1.1323	1.573	1.052	1.1131	1.412
1.520	1.2170	2.200	1.545	1.1982	1.804	1.566	1.1795	1.672
2.045	1.2830	2.395						

The experimental data are given in tables 1 to 5 and are also represented graphically in figure 1. In this paper, m is the molality (moles per 1000 grams of solvent), C is the molarity (moles per liter of solution), and X is the mole fraction. The mole fraction of any constituent is calculated on the assumption that all salts present are completely ionized.

It is readily seen from figure 1 that for a solution of a given ionic strength the effect of a nitrate in increasing the solubility of silver acetate is given in general by the order $KNO_3 < NaNO_3 < Sr(NO_3)_2 < Ca(NO_3)_2$.

THEORETICAL PART

Theory of Debye and Hückel

According to the theory of Debye and Hückel, the mole-fraction activity coefficient f of a univalent ion (or of a uni-univalent salt) at 25°C. is given by the equations

$$\log_{10} f = \log_{10} x_0 - \log_{10} x = -\frac{BS^{1/2}}{1 + AS^{1/2}} \tag{1}$$

$$B = \frac{352.61}{D^{3/2}} \tag{2}$$

$$A = \frac{2.914 \times 10^8}{D^{1/2}} a \tag{3}$$

where D is the dielectric constant of the solvent, a is a suitable mean ionic diameter, and S is the ionic strength of the saturated solution. In equation 1, as applied to our data, X is the mole fraction of silver ion in a given saturated solution and X_0 is the extrapolated value of X for an ionic strength equal to zero; in other words, we may call X_0 the activity of silver ion (or rather the mean activity of silver ion and acetate ion) in any solution saturated with silver acetate. The dielectric constant D of an acetone–water mixture was calculated by linear interpolation from the values given by Åkerlöf (1).

Values of A and X_0 were obtained for each series of solutions by substituting in equation 1 the observed values of X and $S^{1/2}$ for two solutions, one of which was always the solution that contained no added nitrate (in one series, the solution that contained the smallest amount of potassium nitrate). From the two simultaneous equations so obtained, a value of A and a value of X_0 were calculated. We give in table 6 the results of our calculations for 9.81 per cent acetone solutions containing various amounts of potassium nitrate.

Results similar to those given in table 6 were obtained for the other solutions containing potassium nitrate and for the solutions containing sodium nitrate. For solvents containing strontium nitrate or calcium nitrate, the calculated values of A showed much greater variations. A summary of the calculations is given in table 7. The solvents are described as 10, 20, and 30 per cent acetone; the exact composition is given in following tables.

TABLE 6

Silver acetate in 9.81 per cent acetone containing potassium nitrate

m KNO_3	$s^{\frac{1}{2}}$	A	m KNO_3	$s^{\frac{1}{2}}$	A
0.0	0.2234		0.7913	0.9102	1.455
0.04986	0.3200	1.321	1.000	1.006	1.478
0.09878	0.3901	1.404	1.250	1.112	1.476
0.2007	0.5043	1.461	1.500	1.207	1.480
0.3001	0.5933	1.486	2.000	1.373	1.476
0.4002	0.6700	1.484	2.500	1.516	1.507
0.5001	0.7384	1.454			

Average $A = 1.472$; $X_0 = 0.7809 \times 10^{-3}$

TABLE 7

Summary of values of A and of the ionic diameter, a

PER CENT ACETONE	A KNO_3	A $NaNO_3$	A $Sr(NO_3)_2$	A $Ca(NO_3)_2$	a IN A.U. KNO_3	a IN A.U. $NaNO_3$
0	1.43	1.21			4.35	3.69
10	1.46	1.45	1.3 to 1.8	1.2 to 1.6	4.28	4.26
20	1.39	1.35	1.1 to 1.7	1.2 to 1.8	3.93	3.77
30	1.41	1.33	1.0 to 1.7	1.0 to 1.7	3.76	3.59

TABLE 8

Saturated solutions of silver acetate in various solvents

SOLVENT	D	10^3X	10^3X_0	f	C_0	10^7K_x	10^3K_c
Water	78.5	1.200	0.960	0.800	0.0531	9.22	2.823
10 per cent acetone	73.0	0.969	0.779	0.804	0.0397	6.07	1.577
20 per cent acetone	67.0	0.693	0.558	0.805	0.0259	3.11	0.671
30 per cent acetone	61.0	0.504	0.402	0.798	0.0169	1.62	0.285

The data for aqueous solutions containing no acetone are taken from the papers by MacDougall (7) and MacDougall and Rehner (10).

Table 8 gives data referring to saturated solutions of silver acetate in water and several mixed solvents. C_0 is the mean activity of silver and acetate ions when the activity of a constituent is set equal to its molar concentration in a solution of zero ionic strength. The activity products for silver acetate, K_s and K_c, are defined by the equations

$$K_s = X_0^2 \tag{4}$$

$$K_c = C_0^2 \tag{5}$$

From the data presented we can conclude that:

(1) The solubility of silver acetate in a given acetone–water mixture increases with the ionic strength.

(2) The equation of Debye and Hückel is valid up to relatively high ionic strengths when sodium nitrate or potassium nitrate is the added salt.

(3) The solubility of silver acetate in the presence of calcium nitrate or of strontium nitrate is considerably greater than in solutions of the same nominal ionic strength which contain sodium nitrate or potassium nitrate.

Ionization of ternary electrolytes

To account for the observed data the authors suggest the hypothesis of incomplete ionization of whatever ternary salts may be present or may be formed in the solutions investigated. In the present case, such ternary electrolytes would be not only calcium nitrate or strontium nitrate but also calcium acetate or strontium acetate. To simplify the treatment it is assumed that the first stage of ionization, as represented by the equation

$$\mathrm{Ca(OAc)_2} \rightleftharpoons \mathrm{CaOAc^+} + \mathrm{OAc^-}$$

is virtually complete and that the second stage

$$\mathrm{CaOAc^+} \rightleftharpoons \mathrm{Ca^{++}} + \mathrm{OAc^-}$$

is, in general, incomplete.

The assumption that only the added ternary salt, calcium nitrate or strontium nitrate, is incompletely ionized will not account for the observed fact that in solutions of the same nominal ionic strength the solubility of silver acetate is greater in the presence of calcium nitrate or of strontium nitrate than in the presence of sodium nitrate or of potassium nitrate. In fact, the reverse effect should be observed, since the actual ionic strength of a calcium nitrate solution would be less than the nominal value (calculated on the basis of complete ionization). On the other hand, since the solutions considered contain calcium (or strontium) ions and acetate ions, we must consider the possibility of the formation of $\mathrm{CaOAc^+}$ (or $\mathrm{SrOAc^+}$) as well as of $\mathrm{Ca(OAc)_2}$ (or $\mathrm{Sr(OAc)_2}$). The formation of an appreciable amount of the intermediate ion, $\mathrm{CaOAc^+}$ or $\mathrm{SrOAc^+}$, would obviously result in an increased solubility of silver acetate.

We shall simplify our calculations by supposing that for our present purpose we may assume calcium nitrate and strontium nitrate to be completely ionized.

For any solution saturated with silver acetate and containing calcium nitrate, we may write

$$K_e = a_{Ag^+} \times a_{OAc^-} \tag{6}$$

$$K_1 = \frac{a_{Ca^{++}} \times a_{OAc^-}}{a_{CaOAc^+}} \tag{7}$$

Values of K_e are given in table 8. K_1 is the ionization constant of $CaOAc^+$.

The method followed in calculating K_1 for solutions containing either calcium nitrate or strontium nitrate as added salt may now be briefly outlined. In solutions in which the added salt is sodium nitrate, we suppose that the silver acetate is completely ionized and that $C_{Ag^+} = C_{OAc^-}$. Knowing the value of K_e (equation 6), we readily calculate the mean activity coefficients of Ag^+ and OAc^- in solutions of sodium nitrate. We assume further that in a given solution all univalent ions have practically equal activity coefficients, and that the activity coefficient of a divalent ion is equal to the fourth power of the activity coefficient of a univalent ion. We also assume that in a solution containing calcium nitrate the activity coefficient of an ion is practically the same as in a solution of the same ionic strength in which the added salt is sodium nitrate.

The value of C_{Ag^+} in a given calcium nitrate solution is known by experiment. Comparing this solution with a sodium nitrate solution of the same nominal ionic strength, we find the activity coefficient of univalent ions in the calcium nitrate solution and hence from equation 6, the value of C_{OAc^-}. Now according to our hypothesis

$$C_{CaOAc^+} = C_{Ag^+} - C_{OAc^-}$$

The value of C_{CaOAc^+} so obtained is used to make a more accurate estimate of the actual concentration of Ca^{++} and therefore of the actual ionic strength. From this corrected value of the ionic strength, a new comparison is made with a sodium nitrate solution of equal ionic strength and a new set of values of C_{OAc^-}, C_{CaOAc^+}, and $C_{Ca^{++}}$ is obtained. Proceeding in this way, we are finally able to calculate the value of K_1 of equation 7. It should be pointed out that the activity coefficients used in these calculations are molarity activity coefficients, γ_c, obtained readily from the values of the mole-fraction activity coefficients, f. To illustrate our results, we give in table 9 the values of K_1 obtained for $CaOAc^+$ in 10.35 per cent acetone. The first column gives the square root of the ionic strength of the equivalent sodium nitrate solution; the second column gives the corresponding molarity activity coefficient, γ_1, of univalent ions. It will be seen that the values of K_1 given in the last column of table 9 agree remarkably well when one considers the simplifying assumptions made to facilitate their calculation.

In table 10, we summarize the values of K_1 for $CaOAc^+$ and $SrOAc^+$ obtained by the application of our method to the solubility data for water and various acetone–water mixtures. We include also the activity product, K_x, for silver acetate in water and in various acetone–water and alcohol–water mixtures.

TABLE 9

Ionization constant, K_1, of $CaOAc^+$ from solubility of silver acetate in 10.35 per cent acetone in the presence of calcium nitrate

g½ $NaNO_3$	γ_1	c_{CaOAc^+}	$c_{Ca^{++}}$	c_{OAc^-}	K_1
0.3	0.770	0.00223	0.01079	0.04946	0.0841
0.6	0.662	0.01003	0.0914	0.05405	0.0934
0.7	0.635	0.01072	0.1339	0.05622	0.1142
0.8	0.618	0.01458	0.1763	0.05624	0.0992
0.9	0.600	0.01723	0.2304	0.05718	0.0991
1.0	0.582	0.02031	0.2876	0.05761	0.0936
1.2	0.544	0.02236	0.4304	0.06264	0.1056
1.5	0.533	0.03818	0.6804	0.05707	0.0821
1.7	0.522	0.05055	0.8707	0.05445	0.0703

TABLE 10

Ionization constants of $CaOAc^+$ and $SrOAc^+$ and activity product, $K_x = a_{Ag^+} \times a_{OAc^-}$, in various solvents

SOLVENT	$SrOAc^+$		$CaOAc^+$		$a_{Ag^+} \times a_{OAc^-}$ 10^4K_x	SOLVENT	$a_{Ag^+} \times a_{OAc^-}$ 10^4K_x
	K_c	10^3K_x	K_c	10^3K_x			
Water.......	0.34	6.1	0.15	2.7	9.22	Water.......	9.22
10% acetone.	0.12	2.3	0.094	1.8	6.07	10% alcohol.	5.78
20% acetone.	0.087	1.9	0.058	1.2	3.11	20% alcohol..	3.55
30% acetone.	0.037	0.88	0.019	0.44	1.62	30% alcohol..	2.17

Dielectric constant of solvent and equilibrium constant

For a process in a solution of sufficiently low ionic strength, we have the relation

$$\Delta F = -RT \log_e K_x + RT\Sigma\nu_i \log_e x_i \qquad (8)$$

If, for a given solvent, the ionic strength is not low, the mole fraction, X_i, in equation 8 must be replaced by f_iX_i, where f_i is an activity coefficient;

the value of K_x remains, however, essentially unchanged. In passing from one solvent to another, there will be a change in K_x. The magnitude of this change in K_x can be determined if we can calculate the difference between the free energies of an ion in two solvents when the ionic strength is low and when the mole fraction of the ion is the same in both solvents. If we adopt the simple hypothesis that a given ion of charge $z_i\epsilon$, where ϵ is the unit charge and z_i is the valence, remains essentially identical in the various solvents considered and hence is characterized by the same effective radius r_i, this difference in free energy in two media of dielectric constants D_1 and D_2 will be given by the Born equation

$$F_2 - F_1 \text{ (for a given ion)} = \frac{1}{2}\frac{\epsilon^2 z_i^2}{r_i}\left(\frac{1}{D_2} - \frac{1}{D_1}\right) \tag{9}$$

For a given process involving ions in the two media, we find from equations 9 and 8

$$\begin{aligned}\Delta F_2 - \Delta F_1 &= -RT\log_e (K_x)_2 + RT\log_e (K_x)_1 \\ &= \tfrac{1}{2}N\epsilon^2\left(\frac{1}{D_2} - \frac{1}{D_1}\right)\sum\frac{\nu_i z_i^2}{r_i}\end{aligned} \tag{10}$$

For our purpose we may write equation 10 in the form

$$\log_e K_x = \text{constant} - \frac{N\epsilon^2}{2DRT}\sum\frac{\nu_i z_i^2}{r_i} \tag{11}$$

In equations 10 and 11, N is Avogadro's number and ν_i is the coefficient of the ion in the chemical equation. Changing to ordinary logarithms and introducing the numerical values of N, ϵ, and R, we find for 25°C.

$$\log_{10} K_x = \text{constant} - \frac{121.0}{D}\sum\frac{\nu_i z_i^2}{r_i} \tag{12}$$

The radius, r_i, is to be expressed in Ångström units.

We therefore see that the simple theory of Born leads to the result that the equilibrium constant in various solvents of a reaction involving ions should be given by an equation of the form

$$\log_{10} K_x = A - \frac{B}{D} \tag{13}$$

The data presented in table 10 offer an opportunity of testing the relation given in equation 12 or 13. Applying the method of least squares, we find that the dependence of the various equilibrium constants on the dielectric constant of the solvent is reproduced satisfactorily by the following equations.

(1) For $SrOAc^+$ in water and acetone–water mixtures:

$$\log_{10} K_s = 0.379 - \frac{210}{D}$$

(2) For $CaOAc^+$ in water and acetone–water mixtures:

$$\log_{10} K_s = 0.165 - \frac{212}{D}$$

(3) For the activity product, $K_x = a_{Ag^+} \times a_{OAc^-}$, in water and acetone–water mixtures:

$$\log_{10} K_x = \bar{4}.6615 - \frac{211}{D}$$

(4) For the activity product, $a_{Ag^+} \times a_{OAc^-}$, in water and ethyl alcohol–water mixtures:

$$\log_{10} K_x = \bar{4}.1511 - \frac{173}{D}$$

From the equations for the ionization constants of $SrOAc^+$ and of $CaOAc^+$, we find on comparing equations 12 and 13

$$B = 210 = 121.0\left[\frac{4}{r_{Sr^{++}}} + \frac{1}{r_{OAc^-}} - \frac{1}{r_{SrOAc^+}}\right]$$

$$B = 212 = 121.0\left[\frac{4}{r_{Ca^{++}}} + \frac{1}{r_{OAc^-}} - \frac{1}{r_{CaOAc^+}}\right]$$

Assuming that the intermediate ions, $SrOAc^+$ and $CaOAc^+$, are approximately equal in size to the acetate ion, we find

$$r_{Sr^{++}} = r_{Ca^{++}} \cong 2.3 \text{ A.U.}$$

Similarly we obtain

$$B = 121.0\left(\frac{1}{r_{Ag^+}} + \frac{1}{r_{OAc^-}}\right) = 211 \text{ in aqueous acetone}$$

$$B = 121.0\left(\frac{1}{r_{Ag^+}} + \frac{1}{r_{OAc^-}}\right) = 173 \text{ in aqueous alcohol}$$

These equations give for an average value of the radii of Ag^+ and OAc^- 1.2 in aqueous acetone and 1.4 in aqueous alcohol. No claim of course is made for the accuracy of these calculated values of ionic radii. The point of importance is that they turn out to be of the right order of magnitude. In our opinion, the results obtained in these calculations confirm our values for the ionization constants of the intermediate ions, SrOAc$^+$ and CaOAc$^+$.

SUMMARY

We have determined the solubility at 25°C. of silver acetate in various acetone–water mixtures and in the presence of various amounts of potassium nitrate, sodium nitrate, strontium nitrate, and calcium nitrate.

The equation of Debye and Hückel can be applied satisfactorily to the solutions containing either sodium nitrate or potassium nitrate as added salt.

The greater solubility of silver acetate in the presence of strontium nitrate or calcium nitrate is assumed to be due chiefly to the incomplete ionization of the acetates of strontium and of calcium.

From the solubility data, we have calculated the ionization constants of the intermediate ions, SrOAc$^+$ and CaOAc$^+$, in water and in aqueous acetone.

The Born theory, which gives a relation between the equilibrium constant and the dielectric constant of the medium, is applied with some success to the data presented in this paper.

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THE DECOMPOSITION OF AIR-FREE WATER BY ALPHA RAYS[1]

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Experiments by O. Risse (6) and more recently by H. Fricke (3) and his coworkers (4) on the irradiation of water by x-rays led to the conclusion that gas-free water is not decomposed and that hydrogen peroxide, a suspected intermediate compound in the reaction, is not produced. The primary effect of x-rays and of alpha rays on most aqueous solutions is generally considered to be similar. Therefore, the accepted conclusion that water is decomposed by alpha rays is opened to question. The investigations of Cameron and Ramsay (1) and of Duane and Scheuer (2) introduced the original conclusion that water is decomposed by alpha rays and that hydrogen peroxide is formed. In these first experiments no particular effort was made to remove dissolved gases. Their results therefore may not be applicable to gas-free water. In 1934 the author (5) reported some experiments in which approximately normal gas yields were observed, though the water was partially if not completely air-free. Since in these experiments the degree of elimination of dissolved gases may not have been sufficient to give weight to either side of the question, some new tests have been made in which the elimination of air from the water has been emphasized. The results which sustain the decomposition of the water are discussed in this paper, while evidence to support the formation of hydrogen peroxide will be described elsewhere.

EXPERIMENTAL METHOD

The water was prepared in an all-Pyrex vacuum still (figure 1). In order to eliminate contamination of the purified water by contact with air and with testing apparatus the reaction chamber was sealed directly to the still. Thus the irradiation and the analysis of evolved gases were completed without admission of air and without transferring the water to auxiliary gas-testing equipment. The 500-cc. reservoir was half filled with triple-distilled water from a tin laboratory still. The system was sealed. While the water in the reservoir was boiled, a Hyvac pump evacuated the system. Condensation in the reaction chamber was prohibited during the

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[1] The experimental work was done in the Laboratory of Biophysics, Minnesota General Hospitals, University of Minnesota.

first few minutes of boiling. Afterwards, when the condenser was cooled, water slowly collected in the bottom bulb of the reaction chamber. This water was stirred continuously by means of a glass bead with an iron core from the beginning of its collection until the irradiation had stopped.

Alpha rays from radon and its decay products were used. By means of a special device described previously (5), the radioactive gas was forced into the reaction chamber by way of the capillary supply tube. Afterwards the supply tube was either sealed or closed with mercury. The effective radon or that which dissolves in the water, as in the case of any slightly soluble gas, depends on the water temperature and on the volume of the water and of the free space above it. The diffusion of radon is regulated by the size of the exposed liquid surface and by the length of the water column between the liquid and gas phases. Stirring of the water also has some influence. In some preliminary experiments in which diffusion rates were measured, it was found that after three days approximately 50 per cent of the equilibrium amount had dissolved. The slow rate of diffusion is contrary to conclusions expressed in the earlier work; however, in the latter the area of the water surface exposed to radon was considerably larger.

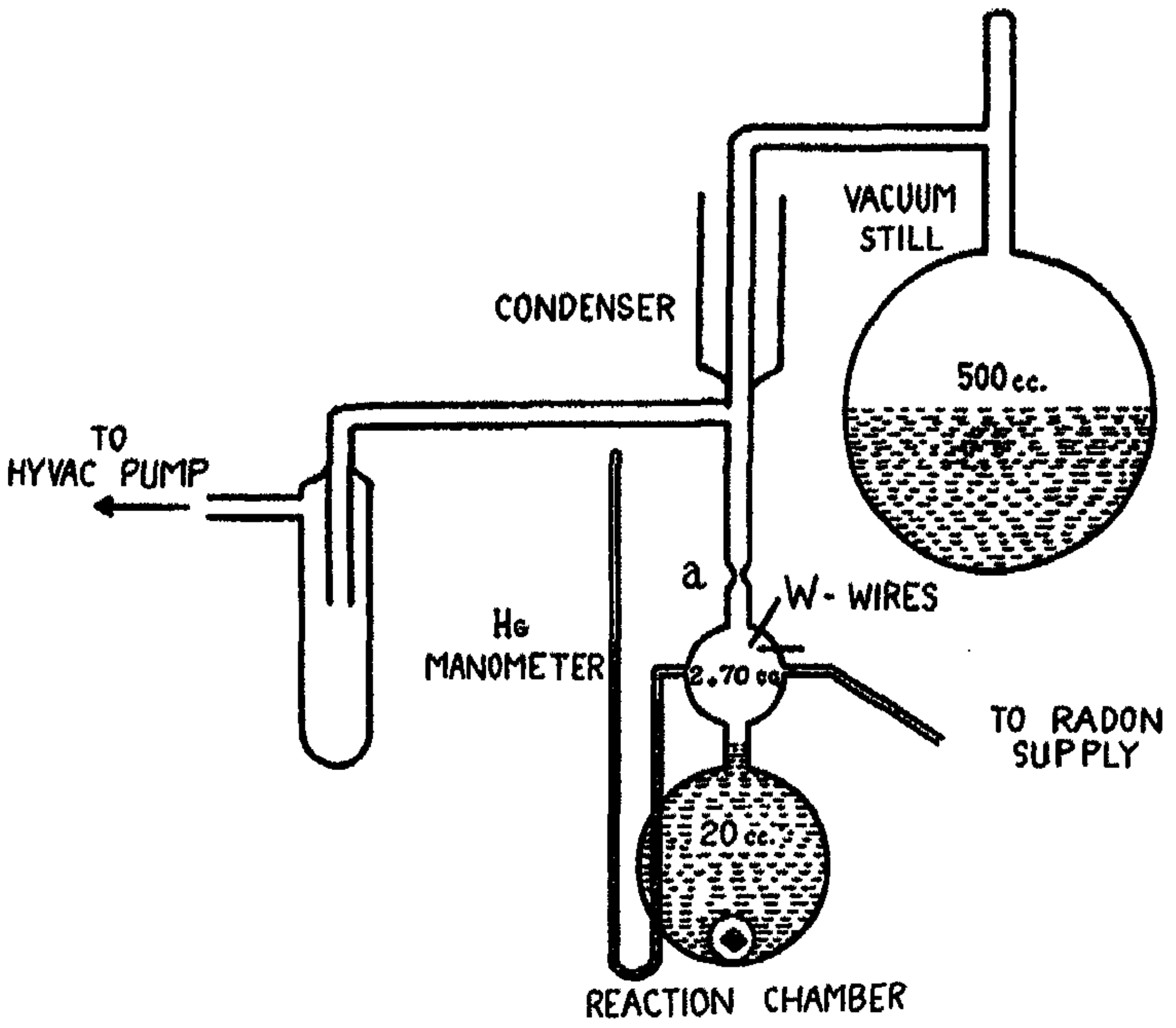

FIG. 1. A vacuum still and reaction chamber for the preparation and irradiation of water by alpha rays

Since gas yields per unit of irradiation intensity are not primarily concerned here, the absolute amount of radon dissolved is not important.

An electric spark between two tungsten wires sealed in the top bulb of the reaction chamber served to explode the gases which collected there. The glass tube above the reaction chamber was sealed at point a previous to the introduction of radon. Gas pressures were measured by means of a mercury manometer having a 2-mm. capillary. Constant temperature was maintained by the immersion of the entire reaction chamber in a water bath. The gases were analyzed quantitatively by means of pressure readings at constant temperature and volume. Qualitative analyses were carried out by exploding the gases with mixtures of either hydrogen or oxygen introduced through the radon supply tube.

TABLE 1

Gas yields from alpha-ray irradiation of air-free water

Initial radon = 76.8 mc.

LENGTH OF EXPERIMENT	WATER TEMPERATURE	WATER VOLUME	GAS VOLUME	GAS PRESSURES	
				Before explosions	After explosions
days	*°C.*	*cc.*	*cc.*	*mm. Hg*	*mm. Hg*
0.0	28.6	20.4	2.70	29.0	29.0
0.21	28.4	20.4	2.70	31.0	31.0
0.92	28.8	20.4	2.70	34.0	34.0
1.42	28.8	20.4	2.70	39.0	39.0
2.17	28.8	20.4	2.70	96.0	60.0
3.34	28.8	20.4	2.70	180.0	82.0

GAS VOLUMES (760 mm. Hg and 0°C.)				
Before explosion	After explosion	O_2 volume	H_2 volume	H_2
cc.	*cc.*	*cc.*	*cc.*	*per cent*
0.011	0.011	0.000	0.011	100
0.022	0.022	0.000	0.022	100
0.058	0.058	0.000	0.058	100
0.221	0.166	0.018	0.202	91.4
0.491	0.177	0.105	0.387	78.8

Total volume of gas produced = 0.644 cc.

RESULTS

The results of a typical experiment are recorded in table 1.

The explosions referred to in the table occurred in the gases produced only by the irradiation and not with mixtures of added hydrogen or oxygen.

Corrections due to water vapor tension are included, but those due to the solubility of the gases in water have been omitted.

The gas pressure, both before and after explosion, increased with the total effective irradiation in all experiments. Therefore the gases cannot be ascribed to organic impurities. The following simple test showed that early in an experiment the gas is all hydrogen, while later it is a mixture of hydrogen and oxygen. When pure hydrogen was added to the first gases evolved and the mixture was exploded, no change in pressure occurred. On the other hand, on the addition of oxygen in the correct proportion, repeated explosions reduced the pressure to its original value at the beginning of the experiment. Reduction of pressure also occurred late in the experiments, either with or without the addition of oxygen.

The lower section of the table contains gas volumes reduced to standard pressure and temperature. The last column gives the percentage of the total gas which is hydrogen. For several hours after the beginning of the experiments, the gas is 100 per cent hydrogen. Later oxygen begins to accumulate, so that the hydrogen percentage is reduced. Hydrogen gas in excess of an electrolytic mixture has been observed before, but in all previous experiments on water the observed excess was not more than 50 per cent. In the earlier experiments dissolved oxygen in the non-degassed water may have reduced the excess hydrogen. The latter is related to the concentration of hydrogen peroxide in the irradiated water, as has been shown in some unpublished work.

DISCUSSION OF RESULTS

The rôle of oxygen in the primary reaction between alpha particles and water molecules is insignificant. There is no apparent mechanism by which oxygen is used and without which the reaction is highly improbable if not impossible. Sensitized reactions are commonly observed in iono- and photo-chemical action. In these a non-reactive substance receives the energy and imparts it to the active substance in a collision of the second kind. The decomposition of water by alpha rays hardly falls into this group of reactions, since no substance is known to absorb alpha rays selectively, and the non-reactive substance, in this case oxygen, is not present in amounts comparable to the active substance, water. If it is generously assumed that a partial pressure of oxygen equal to 1 mm. of mercury still existed after the water had been prepared, then the ratio of water molecules to oxygen molecules would be approximately 10^7. But an alpha particle encounters only about 10^5 molecules in its entire path in air, and, according to Bragg's calculation of their ionization in water, only 0.8 of this number in water before it has lost all power to ionize. Therefore collisions between oxygen molecules and alpha particles, before the latter have lost their power to ionize by collision with water molecules, would be extremely rare.

A simple calculation shows that, if the same original concentration of oxygen is assumed as described in the previous paragraph, each oxygen molecule would be required to dissociate at least one thousand water molecules in order to produce the observed gas yields. From energy considerations this copious dissociation of water by excited oxygen seems highly improbable. Furthermore, oxygen is not needed. The energy of alpha rays is many fold greater than the amount required to dissociate water. If the primary process is activation instead of dissociation, there is still no need of oxygen, for the minimum critical potentials of water and of oxygen are of same order of magnitude.

Calculations on the total gas yields using the assumption that

$$\frac{M_{H_2O}}{N} = 1$$

where M_{H_2O} is the number of water molecules decomposed and N is the number of ion pairs produced, show that the total ionization per cubic centimeter of water was at least 10^3 times greater than the total ionization in Fricke and Brownscombe's experiments with maximum x-ray dosage (150 kiloroentgens). They were able to detect some hydrogen, but were unable to find either oxygen or hydrogen peroxide. They ascribed the hydrogen to some organic impurity. Insufficient x-ray irradiation may possibly account for their failure to find oxygen, since with alpha particles, as was mentioned previously, only hydrogen appeared first and oxygen was not evolved until late in the experiments.

In conclusion, it can be said that air-free water is decomposed by alpha rays and that therefore dissolved oxygen is not necessary to promote the reaction. This conclusion and Fricke and Brownscombe's results on x-ray irradiation of water indicate that the mechanisms of the action of x-rays on water and of alpha rays on water are distinctly different. Before this difference can be definitely accepted many more studies of both reactions must be made.

I wish to express my appreciation of the coöperation of Dr. W. K. Stenstrom of the Division of Biophysics and Cancer Institute, University of Minnesota, Minneapolis.

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THE RATE OF SORPTION OF WATER VAPOR ON SILICA GEL AND IRON-SILICA GEL[1]

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INTRODUCTION

The time necessary for attaining equilibrium in the sorption of water by silica gel, charcoal, etc., has been reported as anywhere from three hours or less (7) up to several months (2). The more rapid sorption rates were found in the absence of permanent gases. Thus the retarding of the diffusion of water vapor by air or other permanent gas present in the apparatus may be sufficient explanation for this enormous difference in rates. However, certain other experiments in the literature indicate that the difference in rates may be due to a more specific effect depending on an interaction of the gas present with the sorbent and even with the sorbate (the substance being sorbed). For example, Burrage (3) found that carbon tetrachloride was taken up almost instantaneously by charcoal, provided that permanent gases (particularly oxygen) were rigidly excluded. Allmand, Burrage, and Chaplin (2) attributed a slow rate of adsorption of various vapors on charcoal to oxygen which probably covers the active centers of the charcoal. Frankenburger and Hodler (5) found, likewise, that minute traces of oxygen hindered the adsorption of hydrogen on tungsten. Furthermore, Patrick and Opdycke (24), using a dynamic sorption method, the vapor being carried in an air stream, found that equilibrium was established rapidly with all vapors studied except water. This last experiment points—at least in the presence of air—to a fundamental difference between the rate of sorption of water and that of other vapors. Since water behaves uniquely, also, with respect to the phenomenon of sorption hysteresis,[2] it is possible that considerable light may be

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[1] A brief summary of the work submitted to the Board of University Studies of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1935.

[2] Sufficient care (removal of impurities and foreign gases) enables one to eliminate hysteresis in the sorption on silica gel of all vapors except water. In only two (references 6 and 13) of the scores of investigations made has hysteresis been reported as eliminated in the case of water on silica gel. Unpublished investigations of one of the authors (4) has always shown hysteresis.

thrown on sorption phenomena in general by a closer examination of the sorption rate (in the presence and in the absence of permanent gases) of water on a sorbent such as silica gel.

The contention that traces of permanent gas have a marked effect on the rate of sorption appears frequently in the literature. The following work was undertaken in order to examine the validity of this contention in the case of the sorption of water vapor by gels.

EXPERIMENTAL

The silica gel used was a commercial sample carefully purified by refluxing with concentrated nitric acid and then washing with distilled water. After first activating the gel by heating in a current of dry air to 300–400°C. for twelve hours, a sample weighing 0.597 g. was placed in the apparatus and evacuated to 10^{-6} mm. at 200–250°C.

The iron–silica gel was prepared according to the method of Klosky and Patrick (8). To 200 cc. of a 1.25 per cent sodium silicate (commercial) solution was added 100 cc. of a 5.2 per cent ferric chloride solution. The silicate solution was stirred mechanically during the addition. The solution gelled nicely in about fifteen minutes; syneresis began within twenty-four hours. The resulting gel was freed from dissolved salts by dialysis and activated. The activation was accomplished by evacuating to 10^{-6} mm. at 150–200°C. The sample weighed 0.716 g.

Distilled water was used. In the experiment carried out in the absence of permanent gases, the pressure of gas in equilibrium with the water was reduced to 10^{-4} mm. The vapor pressure of the water was kept at 4.6 mm. by surrounding the tube containing the water with a bath of ice and water.

The gases used (hydrogen, nitrogen, oxygen, and air) were dried; the first two were freed from oxygen.

A quartz-spiral sorption balance, described by McBain and Bakr (11), was used, and permitted the amount of water sorbed to be determined without withdrawing the sample from the apparatus. The extension of the spiral was read with a cathetometer to an accuracy corresponding to ±0.3 mg. An air thermostat regulated the temperature of the tube containing the spiral and gel to ±0.1°C., the vapor pressure corresponding to this temperature being taken from the International Critical Tables.

A vacuum of 10^{-6} mm. or better could be attained in the apparatus by means of a two-stage mercury-vapor pump backed by an oil pump. However, no attempt was made to exclude mercury vapor.

RESULTS AND DISCUSSION

The first series of measurements (adsorption of water and silica gel, figure 1) shows that the rate of adsorption is independent of the pressure of air present, over the range 4×10^{-4} mm. to 0.5 mm. The pressure of water vapor was 4.6 mm.; the temperature of the gel 25°C. Similar results were obtained with the gel at 23°C. The amount of water adsorbed, *a* (in grams of water sorbed per hundred grams of dry gel), is plotted against the time, *t*, in minutes. *a* is only that water in excess of whatever water is contained in the "dry gel". By "dry gel" we mean the gel in equilibrium with a vacuum of 10^{-6} mm. at 25°C. Under these conditions the gel actually contained about 4.9 per cent water. In order not to confuse the figures, only a few of the points obtained are recorded.[3]

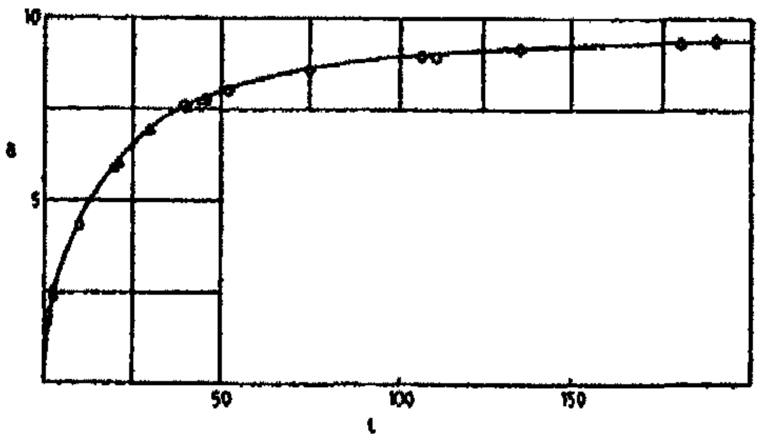

Fig. 1. Adsorption on silica gel in the absence of permanent gases. Ordinate: amount of water adsorbed, *a*, in grams per 100 grams of dry gel. Abscissa: time, *t*, in minutes. Vapor pressure of water, 4.6 mm. Temperature of gel, 25°C. Pressure of air: ⊡, 2.4×10^{-4} mm.; ×, 4×10^{-4} mm.; ⊙, 10^{-2} mm.; △, 2.6×10^{-1} mm.; ◇, 5×10^{-1} mm.

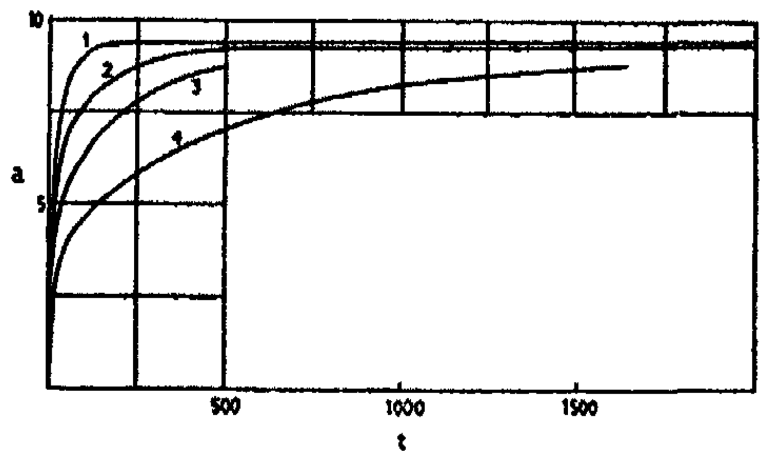

Fig. 2. Adsorption on silica gel in the presence of gases. Ordinate: *a* in grams per 100 grams of gel. Abscissa: time, *t*, in minutes. Vapor pressure of water, 4.6 mm. Temperature of gel, 25°C. Curve 1, copied from figure 1, shows rate of adsorption in absence of gases. Curve 2 shows rate of adsorption in the presence of air, nitrogen, or oxygen at an average pressure of 1 mm. Curve 3 shows rate of adsorption in the presence of hydrogen at 3.9 mm. Curve 4 shows rate of adsorption in the presence of air, nitrogen, or oxygen at 3.6 mm.

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[3] The curve of figure 1 is continuous within the limits of accuracy of the measurements. Slight irregularities could be noticed in the experiments run in the presence of gases (figure 2); however, these are not shown in the figure.

In the second series (also adsorption of water on silica gel) the effect of air, hydrogen, nitrogen, and oxygen at higher pressures is examined. As is shown in figure 2, the rate of adsorption—at 4.6 mm. of water vapor and 25°C.—in gases of similar molecular weight (oxygen, nitrogen, air) is dependent only on the pressure and increases rapidly as the pressure decreases. Further, the rate of adsorption in a gas of low molecular weight, such as hydrogen, is much greater than in a heavier gas at the same pressure. Almost all of the points measured fall, within the experimental limit of error, on the curves given. However, particularly at high values of *t*, some of the points deviated considerably because of the changes of pressure of the permanent gas resulting from the solution of the gas in water. For example, at the start of several experiments the water was gas-free; as the experiments progressed the solution of the gas in the water caused a decrease in the pressure of the gas. These changes amounted in some cases to almost 25 per cent of the total pressure of gas. Experiments (not shown in figure 2) were performed in the presence of hydrogen at 1.1 mm., and oxygen at 3.0 mm. As was to be expected, the former curve lies between curves 1 and 2 (figure 2) and the latter curve between 3 and 4.

We see from figure 1 that the rate of adsorption is independent of the presence of permanent gases when the pressure of the gas is low compared with the pressure of water vapor. From figure 2 we see that at higher pressures the rate depends on both the molecular weight and the pressure of the inert gas. These facts led us to believe that the difficulty of diffusion of the water vapor through the inert atmosphere may alone be sufficient explanation for the behavior of the rate of sorption. In addition, other experiments show that there was no "soaking in effect", i.e., adsorption rates were independent of the length of time the dry gel was allowed to remain in the permanent gas. This, of course, implies that the gas has no specific effect or else the effect is instantaneous. By a specific effect we mean an effect which would slow down the rate of sorption by other means than mere physical hindrance to diffusion of the water vapor. For example, the gas itself might be adsorbed and this might prevent the water from wetting the walls of the gel. The rate of reaching equilibrium would then depend on the rather slow rate of displacement of the adsorbed gas by the water.

The results of series 3—desorption of water from silica gel, figure 3—offer additional evidence in support of the above view. The rate of desorption was measured by connecting the pumps with the tube containing the gel (saturated with water at 4.6 mm.), and measuring the amount of water lost by the gel at definite time intervals. Obviously, gases present in the vapor phase are immediately swept out, and—provided the sorption rate is not dependent on a specific effect—the rate of desorption should be independent of the nature and pressure of the gas present during the previous adsorption. Figure 3 shows this to be, for the most part, the case. However, one interesting exception appears; namely, that the difficulty of

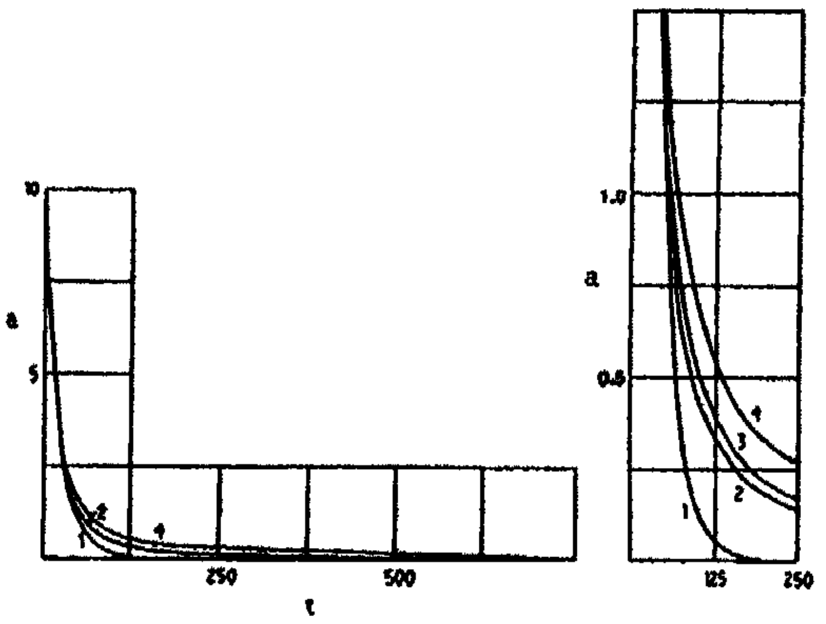

Fig. 3. Desorption from silica gel. Ordinate: a in grams per 100 grams of dry gel. Abscissa: time, t, in minutes. Temperature of gel, 25°C. Desorption followed establishing equilibrium between the gel and water at 4.6 mm. pressure. Curve 1, the pressure of air in the apparatus during the preceding adsorption was 4×10^{-4} mm. Curve 2, the gas present was air, nitrogen, or oxygen at 1 mm. pressure. Curve 3, hydrogen at 3 mm. Curve 4, air, nitrogen, or oxygen at 3.5 mm.

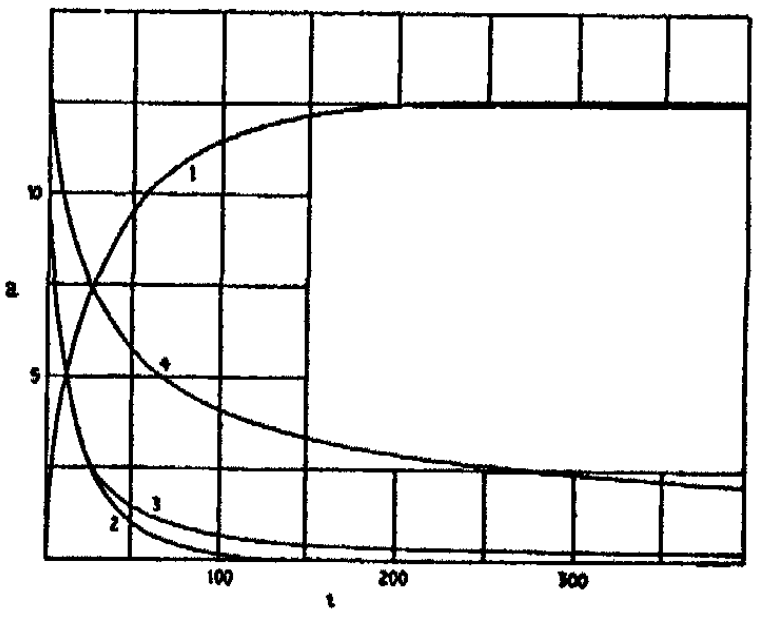

Fig. 4. Adsorption and desorption on iron-silica gel. Ordinate: a in grams per 100 grams of dry gel. Abscissa: time, t, in minutes. Pressure of water vapor, 4.6 mm. Temperature of gel, 25°C. Curve 1, adsorption rate on iron-silica gel in the absence of gases (pressure of gas = 2×10^{-4} mm.). Curve 4, desorption following adsorption in curve 1. Curves 2 and 3 are copied from curves 1 and 4, respectively, of figure 3.

desorbing the last few per cent of the sorbed water (see figure 3, inset) is indeed dependent on both the nature and pressure of the gas present in the apparatus during the preceding adsorption. It is possible that the gas[4] trapped in the capillaries of the gel hinders the desorption of the water, again, merely by physical resistance to diffusion of the water vapor. This hypothesis is supported by the fact that the rate of desorption of the last bit of water is greater in hydrogen—small molecular weight—than in air, oxygen, or nitrogen.

If the above hypothesis is correct, the results of the experiments with the iron–silica gel (figure 4) are particularly interesting. Even following adsorption in a good vacuum (curve 1), the rate of desorption (curve 4) of the last 3 per cent of the water is extremely slow. In fact, we see from figure 4 that curve 4 corresponds more closely to curve 3—desorption from silica gel in the presence of oxygen, nitrogen, or air (at 3.6 mm.)—than to curve 2—desorption from silica gel *in vacuo*. This might well indicate the presence in the pores of this gel of a trace of gas[5] which cannot be eliminated by activation but which is sufficient to hinder the desorption of water.

Of interest in connection with the peculiarities of the iron–silica gel is the work of Lambert and Clark (9), who found that the adsorption of benzene on ferric oxide gel gave an entirely different type of isothermal than the adsorption of benzene on silica gel.[6] Subsequently the same investigators (10) found hysteresis in the sorption of benzene on ferric oxide gel, but no hysteresis with silica gel.

SUMMARY

1. At 25°C. and at a vapor pressure of water of 4.6 mm., two to three hours is sufficient to establish equilibrium between silica gel and water, provided the pressure of the permanent gas present is below 0.5 mm. That is, the rate of adsorption of water on silica gel is independent of the permanent gas present when the pressure of that gas is below 0.5 mm.

2. At higher pressures of gas the rate is an inverse function of the pressure and the molecular weight of the gas present. Thus at a given pressure the rate is most rapid in hydrogen.

3. The rate of desorption of the last part of the water to be pumped off is an inverse function of the pressure and molecular weight of the gas present during the previous adsorption. The desorption of the first and larger portion of water is quite independent of the gas present.

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[4] For example, the gas may have been adsorbed by the gel before or during the adsorption of water, or it may have dissolved in the sorbed water.

[5] Presumably oxygen resulting from the decomposition of ferric oxide. Mellor (12) quotes Sossman and Hostetter to the effect that the decomposition of ferric oxide is measurable as low as 100°C.

[6] Plotting pressure as abscissa and amount sorbed as ordinate, the silica gel gave a curve roughly parabolic; the ferric oxide gave a sigmoid curve.

4. The rate of desorption from an iron-silica gel, following adsorption *in vacuo*, is much less than in the case of silica gel, and is similar to the rate of desorption for silica gel following adsorption in the presence of a gas.

5. All the observed facts may be qualitatively accounted for on the basis of the resistance of an inert gas to diffusion of water vapor, both in the vapor phase around the gel and in the pores of the gel.

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LEAD TITANATE: CRYSTAL STRUCTURE, TEMPERATURE OF FORMATION, AND SPECIFIC GRAVITY DATA

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INTRODUCTION

The study of the kinetics and theory of reactions in the solid state has been carried on principally by Jander (6), Hedvall (4), Tamman (9), Goldschmidt (3), Taylor (10), and their coworkers. Their investigations have dealt principally with reactions between the carbonates, or the halides and metal oxides. In general, the reactions investigated yielded a readily soluble component or evolution of a gas, which affords a ready means of determining the rate of reaction. In some instances, heating curves obtained by means of differential thermocouples have been employed to observe the reaction temperatures. When studying the reactions between oxides, the amounts of resulting components or unreacted components are determined in order to measure the extent or the temperature of the reaction. If these oxides are extremely small particles, as in the case of litharge and precipitated titanium dioxide, the differential thermocouple procedure will give high values for temperature of reaction, owing to low thermal conductivity of the powder and because the deflection in the heating curve is only pronounced when the reaction is rapid and when an appreciable quantity of heat is released or consumed. The formation of alkaline earth metatitanates by reaction of alkaline earth oxides or carbonates with titanium dioxide in the solid state at elevated temperatures was first disclosed in the patent literature (3). The crystal habit, the possibility of other compounds in the system $PbO-TiO_2$, and other physical data on lead titanate have not been published in the literature. Since this compound is now being produced as a commercial pigment, such data are of interest. A discussion of its properties in paints has appeared (8). Other divalent metal metatitanates have been investigated by Goldschmidt (3), Barth (1), Posnjak (7), Zachariasen (12), Hoffman (5), and Taylor (10). According to their researches the $MTiO_3$ compounds crystallize in two types, i.e., ilmenite and perovskite. Wyckoff (11) has questioned the designation of the perovskite type as cubic, and has indicated that orthorhombic might be the proper system for certain titanates now assigned a perovskite structure.

Goldschmidt has used the radius ratio of the ionic radii to predict the probable structure of a compound. The limits of the perovskite structure are between 0.99 and 0.77, according to the formula

$$R_A + R_B = t\sqrt{2}\,(R_B + R_X)$$

The tolerance factor (t) for lead titanate using Pauling's values for the ionic radii is calculated to be 0.985 and using Goldschmidt's values 0.95. Accordingly lead titanate should have a perovskite structure but, as will be shown by the powder diffraction pattern, it does not have such a structure. The ionic radius of Pb^{++} may not be correct, or the radius ratio as postulated by Goldschmidt does not apply in all cases.

PREPARATION OF LEAD TITANATE

Hydrous titanium oxide (99.8 per cent TiO_2) precipitated from an ilmenite solution and freed from sulfates was intimately mixed with fume litharge (99.9 per cent PbO). A second means of compounding the lead titanate was to grind calcined titanium dioxide (commercially known as Titanox-A) with fume litharge in water. The mixtures were filtered, dried, and calcined at various temperatures.

The mole ratios were varied from $3PbO \cdot TiO_2$ to $PbO \cdot 5TiO_2$, in order to determine if $PbTiO_3$ was the only compound in the system $PbO\text{–}TiO_2$. Lead titanate crystallized from $2PbO \cdot 1TiO_2$ at 900°C., at which temperature the composition was a mixture of liquid and crystals. Crystalline lead titanate was also prepared by adding the calcined lead titanate to molten sodium tungstate at 850°C. Microscopic examination of crystals obtained from this melt after three hours heating showed sufficient crystal growth to permit classification.

Since the products of the lead titanate composition showed less than 2 per cent lead monoxide soluble in 5 per cent acetic acid, the reactions were over 98 per cent completed under proper calcination conditions. Long periods of heating at several temperatures were employed in order to ascertain if dimorphism might exist, as in the case of cadmium titanate.

RESULTS OBTAINED

The x-ray data revealed only one compound in the system $PbO\text{–}TiO_2$ between 89 per cent and 25 per cent PbO. Owing to the highly corrosive characteristics of lead monoxide, no attempt was made to obtain the liquidus–solidus curve of the system $PbO\text{–}TiO_2$. The formation of lead titanate, as determined by heating curves, has been reported by Tamman (9) to begin at 470°C. The x-ray data showed that the reaction starts at 360°C. and is complete in forty hours at 375°C., or in four hours at 400°C.

The crystals formed from the partial melt of $2PbO \cdot TiO_2$ and from molten sodium tungstate were yellow-colored octahedrons. Owing to their small size it was not possible to make accurate measurements of their axial ratios. The crystals were readily crushed in an agate mortar and did not scratch glass. A photomicrograph (figure 1) of the crystals shows their general habit. The x-ray data in table 1 indicate that the crystals are orthorhombic holohedral with the axial ratio of 0.95:1:0.92. Owing to their high refraction and birefringence no attempt was made to obtain the optical characteristics of the mineral.

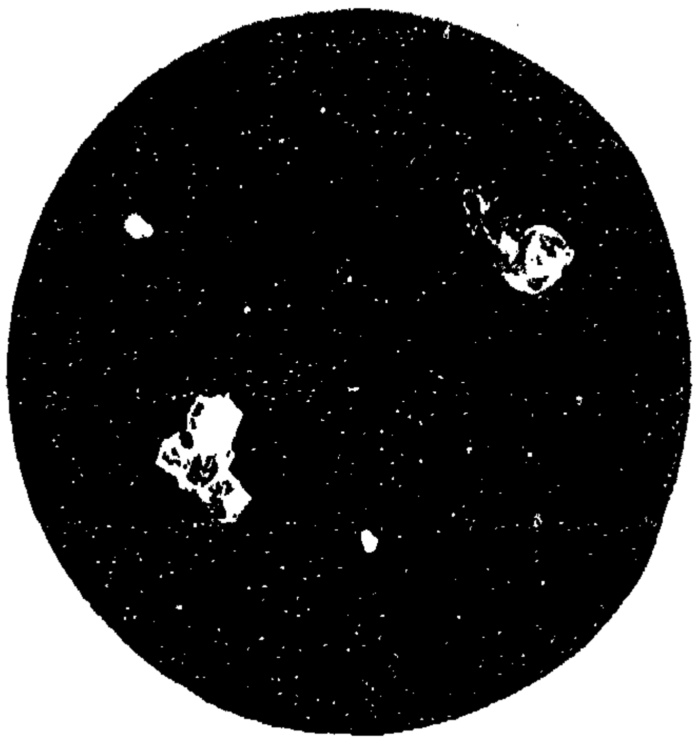

FIG. 1. Lead titanate crystallized from sodium tungstate, magnified 135 ×

TABLE 1

Physical data on lead titanate

Specific gravity:	
Observed	7.52 (average of 4 determinations)
Calculated from x-ray data	7.653 (average of 8 determinations)
Temperature of initial formation	360°C.
Temperature for complete formation	375°C.
Crystal habit	Orthorhombic holohedral
Axial ratio	0.95:1:0.92
Size of unit cell (average of 8 determinations)	a_0 = 4.000 A.U. ± 0.003 b_0 = 4.211 A.U. ± 0.002 c_0 = 3.875 A.U. ± 0.002

The specific gravity was determined according to the method described by Dunn (2) for fine powders and pigments. The value of 7.52 was observed, while 7.65 has been calculated from the x-ray data. This is satisfactory agreement, considering that the average particle size in the sample used for the observed value was less than 1.0 micron. The physical data obtained on this compound are summarized in table 1.

Samples of lead titanate held for twenty-four hours at 400°, 575°, 700°, 775°, 860°, and 1000°C., and then air-quenched, yielded identical diffraction patterns. A hard-sintered sample after two hours at 1200°C. also gave the same pattern. This would indicate that lead titanate exists only in one crystal form from the temperature of its formation to its melting point. A diagrammatic representation of the pattern is given as figure 2.

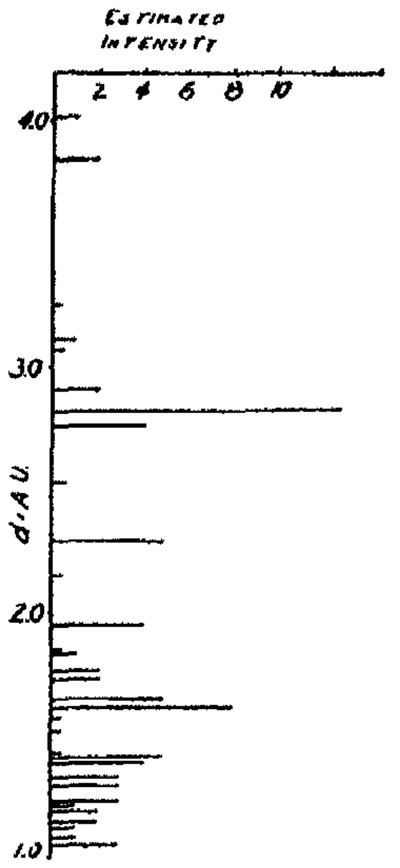

FIG. 2. X-ray pattern of lead titanate

The x-ray data of lead titanate formed at 1200°C. are given in table 2. Patterns of lead titanate calcined at 100° intervals between 400°C. and 900°C. agreed within experimental error. No difference could be observed when an excess of lead monoxide or titanium dioxide was present, or when crystalline lead titanate was examined. The patterns were obtained using a Ksanda gas tube with copper antieathode and cameras having a radius of 57.25 mm. All samples were ground in Canada balsam and mounted on copper wire (32 gauge; 0.23 mm. diameter). All exposures were made with a peak voltage of 38 kilovolts and 5 milliamperes for two hours. The value of 1.539 A.U. for Cu $K\alpha$ was used in the calculations of the unit cell.

The only lines which were not accounted for in the patterns were those

TABLE 2

X-ray data on lead titanate calcined two hours at 1200°C., marked 62C7

ESTIMATED INTENSITY	2d (0.1 mm)	2θ Cu	2θ CORRECTED	$\sin^2\theta$	$(h^2+k^2+l^2)\cdot Q$		hkl
1	220		22.00	0.03641	1.11	0.03280	100
2	230		23.05	0.03992	1.18	0.03383	001
½	273		27.35	0.05590			
1	286		28.65	0.06125	β 011		
½	292		29.25	0.06290			
2	306		30.70	0.07005	2.11	0.03319	110
10⁺	315		31.60	0.07418	2.18	0.03402	011
4	323		32.40	0.07783	2.29	0.03398	101
½	353		35.50	0.09294	β 111		
5	390		39.20	0.11250	3.29	0.03419	111
½	417		41.96	0.12819	β 002		
8	431	43.36					
½	451	45.26					
4	463		46.56	0.15624	4.73	0.03303	002
½	488		49.10	0.17253	5.11	0.03376	120
1	495		49.80	0.17718	β 211		
6	502	50.50					
1	516		51.90	0.19138	5.73	0.03339	012
1	526		52.90	0.19839	5.84	0.03396	102
5	553		55.60	0.21748	6.61	0.03290	211
8	569		57.30	0.22987	6.84	0.03360	112
½	584		58.80	0.24098	β 030		
½	606		61.00	0.25759	β 221		
½	646		65.00	0.28869	β 003		
5	654		65.85	0.29623	9.00	0.03280	030
4	678		68.30	0.31513	9.61	0.03279	221
3	702		70.75	0.33514	9.98	0.03358	300
3	722		72.80	0.35215	10.63	0.03312	003
6	736	74.20					
3	767		77.30	0.39008	11.63	0.03354	013
1	779		78.50	0.40021	12.16	0.03291	311
2	811		81.68	0.42764	12.74	0.03356	113
2	841		84.68	0.45353	13.43	0.03370	230
1	858		86.36	0.46754	13.98	0.03344	320
6	895	90.06					
1	905		91.10	0.50959	15.16	0.03361	321
3	930		93.72	0.53252	16.00	0.03328	040
4	945	95.26					
Average						0.03339	

$a_0 = 4.001$, $b_0 = 4.211$, $c_0 = 3.874$, $d = 7.655$.

which would coincide with copper reflections, i.e., 020, 200, and 210. The structure of lead titanate appears to be a modification of the arrangement of perovskite to accommodate the larger Pb^{++}. The Ti–O distance is increased to 2.1 A.U. along the *C*-axis and to 2.0 A.U. along the *A*-axis from the normal value of 1.95 A.U. found in most titanates. The size of the cell in the direction of the *C*-axis is just slightly greater than that reported for calcium titanate, 3.83 A.U.

The *space group* D_{2h}^1 *with the atomic positions as follows*, Pb:000, Ti:½½½, O:½½0; ½0½; 0½½, seems to be the most probable arrangement for lead titanate. This is primarily a slight change from the calcium titanate arrangement in that the *A*- and *B*-axes are extended with resulting increase in Ti–O distances.

SUMMARY

Lead titanate, $PbTiO_3$, was formed in the solid state from lead monoxide and titanium dioxide.

The temperature of the initial formation of lead titanate was found to be 360°C. and that of complete formation was 375°C.

The specific gravity was found to be 7.52 for powder formed at 800°C., as compared with 7.655 calculated from x-ray data.

Lead titanate crystallized as orthorhombic holohedral pyramids from melts.

The powder diffraction data are calculated and found to agree with orthorhombic structure with an axial ratio of 0.95:1:0.92, yielding the size of the unit cell as $a_0 = 4.000$ A.U., $b_0 = 4.211$ A.U., $c_0 = 3.875$ A.U.

The space group D_{2h}^1 with atomic positions Pb:000, Ti:½½½, O:½½0; ½0½; 0½½ was assigned as the most probable arrangement for lead titanate.

Acknowledgment is due J. L. Turner, Director of Research, Titanium Division, National Lead Company, for the suggestion on which this paper is based.

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THE CONSTANTS OF EBULLIOSCOPY

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The ebullioscopic method for the determination of molecular weights in solution has been the subject of a tremendous volume of study, both theoretically and experimentally. In spite of this, the values of the ebullioscopic constants of various solvents as given by different sources vary widely.

The most consistent and accurate values in use today are those of Rosanoff and Dunphy (5). On the assumption that the slope of the vapor pressure curve of the solution is the same as that of the solvent over a short range and the further assumption that the laws of Henry and Raoult are valid for very dilute solutions, they derive the ebullioscopic constant from the simple mathematical expression for Raoult's law.

If

$$\mathrm{d}p/\mathrm{d}P = n/N$$

then

$$\mathrm{d}p/\mathrm{d}T = p/\mathrm{d}T \cdot n/N$$

Now, when $n = 1$ and $N = 1000/M$, $\mathrm{d}T = K_b$ and

$$K_b = \mathrm{d}T = \frac{pM}{1000\,\mathrm{d}p/\mathrm{d}T} \qquad (1)$$

The gas laws were then utilized to convert the expression into

$$K_b = \frac{RT}{1000v \cdot \mathrm{d}p/\mathrm{d}T} \qquad (2)$$

on the assumption that the gas laws accurately represent the behavior of saturated vapors at the boiling point. This introduces an error of from 0.5 to 5.0 per cent in the calculated constant, which may be eliminated by applying the Berthelot correction to the gas constant. This is unnecessary, however, when the original form of the equation is employed.

As a consequence of the assumptions inherent in the derivation of the equation, this constant is correct only when the solution is very dilute. It constitutes a limiting value of the function which is approached more closely the more dilute the solution.

The thermodynamic cycle at the boiling point has been utilized to derive the boiling-point constant. If proper corrections are made for the failure of the gas laws to represent adequately the state of vapors at the boiling point, the values should be same as those obtained by Rosanoff and Dunphy. In the limiting case, where the concentration of the solution is so small that the heat of evaporation of a mole of solvent from an infinite amount of the solution is equal to the latent heat of vaporization,

$$K_b = \frac{RT^2}{1000 L_v} \tag{3}$$

where T is the boiling point of the solution on the absolute scale and L_v is the latent heat of vaporization. The gas constant R must be corrected by the Berthelot equation, and failure to do so accounts for much of the discrepancy in earlier results.

VARIATION OF EBULLIOSCOPIC CONSTANT WITH BAROMETRIC PRESSURE

The variation in the ebullioscopic constant with change in barometric pressure becomes important when determinations of molecular weight are made at altitudes where the barometric pressure may differ from standard pressure by 40 mm. or more. Menzies and Wright (4) state that the variation is approximately 0.03 per cent for all solvents, based on the value at 760 mm. Rosanoff and Dunphy have furnished a table of variations for each 10 mm. change but, owing to an unfortunate misprint in the original article and the fact that their constants are based on 100 g. of solvent, the corrections as quoted are often in error by one decimal place (2). Moreover, the values as given by these authors in certain cases are otherwise seriously in error.

The variation may be calculated by differentiating K_b with respect to T.

$$K_b = \frac{RT^2}{1000 L_v}$$

$$\mathrm{d}K_b/\mathrm{d}T = \frac{2RT}{1000 L_v}$$

$$\mathrm{d}K_b/\mathrm{d}p = \frac{2RT}{1000 L_v \cdot \mathrm{d}p/\mathrm{d}T}$$

Table 1 gives the values of the ebullioscopic constant of a number of solvents calculated from equation 1 and from equation 3 and the variation in the ebullioscopic constant with change in barometric pressure, using the slope of the vapor pressure curve given by Rosanoff and Dunphy. It is apparent that the constant for all solvents decreases approximately 0.025 per cent for each mm. decrease in barometric pressure. This is in good agreement with the value given for benzene by Washburn and Read (6).

EXPERIMENTAL

The experimental determinations of the ebullioscopic constant were made with the apparatus designed by Menzies and Wright (4). In the original form, as described by these investigators, the solution was drawn by the pump from the bottom of the boiling vessel. Bancroft and Davis (1) have shown that in the Cottrell apparatus superheating occurs when the

TABLE 1

Calculated values of the ebullioscopic constant

SOLVENT	SLOPE OF VAPOR PRESSURE CURVE dp/dT	BOILING POINT t_b	LATENT HEAT OF VAPORIZATION L_v	GAS CONSTANT CORRECTED R	EBULLIOSCOPIC CONSTANT		CORRECTION PER MM.
					Eq. 1	Eq. 3	
Acetone	0.0339	56.00	122.06*	1.926	1.71	1.71	0.0004
Benzene	0.0309	80.15	94.35*	1.925	2.53	2.54	0.0007
Bromobenzene	0.0251	155.83	57.63*	1.920	6.26	6.12	0.0016
Carbon bisulfide	0.0325	46.13	84.07*	1.933	2.34	2.34	0.0006
Chlorobenzene	0.0271	131.98	77.61*	1.921	4.15	4.06	0.0011
Chloroform	0.0329	60.19	58.80*	1.928	3.63	3.64	0.0009
Carbon tetrachloride	0.0306	76.50	46.55*	1.911	5.03	5.02	0.0013
Cyclohexane	0.0301	80.88	85.62*	1.913	2.79	2.79	0.0007
Ethanol	0.0379	78.26	201.88*	1.948	1.22	1.19	0.0003
Ethyl ether	0.0358	34.42	86.08*	1.914	2.02	2.10	0.0005
Ethyl acetate	0.0317	77.13	87.63*	1.919	2.77	2.68	0.0007
n-Heptane	0.0292	98.42	76.35*	1.900	3.43	3.43	0.0008
n-Hexane	0.0313	68.59	79.31	1.902	2.75	2.80	0.0007
Iodobenzene	0.0239	188.47	46.23	1.920	8.53	8.87	0.0021
Methanol	0.0388	64.67	263.31*	1.951	0.83	0.84	0.0002
n-Octane	0.0284	125.80	70.99	1.896	4.02	4.25	0.0010
n-Pentane	0.0354	36.00	85.76	1.904	2.04	2.06	0.0005
Water	0.0357	100.00	538.7*	1.976	0.505	0.510	0.0001

* Data from Matthews: J. Am. Chem. Soc. **48**, 562 (1926).

TABLE 2

Experimental determination of ebullioscopic constants

SOLVENT	MOLES OF SOLVENT	MOLES OF SOLUTE	T_b	K_b
Acetone	0.4029	0.000985	0.0730	1.733
Acetone	0.4182	0.000961	0.0690	1.743
Benzene	0.3269	0.001046	0.1040	2.537
Benzene	0.3314	0.000952	0.0933	2.534
Carbon tetrachloride	0.3087	0.000759	0.0809	5.077
Carbon tetrachloride	0.3087	0.001626	0.1776	5.068
Methanol	0.7774	0.001075	0.0360	0.835
Methanol	0.7472	0.001011	0.0354	0.837

pump is placed close to the bottom. By shortening the pump in the apparatus of Menzies and Wright so that it drew the solution from close to the surface and plugging the efflux end loosely with a plug of glass wool, superheating was eliminated and a steady stream of solution in equilibrium with its vapor flowed over the lower bulb of the differential thermometer. The whole apparatus was placed inside a case with a plate glass window, and the readings were taken with a telescope located several feet away. The use of a micro burner in place of the Bunsen burner gave good control of the boiling rate.

Benzil was chosen as solute, since its boiling point is sufficiently high so that its vapor pressure is negligible at the boiling point of any solvent used. The sample was recrystallized several times from alcohol and melted sharply at 95°C. The solvents were chosen to cover a wide range of internal pressures in order to test the effect when solutions were not ideal (3).

Table 2 shows the experimental values for acetone, benzene, carbon tetrachloride, and methanol.

SUMMARY

A recalculation of the values of the ebullioscopic constants by the equation of Rosanoff and Dunphy has been made for eighteen common solvents. These agree closely with those calculated from the usual thermodynamic equation, provided the gas constant is corrected by the Berthelot equation. Experimental values check the theoretical when superheating is eliminated.

Where any appreciable difference occurs between the two values, that calculated by the equation of Rosanoff and Dunphy is to be preferred.

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THE VAPOR PRESSURE OF BINARY SOLUTIONS OF ISOPROPYL ALCOHOL AND BENZENE AT 25°C.

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As a part of a comparative study of binary and ternary systems made up of water, a hydrocarbon, and a lower alcohol, the following vapor pressure measurements have been made on solutions of isopropyl alcohol in benzene.

MATERIALS

The methods of purification and the physical constants of these materials have been discussed and recorded in a previous article (1).

EXPERIMENTAL

Total pressure

The difference between the vapor pressure of the isopropyl alcohol and each liquid mixture was determined by a differential static method. The apparatus which was used in this measurement was a slight modification of that described by Parks and Schwenk (3). It is sketched in figure 2.

Since considerable difficulty was encountered in closing the tops of the manometer, mercury-sealed stoppers were employed. No measurable leakage through these stoppers was observed in twenty-eight hours when they were subjected to a difference in pressure of 1 atmosphere.

The manometer was placed within a constant-temperature air bath, thermostatically controlled to ±0.10°C. The readings were observed by means of a cathetometer reading to 0.1 mm., and it was found that one could reproduce cathetometer readings to ±0.05 mm., which is the limiting accuracy of the instrument. Each value which is given in the table of data represents the average of many independent determinations, and the agreement is of the order of ±0.05 mm. After the measurement had been completed, a portion of the mixture was removed and its composition was determined by means of a refractive index measurement. The conversion to mole fraction was effected by means of a curve which was plotted from data in table 1.

Analysis of the vapor phase

The composition of the vapor phase in equilibrium with the solutions at 25.00°C. was determined. This was accomplished by passing dry, carbon dioxide-free air through a pair of bubblers (figure 1), each containing 10 cc. of the mixture under consideration. The bubblers were immersed in a constant-temperature water bath. The air thus saturated with the vapor of the mixture was then passed through a freezing-out tube immersed in liquid air. The alcohol-benzene mixture separated as a solid on the walls of this tube, and when about 2 cc. of distillate had been collected, it was analyzed by means of the refractometer.

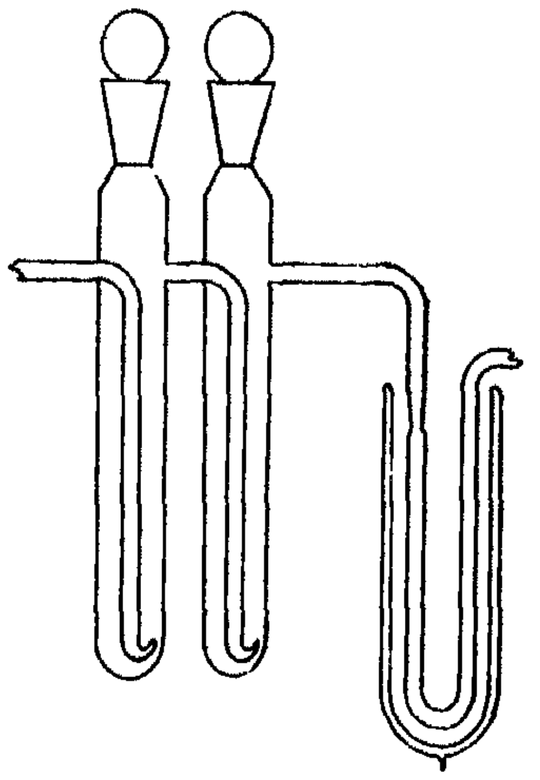

Fig. 1

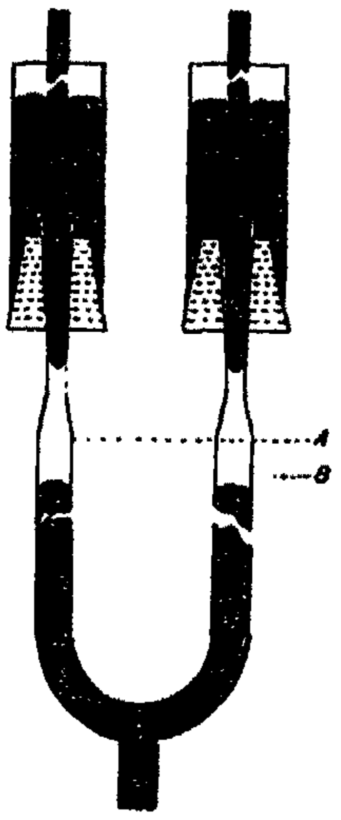

Fig. 2

Fig. 1. Air saturator for vapor analysis
Fig. 2. Differential static manometer

To determine if there were appreciable concentration changes during the time required for the vapor to freeze, the following procedure was carried out. Four bubblers were connected in series and a 10-cc. sample, chosen successively from nine different liquid mixtures and varying in composition from pure alcohol to pure benzene, was placed in each one. It was found that there was no measurable change in composition of the 10-cc. sample in the first bubbler during the time required for the freezing-out process. It was also found that the composition in the first bubbler must change appreciably before a noticeable difference appeared in the second. It was further noted that all the liquid must completely disappear in the first bubbler before a change took place in the third and fourth. The liquids disappeared in the order of their placement in the series. The air bubble as it left the first bubbler must have been completely saturated with the liquid in question during the first part of each determination. A few of the values which are recorded in table 2 were obtained by means of a single unit in which 25 cc. was placed. The values from this procedure compared favorably with those obtained from the two-tube unit. A second bubbler, however, positively insured complete saturation.

TABLE 1

Refractive index of benzene-isopropyl alcohol solutions

MOLE FRACTION OF ALCOHOL	REFRACTIVE INDEX
1.000	1.37479
0.823	1.39861
0.640	1.42162
0.536	1.43444
0.430	1.44725
0.330	1.45954
0.222	1.47159
0.000	1.49800

TABLE 2

Composition of vapor of benzene-isopropyl alcohol solutions

MOLE FRACTION OF ALCOHOL IN LIQUID	MOLE FRACTION OF ALCOHOL IN VAPOR	MOLE FRACTION OF ALCOHOL IN LIQUID	MOLE FRACTION OF ALCOHOL IN VAPOR
0.000	0.000	0.633	0.334
0.114	0.187	0.820	0.450
0.173	0.223	0.861	0.508
0.224	0.231	0.910	0.598
0.330	0.246	0.948	0.739
0.430	0.270	1.000	1.000
0.536	0.290		

The vapor composition data are given in table 2. The values which are recorded are representative values of thirty-four determinations. The average error of a single observation from the mean of the mole fraction of alcohol in the vapor phase over liquid mixtures of identical mole fraction was ±0.005.

Calculation of results

Parks' value of 44.0 mm. was taken as the vapor pressure of the isopropyl alcohol (2). The theoretical and the observed results appear in table 3, and the observed results are plotted in figure 3. The values for the composition of the vapors in equilibrium with these mixtures were not determined directly, but were obtained from a smooth curve plotted from values in table 2. In this sense they are really experimental, and when multiplied by the corresponding total pressures for the various solutions, give the observed partial pressure of isopropyl alcohol. The observed partial pressure of benzene was determined in a similar manner. The ideal pressures in all cases were calculated on the assumption of Raoult's law

TABLE 3

Partial and total pressures at 25.0°C. of benzene–isopropyl alcohol solutions

MOLE FRACTION OF ALCOHOL		PARTIAL PRESSURE OF ALCOHOL		TOTAL PRESSURE OF MIXTURE		PARTIAL PRESSURE OF BENZENE		f_A	f_B
Liquid	Vapor	Observed	Ideal	Observed	Ideal	Observed	Ideal		
0.000	0.000		0.0		94.4		94.4		
0.059	0.123	12.9	2.6	104.5	91.4	91.7	88.7	4.969	1.049
0.146	0.205	22.4	6.4	109.0	87.1	86.7	80.6	3.487	1.075
0.362	0.255	27.6	15.9	108.4	76.2	80.8	60.2	1.733	1.342
0.521	0.288	30.5	22.9	105.8	65.1	75.3	45.2	1.331	1.665
0.700	0.365	36.4	30.8	99.8	59.1	63.4	28.3	1.182	2.239
0.836	0.470	39.5	36.8	84.0	52.3	44.5	15.5	1.074	2.874
0.924	0.635	42.2	40.7	66.4	47.8	24.2	7.2	1.038	3.373
1.000	1.000		44.0		44.0		0.0		

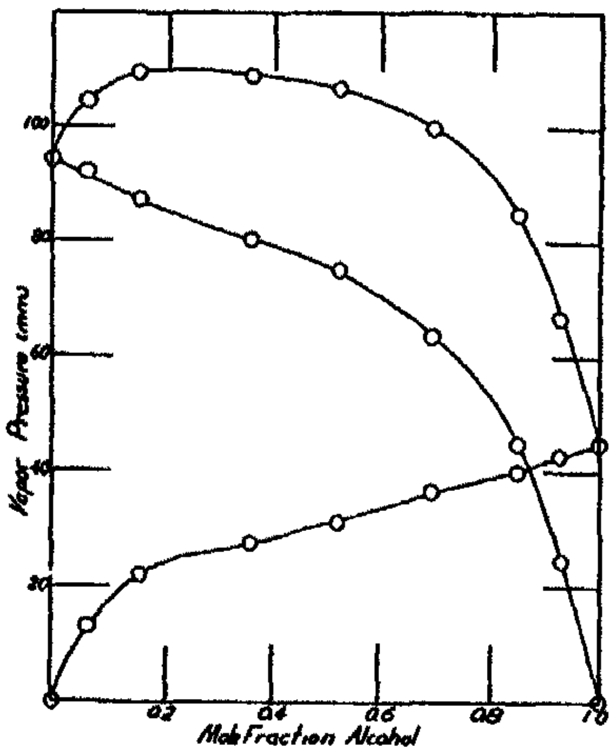

FIG. 3. Observed total and partial pressures of benzene–isopropyl alcohol system

$$p_A = N_A p_A^0$$

where p_A and N_A are respectively the partial pressure and the mole fraction of component A in a given solution and p_A^0 is its vapor pressure in the pure state.

The activity coefficients for alcohol and benzene are recorded in columns 5 and 6, respectively, in table 3. They were calculated by means of the equation

$$f = \frac{p}{p^0 N}$$

where f is the activity coefficient, p is the partial vapor pressure of the component above the solution, p^0 is the vapor pressure of the pure component, and N is the mole fraction of the component in the solution.

DISCUSSION OF RESULTS

The difference between the vapor pressures of the pure components was taken as the criterion of accuracy of measurement. The measurement on this difference, applying many technics, was found to result in an error of 2 to 3 per cent. After having performed the usual routine of technic in removing the visible air, a tiny bubble of air would always remain above the liquids when the mercury reservoir was raised from its lowered position. Still further evidence of dissolved air was found in the observation of abnormal readings at the upper end of the manometer. The usual procedures will never remove the dissolved air, for at the point at which the stoppers may be removed there will be placed the existing atmospheric pressure on the excluded gas, thereby forcing it into the liquid. The effectsof dissolved air were minimized by making pressure measurements well toward the bottom of the manometer.

In a study of vapor pressure data and its subsequent calculation to activity coefficients, it is observed that the alcohol-benzene system deviates in a positive manner from Raoult's law. The wide deviation from ideal behavior took place because of the great difference in polarity of the two components. The polar molecules of alcohol have an abnormally great attraction for each other, producing greater surface tension, cohesion, etc., and tend to "squeeze" out non-polar molecules from their midst. As a result of the tendency of a liquid of high internal pressure to "squeeze" out a liquid of low internal pressure, it is expected that the partial pressure would deviate in a positive manner from Raoult's law. This concept of association does not admit any definite polymers like double molecules. The polar affinities act within the liquid to form groups of molecules which become impregnable to a non-polar molecule like benzene.

In the study of the depression of the freezing point the deviations were ascribed to some combination either of alcohol molecules or alcohol-benzene molecules. There is a small range of concentration near pure benzene where the observed and the calculated freezing points do not deviate appreciably. There is a small range of concentration near pure benzene where the partial pressures of benzene do not deviate far from the theoretical values. The alcohol molecules are randomly and sparsely distributed to such an extent that each is without influence on the other. A decreased value for the internal pressure of the alcohol in the mixture would tend to "squeeze" out a lesser number of molecules of benzene.

SUMMARY

1. The differential static method devised by Parks has been adapted for the measurement of the total and partial vapor pressures of the components of the binary solutions of isopropyl alcohol and benzene at 25°C. The accuracy of the method has been discussed.

2. These data have been used to calculate the activity coefficients which indicate deviations from Raoult's law.

3. Deviations from ideal behavior have been discussed and qualitatively explained on the basis of polarity.

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STREAMING OF LIQUIDS THROUGH SMALL CAPILLARIES[1]

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The present investigation was undertaken to determine the effect of molecular structure on the rate of streaming through diaphragms containing capillaries of small radii. Diaphragms of glass, cellulose, and carbon were used, thus including hydrophilic, hydrophobic, and intermediate materials.

Various workers (7, 5, 1) have reported the rate of streaming of liquids through small capillaries to be governed largely by other factors than viscosity. There has, however, been no systematic study of these relations, and the present communication attempts to provide for this deficiency.

EXPERIMENTAL

The liquids used were water and the first seven normal aliphatic alcohols. Rates were also determined for carbon tetrachloride. All liquids were the purest obtainable; they were distilled and only that portion distilling in a narrow range was used. The viscosities of the alcohols were measured in an Ostwald viscosimeter and these values used in our work. With the exception of the amyl, hexyl, and heptyl alcohols the viscosities found were, within experimental error, equal to those reported in the *International Critical Tables*. Since our values for the viscosities of these last three alcohols yielded a smoother curve when plotted against the number of carbon atoms in the alcohols than did the values from the *International Critical Tables*, we regard our measurements as more reliable.

The diaphragms were of sintered glass, cellulose, and graphite. One of the glass diaphragms (No. I) was a No. 194 Jena sintered glass filter, and the other (No. II), a coarser glass diaphragm, was made from Pyrex glass by the University of Minnesota glass blower. The cellulose was prepared from Schleicher and Schüll filter paper No. 589. It was ground to a pulp in a ball mill with 95 per cent ethyl alcohol. The cellulose was then fil-

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tered and dried *in vacuo* at 95°C. for eight hours and stored in sealed glass containers. It was the same cellulose as that used by Bull and Gortner (2) in their work on the streaming potential. The cellulose was packed into a glass cell 1 cm. thick and 2.2 cm. in diameter to the desired degree of tightness. On both ends of the glass cell were placed well-perforated gold discs. Leakage was prevented by rubber washers. The cell was clamped between two reservoirs containing the liquid in a manner identical with that described by Bull and Gortner (2). The rate of flow was determined by allowing the liquid to flow into a buret and measuring the time required for a certain volume to flow. The pressure was measured with a water or mercury manometer as required.

The carbon diaphragm consisted of a cross section of a dry cell carbon 0.6 cm. thick. This diaphragm was clamped into position and thoroughly washed with ether and benzene by streaming these liquids through it.

The experiments were conducted at room temperature, which varied between 21° and 27°C. An accurate record of the temperature was kept., however, and the viscosities used in the calculations were corrected accordingly.

The average pore radii of the capillaries in the diaphragms were determined by the method of Bull and Moyer (3) by the use of their equation

$$r = \frac{8\eta CU}{P}$$

where η is the coefficient of viscosity in poises, C is the electrical cell constant with $N/10$ potassium chloride, U is the rate of flow in cubic centimeters per second under a pressure P expressed in dynes per square centimeter. The average pore radius was measured both for water and for carbon tetrachloride. It was not possible to evaluate the pore size of the carbon diaphragm by this method, owing to the fact that carbon is itself a conductor. Another method was evolved which consists in substituting in the Poiseuille equation the free volume in the diaphragm as determined by measuring the quantity of carbon tetrachloride taken up by the diaphragm. The free volume is related to the pore radius as follows

$$N\pi r^2 l = V$$

where N is the number of capillaries of average radius r, l is the thickness of the diaphragm, and V is the free volume in the diaphragm. Combining this with the Poiseuille equation we have

$$r = \frac{8l^2\eta U}{VP}$$

from which the average pore radius of the carbon diaphragm was obtained.

In all cases the rate of flow was a straight-line function of pressure. No change of rate of flow with time was noted except in the case of the carbon diaphragm, where there was a slight blocking effect after some time. The initial values for the rates are reported in this case. The results with the carbon diaphragm were the most variable, while those with the other diaphragms were very consistent and reproducible.

RESULTS

The values found for the viscosities are given in table 1.

The diaphragms were found to have the average pore radii given in table 2.

TABLE 1

*Viscosities found at 25°C.**

ALCOHOL	VISCOSITY IN POISES
Methyl alcohol	0.00556
Ethyl alcohol	0.01338
Propyl alcohol	0.01983
Butyl alcohol	0.02507
Amyl alcohol	0.03168
Hexyl alcohol	0.03946
Heptyl alcohol	0.04258

*Measurements made by Mr. John Hollihan.

TABLE 2

Average pore radii of diaphragms

DIAPHRAGM	RADIUS IN WATER	RADIUS IN CARBON TETRACHLORIDE
	cm.	*cm.*
Cellulose (tight)	0.52×10^{-4}	1.13×10^{-4}
Cellulose (moderate)	0.79×10^{-4}	3.04×10^{-4}
Cellulose (loose)	1.10×10^{-4}	6.38×10^{-4}
Carbon	0.155×10^{-4}	
Glass No. I	3.12×10^{-4}	3.70×10^{-4}
Glass No. II	8.85×10^{-4}	9.32×10^{-4}

Rather curiously the permeability as expressed by the factor ηU, where η is the coefficient of viscosity in poises and U is the cubic centimeters of liquid flowing in 1 second under a pressure of 1 dyne per square centimeter, has the dimensions of volume. If this factor ηU is expressed in c.g.s. units, its value comes out in cubic centimeters. We have not as yet been able to interpret this physically. The six graphs in figure 1 show the permeability (ηU) in cubic centimeters plotted against the number of carbon atoms in the alcohol. Water is plotted as having zero carbon atoms.

DISCUSSION

An inspection of the graphs shows that a simple inverse relation between viscosity and rate of flow does not obtain, for if viscosity were the controlling factor, each curve would be a horizontal straight line, parallel to the x-axis.

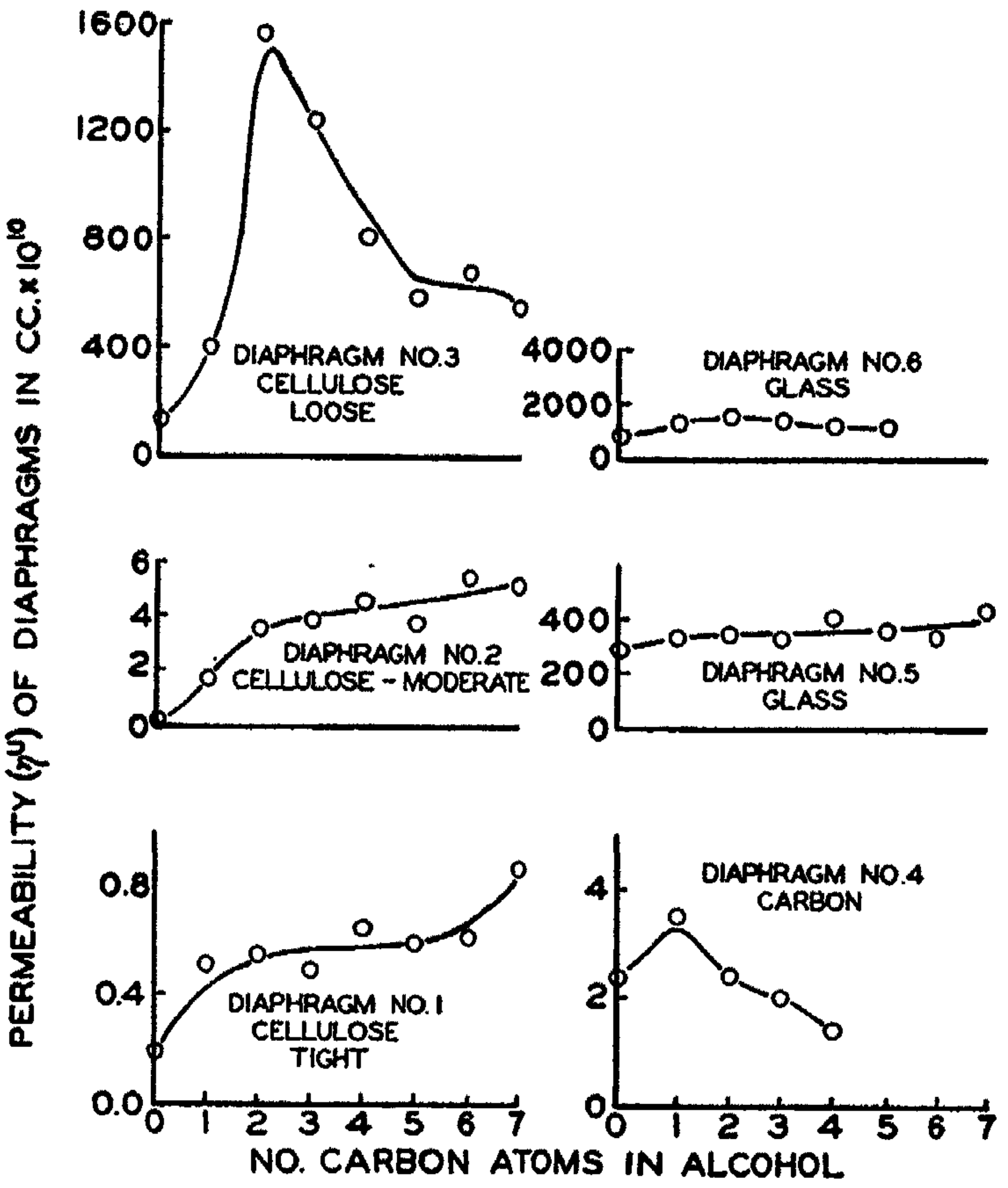

FIG. 1. Showing the effect of molecular structure of the normal aliphatic alcohols on the permeability of diaphragms.

The three graphs, 1, 2, and 3, showing the results with the tightly packed, moderately packed and loosely packed cellulose are interesting but rather difficult to interpret. We are inclined to regard the difference in rate of flow as a surface phenomenon. Ethyl, propyl, and butyl alcohols were evidently able to peptize the loosely packed cellulose with a corresponding increase in rate of flow through the diaphragm. The ζ-potential is probably involved in this peptizing action. Other than this effect the electrokinetic potential probably does not influence the rate of flow to any great extent (4), although the ζ-potential may be related to the factor or factors which influence the rate of flow. Both the moderately and tightly packed diaphragms show increasing rates of flow with increasing length of alcohol chain. In general the non-polar carbon tetrachloride gave the highest rate of flow, although this was not true of the loosely packed diaphragm; evidently there is no tendency for carbon tetrachloride to peptize the cellulose. The peptizing action of the alcohols on the moderately and tightly packed diaphragms did not operate, because the diaphragms were packed, in both cases, too tightly to allow any dispersion of the cellulose. The increasing of the factor ηU with increasing length of carbon chain is probably connected with the decreasing solvation of the cellulose by the higher alcohols, thus allowing greater space for motion of the liquid. Stamm (6) found that the longer alcohol molecules caused less swelling of cellulose than did the shorter ones, which is in good agreement with our results. The reverse of this tendency is exhibited by the carbon diaphragm, where the factor ηU decreases with the carbon number of the alcohols. This is probably due to the increasing attraction of the higher alcohols for the carbon surface with a corresponding decrease in the effective pore radius.

The glass diaphragms exhibited the same general behavior as did those of cellulose. Unfortunately the pore radii were too large in the two glass diaphragms to show a very pronounced effect. In fact the radii in the coarser glass diaphragm are apparently above the critical limit and the rate of flow is normal. We can, therefore, say that the critical pore radius below which anomalous rates of flow occur is between a radius of 8.85×10^{-4} cm. and 3.12×10^{-4} cm. Naturally this estimation of the critical pore radius is only semiquantitative, because the diaphragms are made up of a great variety of pore sizes and even in the coarse glass diaphragm there were no doubt many pores below the critical radius. Probably the critical limit depends on the nature both of the diaphragm and of the liquids and is to be expected to vary from case to case.

The individual points do not fall exactly on a smooth curve. We have not decided whether these variations are experimental errors or are realities. There is some tendency in some cases toward a step-like curve with alternation between even and odd number of carbon atoms. If this is really the case it can be offered as evidence of crystallization of the adsorbed alcohol on the surface.

SUMMARY

1. The viscosities of the first seven normal aliphatic alcohols have been reported.

2. The rate of flow of these alcohols and water has been determined

through diaphragms of cellulose, carbon, and glass, and in general the rate of flow per unit pressure through a given diaphragm appears to be a function both of the viscosity and of the degree of attraction between the liquid and the diaphragm. In loosely packed diaphragms there is a possibility of dispersion of the diaphragm material. Peptization effects may be important in studies such as these.

3. The average pore radii of the diaphragms have been calculated and an estimate made of the critical radius below which anomalous rates of flow occur.

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THE FORMATION OF BENZENE IN THE RADIOCHEMICAL POLYMERIZATION OF ACETYLENE

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In view of the similarity (7) between photochemical and radiochemical reactions it was decided to make an absorption spectral analysis of acetylene polymerizing under the influence of radon. This method has already been applied to the corresponding photochemical reaction by Kato (4), Kemula and Mrazek (6), and Livingston and Schiflett (10), who detected the presence of benzene (4, 6, 10) and naphthalene (6) in the polymerizing gas in addition to the solid cuprene-like polymer reported by various authors (2, 1, 15, 9, 16). The ultra-violet absorption spectrum of benzene (3) is exceedingly distinct and well established, and its presence during the course of the reaction can easily be detected spectroscopically. To anticipate the results of our experiments, we may state that an appreciable quantity of benzene was produced. Actually it was possible to condense a volatile liquid from the acetylene-radon mixture by freezing in solid carbon dioxide plus acetone. This liquid proved to be chiefly benzene.

It is not surprising that in the earlier publications, analysis had failed to reveal the presence of benzene. Mund and Koch (14) weighed the amount of solid polymer ("cuprene") produced, after first pumping out the reaction chamber, and found that the weight of solid corresponded to the disappearance of acetylene. However, weighings were made in air some time after collection of the polymer, thereby permitting absorption of oxygen from the air[2] (5). The procedure of Lind and Bardwell (8) likewise was not designed to detect a volatile liquid.

EXPERIMENTAL

Materials

Acetylene was prepared from calcium carbide in the usual manner (11). The purifying train consisted of strong solutions of sodium hydroxide,

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[2] Kaufmann (5) mentions a pale yellow solid polymer formed from acetylene in the silent discharge. This cuprene-like polymer absorbs oxygen rapidly. Unpublished work by Lind and Schiflett (J. Am. Chem. Soc., February, 1937) indicates a similar absorption of oxygen by the radiochemical polymer.

acidified potassium chromate, and mercuric chloride, as well as tubes of solid calcium chloride and phosphorus pentoxide. The chemically purified gas was frozen in liquid air, and the permanent gases pumped off. After permitting the solid acetylene to evaporate, the process was repeated several times. Before filling the storage containers the solid was fractionated, only the middle portion being collected.

Radon was obtained from the radium chloride solution which serves this laboratory. The method of purifying the radioactive gas has been described elsewhere (12).

The benzene employed was Kahlbaum's "extra pure crystallizable free from thiophene," which was rid of permanent gases by repeating the cycle of freezing in liquid air, pumping while solid, and melting.

Spectroscopic apparatus

The cylindrical absorption tube (C) used was of ordinary glass 2 cm. x 20 cm., with circular quartz plates (2 mm. thick) sealed to each end by means of picein. A Leiss hydrogen lamp (Al electrodes; 4 mm. pressure), designated by D, constituted the source of continuous ultra-violet light. It was operated on 50-cycle A.C. current at 3200 volts and drew 0.1 ampere. The plate included below shows that no photochemical polymerization to benzene resulted from illumination during the thirty minutes exposure time required for distinct pictures. Apparently the cuprene formed in the absorption tube when radon had to be admitted did not obscure the plate.

Spectra were recorded by a Hilger E 1 quartz prism spectrograph (S) set for the region 2700–2300 A.U. Gevaert Super Chromoso # 2000 antihalo plates were employed. The wave length scale was calibrated by means of an iron arc (1.5 min. illumination). Plates were compared by visual inspection.

EXPERIMENTS AND RESULTS

The reaction took place in a cylindrical vessel (A) with a diameter of 4.9 cm. and a length of 50 cm. Container A was first sealed to the radon line (not shown in the diagram), pure radon frozen in the side-arm (a) immersed in liquid air, and stopcock s_1 closed. Then the vessel was transferred to the supply line and filled with acetylene through s_1, after which (with s_1 closed) it was sealed to the light absorption system shown in figure 1. The volume of container A is 4.6 times as great as the volume of the trap system plus the absorption system. High vacuum was obtained by means of mercury vapor pumps.

First the presence of benzene in the polymerizing acetylene was demonstrated. A mixture of 62 cm. of acetylene and 40 millicuries of radon was kept in A for seven days, after which time the gas was allowed to expand into the absorption system. During this interval considerable cuprene had been formed. The total pressure (in the volume including container A, the series of traps between stopcocks s_1 and s_2, the absorption tube and intervening tubing up to s_3) was 41 cm. as read on the mercury manometer M adjusted to a fixed point by leveling reservoir L. This is equivalent to a pressure of 50 to 51 cm. in A alone. Photograph No. 1 on the accompanying plate, the absorption spectrum of the expanded gas, is indisputably the spectrum of benzene vapor. Comparison with photographs 2, 3, and 4, which show the absorption spectra of benzene vapor[3] (supplied by liquid benzene in B) at pressures of 1.3 mm., 4.5 mm., and 2.5 cm. respectively, indicated the presence of more than 4.5 mm. of benzene in the reaction mixture. After the exposure, the gas was transferred to A by freezing in side-arm a and closing s_1.

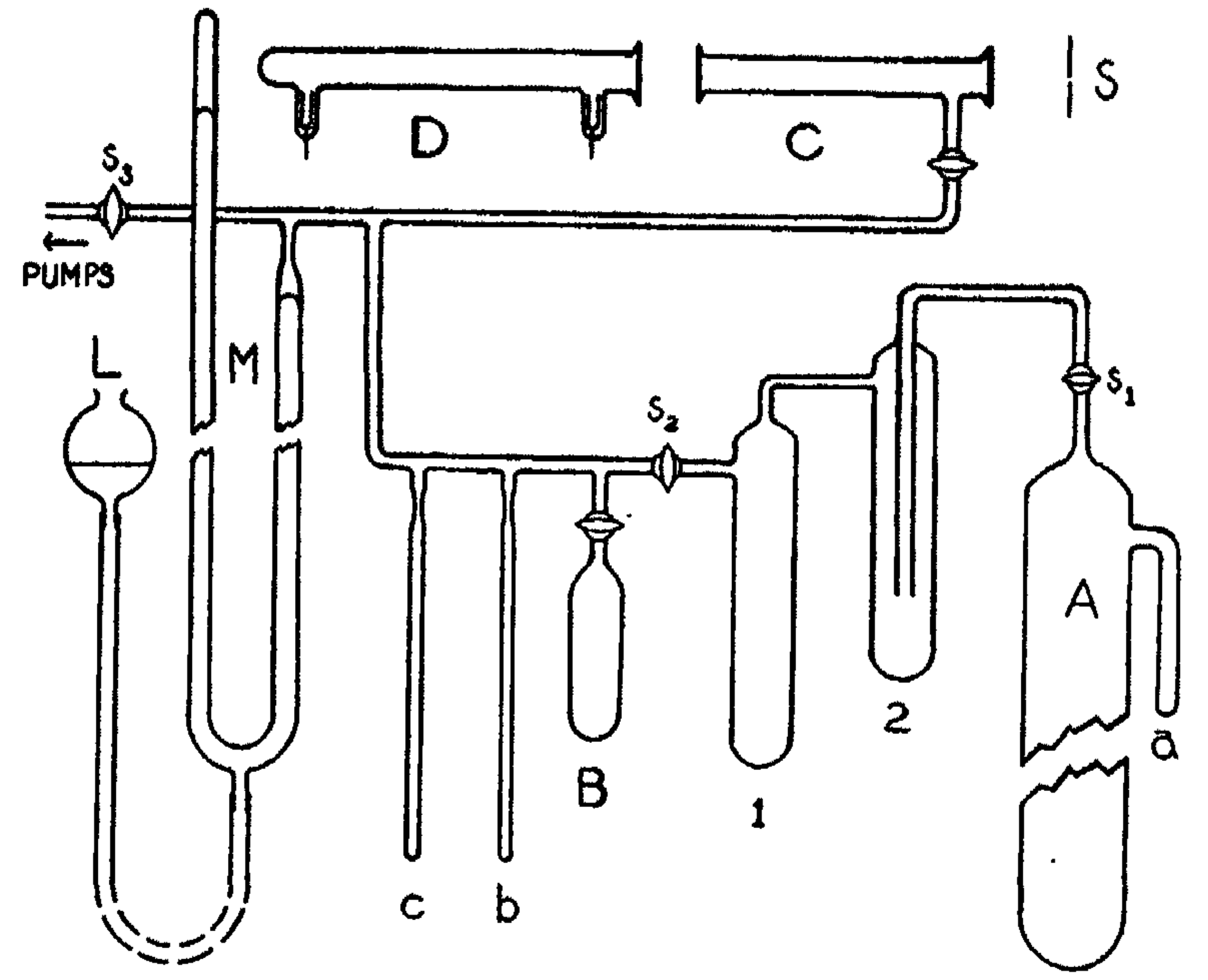

FIG. 1. The apparatus

To see whether appreciable quantities of other substances, which do not absorb in the region examined, are produced, the reaction mixture was passed twice through a carbon dioxide–acetone freezing mixture. Trap 1 was immersed in liquid air and trap 2 in the carbon dioxide plus acetone,

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[3] Spectra 2, 3, and 4 are but three of many such photographs taken at various pressures of benzene vapor.

after which stopcock s_1 was opened. When all the acetylene plus radon had condensed in 1 as indicated by M, the liquid air was transferred from trap 1 to side-arm a, and these gases collected in A. Presumably all substances which melt above about −70°C. were retained in trap 2. With s_1 and s_2 closed, the carbon dioxide–acetone recipient was removed, to reveal a thin deposit of a white crystalline solid which melted only after ten to fifteen minutes but which appeared to melt rather sharply. Droplets of liquid were observable on melting, although the liquid then vaporized, pointing to a rather high degree of volatility. By this procedure, the sensitivity of the examination is increased almost sixfold, since the container A is no longer a part of the space into which the vapor expands.

Connection was made with the absorption tube through s_2, and spectra 5, 6, and 7 photographed at pressures of 2.6 mm., 1.15 cm., and 2.7 cm., respectively, of vaporized liquid. Qualitative visual comparison with the benzene spectra (2, 3, and 4) pointed to partial pressures of benzene equal respectively to < 4.5 mm., < 2.5 cm., and 2.5 to 3.0 cm. In the absence of photometric observations, we are forced to conclude that the principal compound present in this liquid is benzene. The product was frozen in tube b, sealed by fusing the glass at the constriction, and preserved as a liquid (0.2 cc.) for future examination. The liquid was frozen by immersing the tube in a bath at −15°C., and then allowed to warm up slowly. The solid form melted between 6° and 7.5°C. This admittedly approximate measurement again points to the presence of benzene.

The demonstration was repeated with an initial acetylene pressure (in container A) of 85 cm. and 100 millicuries of radon. Five days after the mixture was introduced into A, the higher melting product was separated by freezing in the carbon dioxide–acetone paste as described above, and the absorption spectrum photographed (No. 8) at a pressure of 4.7 cm. Visual comparison with the spectra of pure benzene indicated the presence of more than 3 cm. Again we are led to believe that the product is chiefly benzene. This liquid was preserved by sealing in tube c.

An attempt was made to ascertain whether the benzene was produced by a reaction secondary to cuprene formation or whether it is an intermediate compound necessary to the production of cuprene. With this end in view the acetylene plus radon, freed from "benzene" and collected in container A after the first experiment, was permitted to stand for more than a month, after which time the decay of radon is practically complete and further polymerization has ceased. The initial pressure was thus about 48 cm. and the initial radon 11 millicuries. Stopcocks s_1 and s_2 were opened, thereby permitting the residual gas to expand into the evacuated absorption tube, and the spectrum photographed at a total gas pressure of 37 cm. (equivalent to 45 cm. in A). Again the absorption spectrum was that of benzene.

To make the test more sensitive, condensible products were frozen in trap 2 immersed in carbon dioxide-acetone, and the remaining gases collected in container A. A small pressure of 0.3 mm., presumably due to hydrogen (8), was observable even with side-arm a immersed in liquid air. After pumping off this permanent gas, the liquid air was transferred to trap 1, and the gas mixture again distilled through the carbon dioxide-acetone mixture. The acetylene was collected elsewhere and the carbon dioxide freezing bath removed. A thin film of solid was again in evidence. After melting and evaporation, connection was made with the absorption tube, and the spectrum photographed at a total pressure of 1.06 cm. of volatilized liquid. This spectrum (No. 9) corresponds to 0.6 to 0.7 cm. of benzene.

If we compare the yields of "benzene" for the two successive steps of the reaction, we find that the "benzene" production measured manometrically is proportional to the amount of radon decaying. Hence we must conclude that the reaction proceeds simultaneously with cuprene formation rather than being a step in the latter process. Table 1 shows the data pertaining to this calculation.

TABLE 1

Formation of "benzene"

Δt	RADON IN MILLICURIES	TOTAL PRESSURE OF "BENZENE"	$\frac{\text{"BENZENE" PRODUCED}}{\text{RADON DECAYED}}$
0	40	0	
7 days	11	2.7	0.093
> 1 month	0	1.06	0.096

Of course the acetylene used in these experiments was tested spectroscopically in the absence of radon. Spectrum 10 shows that no benzene vapor is present initially. In fact it is indistinguishable from the continuum (15 min. exposure) of the hydrogen lamp (No. 11). The iron arc is not shown.

It was found furthermore that benzene formation occurred under the influence of β-γ radiation as well. A cylindrical vessel similar to A, filled with stock acetylene but containing no radon, was placed 5 cm. from A. It is known (13) that β-radiation will cause acetylene to polymerize to cuprene. Actually the latter was observed in our vessel. In addition benzene was found to be present. Twelve days after placing the vessel near container A (with 100 millicuries of radon), the contents were permitted to expand into the absorption tube, and photograph 12 obtained at a pressure of 53 cm. in the entire system (container, traps, and absorption tube). This spectrum corresponds to about 1 mm. of benzene. The

Fig. 2. Absorption spectra

mechanism of the β-γ ray reaction thus appears to be the same as that of alpha-ray reactions.

Further experiments now in progress are designed to determine the relative velocities of benzene and cuprene formation, as well as the composition of the liquid product. Consequently a detailed discussion will be postponed until this project is terminated.

SUMMARY

Absorption spectra of acetylene polymerizing under the influence of radon were photographed. By this means the formation of benzene was demonstrated for both the alpha-ray and the beta-gamma ray reactions. That cuprene is not the only polymer produced in appreciable quantities was shown by freezing out in a carbon dioxide–acetone mixture a solid which proved to be a volatile liquid at room temperature. This liquid was chiefly benzene. It appears as a result of a reaction proceeding simultaneously with cuprene formation.

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THE CATALYTIC ACTIVITY OF COBALT SULFIDE FOR THE GAS-PHASE REDUCTION OF NITROBENZENE TO ANILINE

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In earlier studies on the catalytic activity of metals of the nickel group by Sabatier (5) and also by Brown and Henke (2) it was found that they were not satisfactory to use for the reduction of nitrobenzene to aniline. The difficulty lay in the fact that products representing excessive hydrogenation invariably resulted.

This study was suggested by a statement by Sabatier (6) that benzene could not be hydrogenated with a nickel catalyst if thiophene were present as an impurity. This meant that sulfur would inhibit the cyclo-forming property of a nickel catalyst. If this were true for nickel, it should also be true for cobalt. Other studies indicating that cobalt sulfide would reduce the hydrogenation power of catalysts have been made recently by Taylor (7), Tropsch (8), and Roberti (4). The first test of this conclusion was made by the treatment of a cobalt catalyst *in situ* with a stream of hydrogen sulfide gas. The results were so satisfactory that a cobalt sulfide catalyst was made, and it proved to be, in many ways, an excellent catalyst.

EXPERIMENTAL METHODS

The apparatus, preparation and purification of reactants, method of procedure, and analysis of products have been fully described and accepted as reliable in previous papers from this laboratory (3). The calibration of the flowmeter followed the method described by Brown and Hartman (1).

EXPERIMENTAL RESULTS

Pure cobalt catalysis

A pure cobalt catalyst was made from cobalt nitrate and the calculated amount of sodium hydroxide. The hydroxide was dried at 105°C. and ignited at 280°C. A catalyst so prepared, as well as one on an asbestos

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[1] This paper is constructed from a dissertation presented by Fred Albert Griffitts to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, June, 1936.

support, showed little activity (see table 1). The results given in table 1 are in accord with the findings of Brown and Henke (2).

Cobalt catalysts poisoned with hydrogen sulfide

The catalyst used in the following experiments was the same as that used to secure the data given in table 1, except that a stream of hydrogen sulfide gas had been passed through the furnace for fifteen minutes while the temperature was maintained at 260°C. After the passing of the hydrogen sulfide, the furnace was "washed" with hydrogen for thirty minutes before any reduction was attempted. Typical results from a poisoned catalyst are shown in table 2, which summarizes the conversion during forty-four runs.

TABLE 1

The effect of temperature on the activity of a cobalt catalyst

Temperature of reduction, 215°C.; weight of catalyst, 6.5 g.; rate of flow of hydrogen, 10 liters per hour; rate of flow of nitrobenzene, 2.3754 g. per hour

TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY
°C.	*per cent*
215	36.2[*]
260	5.0
250	
243	24.4
243	27.7[†]
235	32.2[†]

[*] All figures given represent rough averages, since excellent checks for low yields are not common.

[†] Rate of flow of nitrobenzene was 4.7509 g. per hour.

TABLE 2

Activity of a cobalt catalyst poisoned by hydrogen sulfide

Weight of catalyst, 6.5 g.; rate of flow of nitrobenzene, 4.7508 g. per hour; rate of flow of hydrogen, 10 liters per hour

NO. OF TRIAL	TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY
	°C.	*per cent*
1	260	43.5
13	272	77.6
14	272	77.3
29	272	100.1
40	272	98.3
41	268	86.9
42	268	94.4
44	268	81.5

Two points of special importance in table 2 are the gradual increase in per cent converted until the maximum was reached, and the fact that the excellent aniline-producing property was maintained so long. In this respect the sulfuretted catalyst was extremely different from the pure metal. No effort was made to determine the amount of sulfur that combined with the cobalt during the treatment. In all trials in which the yield was high the aniline was nearly free from impurities, as indicated by the clear color.

When the cobalt catalyst was treated with hydrogen sulfide before being used for reduction, the product in each run was clear and was apparently nearly pure aniline. The highest yield was at 262°C. (see table 3).

TABLE 3

The effect of treating a cobalt catalyst with hydrogen sulfide before using it for reduction

Temperature of reduction of oxide, 260°C.; temperature of treatment with hydrogen sulfide, 260°C.; rate of flow of nitrobenzene, 4.7508 g. per hour; rate of flow of hydrogen, 10 liters per hour; weight of catalyst, 6.5 g.

TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY*
°C.	*per cent*
262	98.5†
270	95.2
256	88.5
262	97.3

* Figures are the average of three to eight trials.

† Ten runs were made before data were taken.

Preparation of a cobalt sulfide catalyst from cobalt chloride and hydrogen sulfide

Catalyst A. Twenty-five grams of C.P. cobalt chloride ($CoCl_2 \cdot 6H_2O$) was dissolved in 200 ml. of water and treated with washed hydrogen sulfide gas; cobalt sulfide was precipitated slowly. A small quantity of potassium hydroxide was added every five or ten minutes to remove part of the hydrochloric acid formed by the double decomposition reaction. However, the solution was kept slightly acid to litmus throughout the preparation so that the sulfide would not contain any hydroxide, since its presence would result in the formation of metal after drying and reduction. The finely divided and pure black precipitate was washed thoroughly with water, dried at 110°C., and ignited for about thirty minutes at 320°C. This catalyst was treated, in the furnace, with hydrogen gas for about forty minutes before any nitrobenzene was fed into the furnace. No odor of hydrogen sulfide was detectable during the treatment with hydrogen, showing that hydrogen does not reduce cobalt sulfide at this temperature. Table 4 shows the best results from this type of catalyst.

Catalyst B. To study the effect of method of preparation on its activity a catalyst was made as follows: 35 g. of cobalt chloride was precipitated with hydrogen sulfide in acid solution (to prevent hydroxide formation), filtered, washed, and dried in an oven at 110°C. for sixteen hours. It was then placed in the hydrogenation furnace through which a stream of hydrogen was passing while the temperature was at 285°C. It was *not* ignited.

Eight grams of catalyst B at a temperature of 295°C. and under the usual test conditions gave a 95.8 per cent yield.

TABLE 4

Cobalt sulfide as a catalyst, type A

Weight of catalyst, 4.6 g.; rate of flow of hydrogen, 10 liters per hour; rate of flow of nitrobenzene, 2.3754 g. per hour; source of cobalt sulfide, cobalt chloride

TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY*
°C.	*per cent*
262	15.0
275	73.7
295	98.1
305	94.2
320	92.6
295	95.9

* Each figure in this column is the average of several runs.

The best individual yield secured over this catalyst was at 295°C. with a yield of 99.5 per cent. It was not possible, however, to get this value consecutively. When the catalyst was removed from the reaction tube into the air at 295°C., ignition occurred producing sulfur dioxide. This fact shows that at least part of the sulfur is not removed from the sulfide during the catalytic process involving forty or more experiments.

Cobalt sulfide from cobaltous acetate

When the chloride or nitrate of cobalt was used as the source for the preparation of a cobalt sulfide (by treatment with hydrogen sulfide) difficulty was encountered, owing to the solubility of cobalt sulfide in the acid formed. In all such preparations it was necessary to use a base to effect at least partial removal of the acid. This treatment was undesirable, owing to possible hydroxide formation. The acetic acid from an acetate is too weak to dissolve cobalt sulfide appreciably.

Twenty-eight grams of cobaltous acetate (C. P. grade) was dissolved in 700 ml. of water. This salt dissolves very slowly and special care must be taken to prevent a tendency to cake in small granules which enclose cobalt acetate and prevent its solution. If it is not entirely dissolved before the hydrogen sulfide treatment cobalt sulfide will form only on the surface. This will increase the salt content of the catalyst and cause it to be hard and gravel-like after drying. Also, a trace of the color of anhydrous cobalt salt can be detected. It is very difficult to remove the salt by washing because of the fine subdivision of the sulfide. After the ignition and reduction processes the occluded salt is changed to metal. The more nearly pure the sulfide, the more fluffy, porous, and black it will be.

The most satisfactory method of washing was as follows: the precipitated sulfide was washed on a suction filter with about 3 liters of cold distilled water. The residue was returned to a 1-liter beaker and suspended, with occasional stirring, in 700 ml. of water for thirty hours. This mixture was again filtered and washed with 3 liters of water, then dried at 110°C. for twenty-four hours. The weight of the product is usually between 5 and 10 g., depending upon the length of the hydrogen sulfide treatment. Owing to adsorbed and hydration water the compound is very voluminous while wet. After drying it is very porous with low apparent density. In all cases, after the catalyst was placed in the reaction chamber it was treated with a stream of hydrogen for about an hour, to saturate it thoroughly, before any nitrobenzene was passed over it.

About forty experiments were tried on catalysts made in the above manner by varying treatments after removal from the drying oven. Table 9 shows in compact form the properties of several catalysts made by the above method.

Cobalt sulfide catalysts from cobalt nitrate

Thirty-five grams of cobalt nitrate (Merck's, C. P. blue label, showing as the main impurity 0.6 per cent nickel) was dissolved in 200 ml. water and treated with washed hydrogen sulfide until precipitation was nearly complete. To accelerate the precipitation of the sulfide it was necessary to add a few drops of potassium hydroxide solution from time to time to remove the nitric acid formed during double decomposition. The cobalt sulfide was collected on a Büchner filter, washed thoroughly, dried for five hours at 110°C. and ignited for one hour at 320°C. The product was black, fluffy, and very finely divided.

A second catalyst was made in exactly the same manner as given above except for the ignition temperature, which was 295°C.

When the activity of each catalyst was tried under the same conditions of temperature (295°C.) and flow rate (4.7508 g. of nitrobenzene per hour and 10 liters of hydrogen per hour), the values given in table 5 resulted. These results show that the ignition temperature is a very important factor in determining the nature of a sulfide catalyst, the higher temperature evidently oxidizing part of the sulfur to sulfur dioxide and changing the cobalt to an oxide.

Variation of the conversion with the rate of hydrogen flow, rate of nitrobenzene flow, and temperature of roasting

To ascertain the influence of the rate of hydrogen flow (see table 6) cobalt sulfide (from the chloride) was dried fourteen hours at 110°C. and then treated with hydrogen for thirty minutes at 295°C. before testing. During the hydrogen treatment a quantity of water collected in the adapter, showing either that some oxide was being reduced or that some bound water was being expelled.

TABLE 5

Showing the effect of temperature of ignition of cobalt sulfide made from cobalt nitrate

TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY*
°C.	*per cent*
295	93.6
320	75.0

* Each figure is the average of three to eight trials.

TABLE 6

Effect of rate of flow of hydrogen on the per cent yield of aniline

Catalyst, cobalt sulfide from the chloride; weight of catalyst, 6.8 g.; rate of flow of nitrobenzene, 4.7508 g. per hour; temperature of catalyst, 295°C.

RATE OF FLOW OF HYDROGEN IN LITERS PER HOUR	PER CENT OF HYDROGEN REQUIRED BY THEORY	YIELD OF ANILINE IN PER CENT OF THEORY*
12	465	93.5
7	271	95.2
24	930	91.8
4	150	93.7

* Each figure in this column is the average of four to eight trials.

TABLE 7

Effect of flow rate of nitrobenzene on the yield of aniline

Catalyst, cobalt sulfide from the chloride; weight of catalyst, 6.8 g.; temperature, 295°C.; rate of flow of hydrogen, 7 liters per hour

TIME IN MINUTES REQUIRED FOR 2.3754 G. OF NITROBENZENE TO FLOW	RATE OF FLOW OF NITROBENZENE PER HOUR	YIELD OF ANILINE IN PER CENT OF THEORY*
60	2.3754	96.4
12	11.8770	91.3
25	5.7009	93.6
50	2.8505	94.9
120	1.1877	87.6
6	23.7540	78.0†

* Each figure in this column is the average of three to five trials.

† The rate of hydrogen flow was increased to 15 liters per hour in order to furnish enough to reduce 23.7540 g. and have some in excess of theory.

The best flow rate indicated by the data in table 6 is 7 liters per hour. This result is a bit unexpected, because often a larger per cent excess of hydrogen is required over other catalysts to give a similar conversion.

The study of the data in table 7 shows not only that cobalt sulfide is a good catalyst, but that it has the additional quality of being capable of giving high yields at rapid rates of nitrobenzene flow. The optimum flow rate of nitrobenzene was at 2.3754 g. per hour, but much more rapid rates still gave good yields.

TABLE 8

To show the effect of ignition temperature on yield

Catalyst, cobalt sulfide from the chloride; weight of catalyst, 6 to 7 g.; temperature of catalyst, 295°C.; rate of flow of nitrobenzene, 4.7508 g. per hour; rate of flow of hydrogen, 10 liters per hour

TEMPERATURE OF IGNITION	YIELD OF ANILINE IN PER CENT OF THEORY*
°C.	*per cent*
325	90.5
340	82.2
315	90.9
306	96.4
300	95.9
291	91.4
287	76.2

TABLE 9

To show the effects of different methods of ignition

Catalyst, cobalt sulfide from cobaltous acetate; temperature of operation, 325°C.; rate of flow of hydrogen, 10 liters per hour; rate of flow of nitrobenzene, 4.7508 g. per hour

CATALYST NO.	CATALYST WEIGHT	TEMPERATURE OF IGNITION	YIELD OF ANILINE	NUMBER OF EXPERIMENTS IN EACH PER CENT
	grams	°C.	*per cent*	
1	8.6	In air 290	97.4	8
2	9.0	In air 292	97.9	5
3	8.5	In H_2 325	97.3	5
4	6.5	In H_2 325	97.2	7

In table 8 the data were secured over catalysts made as nearly as possible in exactly the same manner. Use was made of 35 g. of the C. P. grade of cobaltous chloride and hydrogen sulfide gas. The quantity of catalyst employed in the following tests was nearly the same in all cases, usually 6 to 7 g. It was customary to dry the catalyst about ten hours at 110°C.

before igniting. Thorough washing of these sulfide catalysts cannot be fully accomplished with much less than 6 liters of water to 6 g. of catalyst.

The best temperature for igniting the catalyst is in the 15° range from 291° to 306°C. Excellent yields have been obtained where the ignition was within this range. It was found during these studies that the point at which cobalt sulfide will ignite and burn is between 306° and 320°C. This reaction evolves sulfur dioxide and forms an oxide of cobalt. The temperatures in table 8 were taken with a thermometer held immersed in the catalyst. The catalyst was in an open dish supported so there would be no superheating by contact with the floor of the muffle furnace.

The data in table 9 show a remarkable agreement for per cent yields of aniline over cobalt sulfide catalysts that have received different treatments. It also gives the final proof that this compound belongs in the class of better aniline-producing catalysts. The chief factors seem to be relative freedom from metallic cobalt, temperature of operation, and the temperature of ignition.

One important question about sulfide catalysts involves the status of the sulfur during its operation: does it remain in the form of the metallic sulfide, or is it oxidized by the nitrobenzene and dispelled as sulfur dioxide? It should be noted that sulfide catalysts after use are very pyrophoric. They will ignite and evolve sulfur dioxide if removed from the hot furnace and exposed to air. This fact shows that the sulfur is not dispelled during use. The pyrophoric quality might be due to the presence of adsorbed hydrogen or nitrobenzene, or possibly to the removal of adsorbed water.

SUMMARY

1. Metallic cobalt has been made a good aniline-producing catalyst by treatment with hydrogen sulfide.

2. Methods are given for the preparation of cobalt sulfide catalysts by the use of different salts as the starting material. Cobaltous acetate is the most convenient substance to use as a starting material.

3. Data are given to show the optimum conditions of operation of cobalt sulfide catalysts.

4. A properly prepared and operated cobalt sulfide catalyst will give, without difficulty, a 97 to 99 per cent yield of aniline.

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THE INTERFACIAL TENSIONS OF SOME MERCURY-HYDROCARBON OIL SYSTEMS

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A study of the literature in the field of lubrication seems to indicate that when an adequate theory of the lubricating action of oils is developed, an important place must be given to the physicochemical relations of bearing surface to lubricant. According to Wilson and Barnard (3) only a very small part of a lubricating oil is actually active as a true lubricant, the rest of the oil acting as a diluent and carrier of the components that are active at the bearing surface. It is to be expected that these active components would have a significant effect upon the surface energies resident in the interface between the lubricant and the bearing, hence the present investigation was initiated in order to study the interfacial tensions of mercury–oil systems in the hope that those metal–oil interfaces would show some characteristics indicative of the surface-active components. While it may not be assumed that the behavior of the oil at the mercury surface is precisely the same as at the surface of bearing metals, as has been pointed out by other writers, somewhat analogous interactions may be expected.

EXPERIMENTAL

Interfacial tension measurements were made with an apparatus similar to that described by Harkins and Brown (1).

Drops of mercury were allowed to fall from the tip of a carefully ground and calibrated glass tube, the drops being formed under the surface of a sample of the oil being studied. From the weight of these drops the interfacial tension of the mercury–oil interface was calculated, using the method and the correction factor developed by the above authors. The calculation of the interfacial tension was made by the use of the equation:

$$\gamma_i = \frac{mg}{2\pi r\phi}\left(\frac{D_{\mathrm{Hg}} - D_{\mathrm{oil}}}{D_{\mathrm{Hg}}}\right)$$

in which m is the mass per drop in grams, r is the radius of the capillary tip in centimeters, ϕ is the correction factor expressed as

$$\psi\left(\frac{r}{V^{1/3}}\right)$$

by Harkins and Brown, and D refers to the density of oil or mercury, while π and g are the usual constants. It is desirable in making these measurements that the capillary tip used be of such dimensions that the value of ϕ does not vary greatly in the range of the work undertaken.

TABLE 1

Densities of the oils at 0°C.

OIL	DENSITY
	grams per cc.
Oil No. 1	0.8943
Oil No. 2	0.8952
Oil No. 3	0.8919
Oil No. 4	0.8960
Oil No. 5	0.9561
Oil No. 6	0.9320

TABLE 2

Interfacial tension data for the system mercury-oil No. 1

TEMPERATURE	WEIGHT OF MERCURY PER DROP	$r/V^{1/3}$	ϕ	INTERFACIAL TENSION
°C.	*grams*			*dynes per cm.*
25	0.1655	0.428	0.674	364
50	0.1644	0.428	0.674	362
75	0.1633	0.428	0.674	360
100	0.1622	0.428	0.674	358
125	0.1607	0.428	0.674	355

TABLE 3

Interfacial tension data for the system mercury-oil No. 2

TEMPERATURE	WEIGHT OF MERCURY PER DROP	$r/V^{1/3}$	ϕ	INTERFACIAL TENSION
°C.	*grams*			*dynes per cm.*
25	0.1652	0.428	0.674	364
50	0.1636	0.429	0.674	360
75	0.1626	0.429	0.674	358
100	0.1611	0.429	0.674	356
125	0.1583	0.431	0.673	350

That this was accomplished in the present investigation is indicated by the values given in tables 2 to 7 inclusive. The radius of the tip used was 0.0985 cm.

The interfacial tension was determined for each oil investigated, at 25° intervals from 25° to 125°C. Efforts to extend the determinations to

TABLE 4

Interfacial tension data for the system mercury-oil No. 3

TEMPERATURE	WEIGHT OF MERCURY PER DROP	$r/V^{1/3}$	ϕ	INTERFACIAL TENSION
°C.	*grams*			*dynes per cm.*
25	0.1566	0.435	0.672	340
50	0.1510*	0.440	0.670	335
75	0.1470	0.443	0.669	326
100	Max. 0.1494	0.440	0.670	332
	Min. 0.1443	0.446	0.668	322
125	Max. 0.136	0.454	0.666	302
	Min. 0.126	0.465	0.662	283

TABLE 5

Interfacial tension data for the system mercury-oil No. 4

TEMPERATURE	WEIGHT OF MERCURY PER DROP	$r/V^{1/3}$	ϕ	INTERFACIAL TENSION
°C.	*grams*			*dynes per cm.*
25	0.1576	0.435	0.672	348
50	0.1553	0.436	0.672	343
75	Max. 0.1530	0.438	0.671	339
	Min. 0.1510	0.439	0.670	335
100	Max. 0.1487	0.441	0.670	330
	Min. 0.1546	0.444	0.669	324
125	Max. 0.1438	0.445	0.669	320
	Min. 0.1337	0.456	0.665	299

TABLE 6

Interfacial tension data for the system mercury-oil No. 5

TEMPERATURE	WEIGHT OF MERCURY PER DROP	$r/V^{1/3}$	ϕ	INTERFACIAL TENSION
°C.	*grams*			*dynes per cm.*
25	0.1541	0.438	0.671	339
50	0.1509	0.440	0.670	332
75	0.1510	0.439	0.670	334
100	Max. 0.1491*	0.441	0.670	330
	Min. 0.1451	0.445	0.669	321
125	Max. 0.1330*	0.457	0.665	297
	Min. 0.1230	0.467	0.662	281

TABLE 7

Interfacial tension data for the system mercury-oil No. 6

TEMPERATURE	WEIGHT OF MERCURY PER DROP	$r/V^{1/3}$	ϕ	INTERFACIAL TENSION
°C.	*grams*			*dynes per cm.*
25	0.1541	0.438	0.671	339
50	0.1510	0.440	0.670	332
75	0.1457	0.444	0.669	325
100	Max. 0.1455	0.444	0.669	322
	Min. 0.1424	0.448	0.668	315
125	Max. 0.1419	0.447	0.668	314
	Min. 0.1350	0.455	0.665	302

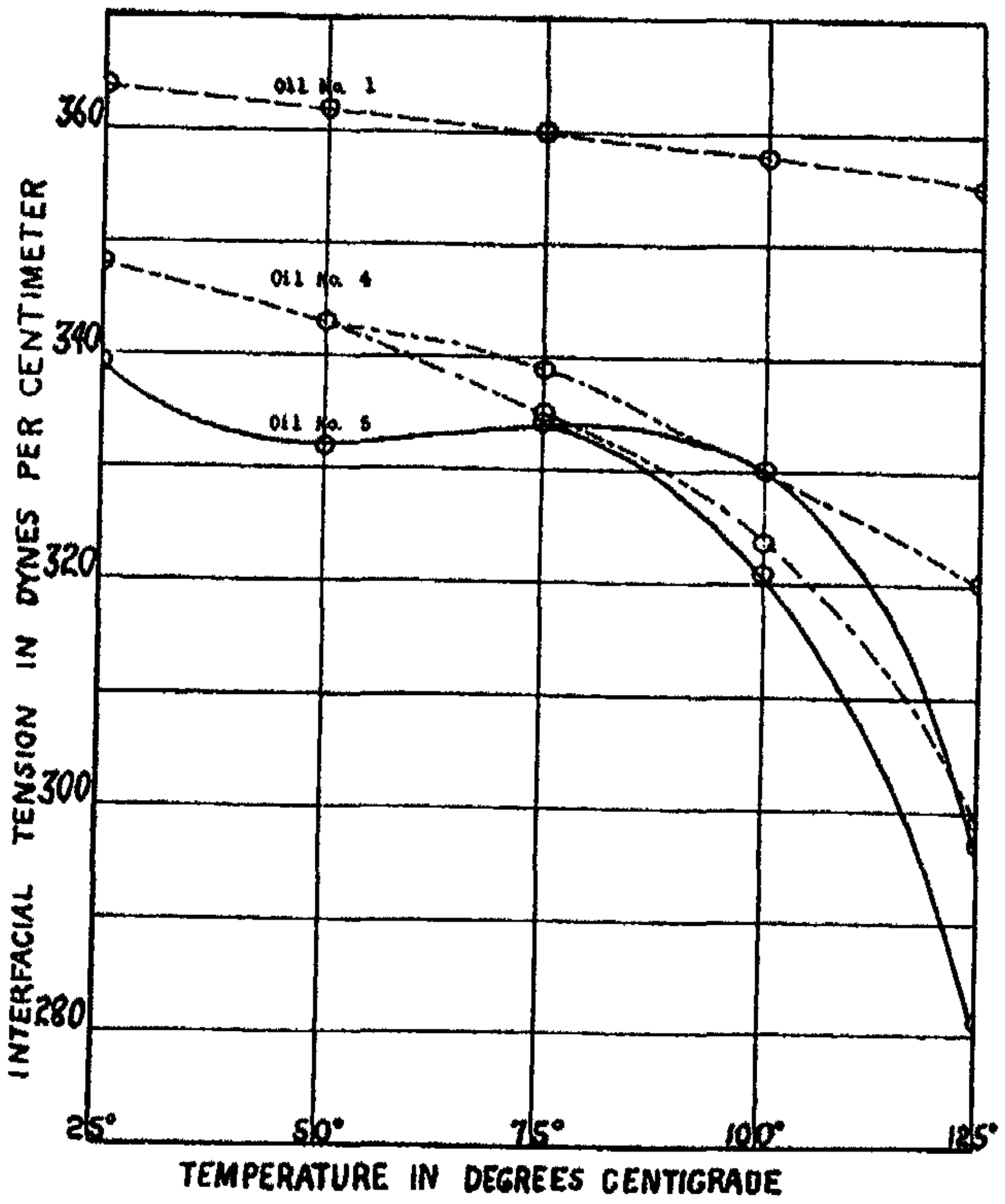

FIG. 1. Interfacial tension data versus temperature from table 2 (oil No. 1), table 5 (oil No. 4), and table 6 (oil No. 5).

temperatures above 125°C. were ineffectual, owing to the tendency of the oil to creep up the inside of the capillary tube at the higher temperatures. The effect of different rates of drop formation was also studied, though the range found permissible for this variable was limited, owing again to the tendency of the oil to creep into the tube when the drops were allowed to form slowly.

The tables and figure show the data obtained from a study of six samples of oils. Referring to the tables, oils 1 and 2 were refined white medicinal oils and oils 3 to 6 inclusive were representative samples of motor oils. The motor oils were all of the same viscosity rating. From the beginning, the apparently justifiable assumption was made that the refined white oils were inferior to the motor oils in lubricating value.

In table 1 are given the densities of the six oils used. It was found for all of them that as the temperature was increased the density decreased by a constant, the value of which is 0.00062 g. per cubic centimeter per degree Centigrade. Tables 2 to 7 inclusive present the interfacial tension data for the six oils. Except for a few cases the drop-weight values represent an average of from two to six determinations, and each determination represents the average of a ten-drop sample. Except for three cases the ± variation from the mean value of the drop weight in duplicate runs was within 1 per cent. In the three cases (indicated in the tables by an asterisk) the maximum variation from the mean was greater than 1 but within 2 per cent. The data from tables 2, 5, and 6 are shown graphically in figure 1. These curves show all of the characteristics of the six oils, since a comparison of the tables will show that oil No. 1 is quite similar to No. 2, No. 4 to No 6, and No. 5 to No. 3.

DISCUSSION

The tables show single values for the mercury–oil interfacial tensions of oils No. 1 and No. 2 at each temperature throughout the range investigated and also for the other four oils through the lower range of temperature. The latter, Nos. 3 to 6 inclusive, showed, however, from the measurements made, that through the upper temperature range the interfacial tension decreased as the time of contact of the mercury with the oil increased. As mentioned above, an attempt was made to follow this decrease with time, but this was partially frustrated by the tendency of the oil to creep into the capillary tip of the drop-weight apparatus. In consequence only two values of the drop-weights and therefore of the interfacial tensions at each of the temperatures at which this decrease was observed were recorded. In the case of each of these pairs of values the maximum corresponds to the drop weight obtained with the minimum time of contact, while the minimum was obtained with the maximum time. The minimum time period allowed for the formation of the drop of mercury at each temperature was approximately 0.5 minute while the maximum time period was 2.5 minutes. It should be noted that in carrying out the determinations the final stages of drop formation were accomplished at as nearly as possible the same rate in all cases. The time differences indicated are due to the different rates at which the drops were brought up to about 90 per cent of their full size. This procedure was necessary in order that at the moment of rupture of the drop from the mercury column in the capillary tip the mercury would be entering the drop so slowly that its mass kinetic energy would be a negligible factor in determining the drop detachment. In all the cases for which single values for the interfacial tensions are recorded no measurable change could be detected as a result of the different rates of drop formation. It is probably not true that the time factor is without effect in these cases, but within the time interval permitted by these experiments by the limitation mentioned above, any variations that may have occurred were smaller than the experimental errors of measurement.

The refined white oils throughout most of the temperature range investigated exhibit mercury–oil interfacial tensions that are approximately straight line functions of the temperature. The motor oils, in sharp distinction, show first a moderately rapid decrease, then a range of temperature in which there is relatively little change, followed by a more rapid decrease. Two of the motor oils show distinct maxima in the interfacial tension–temperature curves in the middle range of temperature.

Wilson and Barnard (3) and also Rhodes and Lewis (2) conclude that adsorption takes place from a lubricating oil on a bearing surface and that this adsorption requires some time for completion. If similar adsorption is taking place at the mercury–oil interface it must certainly be accompanied by a change (a decrease) in the interfacial tension. The changing values at the higher temperatures shown in the tables and by the branched curves are in agreement with this concept. The constancy of the values at the lower temperatures probably means only that the adsorption is so slow that, as was suggested above, these measurements were unable to show it. Since the refined white oils investigated do not, even at the higher temperatures, show evidence of the adsorption process, it is clearly indicated that these oils are much poorer in adsorbable components than the motor oils. It is further indicated by the form of the curves for the motor oils that in the neighborhood of 75°C. some of the more rapidly adsorbed components are broken down, permitting higher interfacial tensions than the values at lower temperatures would indicate should be expected.

SUMMARY

1. Measurements of the mercury–oil interfacial tension have been made on six different systems, to wit, four mercury–lubricating oil and two

mercury-refined white oil systems. Measurements were made at 25° intervals from 25°C. to 125°C.

2. The refined white oils with the mercury show an approximately linear relation between the interfacial tension and the temperature. On the other hand the motor oils show, for this relation, data which seem to indicate a characteristic interaction between such oils and the mercury surface.

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THE MERCUROUS ACETATE ELECTRODE

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INTRODUCTION

The object of this study was to determine whether the electrode $Hg \mid Hg_2(OAc)_2, OAc^-$ would function as a reversible acetate electrode. One test of such reversibility is the constancy of the standard E.M.F. of the electrode when it is measured at various acetate ion activities.

The cell chosen for this study was

$$\begin{array}{llll} Pt \mid & HOAc, & HOAc\ , & Hg_2(OAc)_2 \mid Hg \\ & \text{(Satd. with} & \text{(Satd. with} & \text{(solid)} \qquad\qquad \text{I} \\ & \text{quinhydrone)} & Hg_2(OAc)_2) & \end{array}$$

This cell was chosen because it is simple to make up and measure. The quinhydrone electrode is known to be reliable in solutions whose hydrogen-ion concentrations are of the order of magnitude of those in acetic acid solutions.

Previous studies of the mercurous acetate electrode were not made with the purpose of evaluating its standard E.M.F. Nernst (9) studied the cell

$$Hg \mid Hg_2(OAc)_2,\ KOAc \mid KNO_3 \mid KOAc,\ Hg_2(OAc)_2 \mid Hg \qquad \text{II}$$

in a study of concentration cells. Bugarszky (3) studied the cells:

$$\begin{array}{llllll} Hg \mid Hg_2(OAc)_2, & KOAc \mid & KOAc \mid & KOAc, & KBr, & Hg_2Br_2 \mid Hg \quad \text{III} \\ \text{(solid)} & 1.0M & 1.0M & 1.0M & 0.01M & \text{(solid)} \end{array}$$

$$\begin{array}{llllll} Hg \mid Hg_2(OAc)_2, & KOAc \mid & KOAc \mid & KOAc, & KI\ , & Hg_2I_2 \mid Hg \quad \text{IV} \\ \text{(solid)} & 1.0M & 1.0M & 1.0M & 0.01M & \text{(solid)} \end{array}$$

$$\begin{array}{llllll} Hg \mid Hg_2(OAc)_2, & KOAc \mid & KOAc \mid & KOAc, & KOH, & Hg_2O \mid Hg \quad \text{V} \\ \text{(solid)} & 1.0M & 1.0M & 1.0M & 0.01M & \text{(solid)} \end{array}$$

At 18.5°C., he found for cells III, IV, and V electromotive forces of −0.2474, −0.4277, and −0.2626 volts, respectively.

From these data, it is possible to calculate the standard E.M.F. for the mercurous acetate electrode, $E^0_{Hg_2(OAc)_2}$, if the standard E.M.F.'s for the mercurous bromide, iodide, and oxide electrodes are known, as well as the activity coefficients of the salts involved. The standard E.M.F.'s of the mercurous bromide and iodide electrodes are $E^0_{Hg_2Br_2} = -0.1385$ v., and $E^0_{Hg_2I_2} = +0.0416$ v. (6). The standard E.M.F. of the mercurous oxide electrode, $E^0_{Hg_2O}$, equals −0.13 v. (1). Values for the activity coefficients of the salts must be estimated, since data for 0.01 molar potassium bromide, potassium iodide, or potassium hydroxide in 1 molar potassium acetate solutions are not available. Randall, McBain, and White (10) give the value 0.699 for the molal activity coefficient for 1.0 molal potassium acetate; this is an average value between 0° and 90°C. For potassium bromide and potassium iodide in 1 molal solutions, Harned and Douglas (4) give $\gamma = 0.613$ and $\gamma = 0.649$, respectively, at 25°C. At the same temperature, Scatchard (11) finds $\gamma = 0.743$ for 1 molal potassium hydroxide.

In the calculations, we may assume that the activity coefficients of potassium bromide, potassium iodide, or potassium hydroxide in the solutions in which they are 0.01 molar and in the presence of 1.0 molar potassium acetate are the same as the coefficient for 1.0 molar potassium acetate; on the other hand, we may assume that the activity coefficients are the same as in 1.0 molar potassium bromide, potassium iodide, or potassium hydroxide. Neither of these assumptions is very likely to be correct. Using the first alternative, we obtain from cells III, IV, and V., $E^0_{Hg_2(OAc)_2} = -0.5016$, -0.5018, and -0.50_8 volts, respectively. By the second means, there result the values -0.5049, -0.5040, and -0.50_7 volts from the same three cells. The data of Bugarszky therefore indicate a value of about −0.50 volt for the standard E.M.F. of the mercurous acetate electrode.

MATERIALS AND APPARATUS

Grasselli C.P. glacial acetic acid was used. It was refluxed with chromic oxide (2 g. to 100 cc. of the acid) and distilled.

The mercury used was a commercial product. It was washed first by allowing it to fall from a capillary tip through a 1-meter column of diluted nitric acid (1 part of acid to 4 parts of water), and then in the same way with distilled water. It was next dried by allowing it to run through a filter paper with a hole punched in the apex of the cone. The mercury was then distilled in a current of air under reduced pressure.

Mercurous acetate was made by precipitation from approximately one-tenth normal solutions of mercurous nitrate and potassium acetate. Preparations were made in which the mercurous nitrate contained excess nitric acid, and when it did not. They gave identical results in the cells.

The salt was washed by decantation, collected on a Büchner funnel, air-dried, and stored over anhydrous calcium chloride.

The quinhydrone was prepared by the method of Biilmann and Lund (2) and was recrystallized from water at 60°C.

The water used in the preparation of the solutions was of "conductivity" grade.

For the E.M.F. measurements, a Leeds and Northrup type K potentiometer, a Leeds and Northrup type R galvanometer, and an Eppley cell of the unsaturated type were used. The constant-temperature water bath was at a temperature of 25.00 ± 0.03°C. The temperature was determined by comparison with a thermometer calibrated by the U. S. Bureau of Standards.

The cell-vessels were of Pyrex glass. They were of the customary type. The cell-vessel used for the mercurous acetate electrodes had a stopcock in the side arm to prevent diffusion of mercurous ions into the solution containing quinhydrone. Junction between the two half-cells was made in a small beaker outside the thermostat. Bright platinum electrodes were used in the quinhydrone half-cell.

TABLE 1

Experimental data

C	E	C	E
0.05002	0.1651	0.4138	0.1154
0.07485	0.1565	0.4992	0.1104
0.09956	0.1495	0.7509	0.1001
0.1497	0.1401	0.9943	0.0931
0.2094	0.1315	1.495	0.0826
0.3021	0.1236	2.058	0.0743

The cells were measured in duplicate, and were constant in E.M.F. over a period of at least six hours, when measurements were discontinued. Constancy was usually attained within an hour after making up the cells. Preliminary experiments showed that if the quinhydrone half-cell were renewed each day, the E.M.F. of the cell was constant over a period of several days. The E.M.F. of duplicate cells never differed by more than 0.15 mv.

The acetic acid solutions were analyzed volumetrically with carbonate-free sodium hydroxide, using phenolphthalein as indicator. The solutions more concentrated than 0.15 molar were diluted in calibrated volumetric flasks, and aliquot portions of the diluted solutions were analyzed.

EXPERIMENTAL DATA

Table 1 gives the experimentally observed data; C represents the moles of acetic acid per liter of solution, and E is the electromotive force. The mercury pole was the positive one.

CALCULATION OF THE STANDARD E.M.F.

The values of E in table 1 can be converted to the value of the E.M.F. of the cell,

$$\underset{p\,=\,1\text{ atm.}}{(\text{Pt})\,|\,\text{H}_2},\quad \text{HOAc},\quad \text{Hg}_2(\text{OAc})_2(s)\,|\,\text{Hg} \qquad \text{VI}$$

E_{H}, by adding to them 0.6992 volt, the value of the standard E.M.F. of the quinhydrone electrode (5). The E.M.F. of the left half-cell of cell VI is given by

$$E_L = 0 - \frac{RT}{F}\log_e a_1 \qquad (1)$$

where a_1 is the activity of hydrogen ions in the acetic acid solution. The E.M.F. of the right half-cell is given by

$$E_R = E^0 + \frac{RT}{F}\log_e a_4 \qquad (2)$$

where a_4 stands for the activity of acetate ions in the acetic acid solution saturated with mercurous acetate. If a_2 represents the activity of acetate ions in the acetic acid solution, and a_3 that of hydrogen ions in the acid solution saturated with mercurous acetate, the liquid junction E.M.F. between the two solutions will be given by

$$E_j = n_c\frac{RT}{F}\log_e\frac{a_1}{a_3} + n_a\frac{RT}{F}\log_e\frac{a_4}{a_2} \qquad (3)$$

where n_c and n_a represent the transference numbers of cation and anion, respectively. Now, approximately $a_1a_2 = a_3a_4$, so that $\frac{a_1}{a_3} = \frac{a_4}{a_2}$; and

$$E_{\text{H}} = E_L - E_R + E_j = -E^0 - \frac{RT}{F}\log_e a_3a_4 \qquad (4)$$

or, since

$$K = \frac{a_{\text{H}^+}\cdot a_{\text{OAc}^-}}{a_{\text{HOAc}}} \cong \frac{a_3a_4}{C(1-\alpha)} \qquad (5)$$

if the activity coefficient of undissociated molecules is unity, we have

$$\begin{aligned} E_{\text{H}} &= -E^0 - \frac{RT}{F}\log_e KC - \frac{RT}{F}\log_e(1-\alpha) \qquad (6)\\ &= E + 0.6992 \end{aligned}$$

In table 2 are given results of calculations of E^0 from this equation. The column headed $E^{0\prime}$ gives values of

$$E^{0\prime} = -\left(E_{\mathrm{H}} + \frac{RT}{F}\log_e KC\right) = -\left(E + 0.6992 + \frac{RT}{F}\log_e KC\right) \quad (7)$$

and E^0 gives

$$E^0 = -\left(E_{\mathrm{H}} + \frac{RT}{F}\log_e KC + \frac{RT}{F}\log_e (1 - \alpha)\right) \quad (8)$$

Values of α were approximated from the relation

$$\alpha = \sqrt{\frac{K'}{C}} \quad (9)$$

TABLE 2

E^0 calculated from equation 6

C	E_{H}	$E^{0\prime}$	E^0
0.05002	0.8643	−0.5062	−0.5067
0.07485	0.8557	−0.5079	−0.5083
0.09956	0.8487	−0.5082	−0.5085
0.1497	0.8393	−0.5093	−0.5096
0.2094	0.8307	−0.5103	−0.5105
0.3021	0.8228	−0.5108	−0.5110
0.4138	0.8146	−0.5107	−0.5109
0.4992	0.8096	−0.5105	−0.5107
0.7509	0.7993	−0.5107	−0.5108
0.9943	0.7923	−0.5109	−0.5110
1.495	0.7818	−0.5107	−0.5108
2.058	0.7735	−0.5108	−0.5109

where K' is the dissociation constant for acetic acid, and has the value 1.8×10^{-5} (7). K in equations 6, 7, and 8 is the thermodynamic dissociation constant, and at 25°C. has the value 1.753×10^{-5} (8). The difference between the values in the third and fourth columns of table 2 gives the value of the term

$$\frac{RT}{F}\log_e (1 - \alpha) \cong \frac{\alpha RT}{F}$$

The E^0 values calculated in this way are uncertain in the more dilute solutions, since no allowance for the solubility of the mercurous acetate has been made. The effect of this solubility will be less at higher acid concentrations because in this case the solubility is smaller, and because the contribution of acetate ions from the mercurous acetate is relatively less.

Apparently at an acetic acid concentration of 0.3 molar and above, the effect of the solubility of mercurous acetate upon the degree of dissociation is less than the experimental error in the measurements. Accordingly, the data in this range are considered to give the true value of E^0.

SUMMARY

1. The electromotive forces of the cell

$$\begin{array}{llll} \text{Pt} \mid & \text{HOAc} \quad , & \text{HOAc} \quad , & Hg_2(OAc)_2 \mid Hg \\ & (\text{Satd. with} & (\text{Satd. with} & (\text{solid}) \\ & \text{quinhydrone}) & Hg_2(OAc)_2) & \end{array}$$

have been measured at 25°C., at concentrations of acetic acid varying from 0.05 molar to 2.0 molar.

2. From these data the standard E.M.F. of the electrode $Hg \mid Hg_2(OAc)_2, OAc^-$ has been found to be -0.5109 ± 0.0002 volt at 25°C.

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X-RAY STUDY OF THE STRUCTURE OF COPPER, LEAD, CADMIUM, AND ANTIMONY AT HIGH TEMPERATURES

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Indirect evidence for transitions in the structure of some of the common metals has been cited as proof of such transitions. In some cases direct x-ray examination of the structure of the metals at high temperatures has been made. Nevertheless, in view of the present interest in the metallic state and in the structure of alloys, the need for further and more complete investigations was apparent.

The fact that a metal may exhibit one structure at two different temperatures and yet exist in a second form at intermediate temperatures was not taken into consideration in some of the previous studies. Only by using a camera (9) by means of which the structure could be determined at temperatures readily measurable and controllable was this oversight eliminated. This control in temperature permitted the taking of spectrograms within reasonably small limits of temperature on either side of a supposed transition, with the assurance that the temperatures were those vital to the investigation.

For the x-ray source a self-rectifying gas x-ray tube (10) already described in the literature was used. Throughout the investigation the K_α and K_β lines of copper were employed. The metals copper, lead, cadmium, and antimony were studied with the aid of the camera and x-ray tube developed by us. The frequent occurrence in the literature of calculations from Debye–Scherrer spectrograms of the structure of copper, lead, and cadmium prompted their omission in this article. For these metals only the results are given. In the case of antimony, analyzed heretofore only by the Bragg method, the analysis is included.

I. COPPER

In a series of articles E. Cohen and his coworkers (6, 8) reported that copper has more than two allotropic modifications, stating that one of the transitions occurs within 69.2°C. to 71.7°C. These conclusions were

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drawn from dilatometric and density experiments. From high pressure studies E. Jänecke (14) had evidence of a transition in the range of 66°C. to 103°C. E. Owen and G. D. Preston (18) found it necessary to assume that copper has a second modification in order to explain the β-phase of a zinc–copper alloy. The lattice constant of copper at 475°C. was determined by L. Vegard and Kloster (22), but no investigation of the structure from room temperature to 475°C. was made.

Electrolytic copper in the form of a No. 28 wire was used as a sample. In this case as well as in all subsequent cases the sample was held at the required temperature for at least three hours before irradiation was started. Spectrograms of copper were taken at approximately every fifty degrees from room temperature to 420°C. No change in the position or relative intensity of the lines occurred. Throughout this range copper has a face-centered cubic lattice. No transitions occur. However, in addition to a slight expansion of the lattice the size of the individual crystallites becomes greater at the higher temperatures, as the spotting of the spectrogram illustrates.

II. LEAD

E. Cohen and W. D. Helderman (5) claim they have evidence for the existence of more than two forms of lead. From high pressure studies E. Jänecke (14) concluded that a transition occurs between 59°C. and 62°C. Dilatometric evidence, according to Travers and Houout (21), indicates three modifications of lead, one stable above 180°C. and the remaining two stable below this temperature. P. Saldau (19) claims he has evidence of a transition occurring between 155°C. and 160°C.

Spectrograms of lead in the form of a wire (approximately No. 28) were taken at room temperature, 80°C., 175°C., and 185°C. No change in either the position or intensity of the lines was observed. Throughout this range lead has a face-centered cubic lattice. No transitions occurred. These results are in agreement with those of Washiro Eda (11).

III. CADMIUM

In a series of articles E. Cohen and W. D. Helderman (3) claim that density and dilatometric investigations on cadmium prove the existence of a transition at 64.9 ± 0.1°C. Continuing this study they found that the transition temperature was a function of the previous heat treatment and explained this fact by assuming that more than two allotropic modifications of cadmium exist. Electromotive force experiments led to the same conclusions. The transition $Cd_\alpha \rightleftarrows Cd_\beta$ was deduced to lie between 25°C. and 65.5°C., and the transition $Cd_\alpha \rightleftarrows Cd_\gamma$ at 95°C. From a similar experiment F. H. Getman (12) was led to believe that the transition $Cd_\alpha \rightleftarrows Cd_\beta$ took place at 37.5°C. However a recalculation by Cohen

(1, 7) placed the transition at about 60°C., in fair agreement with the value Cohen had previously determined by means of the dilatometer. In addition E. Jänecke (14) demonstrated that a transition took place within the temperature range of 110°C. to 113°C.

A cursory search for a transition in the structure of cadmium has already been performed by F. Simon and E. Vohsen (20). Three spectrograms of cadmium were taken, one in which the cadmium was heated to 100°C. and then chilled in ice water, a second wherein a high (unknown) temperature spectrogram was taken directly, and a third in which the heated cadmium was chilled in liquid air. No change in structure was found. However, in view of the preponderance of evidence supporting the existence of several transitions, this x-ray work was considered incomplete.

A sample of cadmium was made by plating cadmium onto a No. 28 copper wire from a cadmium sulfate bath. At regular intervals from 23°C. to 120°C. eight spectrograms were taken. No new lines appeared and no changes in the relative intensity of the lines took place. Analysis proved that throughout this range of temperatures cadmium has a hexagonal structure, typical of the common room temperature form. No transitions occur in this range.

TABLE 1

Calculation of a_0 for antimony

hkl	$\sin^2\theta$ (OBSERVED)	$h^2 + hk + k^2$	$\frac{\sin^2\theta}{h^2 + hk + k^2}$
100	0.0430	1	0.0430
110	0.1293	3	0.0431
200		4	
210	0.2986	7	0.0427
300	0.3862	9	0.0429
220	0.5157	12	0.0430
310	0.5562	13	0.0428
400	0.6849	16	0.0428

IV. ANTIMONY

E. Cohen and J. C. van den Bosch (2) concluded that antimony at ordinary temperatures consists of a metastable system of more than two allotropic forms. By means of a dilatometer they demonstrated that one of the transitions occurred at 101°C., but noted that this temperature was a function of the previous heat treatment. E. Jänecke (14) found an anomalous effect within the range 124°C. to 137°C. during his high pressure studies. This he attributed to an allotropic change in structure. Owing to anomalous changes in electrical and thermal conductivities at about

TABLE 2

Antimony at 21 ± 2°C.

INTENSITY	2θ (IN DEGREES)	$\sin^2\theta$ (OBSERVED)	λ	hkl	$\sin^2\theta$ (CALCD.)
s	23.95	0.0430	α	100	0.0429
s	26.1	0.0510	β	102	
ss	28.85	0.0625	α	102	0.0617
s	36.1	0.0960	β	104	
s	37.95	0.1057	β	110	
ss	40.2	0.1181	α	104	0.1181
ss	42.15	0.1293	α	110	0.1287
w	43.6	0.1379	β	006	
	46.35	(calibration line from platinum)			
s	47.15	0.1600	α	105	0.1604
s	48.55	0.1690	α	006	0.1692
ss	51.8	0.1908	α	202	0.1904
w	53.3	0.2012	α	114	0.2039
w	56.05	0.2208	β	107	
ww	59.5	0.2462	α	204 115	0.2468 0.2462
	60.25	(calibration)			
w	61.35	0.2602	β	212	
s	63.05	0.2734	α	107	0.2732
ww	65.0	0.2887	α	205	0.2891
s	66.25	0.2986	α	210	0.3003
	67.65	(calibration)			
s	68.9	0.3200	α	212	0.3191
s	71.85	0.3442	α	108 213	0.3437 0.3426
s	75.6	0.3757	α	214	0.3755
s	76.85	0.3862	α	300	0.3861
s	78.75	0.4025	α	302	0.4049
s	80.6	0.4183	α	215	0.4178
	81.5	(calibration)			
	85.90	(calibration)			
w	86.65	0.4708	α	216 0010	0.4695
s	91.05	0.5092	α	119	0.5094
s	93.65	0.5318	α	222	0.5336
s	96.45	0.5562	α	310	0.5577
s	98.85	0.5769	α	312	0.5765
ww	101.7	0.6014	α	313 218 1110	0.6000 0.6011 0.5987
ww	102.9	0.6116	α	1011	0.6116
s	103.8	0.6193	α	307	0.6164
s	105.55	0.6340	α	314 225	0.6329 0.6323
s	111.7	0.6849	α	400	0.6864
	118.15	(calibration)			

135°C., J. W. Mellor (16) includes in his reference on antimony a transition in structure at this temperature.

Two samples of antimony were employed in this investigation. The first was powdered antimony having the following analysis: Fe, 0.010 per cent; Pb, 0.002 per cent; As, trace; and no Cu, Zn, or Sn. Five spectrograms of this sample were taken at 21°C., 100°C., 110°C., 135°C., and 170°C. The second sample was prepared by plating antimony upon a No. 30 platinum wire from a bath containing 25 g. of potassium antimony tartrate, 25 cc. of 5 *N* hydrochloric acid, and 300 cc. of distilled water. Spectrograms were taken at approximately the same temperatures as in the case of the first sample. All ten spectrograms yielded the same lines and the same relative intensity of the lines. The structure of antimony is unaltered throughout this range.

Heretofore knowledge concerning the structure of antimony was based on experiments (13, 17) employing a single crystal. In H. Kersten's interesting paper (15) on the influence of the temperature of the plating bath on electrodeposited antimony the powder diagrams were not analyzed. Consequently it was necessary to account for each line in order to be assured that in a polycrystalline mixture of antimony one and only one form exists.

The inherent difficulties involved in the solution of powder diagrams of the rhombohedral system were eliminated in the usual manner by solving the spectrogram on the basis of a triply primitive hexagonal lattice and then calculating the rhombohedral constants. Furthermore, in order to avoid the laborious task of making graphs for the solution of the hexagonal system the following semi-graphical method of solution was devised. This method may be readily modified for a rapid and accurate solution of the tetragonal system.

Expressing Bragg's law for the hexagonal system in the form

$$\log \frac{n^2\lambda^2}{4a_0^2} + \log \left\{\frac{4}{3}(h^2 + hk + k^2) + \frac{l^2}{c^2}\right\} \log \sin^2 \theta$$

it is clear that the third term differs from the second by an additive constant which is the first term. If only the *hko* planes are considered they may easily be identified by plotting the log $\frac{4}{3}(h^2 + hk + k^2)$ on a linear graph and log $\sin^2 \theta$ on a second linear graph. The graphs are then superimposed and one is moved parallel to the other until practically all of the lines on the first coincide with lines on the second. If all of the *hko* lines appear on the spectrogram then all of the lines on the first graph will coincide with some of the lines on the second. The remaining lines on the second graph are from *hkl* planes in which $l \gtrless 0$.

After the *hko* planes were identified with their observed $\sin^2 \theta$ values table 1 was made and a_0 calculated. Therefore the mean $\sin^2 \theta_{100}$ value equals 0.0429 ± 0.0002, whence a_0 equals 4.29 ± 0.01 A. U. employing λK_α equals 1.540 A. U.

The following procedure was then used to find $\frac{1}{c^2}$. Lines appearing between the 100 and 110 lines are $10l_1$, $10l_2$, etc., except for an occasional $00l$ line. Writing Bragg's law as

$$\frac{l^2}{c^2} = \frac{4a_0^2}{n^2\lambda^2}\sin^2\theta - \frac{4}{3}(h^2 + hk + k^2)$$

the values $\frac{l_1^2}{c^2}$, $\frac{l_2^2}{c^2}$, etc., may be determined in the range 100 to 110. Remembering that $\frac{l_1^2}{c^2} : \frac{l_2^2}{c^2} : \frac{l_3^2}{c^2}$ as the square of simple whole numbers, l_1, l_2, and l_3 can be determined, from which an approximate value of $\frac{1}{c^2}$ may be found. With this approximate value of $\frac{1}{c^2}$ the remaining hkl lines may be identified. Some lines will remain unidentified. These are $00l$ and can be used for an accurate determination of $\frac{1}{c^2}$. In the case of antimony only the 006 line appeared, from which $\frac{1}{c^2}$ was determined as 0.1460. With $a_0 = 4.29$ and $\frac{1}{c^2} = 0.1460$, table 2 was completed.

From the geometrical relationship of the hexagonal and rhombohedral systems, namely

$$\cos\alpha = \frac{2c^2 - 3}{6 + 2c^2}$$

and

$$\bar{a}_0 = a_0\sqrt{\frac{1}{3} + \frac{c^2}{9}}$$

where α is the angle between the two edges of the rhombohedron and $\bar{a}_0$ the lattice constant, α was found to equal 57.1° and $\bar{a}_0$ 4.49 A. U. This is in fair agreement with the results found by the Bragg method. Wyckoff (23) gives $\alpha = 56.6°$ and $\bar{a}_0 = 4.50$ A. U.

In the above spectrogram all of the lines were accounted for on the basis of a single rhombohedral lattice. Throughout the range of temperatures investigated this lattice is stable. No transition and no evidence of a metastable structure were found.

DISCUSSION

In conclusion it is evident that anomalous changes in the macroscopic characteristics of the metals such as volume or density changes, changes in thermal and electrical conductivity, etc., are not always reliable criteria for postulating the existence of allotropic modifications. Without confirmation by means of x-rays such conclusions may be invalid. It is not the contention of the authors, however, that the experimental results of macroscopic investigations are incorrect. The nature of a metal may readily account for changes in its characteristics without a change in structure. From Debye-Scherrer diagrams a metal consists of a great number of minute crystallites oriented in a more or less random fashion. It is obvious from the tensile strength that these crystallites are cemented together. Near each crystallite this binding matrix must approximate the orientation and structure of the crystallite, causing the matrix to have a highly distorted semi-crystalline structure. This binding matrix may change with temperature and yet, because of its liquid-crystal like structure this change will occur over a range of temperatures and will be influenced by previous heat treatment. This explanation is in agreement with the fact that Cohen found in the case of cadmium and antimony that the transition temperatures were functions of the previous heat treatment. Heretofore attempts to explain the characteristics of a metal have been based on the structure of the crystallites of that metal. It is believed that the intercrystallite matrix is of great importance in a study of the metallic state.

SUMMARY

1. It has been shown that the following metals have the lattices indicated in the temperature ranges given: copper, face-centered cubic, 20°-420°C.; lead, face-centered cubic, 20°-185°C.; cadmium, hexagonal, 20°-120°C.; antimony, rhombohedral, 20°-170°C.
2. In addition, none of the above metals has transitions in the range of temperature investigated, as other authors have postulated. No evidence of metastable forms was found.
3. Antimony was analyzed by the powder method, and the result was found to agree with that previously obtained by the single crystal method.
4. A simple semi-graphical solution of powder diagrams from rhombohedral, hexagonal, or tetragonal crystals was outlined and applied to the case of rhombohedral antimony.

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NEW BOOKS

The Mechanism of Contact Catalysis. By R. H. GRIFFITH. 208 pp. Oxford University Press, 1936. Price: $5.00.

The author presents the theoretical rather than the technical aspects of catalysis, in full recognition, however, of the fact that contact catalysis is still largely in the empirical stage. While much progress has been made in correlating the fields, prediction still rests on analogy, and trial and testing remain the principal guides.

The development of the subject is presented in a logical order with ample citations of the most important literature. The eight chapters deal with experimental methods, adsorption, promoters and carriers, poisoning and retardation, examination and geometry of the catalyst surface, mechanism of catalysis and development of catalysts.

The monograph closes with an interesting discussion of the direction in which future progress is most likely to be made.

S. C. LIND.

Metastrukturen der Materie. By WOLFGANG OSTWALD. 23.3 x 16 cm.; 17 pp. Dresden and Leipzig: Theodor Steinkopff. Price: 0.80 RM.

This little book is a reprint of a lecture delivered by the author in 1935, and contains a survey and classification of material entities of colloidal dimensions, i.e., dimensions lying between ordinary molecular sizes and the wave lengths of visible light. These the author calls "metastructures." The brochure is intended to convey to a non-specialist audience a clear idea of the world of material entities which constitutes the special field of study of colloid science.

F. G. DONNAN.

Schwimmaufbereitung. By W. PETERSEN. 22 x 15 cm.; xii and 337 pp. Dresden and Leipzig: Theodor Steinkopff, 1936. Price: 18 RM.

This book, which forms Volume 36 of the *Wissenschaftliche Forschungsberichte* (Naturwissenschaftliche Reihe) edited by Dr. R. E. Liesegang, gives a valuable account of the theory and practice of the separation of solid particles of different sorts by means of differential flotation. As is well known, this flotation method of concentrating and separating the valuable constituents in ores is of enormous importance in mining and smelting. The main divisions of the work are as follows: (A) Introduction; (B) Flotation Apparatus; (C) Theory of Flotation; (D) Flotation Substances; (E) Flotation Concentration of Ores.

There are given many practical examples, a comprehensive bibliography, and good author and subject indexes. The book can be heartily recommended.

F. G. DONNAN.

Numerical Data on Rotatory Power. By E. DARMOIS. 23 x 28.5 cm.; 68 pp. Paris: Gauthier-Villars, 1936; McGraw-Hill Book Co., Agents.

This fasciculus is an advance reprint from Volume XI of the *Annual Tables of Constants and Numerical Data*, published under the auspices of the International Council of Scientific Unions and of the International Union of Pure and Applied Chemistry by an International Committee with N. Thon as Editor-in-Chief.

It covers the period from 1931 to 1934 under the following headings: Specific Rotatory Powers of Various Groups of Substances in the Homogeneous State and in Solution (12 pp.); Effect of Temperature, Concentration and Solvent on Rotatory Power (7 pp.); Rotatory Dispersion (27 pp.); Resolution of Racemic Compounds (9 pp.); Mutarotation (5 pp.); Effect of Additions (4 pp.); General Theories (1 page). A bibliography with 399 entries for the period 1931-1934 reflects the activity of workers in this field. These data are valuable to students of stereochemistry.

W. M. LAUER.

ERRATA

Vol. 41, Number 3

Page 464. The equation $r = \frac{8\eta CU}{P}$ should read $r = \sqrt{\frac{8\eta CU}{P}}$

The equation $r = \frac{8l^2\eta U}{VP}$ should read $r = \sqrt{\frac{8l^2\eta U}{VP}}$

REDUCTION POTENTIAL AND PHOTOGRAPHIC DEVELOPERS; THE EFFECT OF SULFITE IN DEVELOPER SOLUTIONS[1]

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I. POTENTIAL MEASUREMENTS IN PHOTOGRAPHIC DEVELOPERS

A. Theoretical considerations

If an electrode of a noble metal, such as platinum, is inserted in a solution containing both the oxidized and reduced forms of a thermodynamically reversible chemical system, the electrode attains a definite electrical potential. While the absolute potential of this electrode cannot be measured, it may be compared with that of another which has a known and constant value. In order to accomplish this, an electrode is placed in a solution which has been thoroughly investigated and whose potential is known with respect to that of a "standard hydrogen electrode." This known solution is then connected with the unknown solution by means of a glass tube containing a solution of an electrolyte, usually potassium chloride. The potential difference between the two electrodes may then be determined by determining the potential which it is necessary to apply externally to prevent a current from flowing if the circuit is completed externally. The value so found is characteristic of the ratio of the active oxidized and reduced forms of the agent in the solution being measured. It may be represented by the well-known equation

$$E_h = E_0 - \frac{RT}{nF} \ln \frac{[\text{Red}]}{[\text{Ox}]} \qquad (1)$$

where E_h is the difference of potential against the normal hydrogen electrode, R is the gas constant, T is the absolute temperature, F is the faraday, E_0 is a constant characteristic of the system at unit activity of all components including $[H^+]$, n is the number of electrons in the reaction, and [Red] and [Ox] indicate the concentrations of the active portions of the reduced and oxidized forms, respectively[2] (8).

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[1] Communication No. 601 from the Kodak Research Laboratories.

[2] The notation throughout this paper will follow that of Clark (8).

In the case of a reaction in which a bivalent reduced form loses two electrons in passing over to an unionized oxidized form, i.e.,

$$[\text{Red}^{=}] - 2\epsilon = [\text{Ox}] \tag{2}$$

the value of n is 2. Such a reaction is typical of a great many organic reducing agents, such as hydroquinone, and we may restrict ourselves to this case without changing the essential relations involved in the following discussion. Since the active form in this case is the bivalent anion $[\text{Red}^{=}]$, it is apparent that its concentration will depend not only on the total amount of agent present but also on the extent of its dissociation. If the first and second dissociation constants (K_1 and K_2) are known for the compound being studied, the hydrogen-ion concentration $[H^+]$ may be measured and the concentration of the active form calculated from the known total concentration of the reducing agent $[S_R]$. Equation 1 may then be rewritten for reaction 2 as

$$E_h = E_0 - \frac{RT}{2F} \ln \frac{[S_R]}{[S_0]} + \frac{RT}{2F} \ln (K_1K_2 + K_1[H^+] + [H^+]^2) \tag{3}$$

and, in general, for all reactions involving two electrons as

$$E_h = E_0 - \frac{RT}{2F} \ln \frac{[S_R]}{[S_0]} + \frac{RT}{2F} \ln (f\,(K_1, K_2, [H^+])) \tag{4}$$

If for any reason, such as low solubility of the reaction products or side reactions which remove them from solution, the concentration of the oxidized form is maintained reversibly at a low value, the second term of equation 4 is maintained at a high value and the system has a relatively great (negative) reduction potential. The action of oxidizing agents on such a system then has a tendency to decrease the total reduced form $[S_R]$ only without increasing the total oxidized form $[S_0]$ correspondingly. In the limiting case in which $[S_0]$ is maintained entirely constant independently of both $[S_R]$ and $[H^+]$, it may be included in the constant E_0 and the equation rewritten as

$$E_h = E_0' - \frac{RT}{2F} \ln [S_R] + f(\text{pH}) \tag{5}$$

While this equation represents a condition that is seldom if ever attained in actual solutions, it has been derived to show that a thermodynamically reversible system under suitable conditions may appear to depend only on the logarithm of the concentration of the reductant and the pH of the solution.

An equation exactly similar to equation 4 holds for oxidizing solutions. For silver bromide as an oxidizing agent we may write

$$E_h = E_0 - \frac{RT}{F} \ln \frac{[\mathrm{Ag}]}{[\mathrm{Ag}^+]} \tag{6}$$

In the presence of metallic silver in the solid state, the solution may be considered saturated with silver and this term combined with E_0. The concentration of all components is independent of pH, so that this term becomes zero. The concentration of Ag^+, however, does depend on the concentration of Br^- in such a way that the product of the two is always constant. Since in the case of photographic development it is usually the concentration of Br^- that is known rather than Ag^+, we shall find it convenient to rewrite equation 6 in accordance with the above facts as

$$E_h = E_{\mathrm{AgBr}} - \frac{RT}{F} \ln [\mathrm{Br}^-] \tag{7}$$

By combining equations 4 and 7, we may write an equation for the difference in potential, ΔE, between an oxidizing agent (silver bromide) and a reducing agent (whose oxidation involves the transfer of the two electrons) as

$$\Delta E = E'_{\mathrm{AgBr}} - E'_{\mathrm{Dev}} - \frac{RT}{F} \ln [\mathrm{Br}^-] + \frac{RT}{2F} \ln \frac{[S_R]}{[S_0]} + f(\mathrm{pH}) \tag{8}$$

The experimental data to be presented in this paper are intended to illustrate the application of this equation to photographic developers and to clarify the nature of some of the variables involved.

If a small amount of silver bromide is introduced into an excess of a reducing solution having a more negative value than the silver bromide, reaction takes place. The concentration of Br^- increases, $[S_R]$ decreases, and $[S_0]$ increases until ΔE is equal to zero and the final solution comes to equilibrium at a potential intermediate between that of the original silver bromide and the reducing solution. All the original silver bromide has been reduced to metallic silver and bromide ions except the small amount of silver ion necessary to satisfy the constant product with bromide ion necessary in all solutions.

It will simplify the consideration of actual developers if we discuss at this point the reaction which will take place if, instead of an oxidizing agent, we add another reducing agent to the above solution. If this added reducing agent is the reduced form of an oxidation-reduction system having a more positive potential than the system under consideration, then it cannot itself be reduced. The slight amount of its oxidized form which is always present will be reduced, however, until the potential of this added system is just the same as the potential of the solution as a whole. This reaction will use up only an infinitesimal amount of the original reducing agent and consequently the resulting potential will be that of the original system.

In many solutions containing organic oxidation–reduction systems, it is found that electrodes come to equilibrium rather slowly, and it is sometimes difficult to determine the exact point at which equilibrium has been attained. In such cases, it has been found convenient to add to the solution a small amount of the reduced form (in measuring reducing solutions) of a system having a more positive potential. From the reasoning of the preceding paragraph it is seen that this does not appreciably affect the true reduction potential of the system being measured and, if the added system is characterized by readily recognized electrode equilibria, it is found that measurements are greatly facilitated. Such added agents are known as "potential mediators." A more complete discussion of their action may be found in Clark (9).

B. Experimental technique

By the use of a suitable potential mediator, it has been found possible to measure the reduction potentials of photographic developer solutions directly. The apparatus used in the work to be described below was of the conventional type for oxidation–reduction measurements. As a standard reference potential the "saturated calomel electrode" was chosen because of its low temperature coefficient. This electrode consists of platinum foil immersed in a solution which is saturated with respect to mercury, mercurous chloride, and potassium chloride. At 20°C. it maintains a constant potential of +0.250 v. with respect to the "standard normal hydrogen electrode." All potential measurements reported in this paper will be in terms of differences with respect to this saturated calomel electrode and are given negative values when the system in which measurements are being made is either a more powerful reducing system or is less easily reduced than this reference system. The solution of the standard electrode was connected to that being measured by a salt bridge consisting of a glass tube filled with saturated potassium chloride solution. The end of the tube which was immersed in the solution being measured was partially closed by means of a cap fitted to the end by a ground-glass joint.

Bright platinum foil electrodes with a surface area of around 2 cm.^{2} were inserted into the unknown solution immediately before measurements were made. The unknown solution was kept at a temperature of 20°C. during all measurements. The difference of potential between the two electrodes was determined by opposing an opposite potential with a Leeds and Northrup student potentiometer and determining the potential at which no current flowed in the circuit by means of a high-sensitivity current galvanometer. All measurements were made in air with all parts of the equipment at room temperature except the solution being measured. When the electrodes were not in use, they were kept in alcohol. This was found necessary in order to maintain proper surface conditions.

It was found experimentally that potassium ferrocyanide would serve as a satisfactory potential mediator for photographic developers. This compound is the reduced form of an oxidation-reduction system having an E_0' of approximately +0.20 v., and this potential is independent of the value of pH between 4 and 12.5. It is available commercially in a sufficiently pure form for the purpose and is relatively stable in water solution. From the considerations of section A above, it may be shown that additions of small amounts of this compound to a developer solution have no appreciable effect on the true potential of the solution. In practice, it was found that the factor limiting the amount which could be added without appreciable change was dilution rather than chemical reaction.

In all cases the procedure of making a measurement was as follows: Approximately 150 cc. of the developer was placed in a water-jacketed glass beaker and 0.5 to 1 cc. of $N/10$ potassium ferrocyanide was added. The platinum foil electrode was rinsed with distilled water before immersing it in the solution whose potential was to be measured. The solutions were constantly stirred by a glass paddle during all measurements, and the readings were independent of the rate. Balancing of the potential was commenced immediately on insertion of the electrode. The potential customarily fell very rapidly at the start and then tapered off gradually to a well-defined equilibrium. This equilibrium was maintained anywhere from 30 seconds to one half-hour, depending on the nature of the solution, and then drifted slowly to more negative values. Tests with many electrodes of different metals and under varying conditions showed that this plateau was characteristic and repeatable for a given solution, and its value has been taken throughout this work as the true electrode potential for the solution under consideration. There appears to be a close analogy between the action of our electrodes and those reported by Clark in his work on indophenols. In his work he observed the same type of plateau and used it as the true equilibrium potential. He gives an interesting discussion of the phenomenon in his first paper on the subject (7).

No solutions of developers at any value of pH have been encountered which cannot be read by the above method, although some alkaline solutions not containing sulfite are characterized by an additional continuous drift due to aerial oxidation. Values for typical mixed developers are presented in table 1 to show the range of potentials encountered in commercial solutions. The values given are those actually measured against the saturated calomel electrode at room temperature and with the developer at 20°C.[3] All values given are uncertain in the third place. All solutions were mixed with Eastman tested chemicals as supplied to the trade.

The pH values recorded in table 1 and used throughout this paper were obtained by means of a glass electrode measured against the same calomel electrode used for the oxidation-reduction potential work. By careful calibration and frequent checking for drifts, it was found practicable to measure the pH values of all developer solutions up to a value of 12 to 12.5. Sulfite and sodium ion errors have been neglected, but represent a small error which is constant for a given environment. The values as given are believed to be correct to within 0.1 pH.

TABLE 1

Reduction potentials for typical mixed developers

FORMULA*	TYPE	pH	REDUCTION POTENTIAL
			volts
D-1	Pyro	9.6	−0.364
D-9	Caustic hydroquinone	12.5	−0.446
D-16	Positive MQ	9.0	−0.295
D-72	Paper MQ	9.9	−0.407
D-76	Borax MQ	8.1	−0.259
D-76d	Buffered borax MQ	7.8	−0.253
D-82	High energy MQ	10.3	−0.420

* The formula designations refer to those published by the Eastman Kodak Company in its trade pamphlets. For the collected formulae, see *Elementary Photographic Chemistry*, published by the same company.

The nature of the dependence of potential on the concentration of the main constituents of the developer solution is shown by figures 1, 2, and 3. In figure 1 the potential is plotted against the pH of a solution containing 10 g. of amidol (Eastman Acrol) and 20 g. of sodium sulfite (anhydrous) per liter. The pH was varied by the addition of either concentrated hydrochloric acid or 1 *N* sodium hydroxide solution. Above a pH of 11.0, air oxidation of the amidol is so rapid, even in the presence of sulfite, that potential measurements could not be made accurately. Figure 2 shows the relationship between the potential and the logarithm of the concentration of the amidol in grams per liter. These measurements were made in the presence of 20 g. of sodium sulfite per liter and at a pH of 7.9. Since the addition of varying amounts of amidol caused fairly large changes in the pH of the solution, it was necessary to readjust this to 7.9 by the addition of small amounts of 1 *N* sodium hydroxide. It is seen

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[3] All data given in this paper will be those found under these same conditions.

that a linear relation exists over the entire range studied. Figure 3 shows the relationship found when the sulfite concentration is varied while the pH and amidol concentration are held constant (pH, 6.1; amidol concentration, 10 g. per liter). The first small addition of sulfite causes a very decided drop in potential to more negative values, and above 20 g. per liter there is little further change.

It should be mentioned that the literature of photography contains many scattered references to potential measurements by electrochemical means. They are found for the most part in the work of Bancroft, Bredig, Sheppard, and Nietz. In more recent times there have been papers by Abribat and by Faerman and Bogdanov describing work which involves potential measurements, but, as far as can be determined, this is the first time in which the potentials of mixed developers containing sulfite have been measured and their dependence on the constituents of the solution investigated systematically.[4]

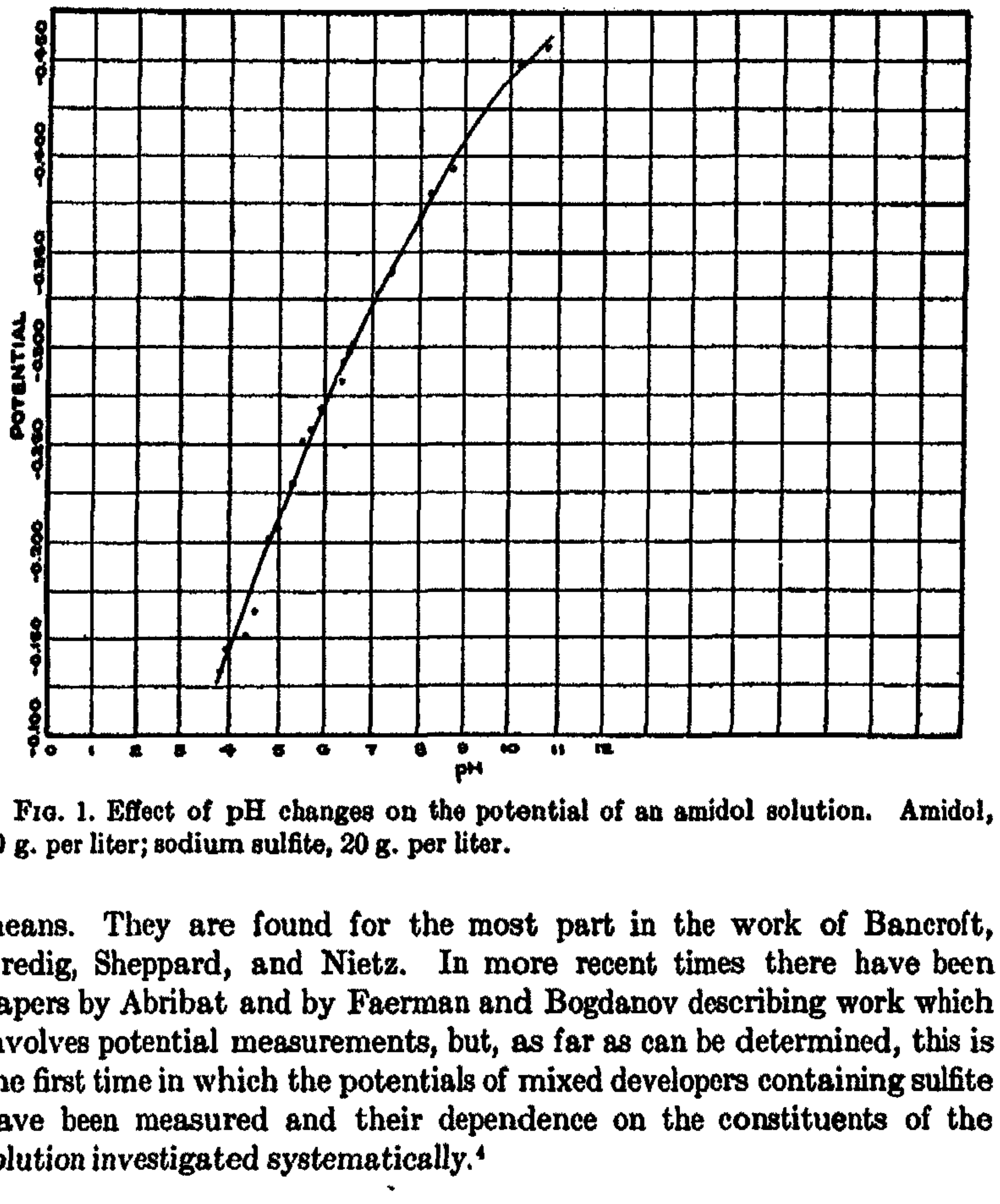

FIG. 1. Effect of pH changes on the potential of an amidol solution. Amidol, 10 g. per liter; sodium sulfite, 20 g. per liter.

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[4] The authors desire at this point to acknowledge the work done by Mr. W. H. Bahler of these laboratories in the development of this technique.

C. The reversibility of development

Sheppard and Mees (18), in their fundamental work on photographic developers, demonstrated as early as 1906 that development with ferrous oxalate complexes is a reversible process. Their experimental method consisted in varying the ratio of ferrous to ferric complexes present in a given solution, keeping the bromide constant, and determining the effect the mixture had on both a latent image and a developed and fixed image. In certain solutions the predeveloped image was found to bleach, and in other solutions the latent image was developed. Bromide ion was found to affect the results. On the basis of certain theoretical considerations similar to those of the first section of this paper, they investigated a series of solutions in which the ratio $\frac{[Fe^{+++}]}{[Fe^{++}][Br^-]}$ was varied in a known manner.

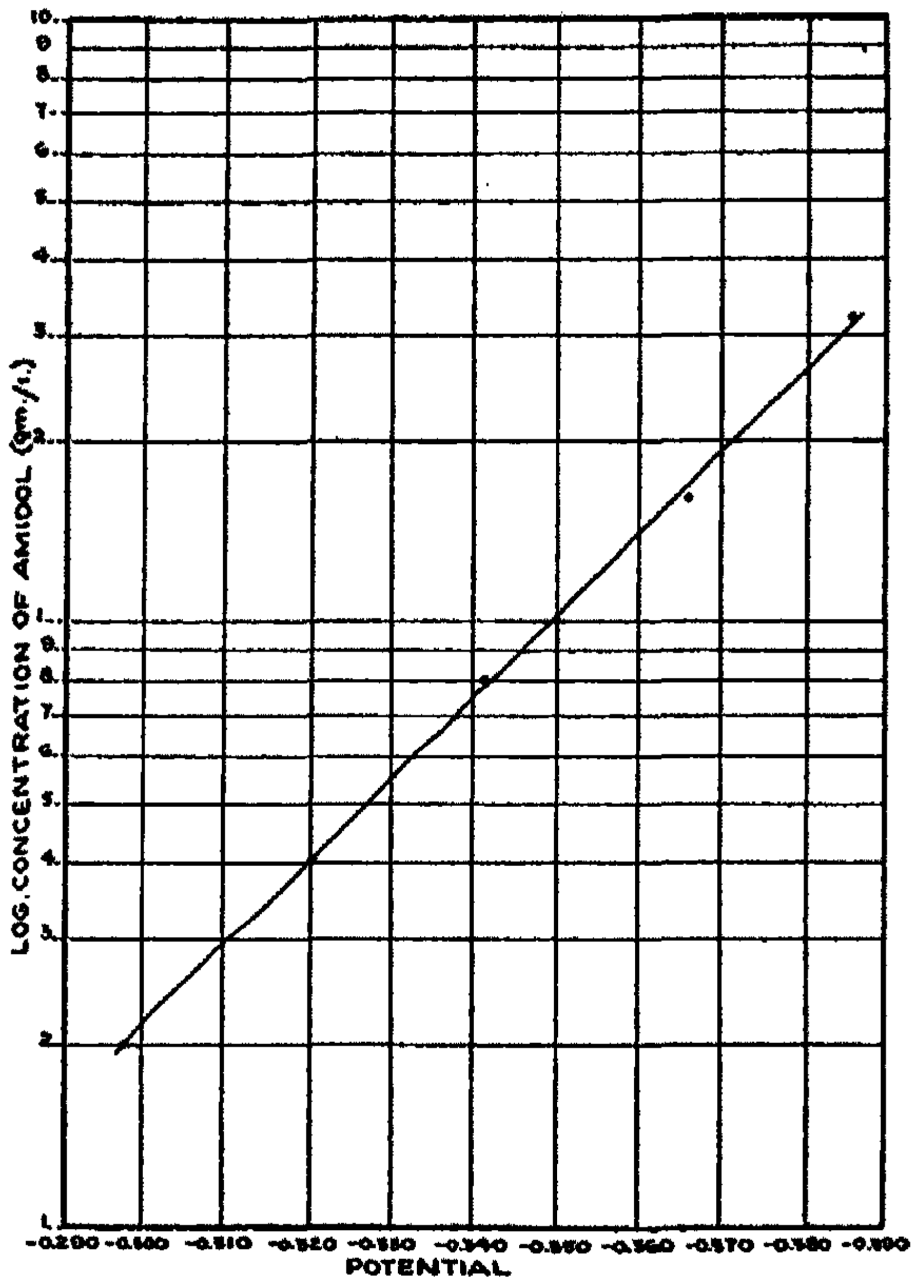


FIG. 2. Relation between potential and amidol concentration. Sodium sulfite, 20 g. per liter; pH = 7.9.

They found that as this ratio was varied, all solutions in which it had a value greater than approximately 700 were oxidizing agents for the silver image and would convert it to silver bromide. All those in which the ratio was less than 700 were found to be reducing agents for the latent image. The sensitivity of the method was rather low because of the slowness of the reactions involved, and they came to the justifiable conclusion that, within experimental error, as the value of this ratio increased, the solution ceased to be a developer, passed through an equivalence point at which no action took place, and became an oxidizing agent for a silver image in a continuous manner. As a matter of fact, their published data do not show this. They do not appear to have been able to find two solutions whose ratio values had a difference of less than ten which would show the two effects. Most of their data shows a ratio difference of at least thirty between the highest value a solution could possess and still develop, and the lowest it could have and still oxidize a silver image.

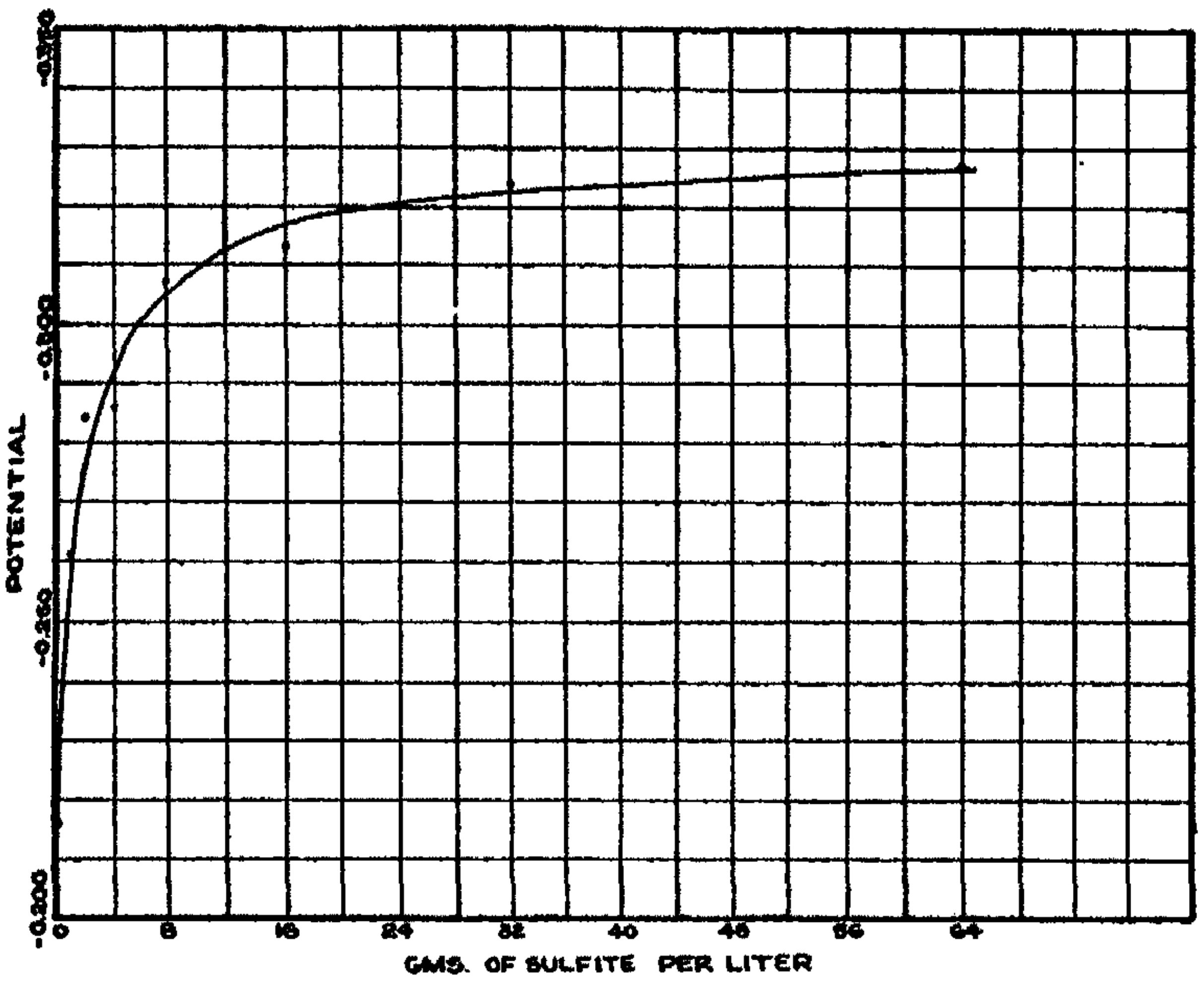


FIG. 3. Effect of sodium sulfite on the potential of an amidol solution. Amidol, 10 g. per liter; pH = 6.1.

The above ratio of Sheppard and Mees may be rewritten in terms of the potential of such a solution and gives rise to equation 8 of the first section above. Their proof of the reversibility of development accordingly may be stated as follows: All solutions containing ferrous and ferric oxalate complexes in the presence of soluble bromides act as oxidizing agents for a silver image if the potential of the solution is higher than a certain value, and as reducing agents for a latent image in silver bromide if the potential is less than a somewhat lower value.

It remained for Reinders (15) and his student Beukers (5), nearly thirty years later, to clear up the discrepancy between the limiting values by the application of actual potential measurements to similar solutions.

They found that by the use of suitable ratios of ferrous and ferric complexes with oxalates, malonates, citrates, etc., a series of solutions having a wide range of potentials could be obtained. These potentials were independent of pH over a rather wide range and were readily measurable. They were able to obtain a total range of potentials with the various salts of from −0.050 v. to +0.650 v. on the hydrogen scale. (Approximately −0.300 v. to +0.400 v. on the scale used in this paper.)

The technique followed by these investigators was as follows: Pairs of identically exposed strips, one of which had been developed in a metol developer to a density of approximately 1.5 and washed but not fixed, and the other of which had received no treatment, were placed in each of a series of the above solutions. Each set was then agitated for four to five hours in closed vessels to insure complete development unaffected by aerial oxidation. After fixing the strips the density of each was read, and the values plotted on a potential vs. density graph. A standard strip, which received the metol predevelopment but which was then fixed without further treatment and its density determined, served as the control from which the density of all the predeveloped strips was known.

The accompanying figure (figure 4), taken from Beuker's thesis (6), shows the nature of the results obtained in a series of solutions containing malonate complexes. It is seen that the silver image in silver halide which was obtained by predevelopment is completely and continuously reversible about a single potential. Each curve of the figure represents a different exposure, and it is seen that the value of this equivalence point potential is independent of the original exposure and predeveloped density to within experimental error. The developer is, accordingly, reversible in the same sense, acting either as an oxidizing or reducing agent depending on its potential relative to that of the silver image.

The curves for the latent images, however, show that a greater reduction potential is necessary to initiate development than is required to continue a development that has already been started. It is this discovery which explains the fact that Sheppard and Mees were unable to obtain the same value for the equivalence point when they tried to approach it from the two directions by different methods.

Reinders and Beukers ascribe this difference to the solubility of the silver of the latent image, and obtain a value sixteen to fifty-three times as great as that for massive silver. It is not within the scope of this paper to discuss this interesting point, although the dependence of the threshold potential for development on the amount of the exposure is particularly suggestive.

No measurements are reported by Beukers on conventional formulae containing organic developers. Predeveloped strips were tested in buffer solutions having pH values ranging from 7.0 to 8.0 and saturated with quinhydrone. In these solutions he obtained a reversible equivalence point in the same manner as for iron salts. The value of this point was found to be about 0.025 v. higher than before (apparently owing to differences in the bromide-ion concentrations of the solutions). He does not report any latent-image development over the potential range studied (+0.299 v. to +0.178 v. on the hydrogen scale). Only two solutions were tested which contained both sulfite and quinhydrone. In one of these at a pH value of 7 he found no change in density, while an increase was observed in the other which had a pH of 8.

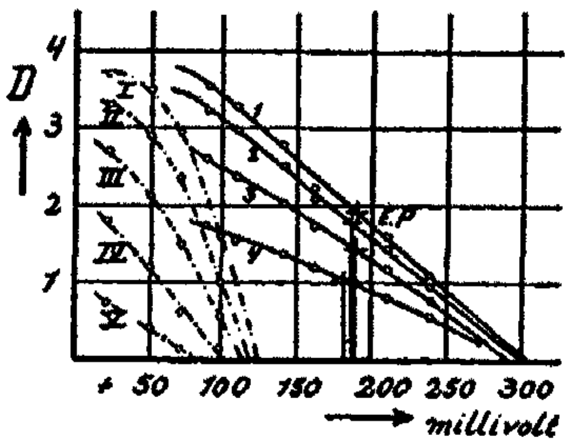


FIG. 4. Equivalence point curves (from Beukers)

Since it has been found in the present work that, by using the experimental technique described above, the reduction potential of organic photographic developers can be measured, it becomes possible to extend the work of Reinders and Beukers to include that type of developer. The approach has followed that of Beukers rather closely.

The greater part of our work to date has been done with amidol, and only the results obtained with this agent will be reported here. The ease with which amidol will develop a latent image at pH values as low as 4 makes it particularly suited for this kind of study, but this property is by no means essential. Entirely analogous data have been obtained using elon and hydroquinone.

In order to cover a sufficient range of potential to study both the oxidizing properties of the developer and its latent-image development characteristics, a spread of nearly 0.400 v. was found necessary. Since in high concentration the primary oxidized forms of organic developers are not stable in solution, the potential range was covered for the most part by varying the pH of the solutions. For the more positive solutions, however, the necessary pH was so low that the gelatin of the photographic material was attacked. In these cases a slightly different method of decreasing the reduction potential was used. It was found that if an alkaline solution of amidol was agitated for about five minutes by means of a stream of air, the solution became very dark red, and on acidifying to a pH of around 2 had a potential of approximately +0.125 v. If this is mixed with an unagitated solution, or made slightly less acid, potential values more negative than +0.125 are obtained. The slight variation of the concentration of neutral salts caused by the addition of acids (hydrochloric and acetic) and alkalies (sodium hydroxide or sodium carbonate) in adjusting the pH has been neglected.

A typical bromo-iodide negative emulsion, Eastman Par Speed No. 1201, was chosen for this work. A series of strips 35 mm. wide was exposed on a Type II B Eastman sensitometer to tungsten light corrected to a color temperature of 5400°K. This instrument gives a range of twenty-one light exposures, each with an intensity of 1.075 meter candles and with times increasing by a factor of $\sqrt{2}$ from 0.004 second to 4.16 seconds. This series of strips was then developed uniformly for five minutes in an MQ developer (Eastman D-16 formula), washed thoroughly, and dried in the dark without fixing. As a standard for comparison, one strip in each series was removed and fixed and the densities carefully read.

One of the above developed and dried strips and an identically exposed but untreated strip were then placed in each of a series of developers having potentials covering the range to be studied. The strips were supported on heavy celluloid to prevent overlapping and to give free access to the solutions. The developer solutions were contained in four-liter beakers which were covered with heavy paper to exclude as much air as possible, but no further protection was provided to eliminate the action of oxygen. Consequently the potentials of the solutions drifted somewhat during the course of a development. In every case the potential was read immediately after the development was completed, and this reading is the one that is used in the presentation of the data. The development was continued for from five to six hours with no agitation other than a frequent shaking of the beakers.

Figure 5 shows graphically the results obtained using a developer containing 10 g. of amidol per liter, no sulfite, and no bromide. The measured potentials of the solutions at the end of the development are plotted against the densities read for single exposure values after the films had been fixed in acid hypo, thoroughly washed, and dried. The full line curves give the values of the densities of the predeveloped strips corresponding to the step whose number is indicated in parentheses. The density value of the control strip removed and read after predevelopment only is indicated by a short horizontal line across the curve, and a dotted line is carried down to the potential axis to show the value of the potential corresponding to a solution which would have produced no change in density. The densities read on the strips which had not been predeveloped and which, accordingly, represent the density reached by a latent image for the given exposure and developer potential are shown as dashed lines. A heavy red stain was obtained on many of the strips of this series. In order to eliminate this from the density readings, the silver of the image was removed by ferricyanide and hypo after a careful determination of silver plus stain, and the stain alone read in the same manner. This value was then subtracted from the sum of the two.

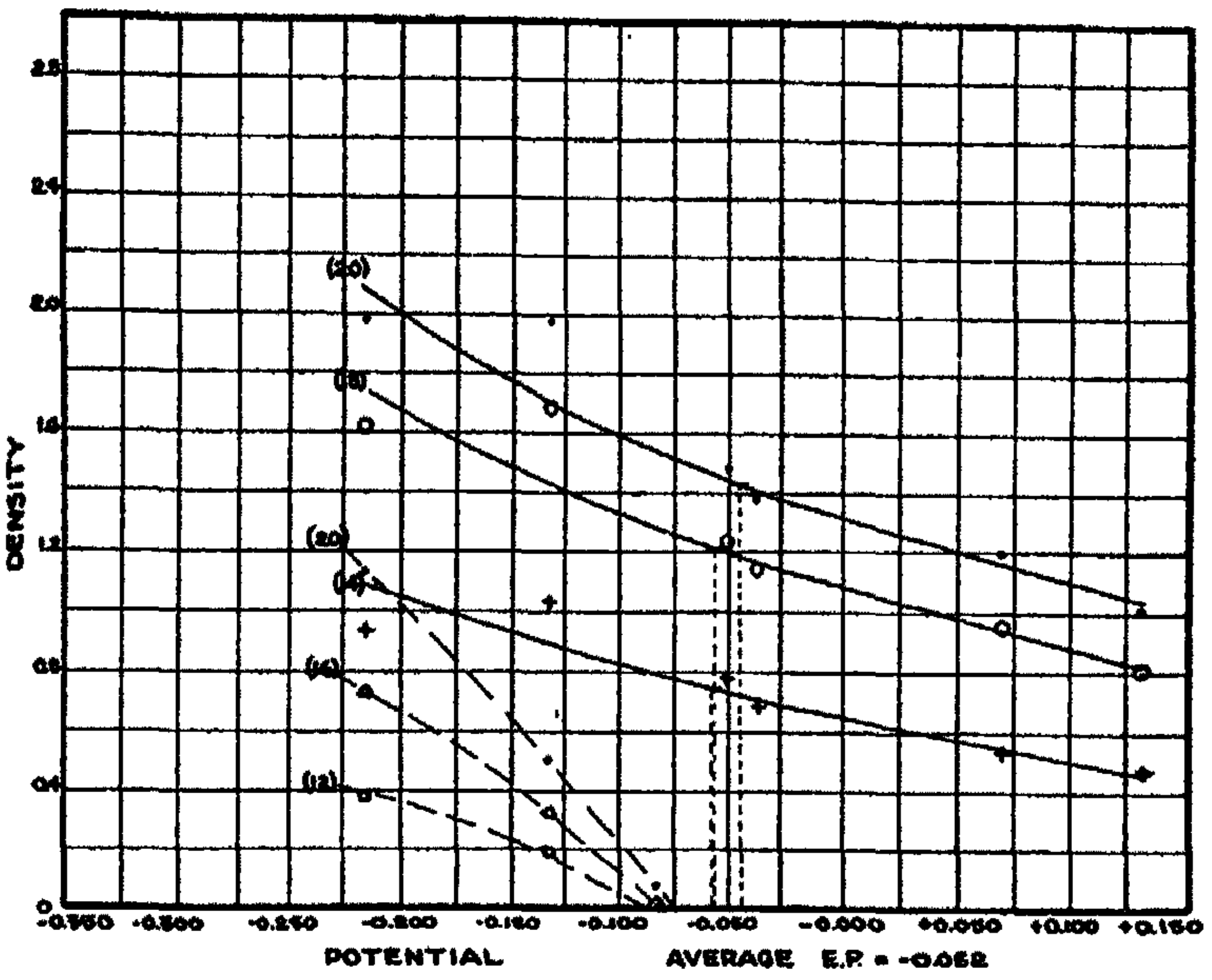


FIG. 5. Equivalence point curves. Emulsion No. 1201; amidol, 10 g. per liter

A comparison of this figure with figure 4 shows that in all essential respects the results so obtained with amidol are the same as those found by Reinders and Beukers for development with ferrous complexes. It is interesting to note that if correction is made for the fact that their data are given in terms of a hydrogen rather than of a saturated calomel electrode, the two graphs show the same value for the equivalence point within 10 mv.

As was shown in figure 3, the addition of sulfite to an amidol solution gives rise to a large shift in the potential of the solution toward more negative values. It was thought interesting to repeat the series of figure

5 with solutions which covered the same range of potentials, but each of which contained 5 g. of sodium sulfite (anhydrous) per liter. The results of such a series are presented graphically in figure 6. It is seen that the same type of family of curves is obtained as in the preceding case but that the slope of the curves for predeveloped images is less to the right of the equivalence point than before, although this comes at the same value of potential. This change in slope and the cause of the drop in potential when sulfite is added to an amidol solution will be discussed more fully in part II of this paper. The rather large experimental errors found, particularly in the values for the equivalence point, are due to a large extent to small fluctuations in the bromide-ion concentration of the solution. No bromide was added except that which washed out of the film after immersion in the developer. In the subsequent series which are discussed below and in which added bromide was used smaller errors were encountered.

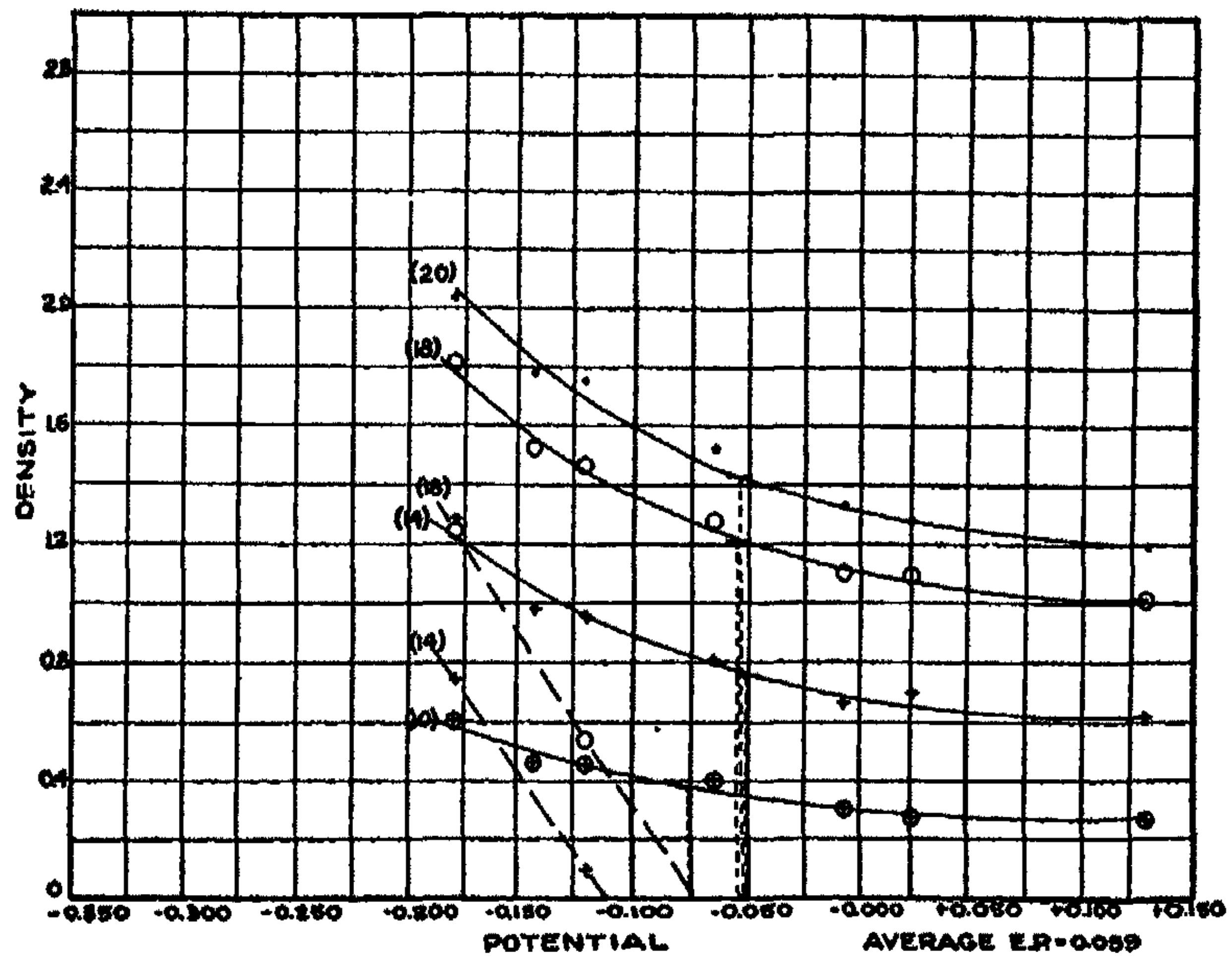


FIG. 6. Equivalence point curves. Emulsion No. 1201; amidol, 10 g. per liter; sodium sulfite, 5 g. per liter.

Since equivalent results were obtained in the presence and absence of sulfite, all of the following experiments have been carried out using 6.25 g. of sulfite per liter. This eliminates the heavy stain and consequently greatly increases the accuracy of the density measurements.

Referring to equation 8 of section A, it is seen that the addition of potassium bromide to a developer solution should decrease the potential difference between the developer and the silver of the image by an amount equal to $\frac{RT}{F}$ ln [Br$^-$]. At 20°C. RT/F has a value of approximately 0.06, including the factor for the conversion to $\log_{10}$, and accordingly for each time that the bromide-ion concentration is doubled the potential difference should decrease by about 0.018 v.

To test whether or not correspondingly lowered values of the equivalence point and the threshold potentials for development of the latent image could be demonstrated experimentally, two series were run which were similar to the previous one but contained bromide. In the first of these, for which the data are presented in figure 7, solutions were employed each of which contained 10 g. of amidol, 6.25 g. of sodium sulfite, and 2 g. of potassium bromide per liter. In the second series each solution contained 8 g. of potassium bromide per liter. The data are shown in figure 8.

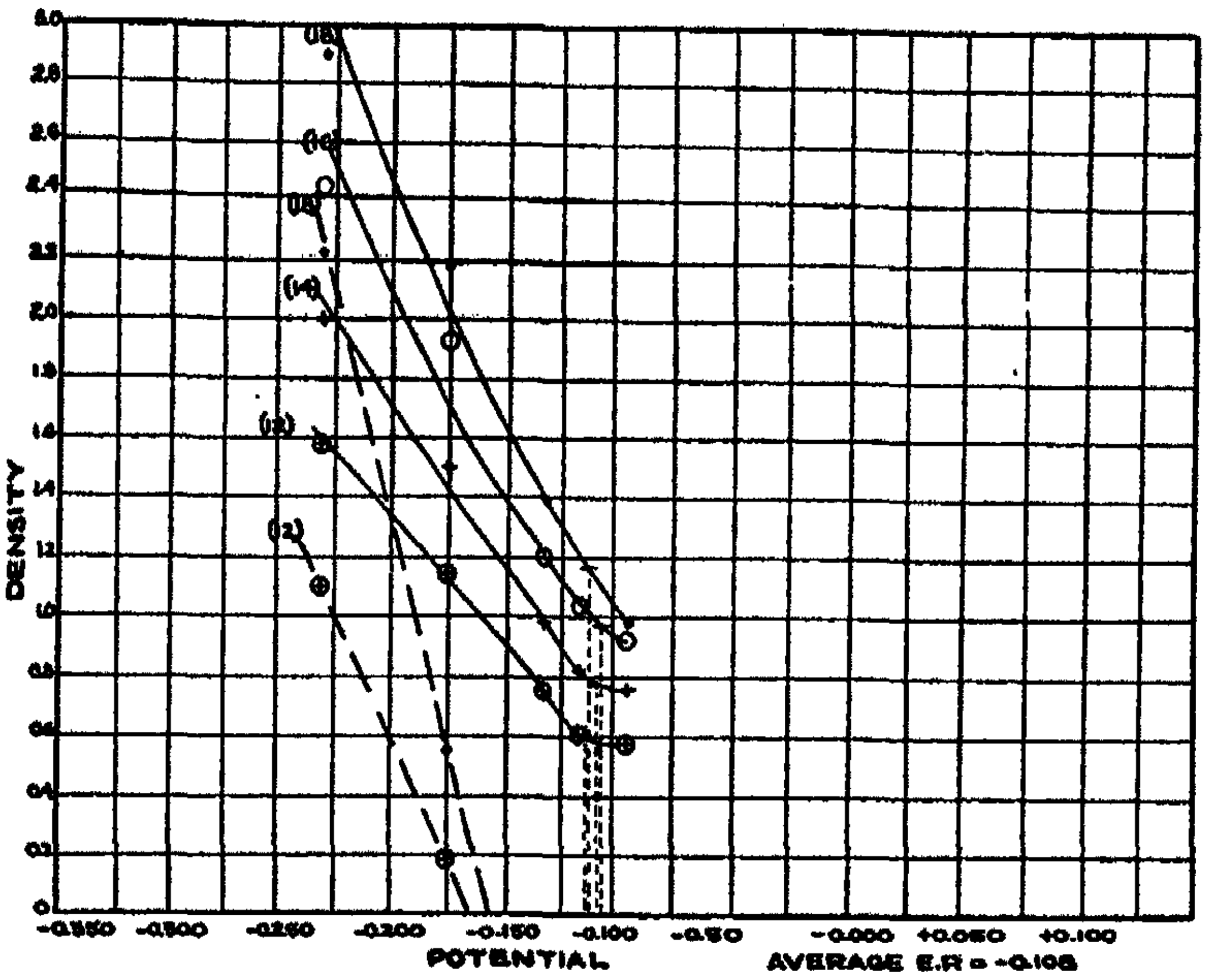


FIG. 7. Equivalence point curves. Emulsion No. 1201; amidol, 10 g. per liter; sodium sulfite, 6.25 g. per liter; potassium bromide, 2 g. per liter.

A comparison of the two figures shows that the equivalence points as well as the threshold potentials for latent-image development are separated by approximately 40 mv., in good agreement with the 36-mv. shift

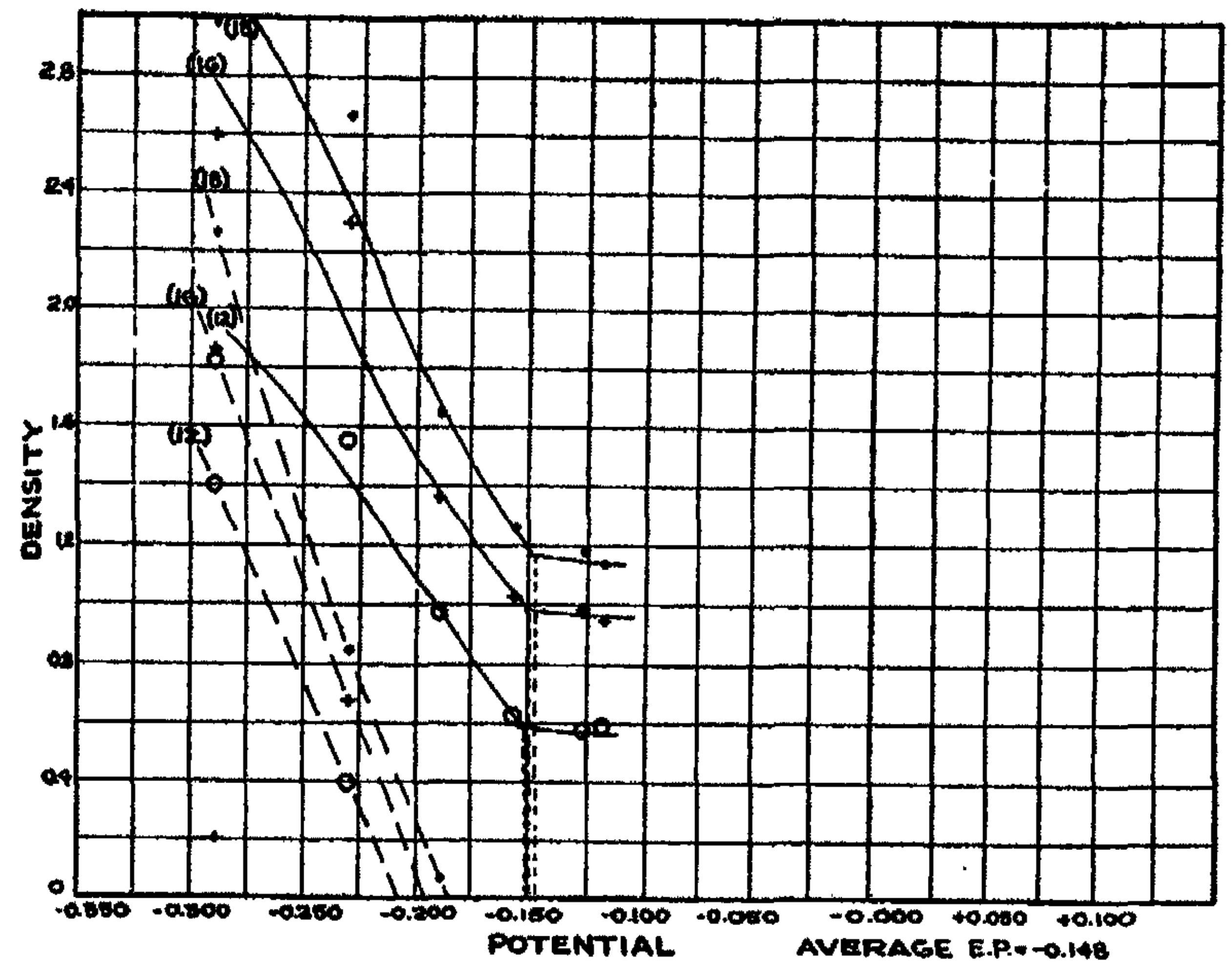


FIG. 8. Equivalence point curves. Emulsion No. 1201; amidol, 10 g. per liter; sodium sulfite, 6.25 g. per liter; potassium bromide, 8 g. per liter.

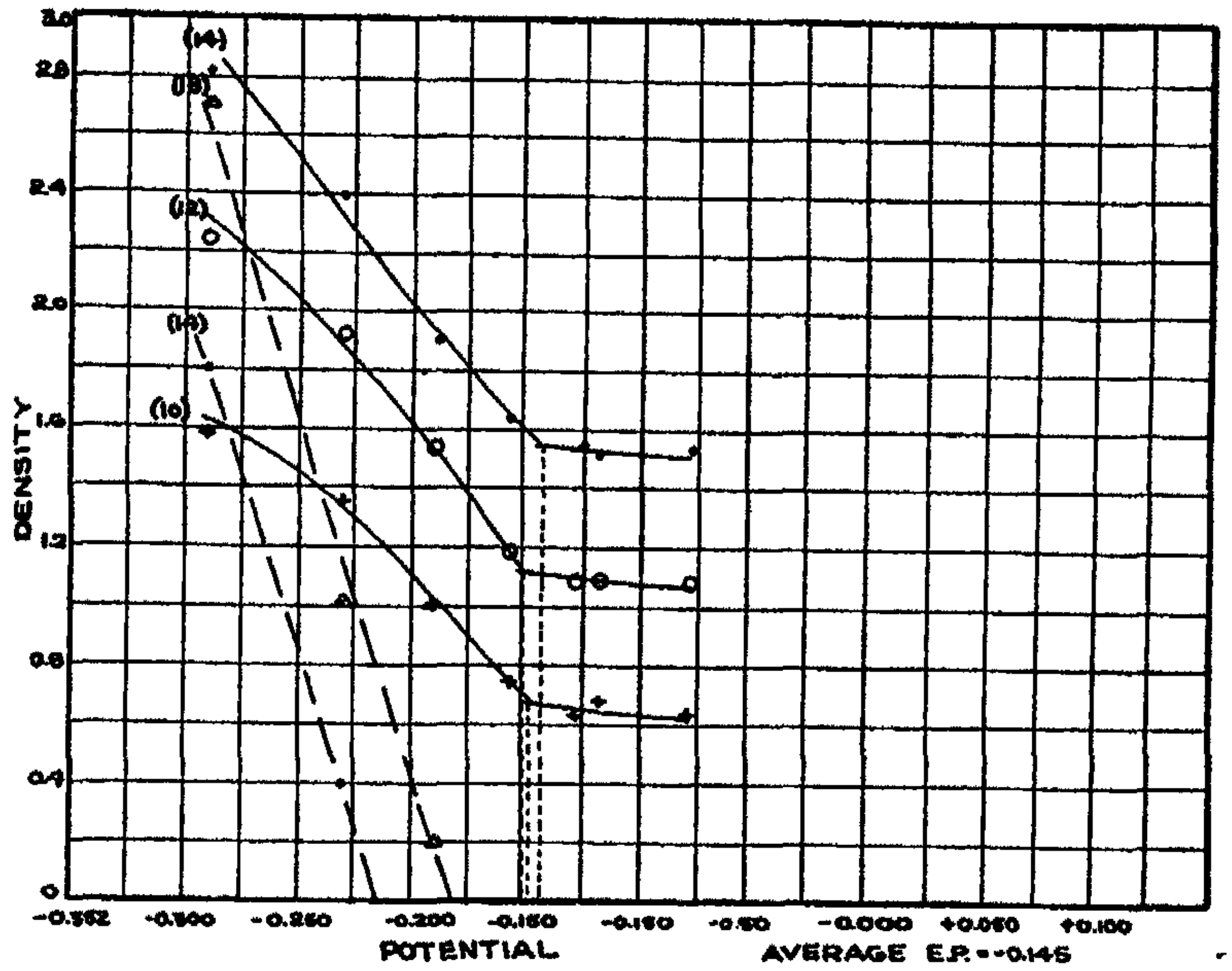


FIG. 9. Equivalence point curves. Emulsion No. 1301; amidol, 10 g. per liter; sodium sulfite, 6.25 g. per liter; potassium bromide, 8 g. per liter.

predicted by the equation. Figure 7 in comparison with figure 6 also shows a shift to more negative values, which is consistent with a greater bromide-ion concentration.

To test the effect of a different grain size frequency distribution in the emulsion material on the value of the equivalence point, a series was also run on the same solutions as used for the data of figure 8 but using Eastman Motion Picture Positive Film No. 1301. The data are presented in figure 9. Within the experimental error the same value is found for the equivalence point. The strips were exposed to light having a color temperature of 3000°K. and an intensity of 27 meter candles, so that the position of the latent-image curves cannot be compared. They were predeveloped in the same developer as the negative strips.

From the foregoing discussion and data, it appears safe to conclude that organic developers both in the presence and in the absence of sodium sulfite are continuously reversible in the same sense as ferrous complex developers, and that the primary effect of the addition of potassium bromide to a developer is to decrease the potential difference between the developer and the image by an amount equal to that predicted by the application of the mass action law.

II. THE EFFECT OF SULFITE IN PHOTOGRAPHIC DEVELOPERS

A. Brief résumé of the literature

Sodium sulfite is the one chemical customarily found in all formulae for organic photographic developing agents. Its use as a protective against aerial oxidation dates back to 1882 and appears to have been suggested by Berkeley (4). In addition to this protective property, sulfite tends to prevent the formation of colored end products in the development reaction, and so has found wide use for many years in pyro developers. By varying the sulfite content of an alkaline pyro solution, the density of the brown stain image formed in the vicinity of the silver during development may be altered at will or, at high sulfite concentrations, practically eliminated.

Recent writers have pointed out other properties of sulfite solutions, and we may summarize the matter as follows: Sulfite is an agent which (1) protects organic developers against aerial oxidation, (2) tends to prevent staining development products, (3) acts as a solvent for silver halides by the formation of complexes, (4) is a weak alkali, and (5) gives increased development under special conditions. In the present paper, experimental evidence will be presented to show that effects 1, 2, and 5 may be explained by the assumption of a single reaction mechanism from which new effects may be predicted. The other two effects noted above will not be discussed here, but have been eliminated or held constant in the experimental work.

The chemical reactions of sulfite in solution are the subject of an extensive literature which cannot adequately be reviewed here. We shall consider only a few of those papers which have a direct bearing on our subject matter.

Sodium sulfite by itself in water solution is rapidly and completely oxidized by air to sodium sulfate. The rate of this oxidation is independent of the concentration of the sulfite but directly proportional to the rate of solution of oxygen in the mixture. Thus, the addition of alkalies to the solution will decrease the oxidation rate to a marked degree. The addition of slight amounts of substances called antioxygens, of which hydroquinone is an example, will also greatly prolong the life of the sulfite.

Hydroquinone similarly, in neutral or alkaline water solution, is rapidly oxidized by air. In this case increase in the alkalinity greatly accelerates the reaction, the reactivity of the compound apparently increasing more rapidly than the rate of solution of oxygen decreases. The end products of the oxidation are not fully known, but the work of Eller (10) has gone far toward showing that for hydroquinone as well as many other developing agents they are polymerized bodies formed from the corresponding quinones and higher oxidized forms. Eller has shown that they are of the group of compounds known as humic acids.

The addition of a slight amount of sulfite to a water solution of hydroquinone will so decrease the rate of oxidation by air that it proceeds at a much lower rate than it would have in either compound alone. In fact it is found that if about 10 per cent of either compound is added to a solution of the other the rate of oxidation becomes the same in either case and the solutions are relatively stable.

Considerable research has been undertaken to determine the nature of the reaction products when both compounds are present. Perhaps the earliest investigator to accomplish their isolation and identification was Pinnow (14), who found in 1912 that the chief product was hydroquinone monosulfonate. This he isolated and identified by comparison with the monosulfonate formed by direct sulfonation with concentrated sulfuric acid. He also found that hydroquinone mono- and di-sulfonates were formed when silver halides were the oxidizing agents. The reaction was assumed to take place in two steps, the hydroquinone first being oxidized to quinone and this then being converted to the monosulfonate by the sulfite under the influence of the alkali present. In explaining the mechanism by which this could take place, he reviewed the literature up to that time and gave references dating back to Carstaujen in 1877 and to Storch in 1893 to show that quinone in alkaline solutions containing sodium sulfite reacted at once to form sulfonates of hydroquinone. Andresen (1) had previously suggested, in 1898, that sulfonates might be a reaction product of hydroquinone developers, but had not demonstrated their presence.

The exact reason why this formation of a monosulfonate results in such a marked decrease in the aerial oxidation of the solution has not been found. It appears probable that by the reaction a chain mechanism, by which one oxidized molecule is able to cause the oxidation of others, is prevented. To explain this, however, it seems necessary to postulate that the first oxidation product produced by oxygen is more of the nature of a peroxide of hydroquinone than quinone itself. This assumption appears to gain some support from the fact that the humic acid end products in the absence of sulfites have been shown by Eller to have the general formula $(C_6H_5O_3)_x$, but the whole subject is in need of investigation before the actual mechanism may be stated. In the case of oxidation by silver halides, there appears to be little difficulty in assuming that quinone is the first product.

In 1933 and 1934 Seyewetz and Szymson (16, 19) at Lyons, and Lehmann and Tausch (12, 20) at Dresden independently investigated the oxidation products of photographic developers. These workers succeeded in showing that in the case of both hydroquinone and elon, sulfonates were formed as oxidation products whether the oxidizing agent was air or silver bromide. Seyewetz and Szymson later showed (17) that either air or silver halide oxidation of hydroquinone, pyrocatechol, pyrogallol, *p*-phenylenediamine, *p*-aminophenol, metol, glycine, *o*-aminophenol, *o,p*-diaminophenol, and the sodium sulfonate of *p*-amino-α-naphthol (eikonogen) produced in all cases either the mono- or di-sulfonates of the original compounds. Since these represent nearly all the known types of organic developers, it seems safe to conclude that in practically every case the principal reaction product of the developing agent in photographic development consists of the sulfonated form of the developing agent itself.

Since all of the above sulfonates are colorless, water-soluble compounds, it becomes immediately apparent how it is possible for sulfite to prevent the formation of staining end products. The fact that all stain is not removed, in the case of pyro for example, unless large quantities of sulfite are present, is explained by the findings of Tausch (20). He showed that, in the case of both elon and hydroquinone in solutions containing sulfite, a certain proportion of the reaction products was humic acids and that this proportion was frequently as high as 5 per cent. The formation of sulfonates, therefore, is to be considered as the chief reaction but not the only one.

It has been noted by several investigators, notably Andresen (3), that the addition of even slight traces of sulfite to an alkaline solution of such varying developing agents as hydroquinone, *p*-aminophenol, and metol has a tremendous effect on the maximum density obtainable by prolonged development. Thus in an alkaline solution of chlorohydroquinone he obtained a density of 1.67 with no sulfite present and 2.59 when 4 g. was added per liter. Nietz (13) also came to the conclusion that in a hydroquinone–carbonate developer the maximum developable density (D_∞) for a given exposure increased as the concentration of sulfite in the solution was increased. This effect is not to be confused with an increase in development velocities. In the present work we are concerned only with the effect of development which has been carried to the point at which the density produced by a given exposure has reached its maximum attainable value.

The cause of this increase may be seen by reference to figures 3 and 5 to 9 inclusive. In figure 3 is shown the dependence of the potential of an amidol solution on the sulfite concentration. As sulfite is added to the solution, the potential at first drops very rapidly and then more slowly. Figures 5 to 9 show the dependence of the maximum developable density on the potential of the solution. Since the density obtained for a given exposure varies almost linearly with the potential, it follows that the addition of small amounts of sulfite should increase the density greatly, as has been found to be the case. The cause of the drop in potential will be discussed in the following section.

B. Generalized hypothesis for the action of sulfite in photographic developers

From the considerations set forth above and in part I of this paper, it appears that in any conventional alkaline organic developer solution containing sulfite, oxidizing agents, such as air or silver halide, produce as a principal reaction product the monosulfonated form of the developing agent. This reaction is assumed to take place in two steps which may be different for the two cases. The intermediate product in each case, however, is an oxidized form of the developing agent, and in each case this form reacts with the sulfite to produce the reduced form of the monosulfonated compound. Owing to the substitution of an acidic group in the ring, the E_0 of the system (of which it is the reduced form) is more positive than that of the system from which it originated.

The monosulfonates of hydroquinone and elon have been synthesized in these laboratories by Mr. L. A. Smith, following the methods of Pinnow and Tausch. Hydroquinone and elon were eliminated as impurities as far as possible, but no great attempt was made to obtain 100 per cent purity as regards inert material. The purity as obtained by analysis appears to be better than 90 per cent in both cases. Reduction potential measurements were made on these compounds in comparison with equivalent amounts of hydroquinone and elon in the same environment. The results obtained are given in table 2. The formula was as follows, except that small amounts of sodium hydroxide or hydrochloric acid were added where necessary to give the desired value of pH: elon, 5 g., or hydroquinone, 10 g., or the monosulfonates in equivalent amounts; sodium carbonate (anhydrous), 30 g.; sodium sulfite (anhydrous), 75 g.

From the data it is seen that in a normal developer solution the potentials given by the sulfonates are definitely more positive than those found for the unsulfonated forms. It follows from the considerations on potential mediators in part I, section A above, that the sulfonates play no part in the potential of a developer solution, nor in the actual development of an image. For each molecule of sulfonate which is formed, however, a molecule of the *oxidized* form of the developer has been removed from the solution. The remaining form does affect developer potential directly, decreasing amounts of it increasing the reduction potential of the solution according to equation 4. Accordingly the formation of sulfonates tends to maintain the reduction potential of the solution against oxidizing agents. This effect has been reported by Faerman (4) and Bogdanov, who found that the effect of the presence of sulfite when metol was titrated with potassium ferricyanide in the absence of oxygen was to oppose the normal increase in the potential of the solution as the metol was oxidized.

TABLE 2

Reduction potential measurements

AGENT	pH	POTENTIAL
		volts
Elon	10.1	−0.305
Elon monosulfonate	10.1	−0.286
Hydroquinone	10.0	−0.400
Hydroquinone monosulfonate	10.0	−0.345

It follows, therefore, that *the primary action of sulfite in a developer solution is that of an acceptor for the oxidized form.*

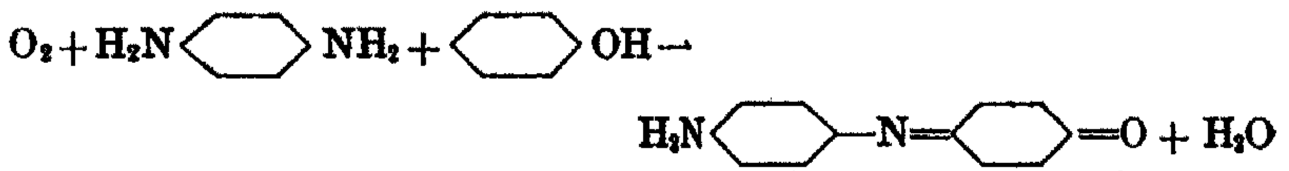
Such an acceptor action has been formulated in electrochemical terms in part I, section A, where it was shown that if the concentration of the oxidized form were held at low values, the reduction potential of the solution no longer followed equation 4. In the limiting case in which the concentration of the oxidized form was held constant during oxidation of the solution, it was shown that the potential was then governed by the logarithm of the concentration of the reduced form alone, i.e.,

$$E = E_h' - \frac{RT}{2F} \ln [S_R] + f(\text{pH})$$

This is in fact what is found to be the case experimentally. Figure 2 shows that with constant pH and sulfite concentration the potential of an amidol solution varies linearly with the logarithm of the amidol concentration. From the nearly linear relationship shown above (figure 5, for example) to exist between the reduction potential and the maximum developable density for a given exposure, it should follow directly that this density for a given developing solution should vary linearly with the logarithm of the concentration of the developing agent. Unfortunately, a search of the literature has failed to reveal a study in which this effect is clearly shown. In most cases which we have found the data are not admissible because the pH has not been held constant. There are many papers which show that development *velocity* has such a relationship to concentration, but while this may be considered as contributory evidence, a study must first be made of the connection between potential and velocity before any conclusions may be drawn.

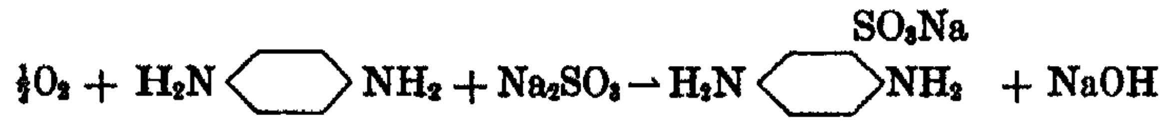
The assumption that in the presence of sulfite the oxidized form of a developing agent is held at almost constant low values for any given value of pH carries with it certain other necessary assumptions. It is first necessary to assume that the reaction between sulfite and the oxidized developer to form a sulfonate is reversible. For this assumption we have no direct evidence. However, from the fact that a potential can be read at all and the fact that this potential is dependent on the *quantity* of sulfite rather than merely being affected by its presence, the conclusion that an equilibrium exists appears to be inevitable. A second necessary assumption is that the developing agent itself and its first oxidation product are in reversible equilibrium. For this assumption we have the evidence presented in the first part of this paper. It was shown that as the reduction potential of a given developer solution was decreased, a point was reached at which it would act as an oxidizing agent for the silver of a partially predeveloped image. It may be considered that the reversibility of developers, at least in the first stages of the reaction, is well established, both by the evidence presented here and by that found in the literature cited. A further indication that both of the above assumptions are admissible is found in the sets of data for solutions which contained sulfite (see figures 6 to 9 inclusive). In all of these sets it is found that the amount of oxidation which has taken place in the duration of the experiment is less than that found for solutions not containing sulfite. The densities, in fact, are found to vary only slightly as the potential changes but, if the above acceptor hypothesis is correct, since we are dealing here with very small quantities of oxidized form, this is exactly what would be expected. The fact that oxidation takes place at all is sufficient indication that both assumptions have some basis in fact. Until further studies have been made as to the rate of this oxidation, it is not safe to assume that sufficient time was permitted in these sets for complete equilibrium to take place. Calculations based on the observed potentials indicate that the quantity of oxidized developer is extremely low, and it does not appear probable that six hours is sufficient under these conditions. Because of this uncertainty we cannot draw any conclusions from the difference in slope of the density lines on the two sides of the equilibrium point. Theoretical considerations indicate that in the presence of sufficient sulfonated form the final equilibrium should be the same as in developers of the same potential which do not contain any sulfite. The experimental verification of this, however, is extremely difficult, owing to the shifts of potential encountered when development is extended for long times.

An interesting extension of the concept of sulfite as an acceptor can be made in the case of the coupler developers of Homolka (2). In these solutions a coupling agent is present which has the property of uniting with the oxidized form of the developing agent as it is formed, precipitating an insoluble dye in the vicinity of the developing image. A typical reaction is as follows:



(colored precipitate)

It is apparent that this is the same type of acceptor action which we have postulated in the case of sulfite except that the steps of the reactions are probably quite different. We may write the sulfite reaction as



(colorless, soluble)

The analogy may be carried somewhat further. It is found that the *amount of dye* formed by a Homolka coupler developer, when a given amount of silver halide is reduced, depends markedly on the ratio of coupling agent to sulfite in the solution, as would be expected in the case of two acceptors competing for the same product. Also it is found that couplers will act in the same sense as sulfite in protecting the developing agent from aerial oxidation. It is thought that the mechanism is somewhat similar to the protective action of sulfite, i.e., the prevention of a chain reaction, but this has not been established definitely. Also, it appears that the same dye is formed by both oxygen and silver halides.

In customary developer solutions the effect of an acceptor action may be seen readily by considering the reactions taking place in the vicinity of a developing photographic image. In the case of a ferrous oxalate developer in which no acceptor is present, the oxidized form of the developer builds up in concentration at the point in the gelatin where reduction of the silver halide is taking place. A two-way diffusion is then necessary to carry away this product and bring in fresh developer before the image can come to equilibrium with the main body of the solution. Under such conditions the attainment of equilibrium will be slow and we should expect the reaction to proceed with little energy. With organic developers on the other hand, as oxidation proceeds, there is always plenty of sulfite present (frequently fifty times as much as the total developing agent), so that the oxidized form of the developing agent is immediately greatly reduced without the necessity of any outward diffusion process. Coupled with the diffusion in of fresh developer the total effect at the image is to maintain a potential throughout development which is only slightly lower than that of the solution as a whole. (Since Tausch has demonstrated that the sulfonates are not only not restrainers but in some cases—notably elon—may actually be used as developers, it should be noted that the severe restraining action indicated by the Eberhard and similar effects are to be ascribed to outward diffusion of the hydrogen bromide formed by the reaction and not to the oxidized developer, as is frequently stated.)

We should further note at this point that in the case of organic developer solutions not containing sulfite, we should still expect development to proceed with greater energy than that of the ferrous complexes at the same solution potential because of the ease with which the oxidized form of these developing agents can polymerize to form multiple quinoidal products of the humic acid type. This polymerization also removes the primary oxidation products, usually depositing a stain either in the vicinity of the image or throughout the gelatin, and so also tends to maintain the reduction potential against oxidizing agents.

This section of this paper may be summarized as follows: It appears consistent with the known facts concerning the reactions of developing solutions containing organic developing agents and sodium sulfite in an alkaline environment that the primary effects of the sulfite are due to its action as an acceptor for the oxidized form of the developing agent. This action explains its protective properties against the oxygen of the air, its preventive action against the formation of staining products of development, and its augmenting action on the maximum developable density for a given exposure.

SUMMARY

Part I

1. By the use of a suitable potential mediator it has been found possible to obtain consistent and repeatable measurements of the oxidation-reduction potentials of customary organic developing solutions.

2. By the use of this technique the reversibility of development when these solutions are used has been demonstrated. The facts observed by

Reinders and Beukers for ferrous complex development are demonstrated for organic developers both in the presence and in the absence of sulfite.

3. The potential of a developer solution is found to vary linearly with the logarithm of the concentration of the developing agent, and to depend on the sulfite concentration as well as on the pH value.

4. It is found that if the variables under 3 above are held constant, the effect of Br^- in the solution is that formulated by Sheppard and Mees, the potential difference between the photographic image and the developer solution decreasing by an amount equal to that predicted from mass action considerations.

Part II

1. It is postulated that the effect of sulfite in a photographic developer is that of an acceptor for the oxidized form of the developing agent.

2. It is found that this hypothesis satisfactorily explains the protective and stain-preventive properties of the sulfite. It also explains the dependence of the potential of the solution on the logarithm of the concentration of the reducing agent, and on the sulfite concentration. The potential–sulfite relationship is shown to explain the increase in developable density caused by the addition of sulfite to a developer.

3. The postulated acceptor action of sulfite is shown to have a close analogy in the action of the coupler in the Homolka coupler developers. The effect of the presence of sulfite in such a developer is also satisfactorily explained by the same reasoning.

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THE VAPOR PRESSURES OF AQUEOUS SOLUTIONS OF SODIUM NITRATE AND POTASSIUM THIOCYANATE

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This paper presents briefly the results obtained in a study of the vapor pressures of aqueous solutions of sodium nitrate and potassium thiocyanate at 25°C. The apparatus and the technique are the same as that employed in our previous work (3, 2).

Large samples of the "analyzed" salts were further purified by recrystallization, twice from distilled water and once from conductivity water. All solutions were made up on a weight molal basis. Solutions of sodium nitrate were made by direct weighing of the dry salt, previously heated to constant weight at 140°C. The saturated solution was prepared by first filling the saturators with a solution of the salt saturated at a temperature a few degrees higher than the temperature of the bath. The saturators were then transferred to the constant-temperature thermostat and the electrolytic gas was allowed to pass for two days while the solution was coming to equilibrium with the solid crystals at 25°C. ± 0.005°.

Concentrated stock solutions of the thiocyanate were prepared and stored in glass-stoppered, mercury-sealed flasks in the dark. The thiocyanate content of each was determined gravimetrically as silver thiocyanate. The experimental solutions were made by diluting definite weights of these solutions to the desired molality. The densities, $d_{4°}^{25°}$, are the mean of at least three determinations and are accurate to 1 part in 300,000.

The final experimental and calculated data are collected in tables 1 and 2. In these m is the molality of the salt solution, c is the molarity, and p_1 is the vapor pressure of the solvent. Each value of p_1 is the mean of at least three values whose deviation from the mean does not, except in one case, exceed 0.007 mm. The activity of the solvent was obtained directly by the relation, $a_1 = p_1/p_1^0$. The change in free energy accompanying the transfer of one mole of water from pure solvent to a solution of concentration m was calculated by means of the relation, $\Delta \bar{F}_1 = RT \ln a_1$. The remaining symbols possess their usual significance and will be mentioned later.

Perhaps no graphic method illustrates better the deviations of solutions

TABLE 1

Experimental and calculated data for solutions of sodium nitrate at 25°C.

m	$d_4^{25°}$	c	p_1	a_1	$-\Delta\bar{F}_1$ calcd.	$\varphi_{obsd.}$	$\varphi_{eq.}$	$\bar{v}_2$
			mm.			*cc.*	*cc.*	*cc.*
0.0	0.997074	0.0000	23.752	1.0000			27.571	27.571
0.1	1.002711	0.0994	23.674	0.9967	1.93	28.393	28.362	28.757
0.2	1.008245	0.1983	23.596	0.9934	3.91	28.749	28.689	29.249
0.4	1.019128	0.3942	23.440	0.9871	7.69	29.151	29.153	29.941
0.6	1.029723	0.5878	23.299	0.9809	11.42	29.552	29.506	30.467
0.8	1.040108	0.7791	23.152	0.9747	15.17	29.857	29.803	30.905
1.0	1.050308	0.9680	23.006	0.9686	18.92	30.100	30.062	31.287
1.5	1.074970	1.4301	22.650	0.9534	28.17	30.626	30.608	32.081
2.0	1.098511	1.8778	22.332	0.9402	36.54	31.076	31.060	32.728
2.5	1.121130	2.3116	21.998	0.9261	45.54	31.430	31.450	33.279
3.0	1.142706	2.7315	21.691	0.9132	53.81	31.783	31.795	33.758
4.0	1.183332	3.5323	21.092	0.8880	70.41	32.369	32.390	34.562
5.0	1.220751	4.2833	20.534	0.8645	86.30	32.880	32.892	35.217
6.0	1.255220	4.9875	19.999	0.8420	101.9	33.344	33.326	35.764
7.0	1.287413	5.6499	19.484	0.8203	117.4	33.716	33.709	36.236
8.0	1.317351	6.2729	18.987	0.7994	132.7	34.048	34.050	36.032
9.0	1.345199	6.8592	18.448	0.7767	149.8	34.352	34.357	36.981
10.0	1.371117	7.4112	17.957	0.7560	165.8	34.637	34.636	37.312
10.8300*	1.391372	7.8457	17.554	0.7391	179.2	34.851	34.847	37.513

* Saturated.

$\varphi = 27.5078 + 2.4968c^{\frac{1}{2}} + 0.03597c.$

TABLE 2

Experimental and calculated data for solutions of potassium thiocyanate at 25°C.

m	$d_4^{25°}$	c	p_1	a_1	$-\Delta\bar{F}_1$ calcd.	$\varphi_{obsd.}$	$\varphi_{eq.}$	$\bar{v}_2$
			mm.			*cc.*	*cc.*	*cc.*
0.0000	0.997074	0.0000	23.752	1.0000			49.212	49.212
0.1000	1.001788	0.0992	23.672	0.9966	2.00	49.797	49.793	50.083
0.2000	1.006405	0.1974	23.597	0.9934	3.88	50.051	50.033	50.441
0.4000	1.015432	0.3909	23.439	0.9868	7.87	50.357	50.369	50.940
0.6000	1.024202	0.5807	23.283	0.9802	11.83	50.594	50.624	51.315
0.8000	1.032707	0.7666	23.131	0.9738	15.71	50.830	50.836	51.623
1.0000	1.041001	0.9488	22.969	0.9670	19.87	51.016	51.021	51.889
1.5000	1.060773	1.3888	22.598	0.9514	29.53	51.447	51.405	52.433
2.0000	1.079491	1.8077	22.246	0.9366	38.83	51.723	51.718	52.807
3.0000	1.113790	2.5872	21.533	0.9066	58.15	52.204	52.218	53.535
4.0000	1.144565	3.2969	20.807	0.8760	78.47	52.582	52.613	54.036
4.9865	1.171667	3.9357	20.143	0.8480	97.00	52.957	52.934	54.426
5.9785	1.196605	4.5252	19.438	0.8184	118.8	53.227	53.210	54.746
6.9786	1.219557	5.0718	18.757	0.7897	139.9	53.454	53.449	55.012
7.9742	1.240376	5.5730	18.120	0.7629	160.4	53.664	53.659	55.234
8.9693	1.259495	6.0362	17.486	0.7362	181.5	53.847	53.844	55.424
10.0000	1.277894	6.4814	16.827	0.7084	204.3	53.995	54.016	55.593

$\varphi = 49.2123 + 1.8382c^{\frac{1}{2}} + 0.01918c.$

of strong electrolytes from the laws of perfect solutions than does the plot of the fractional lowering of the vapor pressure against the molality. If we assume complete dissociation and that the ions behave as perfect solutes, the experimental fractional lowering curve for binary electrolytes should coincide exactly with the slope of the curve of the molality plotted against $2n_2/(n_1 + 2n_2)$. Here n_1 is the number of moles of solvent and $2n_2$ is the number of moles of ions from n_2 moles of salt. With all of the salts previously studied the experimental fractional lowering curve for a given salt of a given type lies below the theoretical curve up to a characteristic concentration. Above this concentration the experimental curve lies above the theoretical curve, and its deviation from the theoretical curve increases more or less rapidly with further increase in concentration. For similar salts with a common anion the concentration at which the two curves intersect is lower the smaller the radius of the bare cation. Potassium thiocyanate behaves in a similar manner. The concentration at which the two curves intersect is higher than for any binary salt studied thus far. At both high and low concentrations it deviates but little from the theoretical curve representing complete dissociation. Sodium nitrate, however, presents a striking relation in that the experimental curve lies below the theoretical curve at all concentrations.

The apparent molal volumes of the salts are very sensitive to errors in density measurements. To eliminate these errors in the calculation of the apparent molal volumes we first plotted the values of

$$F = [1000(d_1 - d)]/c$$

against the square root of the molar concentration, $c^{1/2}$. Here d_1 and d are the densities of the pure solvent and solution, respectively. In no case did the experimental value of $\varphi_{\text{obsd.}}$ deviate from the smooth curve by more than 0.1 of an F-unit. Using the apparent molal volumes thus calculated from the densities, we derived by the method of least squares an equation for the dependence of the apparent molal volume upon the concentration. That is,

$$\varphi_{\text{eq.}} = \alpha + \beta c^{1/2} + \gamma c$$

The final equations for the two salts are inserted below their respective tables. The agreement between the values of $\varphi_{\text{obsd.}}$ and $\varphi_{\text{eq.}}$ is excellent throughout; in no case do they differ by more than 0.06 cc.

The partial molal volumes of the salts for each concentration have been calculated by means of the relation derived by Gucker (1), namely,

$$\bar{v}_2 = \varphi_{\text{eq.}} + c^{1/2}\left[\frac{1000 - \varphi c}{2000 + c^{3/2}\partial\varphi/\partial c^{1/2}}\right]\partial\varphi/\partial c^{1/2}$$

The values of $\bar{v}_2$ thus calculated are incorporated in the accompanying tables.

It would be interesting to compare these volume relations with those calculated on the basis of the Debye-Hückel theory. From this theory Redlich and Rosenfeld (4) have deduced an equation which they claim satisfactorily reproduces partial molal volumes for dilute solutions. The lack of definite knowledge of the ionic radii, and of the dielectric constant and its dependence upon the pressure and the concentration, preclude for the present at least the employment of Debye-Hückel equations for the calculation of partial molal volumes in the high concentrations which we have studied.

SUMMARY

The vapor pressures of aqueous solutions of sodium nitrate and potassium thiocyanate have been determined at 25°C. The apparent and partial molal volumes of the salts in these solutions have been calculated.

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ELECTRODE POTENTIALS OF PLATINUM, GOLD, AND SILVER IN VARIOUS SOLUTIONS OF ELECTROLYTES

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Essin and Lozmanova (2) studied the potentials of gold electrodes in solutions of copper sulfate, copper nitrate, and silver nitrate in the absence of air. It was found that the potential of the gold electrode in copper sulfate solutions depends upon the copper concentration in a way somewhat similar to that of the copper electrode in the same solutions, although the potential of the gold electrode changed about three times as much as that of the copper electrode for a given change in the copper-ion concentration. The following relation was found between the potential of the gold electrode ($E_{\mathrm{Au/CuSO_4}}$) and that of the copper electrode in the same solution ($E_{\mathrm{Cu/CuSO_4}}$):

$$E_{\mathrm{Au/CuSO_4}} = A + bE_{\mathrm{Cu/CuSO_4}}$$

in which A and b are constants. Similar equations were found for other combinations of electrolytes and electrodes. Nierstrasz and Tendeloo (4) made use of the potential of the system, noble metal–copper oxalate (solid–saturated solution) as an indicator of copper-ion concentration in the presence of air, and they applied these systems to the potentiometric titration of calcium with oxalate.

No explanation has been offered for the above behavior of the noble metals; theoretically it seems hardly justifiable to attribute a copper electrode function to the noble metals, since the potential is also dependent upon the nature and concentration of the anions present in the solution. In the presence of air and in solutions of low oxidation potential, noble metals may be expected to adopt the air potential determined by the net electrode reaction,

$$O_2 + 2H_2O + 4e \rightleftharpoons 4OH^-$$

Although, under carefully regulated conditions, air electrode potentials are fairly reproducible (see Richards (6)), the values obtained for the

[1] This article is based upon a thesis submitted by Chin Wang to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Master of Science, June, 1936.

oxygen-hydrogen cell are far below the theoretical values calculated from other thermodynamic data. This is partly explained as being due to the formation of oxide films on the noble metal and, as shown by Hoar (3), to irreversible autopolarization of the oxygen electrode. The potentials of gold and platinum electrodes in solutions of copper salts in the presence of air may therefore be expected to depend upon the hydrogen-ion concentration of the solutions. Changing the concentration of the copper salt in the solution also changes the hydrogen-ion concentration (hydrolysis) and hence also the potential. The potential is mainly determined by the hydrogen-ion concentration (activity) and not by the concentration (activity) of the copper ions. In the present study this view was actually shown to be correct. Addition of acid to solutions of copper salts resulted in a marked increase of the potential of gold and platinum electrodes immersed in these solutions. In acetic acid–sodium acetate buffers the potential was found to be determined by the pH and not by the concentration of the copper ions. When, after measuring the potential of gold and platinum electrodes in solutions of copper salts, nitrogen was passed through, the potentials dropped slowly, until after five to ten hours a more or less constant potential was obtained which differed by about 0.25 volt from the "air potentials." The above results show conclusively that in air the noble metals do not function as copper electrodes.

The potential of a silver electrode has also been measured in solutions of copper sulfate and copper nitrate of various concentrations. It was found that in general the potential was not affected by air or by a change in the pH of the solutions.

The potentials of platinum and gold in solutions of copper salts, after removal of the air by nitrogen, were not affected, or only very slightly, by the addition of a strong acid. Under these conditions the partial pressure of oxygen is reduced to such a small value that the noble metals no longer function as oxygen electrodes. Apparently in nitrogen the oxidation potential of the dissolved copper salts is measured with platinum or gold electrodes. These potentials are not very reproducible, because the concentration of the reduced form (cuprous ions or metallic copper) is indefinite and exceedingly small. The case is somewhat comparable to the measurement of the oxidation potential of a *pure* solution of an oxidizing or reducing agent in which the concentration of one of the electromotively active forms is indeterminate. In a nitrogen atmosphere the potentials measured with platinum and gold electrodes in copper sulfate and nitrate solutions were nearly identical at the same copper concentration, this result lending support to the above interpretation.

Erich Müller (5), and later Böttger and Schall (1), found that the chloride–silver titration could be carried out using electrodes of gold, platinum, and palladium, instead of silver. Apparently, here again the oxidation potential of the silver solution ($Ag^+ + e \rightleftharpoons Ag$) is measured with the noble metal electrodes. In order to substantiate this view experimentally, measurements of the potential have been made in silver nitrate solutions of varying concentrations using platinum, gold, and silver electrodes. In 0.5 molar silver nitrate solutions the potentials were found to be identical, indicating that under these conditions enough metallic silver was formed on the noble metals to enable them to function as silver electrodes. In dilute silver nitrate solutions the potentials of the noble metals were more positive than those of the silver electrode. Under these conditions the amount of metallic silver formed on the noble metals is not sufficient to make them identical with silver electrodes. The activity of the reduced form (silver) is not fixed and the potentials become more or less indeterminate. (Compare with behavior of copper solutions in nitrogen.) A further substantiation of the fact that the noble electrodes do not function as air electrodes in solutions of silver salts of adequate concentration is that the potentials were found to be unaffected, or only slightly affected, by the addition of acid or by the removal of oxygen from the solution.

In mixtures of copper and silver nitrate the potential was found to be determined by the silver concentration in the solution.

EXPERIMENTAL

Electrodes

Gold electrodes: (1) plate electrode, 1 x 2 cm., 1 mm. thick; (2) wire electrode, 1.5 mm. in diameter; (3) a gold-plated platinum gauze electrode.

Platinum electrodes: (4) plate electrode, 1 x 2 cm., 1 mm. thick; (5) wire electrode, 1.5 mm. in diameter; (6) a gauze electrode.

Silver electrodes: (7) plate electrode, 2.5 x 1 cm., 0.5 mm. thick; (8) silver gauze electrode; (9) a silver-plated platinum gauze electrode.

The most reproducible results were obtained with electrodes 3, 6, and 8, which were used in most of the work. The gold and silver electrodes were connected directly with the copper lead-wire. The platinum electrode was sealed into a glass tube and connection made in the ordinary way with mercury. Before the measurements the electrodes were cleaned with a mixture of sulfuric and chromic acids and then washed thoroughly with distilled water.

Electrode cell

The cell was made of Pyrex glass and was about 7 cm. in diameter and of 150-ml. capacity. It was closed with a rubber stopper provided with holes for the admission of the electrodes, for the salt bridge filled with sodium sulfate or potassium nitrate making electrolytic contact with the saturated calomel electrode, for the inlet and outlet tubes for air or nitrogen, and for the thermometer (25°C.). The potentials were measured against the saturated calomel electrode.

Potentiometric outfit

The ordinary compensation method was used, employing a Leeds and Northrup student potentiometer. Since the electrodes are easily polarizable, measurements have been made also with a vacuum tube potentiometer as a null point instrument. Both methods gave corresponding results if the final data were taken after long enough periods of time.

Chemicals and gases used

All chemicals were of C.P. quality and were recrystallized before use. Tank nitrogen was purified by washing with sodium hydroxide, by passing over copper turnings heated electrically to about 600°C., and finally by washing with the same solution as used in the cell. The air was obtained from the air pressure supply in the laboratory, and was washed through the same solution as used in the cell.

EXPERIMENTAL RESULTS

A detailed account of all measurements in air and nitrogen before and after addition of acid are given in the thesis of the junior author (see footnote 1). They are not reported here as the figures have no exact significance, owing to the great polarizability of the electrodes. As an illustration a few figures obtained with 0.05 molar copper sulfate are given in table 1. One hundred ml. of this solution was placed in the cell and the latter closed air-tight after introduction of the electrodes and various tubes. Air was passed through and the potentials were measured after regular intervals. After the potentials had become fairly constant, acid was added (in the case of copper sulfate, sulfuric acid; in the case of copper nitrate, nitric acid), the final normality being known. The potentials were measured again after definite intervals of time until they were constant, or approached constancy. A fresh sample of solution was then placed in the cleaned cell and the entire manipulation repeated in nitrogen. The gold and platinum electrodes give almost identical results. The air electrode function is evident from the great effect of acid upon the potential (increase about 80 mv.) and the effect of removal of air by nitrogen (decrease about 200 mv.). The potential of the silver electrode, on the other hand, is only slightly affected by these changes.

In table 2 the final potentials measured with platinum and gold electrodes in neutral and acid solutions of copper sulfate and nitrate of various concentrations in a nitrogen atmosphere are given. The gold and platinum electrodes behave in an almost identical fashion. The results show definitely that under the conditions of these experiments, the noble elec-

TABLE 1

Measurements in 0.05 M copper sulfate (against saturated calomel electrode; 25°C.)

a. In air | b. In nitrogen

TIME IN HOURS	POTENTIAL IN VOLTS			TIME IN HOURS	POTENTIAL IN VOLTS		
	Au	Pt	Ag		Au	Pt	Ag
0	0.3640	0.3840	0.2810	0	0.3670	0.4320	0.2610
6	0.3750	0.3850	0.2570	2	0.1900	0.1820	0.2520
8	0.3890	0.3920	0.2510	5	0.1770	0.1730	0.2400
30	0.3870	0.3910	0.2490	6	0.1800	0.1780	0.2400
Acidified to 0.05 *N* with sulfuric acid							
0.5	0.4260	0.4360	0.2335	¼	0.1770	0.1900	0.225
4	0.4660	0.4780	0.2440	1	0.1920	0.1840	0.225
6	0.4680	0.4780	0.2480	2	0.1930	0.1840	0.223
7	0.4680	0.4790	0.2480	3	0.1940	0.1850	0.225

TABLE 2

Measurements in nitrogen in solutions of copper sulfate and nitrate

	IN 0.5 *M* $CuSO_4$		IN 0.05 *M* $CuSO_4$		IN 0.005 *M* $CuSO_4$	
	Au	Pt	Au	Pt	Au	Pt
Neutral	0.240–0.245	0.226	0.180	0.178	0.128	0.128
0.05 *N* H_2SO_4	0.250	0.233	0.194	0.185	0.120	0.120

	IN 0.5 *M* $Cu(NO_3)_2$		IN 0.05 *M* $Cu(NO_3)_2$		IN 0.005 *M* $Cu(NO_3)_2$	
	Au	Pt	Au	Pt	Au	Pt
Neutral	0.227	0.219	0.182	0.185	0.137	0.132
0.05 *N* HNO_3	0.216	0.210	0.140	0.140		

TABLE 3

Measurements in silver nitrate solutions

	IN 0.5 *M* $AgNO_3$			IN 0.05 *M* $AgNO_3$			IN 0.01 *M* $AgNO_3$		
	Au	Pt	Ag	Au	Pt	Ag	Au	Pt	Ag
In air									
Neutral	0.510	0.510	0.5105	0.489	0.498	0.460	0.469	0.490	
0.01 *N* HNO_3	0.509	0.519	0.5110	0.462	0.490	0.450	0.471	0.480	
In nitrogen									
Neutral	0.5055	0.504	0.5085	0.476	0.484	0.460	0.410	0.520	0.410
0.01 *N* HNO_3	0.508	0.507	0.5085	0.455	0.467	0.450	0.455	0.485	0.400

trodes do not function as air electrodes (hardly any effect of acid). The potentials measured in neutral copper sulfate and nitrate solutions are practically the same at the same copper concentration, the potential changing 0.045 ± 0.005 volt with a tenfold change of the copper concentration.

All measurements were repeated with 0.5, 0.05, and 0.005 molar solutions of lead nitrate. The results were still less reproducible than in the copper solutions, but qualitatively the same effects were found.

In table 3 a summary of the measurements in solutions of silver nitrate is given. The figures are interesting in so far as they show that particularly in the more concentrated solution the potentials of gold and platinum are hardly affected by the addition of acid or the removal of air by nitrogen. The results show conclusively that the oxidation potential of the silver solution is measured, which in the more concentrated solutions was found to be identical with the silver–silver ion potential.

In 0.01 molar silver nitrate the gold and platinum electrodes apparently become easily polarized.

SUMMARY

1. Gold and platinum electrodes in solutions of copper sulfate and nitrate behave as air electrodes. The potential is not affected by the concentration of copper ions. After removal of air by nitrogen, the electrodes no longer behave as air electrodes. Apparently the oxidation potential of the copper solutions is measured.

2. Gold and platinum electrodes in solutions of silver nitrate of a concentration greater than 0.01 *M* indicate the oxidation potential of the silver solution ($Ag^+ + e \rightleftharpoons Ag$). The potentials are not affected, or only very slightly, by a change of the hydrogen-ion concentration or by the removal of oxygen by nitrogen.

3. In all cases the noble metals are easily polarized and the systems are not suitable for exact measurements.

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THE EFFECT OF EVAPORATION UPON THE STABILITY OF LIQUID FILMS

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It is recorded that the stability of bubbles and foams produced from certain solutions is decreased when free evaporation is prevented. This effect has been investigated somewhat quantitatively by Talmud and Suchowolskaya (4) for aqueous solutions of ethyl alcohol, potassium chloride, and potassium sulfate. The following paragraphs are translated from their paper:

> "In the case of insoluble films, formed of substances with high boiling points and low vapor pressures, there is no reason to assume that evaporation can affect the stability of single bubbles in any way. On the other hand, in the case of volatile, soluble, surface-active substances, it is to be expected that the surface layer will lose molecules of solute through evaporation more rapidly than they can be replaced by diffusion, and hence the concentration of surface-active solute in the adsorption layer will decrease and the stability of the bubble will be changed. Further, at certain concentrations, water may evaporate more rapidly than the solute . . .
>
> "We see that the stability of single bubbles formed without evaporation in ethyl alcohol solutions has a totally different character from that which obtains when evaporation is permitted . . .
>
> "Evaporation plays a special part in stabilizing bubbles formed in solutions of electrolytes. In closed glass cylinders the stability is significantly less . . . The explanation of this fact lies probably in a concentration of the surface layer by the evaporation of water . . .
>
> "We see that the suppression of evaporation strongly diminishes the stability of the bubbles but does not change the nature of the dependence of bubble stability upon concentration."

The above explanation of the stabilizing effect of evaporation requires that, in general, the stability of the film shall be increased by a decrease in concentration of a solute more volatile than the solvent and by an increase in concentration of a solute (e.g., an electrolyte) less volatile than the solvent. That is, the relationship of concentration of solute to film stability is used rather indiscriminately. Furthermore, the data for electrolytes in the paper cited show that beyond a certain concentration (about 0.3 *N*) the stability of single bubbles is independent of concentration. This is true whether evaporation is free or is prevented, but the stability of the bubbles is consistently greater when evaporation is free. That is, in this range the stability curves are parallel to the concentration axis, and the curve for free evaporation lies above the other. This relationship is obviously inconsistent with the explanation given. It would appear that some factor other than change in concentration of the solution must be considered to account for the effect of evaporation upon the stability of liquid films.

Concentration changes can be eliminated by working with films of individual pure liquids. It is generally stated that films of pure liquids can not be formed. This is not strictly true, for hemispherical bubbles or calottes of pure liquids have been studied by various investigators, notably by Plateau (3). It is true that these films are relatively unstable; they do not form foams because of the brevity of their existence and the tendency of two such films to coalesce upon contact.

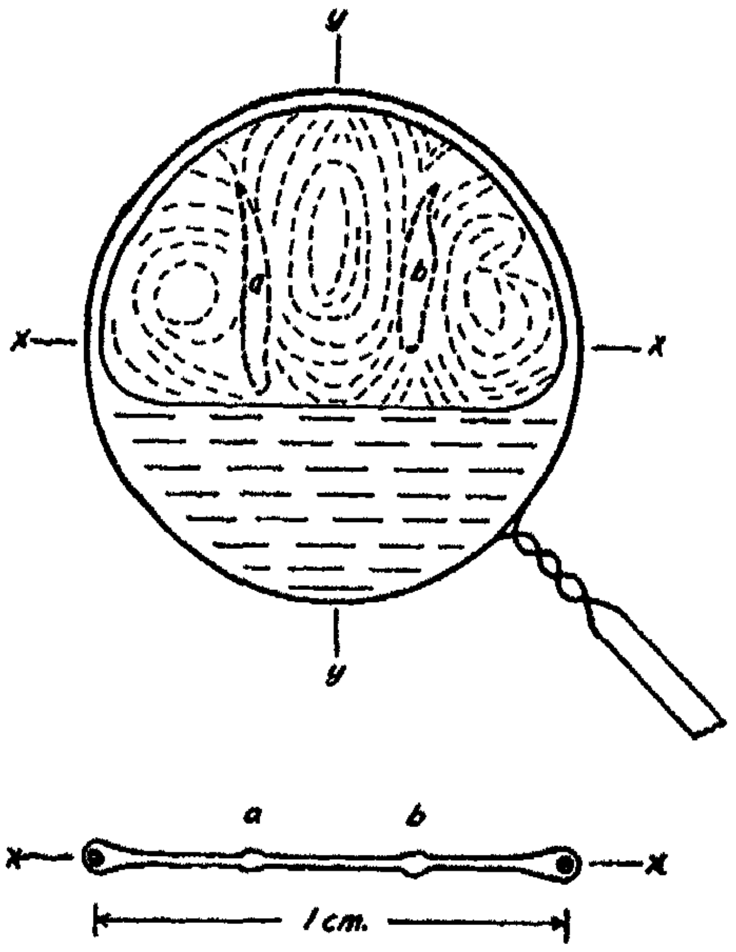

FIG. 1. Diagram of vertical liquid film. xx and yy, horizontal and vertical cross sections

We have studied the effect of evaporation upon the stability of films of pure liquids for a variety of liquids, including water, alcohol, and aliphatic and aromatic hydrocarbons. For this purpose it is convenient to form the films upon a circular loop of wire or glass by dipping the loop into the liquid and lifting it quickly. A film is not obtained on every attempt, but with many liquids a film can be formed on a circle at least as large as 1 cm. in diameter. Such a film is produced by the necking-off of the column of liquid lifted by the loop, and a varying amount of liquid will be retained by the loop. Excess liquid can be removed from the loop by means of a smaller loop, a capillary tube, or filter paper, but it is doubtful if two films which are exactly comparable can be prepared in this way. Individual films of this type last for a few seconds to several minutes, depending upon the liquid and the attendant conditions. The tendency of the total surface to become a minimum causes these films, when horizontal, to drain to the periphery, and this tends to produce a thin central region (1). When the film is tilted toward the vertical position, gravitation causes additional drainage to enlarge the thin region. This portion inevitably thins further to the point of rupture unless there is a restoring counter-flow.

The typical structure of the vertical film is shown in figure 1. The liquid tends to drain from the thin film into the wedge or Gibbs' ring adjacent to the wire and into the thick lower portion of the film, as indicated by arrows in the cross section *yy*. The suction into the Gibbs' ring or into any thicker portion is conditioned by the curvature of the film at that point as expressed in the equation

$$P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

where γ is the surface tension of the liquid, and R_1 and R_2 are the principal radii of curvature. If the central portion is truly plane its counter-suction is zero regardless of the surface tension, but it is almost never truly plane and when any finite curvature exists here it also produces a suction. The opposing suctions would balance if

$$\gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \gamma'\left(\frac{1}{R_1'} + \frac{1}{R_2'}\right)$$

While such a condition is perhaps conceivable, it would be highly unstable and practically impossible to maintain. It follows that a steady state is ephemeral; there is no static condition of equilibrium in these films. The thin film can persist only so long as flow of liquid into the thin portion counteracts drainage from it by setting up a dynamic equilibrium.

The flow of liquid into the thin portion of the film is caused principally by evaporation of the liquid. Assuming uniform evaporation from the whole surface of the film, the resultant cooling effect will be greatest where the film is thinnest because (1) here the heat capacity is least and (2) the thermal conduction is reduced by the thinness of the film. The equalization of temperatures in a liquid film by conduction, diffusion, and distillation is relatively slow, and some of the important consequences of a lowered temperature in the thin region are as follows: (1) The density, viscosity, cohesion, and surface orientation of the liquid are increased, thereby opposing further drainage and increasing the strength of the film. (2) Convection currents are set up in the plane of the film and perpendicular to this plane. (3) The surface tension of the liquid is increased and more liquid is drawn into the thin portion if there is any curvature in this region. (4) The warmer liquid in the thicker portions of the film, owing to its lower surface tension, spreads over or floods the thin areas. The warmer liquid may be considered a liquid of positive spreading coefficient equal to the difference in surface tensions caused by the thermal difference. That is, $S = \gamma_a - (\gamma_b + \gamma_{ab})$, where γ_a refers to the surface tension of the cold liquid, γ_b to that of the warm liquid, and γ_{ab} to the interfacial tension, which is presumably zero in this case.

The flooding of the thin areas of the film will continue as long as there is a thermal gradient, and this gradient can be maintained if the liquid is free to evaporate. Since the heat of evaporation is large relative to the specific heat of the liquid, the evaporation of a small amount of liquid from the film provides motive power for the transport of a much larger quantity of liquid into the thin film. As a result, the liquid in the thin portion of the film is in continuous turbulent motion, for liquid is also constantly draining from this region.

The decrease in thickness of the film due to evaporation of the liquid may be relatively small while the cooling effect becomes considerable. It has been noted that moisture from the air condenses on carbon disulfide films and separates as fine particles of ice in the thin portion of these films as evaporation occurs. Of course the decrease in temperature also lowers the vapor pressure of the liquid, and this would oppose thermal fluctuation. Those liquids having a low vapor pressure–temperature coefficient may continue to evaporate considerably even after an initial cooling and so continue to produce a temperature gradient. However, the heat of evaporation, which is also a prime factor in determining the degree of cooling, is roughly proportional to dp/dT and the two effects thus tend to cancel.

As the films of liquids decrease in thickness by drainage, interference colors may be observed ranging from the high order down to the white film. A few liquids, especially hydrocarbons, will sometimes thin further to the incipient black stage before rupturing. Color phenomena in thin films have been ably discussed by Lawrence (2)

The changes in thickness of the film may be followed by observing the rapid fluctuations in color while evaporation is occurring. The color distribution in the thin area indicates that a plane surface almost never exists in this region. Very frequently relatively thick ribs of liquid can be observed in the thin film. Such ribs are indicated at *a* and *b* in figure 1. They are often almost stationary for a few seconds if protected from air currents, but are usually in rapid motion. The thickness and activity of these ribs are the more pronounced the more rapid the evaporation of the liquid. They are apparently started by the junction of two opposing or converging currents and are enlarged by suction due to the curvature and thermal gradient. It seems probable that they are return channels for the cooled liquid. It is very difficult to chart the currents in these films or to state the direction of flow at any point, since these fluctuate rapidly. There have been noted as many as three vortical movements in a film simultaneously, even when the color pattern indicated that the depth distribution was almost constant.

Since the flow or pumping of the liquid into the thin film is essential to its preservation, and since this is caused by local temperature differences resulting from evaporation, it follows that the film must become unstable and rupture when evaporation from it is prevented. This conclusion is amply supported by experiment. Thin films of pure liquids are highly sensitive to their own vapors. When immersed in their vapors the films rapidly become thinner and burst. The sensitivity of the film varies with the liquid, the temperature, and the degree of saturation of the vapor. Xylene films burst at once when placed in a small enclosed space. Water and alcohol films are quickly burst by their vapors. A film of kerosene persists for some time in the presence of kerosene vapor unless this is appreciably warmer than the film.

Kerosene films were found to be particularly suitable for continuous detailed study, because of their high stability. It is possible to insert them in test tubes to avoid air currents and to retard the movements of the liquid by decreasing the net rate of evaporation. Such films can be studied conveniently under the microscope or projected in color upon a translucent screen, since they often last for fifteen minutes or more.

Although kerosene is not strictly a pure liquid the phenomena exhibited in its films are essentially similar to those observed in liquid films which consist of a single molecular species. The effects of evaporation set forth in this paper for pure liquids apply equally well to liquid mixtures and other types of solutions. However, other factors, including adsorption, orientation of solute and solvent molecules, and especially the formation of rather rigid structures (as with soap, saponin, or proteins), may increase the strength of such films to the extent that the influence of evaporation is not apparent. It is intended to discuss some of the characteristics of solution films in a subsequent article.

Liquid films are thinned and broken by any means which imparts heat to the thin portion of the film. The application of a slight air pressure to an enclosed film forces the surrounding blanket of vapor against the film and increases the net rate of condensation. This warms the thin film and causes further thinning; if it does not break it shortly returns to its previous condition. A slight decrease in the air pressure causes the opposite result,—a temporary thickening of the film until equilibrium is reëstablished.

If a short piece of platinum wire, held by glass or wood, is thrust into the thin film, the heat conducted by the wire to the cooler film causes rupture of the film. If the wire and holder are previously chilled, the thin film is not ruptured when the wire is inserted. The wire at room temperature may be thrust into the thick portion of the film and then slowly raised into the thin portion without destroying the film. If this is repeated with a wire held directly in the fingers, the conduction of body heat causes the thin film to become thinner and to burst. Heat may also be supplied through the supporting wire,—for example, by touching the lead-in wire with a warm file. If this wire leads to the thin part of the film, bursting occurs when heat is supplied; if to the thick part it does not.

Besides its own vapor, other vapors and gases may supply heat to a film and affect its stability. This effect for a given quantity of vapor will depend upon its temperature and upon whether it transfers heat by contact only or by solution in or condensation upon the film. More heat is supplied if condensation or solution occurs. If the vapor is insoluble in the liquid film, condensation will occur only if the vapor pressure is greater than the saturation pressure at the temperature of the thin film. The vapors of liquids having high vapor pressures and large heats of vaporization are the most effective in destroying films. For example, kerosene films are burst by the vapors of ether, methyl alcohol, ethyl alcohol (95 per cent), and ethyl alcohol (75 per cent) at room temperature with decreasing ease, by water vapor at body temperature with ease, and by air at body temperature with difficulty. If the vapor is soluble in the film a smaller vapor pressure will suffice to produce condensation and to impart heat in this manner to the film. Thus kerosene films are readily burst by vapors of volatile hydrocarbons such as benzene, toluene, xylene, and hexane at room temperature.

The possibility should be noted that if condensation and solution of a vapor in a film do not occur so rapidly as to destroy it, the resulting film may become more stable if the solution forms stronger films than the pure liquid. For example, this might occur when a film of water is exposed to alcohol vapor.

SUMMARY

Liquid films thin by drainage and by suction, owing to surface tension where curvature exists. No static condition of equilibrium can be established. A film can persist only so long as flow of liquid into the thin portion counteracts drainage.

The flow or pumping action into the thin region results from evaporation of the liquid. Uniform evaporation produces the greatest cooling where the film is thinnest, and warm liquid floods the colder areas with resultant decrease in surface energy.

When evaporation is prevented by surrounding the film with its own saturated vapor, the temperature of the film becomes uniform and flow into the thin portion ceases, while drainage continues to decrease its thickness until rupture occurs. Condensation of other vapors upon the film, metallic conduction, or any other means which supplies heat to the thin portion of the film, tends to destroy the film.

The dynamic equilibrium in liquid films can be studied by observing the remarkable display of changing interference colors in thinned films, where the thickness at any point can be estimated from the reflected color.

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STUDIES ON SILICIC ACID GELS. VII

The Effect of the Soda-Silica Ratio upon the Time of Set

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INTRODUCTION

One of several theories, proposed to explain the mechanism involved in the setting of gels of hydrated silica, or silicic acid gels as they are often called, assumes that the molecular silicic acid reacts to form long chains by a process of condensation. This branching or fibrillar structure is believed to provide sufficient rigidity, so that the gel may set (8). With this theory in view it might be assumed that a gel would be produced more rapidly if one started with di- or tri-silicic acid molecules than if the starting point were a monosilicic acid such as ortho- or meta-silicic acid. In order to check this theory, two investigations have been completed in this laboratory. The result of the first investigation, as reported by Hurd and Miller (6), has shown that the effect of temperature upon the time of set of gel mixtures produced by mixing solutions of acetic acid and solutions of sodium silicate is the same, over a variation of the soda-silica ratio from 1:1.58 up to 1:3.86.

In the present investigation we have been able to show that the original soda-silica ratio has no effect upon the time of set where the compositions of the final mixtures are identical in every particular. It can thus be seen that the original soda-silica ratio does not have the result which was logically expected.

GENERAL CONSIDERATIONS

In general, it is well known that the time of set of gels of hydrated silica is affected by a number of factors. The influence of the temperature has been reported (6). The concentrations of silica, of excess acid, of the hydrogen ion, and of certain sodium salts have been shown to exercise a powerful influence upon the time of set. It was not known whether the soda-silica ratio of the sodium silicate possessed any influence, although Bogue (1) has voiced the opinion that it should be studied.

In the investigation which we report here concerning the influence of the soda-silica ratio of the original silicate upon the time of set, it was clear, of course, that no factor should be allowed to vary except the soda–silica ratio. This meant that the composition of two mixtures which were to be compared for time of set should be identical in every respect, except that the sodium silicates used possessed different soda–silica ratios. This involved building up the soda deficiency in a silicate with a higher ratio such as 1:3.25 to compare, for example, with one whose ratio would be 1:2.00. This might be done in any one of four ways. First, the extra sodium hydroxide could be added to the sodium silicate which was lower in soda, using the same amount of acetic acid for both mixtures. Secondly, the extra sodium hydroxide could be added to the acetic acid before pouring in the silicate. Third, less acetic acid could be used and the deficiency of both sodium and acetate in the one solution could be built up by adding the necessary amount of sodium acetate, placing it in the acetic acid before mixing. In a fourth procedure, the sodium acetate could be added to the one sodium silicate solution before mixing. Of these possible procedures, the first three have been tried in our investigations. We have not added the sodium acetate to the silicate, inasmuch as the addition of a strong salt solution causes the silicate to curdle.

In all of the determinations, the temperature was kept constant by means of a good thermostat such as has been used here in previous investigations.

The silicates used in this study have been described previously by Hurd, Raymond, and Miller (7). The time of set was determined always in 80-cc. mixtures in 100-cc. Pyrex Griffin beakers, by the tilted-rod method (1). Thermostats employed gave a variation in temperature of less than 0.1°C. Hydrogen-ion concentration was determined by the quinhydrone method, which was found satisfactory by Hurd and Griffeth (4).

THE EFFECT OF THE ADDITION OF SODIUM HYDROXIDE

The silicates used are classified by letters by their manufacturer.[1] Their composition is shown in table 1. These were fresh silicates and were used fairly quickly. Reagent acetic acid and reagent sodium hydroxide were used. Standard quantitative methods were used for the analysis of solutions of the latter. Solutions of the sodium silicates were analyzed by determining their normality equivalent in sodium hydroxide by titration with standard sulfuric acid solution, using methyl orange as the indicator. From this and the soda–silica ratio supplied by the manufacturer, the silica content of the solution was determined.

The "natural" gel mixtures were produced by pouring a measured volume, 25 cc., of the solution of sodium silicate of the K, U, or C brands into 55 cc. of a mixture of standard acetic acid solution and water. The

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[1] The writers wish to express their appreciation to the Philadelphia Quartz Company, which has kindly supplied the silicates used in this and in other studies.

solutions before mixing had been kept in a thermostat at such a temperature that the heat of the immediate ionic reaction raised the temperature exactly to the temperature of the thermostat in which the time of set was determined. In each case the silicate solution was of such a strength as to give exactly the same concentration of silica in the gel mixture.

TABLE 1

Composition of silicates used

BRAND	SODA:SILICA WEIGHT RATIO	SODA:SILICA MOLE RATIO
E	1:3.25	1:3.36
K	1:2.84	1:2.93
U	1:2.44	1:2.52
C	1:2.00	1:2.06

TABLE 2

Time of set of synthetic mixtures produced by adding sodium hydroxide

TEMPERATURE	MIXTURE	CONCENTRATION OF ACETIC ACID	TIME OF SET IN MINUTES	
			Sodium hydroxide added to acid	Sodium hydroxide added to silicate
°C.				
27.4	K-1	0.680	75.	76.
	K-2	0.805	113.	111.
	K-3	0.930	146.	146.
	K-4	1.055	181.	178.
	K-5	1.180	207.	206.
	K-6	1.300	236.	236.
25.9	U-1	0.748	82.	82.
	U-2	0.873	119.	118.
	U-3	0.998	155.	155.
	U-4	1.123	187.	188.
	U-5	1.248	218.	217.
	U-6	1.373	248.	249.
25.9	C-1	0.865	70.	70.
	C-2	0.990	103.	102.
	C-3	1.115	132.	131.
	C-4	1.240	165.	163.
	C-5	1.365	193.	194.
	C-6	1.490	215.	215.

Concentrations are all in gram moles per liter. Constant are SiO_2 = 0.645; NaOH from E brand = 0.385; NaOH total in K runs 0.440, in U runs 0.508, and in C runs 0.625.

The "synthetic" gel mixtures were all made from the solution of E brand silicate, which has the least soda per mole of silica of any considered in this work.

As a result of the study of these synthetic mixtures, it was found that it made no difference whether the sodium hydroxide was added to the E brand silicate or to the acetic acid. This will be shown in table 2. It was also found, however, that while the curves for time of set against concentration of excess acid checked very well for natural and synthetic mixtures in the case of the K brand silicate, the curves were parallel but did not check in the case of the U and C brands. We suspected this to be due to a small error in the analysis, which was later shown to be true. Accordingly, that part of the investigation was reserved until more satisfactory methods of analysis were worked out.

The data of table 2 show that no significant difference could be found in the time of set of these mixtures whether the sodium hydroxide was added to the sodium silicate solution or to the acetic acid solution. In addition to these data shown, several series of determinations were made where the sodium hydroxide was added to the E brand silicate solution and the result allowed to stand or age for from a few seconds up to seventy-two hours. Then this mixture was poured into the acetic acid solution. No change in the time of set could be found.

It is evident, therefore, either that the sodium hydroxide has no effect upon the structure of the E brand silicate in the three different concentrations needed for the synthetic K, U, or C brands, or that the changes in the structure resulting have no effect upon the time of set.

DEVELOPMENT OF METHODS OF ANALYSIS

From the fact that the curves for the natural and synthetic mixtures from the first investigation either checked satisfactorily, as in the case of the K mixtures, or were parallel but failed to check, as in the case of the U and C mixtures, there was doubt as to whether we were dealing with actual differences or with the results of inaccuracies in the analysis. Since the materials were supplied with a trade analysis and since, more particularly, a small difference in analysis and hence in the composition of the mixtures would produce a considerable difference in the time of set, it was decided that all mixtures must be checked by some satisfactory method of analysis. After receiving considerable help from the manufacturer and studying the various methods here in our laboratory, we have decided to adopt the following methods. It may be possible that they do not give results of absolute accuracy, satisfactory to all, but we have found them entirely reliable and always capable of giving results perfectly reproducible. After all, we must make absolutely certain that the compositions of the natural and synthetic solutions are identical.

Sodium silicate

About 2 g. of the sodium silicate was weighed accurately into a clean platinum crucible, placed in a 250-cc. casserole, and dissolved in about 100 cc. of boiling water. The sodium hydroxide equivalent was determined in the cooled solution by titration with standard hydrochloric acid, using one or two drops of methyl orange indicator. The hydrochloric acid solution was of such strength that about 40 cc. was required. The silica in the solution was dehydrated with hydrochloric acid instead of sulfuric acid, ignited and weighed in the regular manner. The silica was volatilized with hydrofluoric and sulfuric acids. We have had very much better success in dehydrating the silica with hydrochloric acid than with sulfuric acid.

When a solution of sodium silicate was analyzed, it was measured by volume, otherwise the same procedure was used.

The silicates used have given the results shown in table 3, three check determinations having been made in each case.

TABLE 3

Composition of silicates from analysis

BRAND	SODA:SILICA WEIGHT RATIO	SODA:SILICA MOLE RATIO	AVERAGE DEVIATION FROM MEAN IN PARTS PER THOUSAND
E	1:3.208	1:3.313	1.3
K	1:2.830	1:2.923	0.7
U	1:2.358	1:2.435	1.1
C	1:1.948	1:2.011	1.9

Acetic acid

Solutions were made from reagent grade glacial acetic acid. They were standardized against an approximately 1 *N* sodium hydroxide solution. This contained enough barium hydroxide to be free from carbonate and was kept in a Squibb automatic buret assembly, protected by fresh soda lime tubes. The base was standardized against hydrochloric acid, gravimetrically standardized.

Sodium acetate

A study was made of the accuracy and precision of two methods for the analysis of sodium acetate, both solid and in solution (3), namely, the pyrolytic and the distillation methods. The former method is much more rapid. The sodium acetate was converted to carbonate by careful ignition at low red heat, as recommended by Scott (9). It was weighed as carbonate. The results were found to check to 1 or 2 parts per thousand.

The sodium acetate solutions were prepared from reagent sodium acetate and analyzed by the pyrolytic method.

COMPARISON OF TIME OF SET FOR NATURAL AND SYNTHETIC MIXTURES

Preparation of sodium silicate solutions

These were prepared by weighing out slightly more than the calculated amount of the particular sodium silicate. This was dissolved in recently boiled distilled water, and the solution was allowed to stand for a week. The sediment was then removed by decantation and filtration. Only in the case of the K brand was the sediment appreciable. Here it was found by analysis that a loss in content of silica of 4 parts in 1000 had occurred. A correction was made. The filtered solutions were titrated for the sodium hydroxide equivalent with standard 1 *N* hydrochloric acid, using methyl orange. From the soda-silica ratios the content of silica was calculated. The solutions were diluted to make them all 2.064 *M* with respect to silica.

TABLE 4

Time of set and pH of natural and synthetic gel mixtures

MIXTURE	MOLARITY OF EXCESS ACETIC ACID	NATURAL MIXTURE		SYNTHETIC MIXTURE	
		Time of set	pH	Time of set	pH
U-11	0.400	125.0	4.70	125.0	4.69
U-12	0.300	98.0	4.82	97.0	4.82
U-13	0.200	70.0	4.94	66.0	5.00
U-14	0.100	35.0	5.30	34.5	5.31
U-15	0.050	18.3	5.60	17.8	5.58
C-11	0.400	105.0	4.75	104.0	4.75
C-12	0.300	84.0	4.87	80.3	4.89
C-13	0.200	56.0	5.07	55.5	5.07
C-14	0.100	30.5	5.39	30.0	5.39
C-15	0.050	15.7	5.70	15.9	5.67
K-11	0.400	140.0	4.61	139.5	4.63
K-12	0.300	105.7	4.75	106.8	4.76
K-13	0.200	72.6	4.93	74.7	4.95
K-14	0.100	39.2	5.24	39.0	5.25
K-15	0.050	20.0	5.56	20.3	5.55

The gel mixtures were prepared as usual. Into one 250-cc. beaker was placed 50 cc. of silicate solution. This would make each mixture 0.645 *M* with respect to silica, which, experience has shown, produces satisfactory gels. The remaining items were measured into another 250-cc. beaker containing 110 cc. in all of acetic acid solution and distilled water in the natural mixtures and of acetic acid solution, sodium acetate solution, and distilled water in the synthetic mixtures. Mixing and determination of time of set and of pH were carried out as usual. The tilted-rod method was used to determine the time of set. The thermostat in which setting occurs was kept at 25.0°C. As explained before, the heat of mixing of the silicate and acetic acid solutions brought the mixture exactly to 25°C.

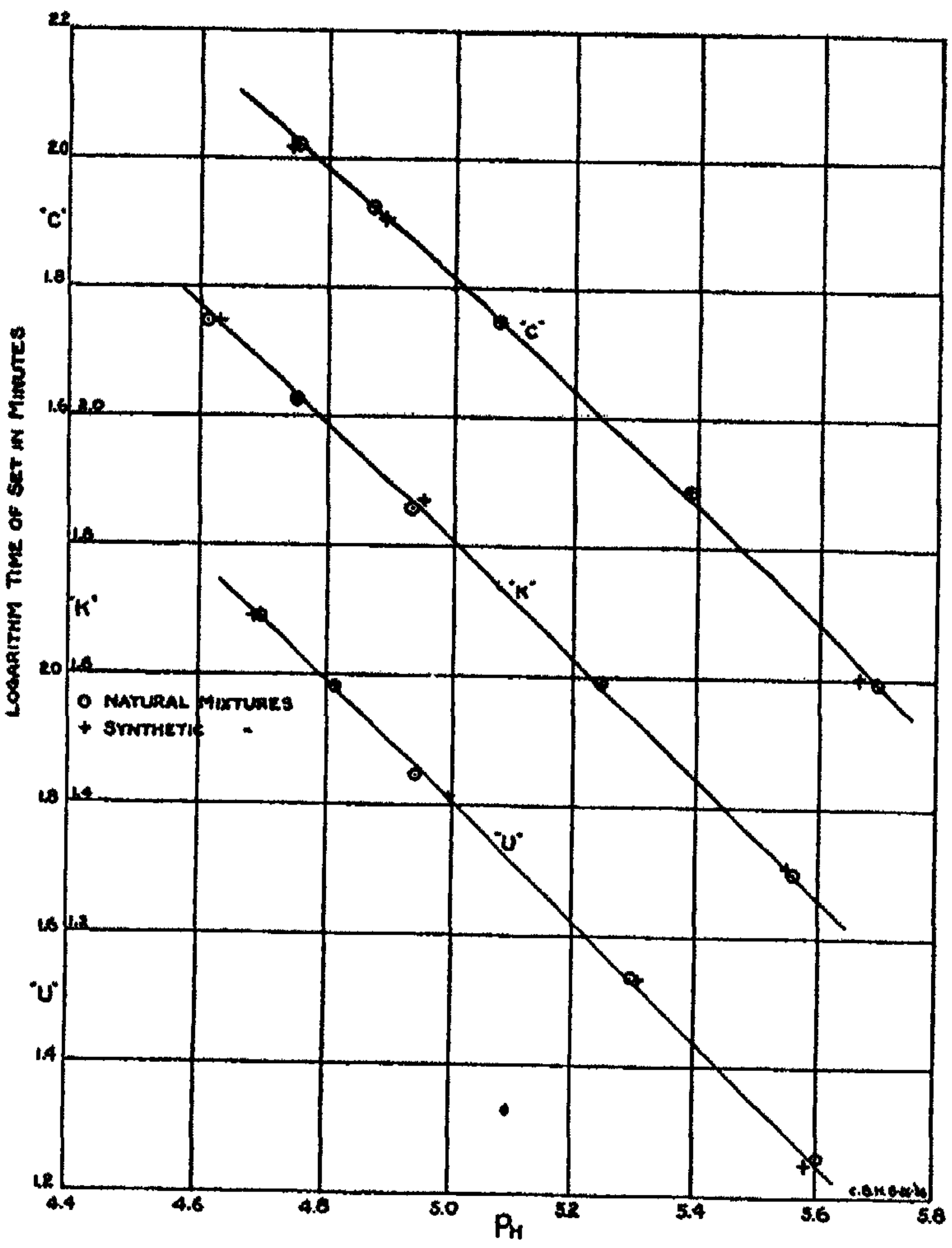

FIG. 1. Relation between logarithm of time of set and pH for natural and synthetic mixtures for three series

At least four check determinations were made for each mixture. The results are given in table 4, although the curves of figure 1 show them somewhat more clearly. Discrepancies are well within the limits of experimental error and the conclusion is obvious that gel mixtures of the same composition and temperature and particularly, with the same pH, set in the same time, regardless of the soda–silica ratio of the original silicate. It may be thought that a wider range might have been chosen. The answer is that such work is very laborious and time-consuming, and we have considered that five different compositions each for three different soda–silica ratios is sufficient to prove the point.

We do not have sufficient data to be able to show that the gels prepared from the natural and synthetic mixtures are identical. However, it should be evident here, we believe, that the most striking property and, probably, the most fundamental—namely, the setting time—is the same for both. We are studying other properties, but the results will not be available for at least two years.

DISCUSSION OF RESULTS

It was expected, naturally, in view of the theory mentioned at the beginning of this article, that a gel should set more rapidly coming from a silicate with more silica per mole of soda. This would be on the assumption that such a silicate was a salt of a polysilicic acid or a mixture of such salts. For example, the C brand with its soda–silica ratio of 1:2.06 might be considered as a disilicate and hence considerably simpler than the salts present in the E brand with its ratio of 1:3.36. However, no difference in time of set was noted.

Possibly this assumption of the polysilicate structure is untrue, and the theory advanced by Harman (2) is correct, namely, that in sodium silicate of soda–silica ratio 1:1.0 the metasilicate ion, $SiO_3^{=}$, is present but that in silicates of ratio 1:2 and on up to 1:4, the extra silica is present as colloidal silica.

The results presented in the first portion of this paper may be taken to bear upon this idea of the colloidal silica present in silicates of ratios 1:2 to 1:4. It is a well-known fact that colloidal silica is rapidly peptized by sodium hydroxide. In the synthetic C runs, for example, no difference in time was noted where the extra sodium hydroxide was added to the E brand solution, being permitted to remain up to three days before mixing, and in those cases where it was added to the acetic acid before pouring in the sodium silicate solutions. This corresponded to exposure to about 0.5 *N* sodium hydroxide for up to three days, which treatment will even peptize a silicic acid gel. In spite of this long exposure, no difference in time of set was found.

Two alternative theories appear possible. According to the first theory, the silica goes into the same form when the sodium silicate solution is poured into the acetic acid solution regardless of the soda-silica ratio. The building up of the gel structure starts from this basic material.

The second theory postulates that the slow stage in the formation of the silicic acid gel occurs considerably farther along the line than would correspond to the difference between these di- or tri-silicic acids.

At present we do not have sufficient data to permit a choice between these theories. An attempt was made by Hurd and Letteron (5), described in an early paper in this series, to measure the order of the reaction. Had the attempt succeeded, we should have had valuable data to aid us in a choice of theory. The attempt failed since there was also a variation of the hydrogen-ion concentration, a factor which has a very powerful effect upon the time of set. In the papers which have followed the one mentioned, the effects of the different variables have been isolated and studied, one by one.

It is hoped that an investigation already partially completed in this laboratory will help in a choice of the correct theory.

SUMMARY

A study has been made to determine the effect, if any, of the soda-silica ratio of the original sodium silicate upon the time of set of silicic acid gels. The gel mixtures were made by mixing solutions of sodium silicate and acetic acid. The soda-silica ratio was varied from 1:2.00 to 1:3.25.

All variable factors except the original soda-silica ratio were carefully controlled.

No measurable effect of the soda-silica ratio of the original silicate upon the time of set of the silicic acid gel could be found.

Solutions of sodium silicate lower in soda and higher in silica were exposed to the action of excess sodium hydroxide for varying lengths of time. This was found to have no effect upon the time of set of gel mixtures made with these solutions and acetic acid solutions.

A brief discussion of several theories for the setting of these gels is given.

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THE VAPOR PRESSURES AND SOME THERMODYNAMIC PROPERTIES OF AQUEOUS SOLUTIONS OF NICKEL CHLORIDE AT 25°C.

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A large supply of nickel chloride, prepared from C.P. nickel carbonate and pure hydrochloric acid, was further purified by repeated crystallization from a hot saturated solution of the salt in pure distilled water. The crystals were sucked dry and then dissolved to a nearly saturated solution, which was preserved in a mercury-sealed flask to prevent evaporation. Accurately weighed portions of this solution were diluted to a suitable volume and the nickel chloride content was determined by precipitation as silver chloride. The experimental solutions were prepared on a weight-molal basis by diluting accurately weighed portions of the mother solution to the desired molality. The densities are accurate to 1 part in one million. The apparatus and technique employed have been fully described in previous papers (2).

Because of the lack of agreement in the solubility data to be found in the literature, we redetermined the solubility of nickel chloride at 25°C. A practically saturated solution of the salt in contact with solid crystals was first made at about 32°C. The saturation vessel was then transferred to the large Freas water bath at 25° ± 0.01°C. and stirred with a high speed motor-driven stirrer for ten days. At the end of this time triplicate samples were withdrawn at various times over an additional period of two weeks. The data obtained for the solubility of nickel chloride are as follows:

Grams of saturated solution.....	2.75458	2.62211	2.70519	2.57363
Grams of $NiCl_2$ per gram of solution....................	0.38881	0.38918	0.38891	0.38896

The mean, 0.38896, corresponds to a solubility of 4.9116 ± 0.0020 moles of $NiCl_2$ in 1000 g. of water at 25°C.

The essential experimental data are given in table 1. Each value of the vapor pressure of the solvent, p_1, is the mean of at least three consecutive determinations. For no solution did the maximum deviation from the mean exceed 0.004 mm. The activity of the solvent, a_1, is calculated directly from the ratio, $a_1 = p_1/p_1^0$. Employing these values of a_1 we calculated the increase in free energy accompanying the transfer of one mole of solvent from the pure solvent to a solution of molality, m, by means of the relation, $\Delta \bar{F}_1 = RT \ln a_1$.

To eliminate the influence of slight errors in density upon the values of the apparent molal volumes, we first calculated the values of

$$F = 1000\,(d_1 - d)/c$$

where d_1 and d are the densities of the pure solvent and solution, respectively. We then plotted the values of F against the corresponding values

TABLE 1

Experimental and calculated data for nickel chloride solutions at 25°C.

m	p	a_1	$-\Delta\bar{F}_1$ calcd.	$d^{25°}_{4°}$	$\varphi_{\text{obsd.}}$	$\varphi_{\text{eq.}}$	$\bar{v}_2$
	mm.				*cc.*	*cc.*	*cc.*
0.0	23.752	1.000		0.997074		7.016	7.016
0.1	23.648	0.9956	2.60	1.009105	8.861	8.971	9.957
0.2	23.541	0.9911	5.29	1.020930	9.769	9.791	11.197
0.4	23.312	0.9815	11.08	1.044193	10.976	10.960	12.964
0.6	23.063	0.9710	17.45	1.067009	11.906	11.863	14.328
0.8	22.788	0.9594	24.56	1.089483	12.624	12.627	15.480
1.0	22.485	0.9466	32.51	1.111579	13.281	13.301	16.494
1.5	21.598	0.9093	56.34	1.165334	14.675	14.735	18.639
2.0	20.548	0.8651	85.89	1.216740	15.984	15.939	20.420
2.5	19.354	0.8148	121.4	1.266389	17.026	16.993	21.957
3.0	18.044	0.7597	162.9	1.314339	17.909	17.984	23.361
4.0	15.209	0.6403	264.2	1.406068	19.242	19.586	25.627
4.9116*	12.579	0.5287	377.8	1.485417	20.119	20.890	27.391

*Saturated.

of the square root of the molar concentration, $c^{1/2}$, calculated from the density. Although the relation (1), F, is very sensitive to slight errors in density, all of the experimental points, except those of the lowest and the two highest concentrations, fall upon a perfectly smooth curve. Using only those values of $\varphi_{\text{obsd.}}$ for the solutions for which the F-values fall upon the curve, we deduced by the method of least squares the relation,

$$\varphi_{\text{eq.}} = 7.0164 + 6.1267c^{1/2} + 0.2103c$$

Except for the three solutions mentioned, the agreement between the observed and calculated apparent molal volumes, $\varphi_{\text{obsd.}}$ and $\varphi_{\text{eq.}}$, is exceptionally good.

Gucker (1) has derived the following relation between the molal and apparent molal volumes:

$$\bar{v}_2 = \varphi + c^{1/2}\left[\frac{1000 - \varphi c}{2000 + c^{3/2}\partial\varphi/\partial c^{1/2}}\right]\partial\varphi/\partial c^{1/2}$$

Upon substituting in this equation the values of $\varphi_{\text{eq.}}$ for the corresponding concentrations, c, we obtain the partial molal volumes, $\bar{v}_2$, of the nickel chloride at the various dilutions. All of the data thus calculated are incorporated in table 1.

SUMMARY

The densities of aqueous solutions of nickel chloride and the vapor pressures of the solvent over these solutions have been determined at 25°C. From this data have been calculated the activity of the solvent and the partial and apparent molal volumes of the dissolved salt.

The solubility of nickel chloride in water at 25°C. has been found to be 4.9116 moles per 1000 g. of water.

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ELECTROKINETICS. XVIII

INTERFACIAL ENERGY AND THE MOLECULAR STRUCTURE OF ORGANIC COMPOUNDS. IV. THE ELECTROKINETIC BEHAVIOR OF CHARCOALS IN AQUEOUS SOLUTIONS OF ORGANIC ACIDS[1]

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INTRODUCTION

Many of the papers which have been published on charcoal deal with (a) the adsorption of homologous series of organic compounds together with the application of the Langmuir or Freundlich adsorption isotherms or the testing of Traube's rule, (b) the adsorption of inorganic acids, and (c) the hydrolytic adsorption of salts of organic and inorganic acids. One of the generalizations which has grown out of these studies is that the adsorption of weak electrolytes on carbon is apolar. For example, Phelps and Peters (14) have noted that the adsorption of organic acids on charcoal increases with decreasing pH, and Fromageot and Wurmser (6) and Angelescu and Comanescu (2) point out that the adsorption of the acids is reduced in the presence of their salts. Kolthoff (7) states that the adsorption of acids is molecular (non-ionic) and non-polar, and follows the order of the depression of the surface tension at an air-water interface. Gas adsorption on charcoal of substances which are weakly electrolytic in aqueous solution is largely parallel to adsorption from solution. Freundlich (5) has pointed out that this may be construed as evidence that weak electrolytes are adsorbed apolarly on charcoal. This interpretation arises from the consideration that, because of the non-electrolytic nature of gases, the adsorption of gases is of necessity apolar.

A second concept arising from adsorption studies on charcoal is that oxides of carbon (other than carbon monoxide or carbon dioxide) are formed on the surface of the char during its preparation. These oxides

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[1] Paper No. 1456 Journal Series, Minnesota Agricultural Experiment Station. Greatly condensed from a thesis presented by Vernon L. Frampton to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1936. The detailed thesis is on file in the Library of the University of Minnesota.

have been postulated to be either acidic or basic, depending on the type of the activation. Thus it has been observed by practically all workers studying charcoal that charcoal activated at higher temperatures (900° to 1200°C.) will adsorb little or no alkali hydroxide, but will adsorb appreciable quantities of acids. However, if the activation is at lower temperatures (400°C.) the char will be a good adsorbent for alkali hydroxides, but a relatively poor one for acids. The interpretation of these observations has been that basic oxides of carbon were formed on the charcoal heated at the higher temperatures, whereas acidic oxides of carbon were formed on those chars heated at the lower temperatures. Kruyt and de Kadt (8) report that charcoal which has been heated at 900°C. in an atmosphere of carbon dioxide has on its surface a basic oxide of carbon, and that the charcoal particles are positively charged. Various postulates have been advanced regarding the structural formulas of these oxides of carbon, but the oxides themselves have not been isolated, and the evidence for their existence is circumstantial and is based on adsorption characteristics. We have been unable to find any electrokinetic evidence for positively charged charcoal.

If adsorption of weak electrolytes on charcoal is apolar (molecular), the electrokinetic charge on the surface of the charcoal particles should be independent of the amount of material adsorbed, its concentration in solution, or its chemical configuration. Likewise the presence of acidic or basic oxides of carbon on the surface of the char preparation should be reflected in its behavior in a cataphoresis cell. The objective in this research was to study charcoal, using electrokinetic technics as a tool.

EXPERIMENTAL

Methods

Cataphoretic mobility determinations were used, chiefly because of the simplicity of measurement. The cell used was a slight modification of the one described by Bull (3). The modification consisted in the replacement of the plaster of Paris, in which the copper wires were imbedded, by parchment bags. A small amount of potassium chloride solution was placed in the bags before sealing to provide for the initial conductivity in the early part of the determination. The bags were sealed in place at either end of the cell by means of paraffin, and the cover glass sealed on in the usual manner. The cover glass was of the same type of glass as the cell proper. It is desirable in studies of this type that the entire cell be composed of the same glass, since small differences in the charge on the glass composing the bottom and top of the cell cause appreciable distortions in the distribution of the velocity of the water in the cell. That is, the water velocity caused by electrosmosis should be identical at the top and bottom of the cell.

The cell was placed on the stage of a microscope equipped with a 16 mm. objective and a No. 10 eyepiece. The microscope tube length was set at 181 mm. The depth of the cell was measured by means of the calibrated screw micrometer of the microscope. The copper electrodes were connected with a D.C. source of current, the potential drop across the cell being usually some 200 volts.

Velocity determinations were made at levels one-third, one-half, and two-thirds the depth of the cell, and from these measurements the velocity of the suspended particle with respect to the water was calculated. In some cases the speeds of the particles were determined at depths of 0.211 and 0.789 the depth of the cell. Observations were made only on particles which were sharply in focus.

Smoluchowski (16) has shown that for laminar streaming of a viscous liquid between parallel plates

$$V_w = U[1 - 6\{x/d - (x/d)^2\}] \qquad (1)$$

where V_w = velocity of water, d = total depth of the cell, x = depth of cell at which V_w is measured, and U = the endosmotic velocity of the water at the top and bottom of the cell. Now

$$V = V_o - V_w \qquad (2)$$

where V = velocity of particle with respect to the water, V_w = velocity of the water, and V_o = observed velocity.

Values for $V_o - V$ may be substituted in equation 2 and the resulting equation will relate the observed velocity, the velocity of the particle with respect to the water, the endosmotic velocity at the walls of the cell, and the depth of observation. The unknowns are V and U. Speeds determined at $x/d = \frac{1}{3}$ and $\frac{1}{2}$ may be substituted for the values of V_o at the respective levels, and the two resulting equations solved simultaneously for V. The relation

$$V = (V_o)_{\frac{1}{2}} - 3[(V_o)_{\frac{1}{2}} - (V_o)_{\frac{1}{3}}] \qquad (3)$$

is obtained, where $(V_o)_{\frac{1}{2}}$ and $(V_o)_{\frac{1}{3}}$ are the observed velocities at depths $x/d = \frac{1}{2}$ and $\frac{1}{3}$, respectively. It will be noted that at depths of 0.211d and 0.789d the water is stationary, and at this point $V = V_o$.

In checking equation 3 to determine its usefulness, observations of speeds of the suspended particles were made at depths of 0.211d and 0.789d, and these were compared with those calculated from the observations of speeds at depths of $\frac{1}{3}d$, $\frac{1}{2}d$, and $\frac{2}{3}d$. An average of thirty determinations each at levels of 0.211d and 0.789d gave, respectively, for a suspension of charcoal particles in water, 3.29 and 3.28 microns per second per volt per centimeter. The average for the determinations for depths of $\frac{1}{3}d$, $\frac{1}{2}d$, and $\frac{2}{3}d$ gave 5.42, 6.50, and 5.45 microns per second per volt per centimeter respectively. These values substituted in equation 3 gave a value of 3.32 microns per second per volt per centimeter as the true cataphoretic velocity. The error due to faulty focusing of the microscope or to the settling out of the particles during the determination in the case of direct measurement of speed at depths of 0.211*d* and 0.789*d* is about half that found in the case of the calculated values of the speeds from the observations at depths one-half, two-thirds, and one-third the depth of the cell. It may be said in general that the measurements reported in this paper have an accuracy of about 95 per cent.

Determinations of the speeds of the suspended particles were made with a stop watch, observing the time required for the particles to traverse a given distance under a given potential gradient. The direction of the field was reversed after each measurement. On the average, about twenty-five observations were made at each level of the cell. All determinations were made at room temperature, since the errors in observations are probably larger than those introduced by variations in temperature which occurred.

All of the adsorption studies reported were made on 0.5 g. of charcoal suspended in 35 cc. of solution. Phenolphthalein was used as an indicator in the case of the titrations of the organic acids, the first portion of the filtrate from the char suspensions being discarded, and titrations made on later aliquots. The char was left in suspension in the liquid for 30 minutes as a minimum in order to ensure complete adsorption equilibrium.

PREPARATION OF MATERIALS FOR STUDY

The organic acids were redistilled from an all-Pyrex still. Only those fractions which had a boiling-point range of less than 1°C. were used. In the case of the inorganic materials, the precautions taken were those usually taken in quantitative procedure.

The Norite used in these studies was a sample of the lot used by Linner and Gortner (9). This charcoal was electrodialyzed across parchment paper at 530 volts for a week, thus reducing the ash content from 1.29 per cent to 0.47 per cent. The residual ash appeared to be almost wholly silica. It was non-hygroscopic and was neutral to phenolphthalein. The char was dried at 100°C. in the air, and finally at 100°C. *in vacuo.*

Charcoal No. 0 was prepared by charring sucrose with C.P. sulfuric acid. After the charring was complete, the char was washed with boiling distilled water until the washings were alkaline to methyl red. It was then ground in a porcelain ball mill, rewashed with water, and finally electrodialyzed for a week across parchment paper at 220 volts. The ash, 1.66 per cent after the dialysis, was apparently porcelain dust derived from the ball mill. The ash was non-hygroscopic and neutral to phenolphthalein. No sulfate could be extracted from the dialyzed char by boiling sodium hydroxide solution. Apparently all of the acid had been removed by the electrodialysis, since Miller (11) states that mineral acids are quantitatively removed from charcoal by boiling solutions of sodium hydroxide.

Charcoal No. 1 was prepared by activating charcoal No. 0 at 750°C. for seven hours in a muffle furnace. Charcoal No. 0 was placed in 8-in. test tubes (Pyrex) and the open end nearly sealed; the test tubes were subsequently placed in the furnace. The loss of material during activation was nearly 80 per cent.

Charcoal No. 2 was prepared by activating charcoal No. 0 in the manner indicated above, except that it was heated for seven hours at 450°C., and then for two hours at 750°C.

Charcoal No. 3 was charcoal No. 0 activated at 400°C. in the manner indicated for charcoal No. 1. The heating was for two hours. Charcoal No. 4 was similarly activated at 600°C. for two hours.

Charcoal No. 5 was prepared by activating charcoal No. 0 in a covered platinum dish over a blast lamp for two hours. From the color scale of approximate temperatures it appeared that the char had been heated to approximately 1300°C. It was heated in separate small portions, so that all portions of the charcoal received as nearly as possible the same treatment.

Charcoal No. 6 was prepared by extracting charcoal No. 0 with water continuously in a Soxhlet extractor for five days. During the early part of the extraction the extracts were acidic. The water in the extractor was changed frequently.

Charcoal No. 7 was prepared by boiling charcoal No. 0 in a solution of approximately 0.1*N* sodium hydroxide, filtering, and then extracting the residue with water in a Soxhlet extractor until no further alkali was removed.

Charcoal No. 8 was prepared by activating charcoal No. 0 in an atmosphere of hydrogen at 600°C. for three hours.

Charcoal No. 9 was prepared by moistening charcoal No. 0 with nitric acid and then heating in a covered platinum crucible to a dull red heat.

Charcoal No. 10 was prepared by carbonizing sucrose over a flame in a porcelain dish. It was then heated, small portions at a time, in a covered platinum dish over a blast lamp.

Charcoal No. 11 was prepared by heating charcoal No. 10 in an atmosphere of hydrogen to 1000°C. for three hours. In this case, as in the case of the other gas treatments, the charcoal was permitted to cool in the gas stream.

Charcoal No. 12 was prepared by heating charcoal No. 10 in an atmosphere of carbon dioxide for two hours to 1000°C.

Charcoal No. 13 was prepared by heating charcoal No. 10 in an atmosphere of carbon dioxide to 1000°C. for five hours. Some portions of this sample received heat treatment for as long as twenty-four hours.

Charcoal No. 14 was a sample of Norite that had been heated in an atmosphere of nitrogen to 900°C. for about one and one-half hours. This treatment was given the char about a year before the electrokinetic observations were made.

The graphite used was a sample of synthetic Atcheson graphite, grade BB.

THEORETICAL

The theoretical treatment relating the potential across the Helmholtz double layer and the mobility of a charged particle suspended in a medium is adequately treated elsewhere (1). The relation derived is

$$\zeta = \frac{4\pi\eta u}{DX} \tag{4}$$

where ζ = potential across the double layer, u = observed velocity of the suspended particle, η = viscosity of the medium in which the particle is suspended, D = dielectric constant of the liquid medium, and X = potential gradient through which the suspended particle moves.

The relation between the potential, the ionic concentration, and the charge per unit area on the particle is given (1) by the equation

$$\sigma = \sqrt{\frac{NDkT}{2000\pi}} \sqrt{\sum C_i\left(e^{-z_i\frac{e\zeta}{kT}} - 1\right) + \sum C_j\left(e^{+z_j\frac{e\zeta}{kT}} - 1\right)} \tag{5}$$

σ = the charge per unit area on the particle, N = Avogadro's number, k = the Boltzmann constant, T = the temperature, C = the concentration of electrolytes in moles per liter, e = the elementary charge, Z = the valence of the ions, and i and j indicate the anion and cation, respectively.

When the valences of the ions making up the electrolyte are the same, equation 5 reduces to

$$\sigma = 2\sqrt{\frac{NDkT}{2000\pi}}\, \sqrt{C} \sinh Z\frac{e\zeta}{2kT} \tag{6}$$

In the calculations of the charge per unit area on charcoal particles suspended in solutions of organic acids in water, it was assumed that the un-ionized portion of the acid did not influence the charge, and the concentration C was taken as that of the ions in solution. The values for C were obtained by calculation, using the ionization constants of the acids.

THE EXPERIMENTAL DATA

Figure 1 shows the effect of concentration of acid on the mobility of Norite particles suspended in aqueous solutions of several aliphatic acids. It will be noted that the curves for the various acids are essentially superimposable. It is not possible to distinguish one acid from the other. Within the experimental error the values for the speeds at a given concentration are the same. However, there is a considerable difference in the number of equivalents of the various acids which will be adsorbed on a gram of this particular char from solutions of the same concentration. The data of Linner and Gortner (9) indicate that there are nearly twice as many equivalents of caproic acid as of acetic acid adsorbed from a 0.05 molar solution by a gram of Norite. This difference is not reflected in the mobility of the char suspended in solutions of these acids.

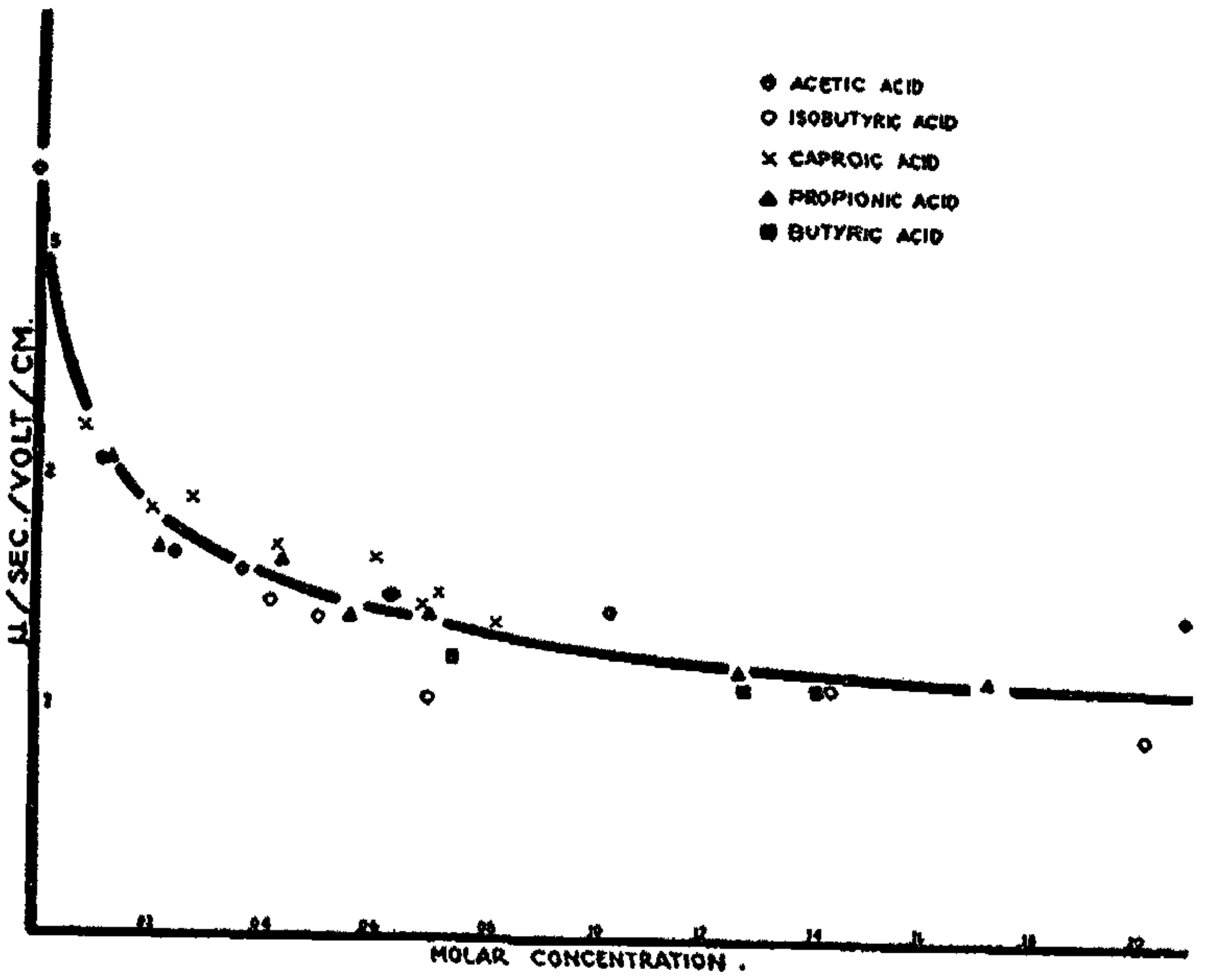

FIG. 1. The electrokinetic mobility–concentration curve for Norite in solutions of aliphatic acids. The isobutyric acid data were obtained by using a sample of activated charcoal obtained from Dr. I. M. Kolthoff. This particular charcoal sample had probably been made ash-free by the method of Miller (11), as it contained detectable quantities of hydrochloric acid. The char was washed with boiling distilled water until the washings were alkaline to methyl red before the preparation was used.

A hint at the interpretation of these results is found in the values of the ionization constants for the various aliphatic monobasic acids. These vary only from 1.86×10^{-5} for acetic acid to 1.4×10^{-5} for caproic acid. Since there are only slight differences in the strengths of the various acids, the value of $\sqrt{C}$ in equation 6 will be essentially the same for all acids. As a matter of fact, the value of $\sqrt{C}$ at a given concentration of acid will vary from acid to acid very nearly as the fourth root of the ionization constants vary. If, however, the adsorption of aliphatic acids on Norite is *apolar*, the quantity of acid adsorbed on the charcoal should not influence the charge on the particles, and the product of their speeds by $\sqrt{C}$ should be constant through all ranges of concentration. The calculations for propionic acid, which may be taken as a representative of the group, are given in table 1. The data are in accord with the rule that the adsorption of weak electrolytes from aqueous solutions is primarily the adsorption of un-ionized molecules.

TABLE 1

Charge on Norite particles suspended in solutions of propionic acid

CONCENTRATION OF ACID	CONCENTRATION OF H^+ ION	SQUARE ROOT OF H^+ ION CONCENTRATION	SPEED OF PARTICLE	CHARGE PER UNIT AREA
normality	$\times 10^4$	$\times 10^2$	*μ/sec./volt/cm.*	*e.s.u.*
0.0123	4.34	2.06	2.07	461
0.0216	5.50	2.34	1.69	428
0.0431	7.77	2.78	1.63	492
0.0561	8.86	2.97	1.40	435
0.0686	9.80	3.13	1.41	479
0.1263	12.4	3.52	1.00	445
0.1723	15.6	3.95	1.15	492
0.2169	17.4	4.17	0.99	451
0.2416	20.4	4.52	0.98	482

The data for suspensions of charcoals No. 0 and No. 1 in solutions of formic acid are shown in figure 2. It will be noted that for these charcoal preparations the same curve is obtained. The adsorption of formic acid on charcoal is likewise apolar, since the charge per unit area (cf. table 2) is constant. The difference in the charge in the cases of the data presented in tables 1 and 2 is unaccounted for.

The specific treatment of a charcoal may have an enormous effect on its adsorptive capacity. It might be expected that an equally marked effect would be produced in the electrokinetic properties of a charcoal by various treatments. However, mobility studies on the various chars indicate that the history of the charcoal is not reflected in its electrokinetic behavior. The results of a study of the mobility of various charcoals in acetic acid solutions are presented in figure 3. Charcoal A in these studies is a portion of charcoal No. 0 which was not electrodialyzed. These studies do not indicate a difference in the surface properties of the various charcoals. That these charcoals do differ greatly in adsorptive capacity is shown by figure 4. Furthermore the charcoals used in figure 3 show large differences in adsorptive capacities toward sodium hydroxide.

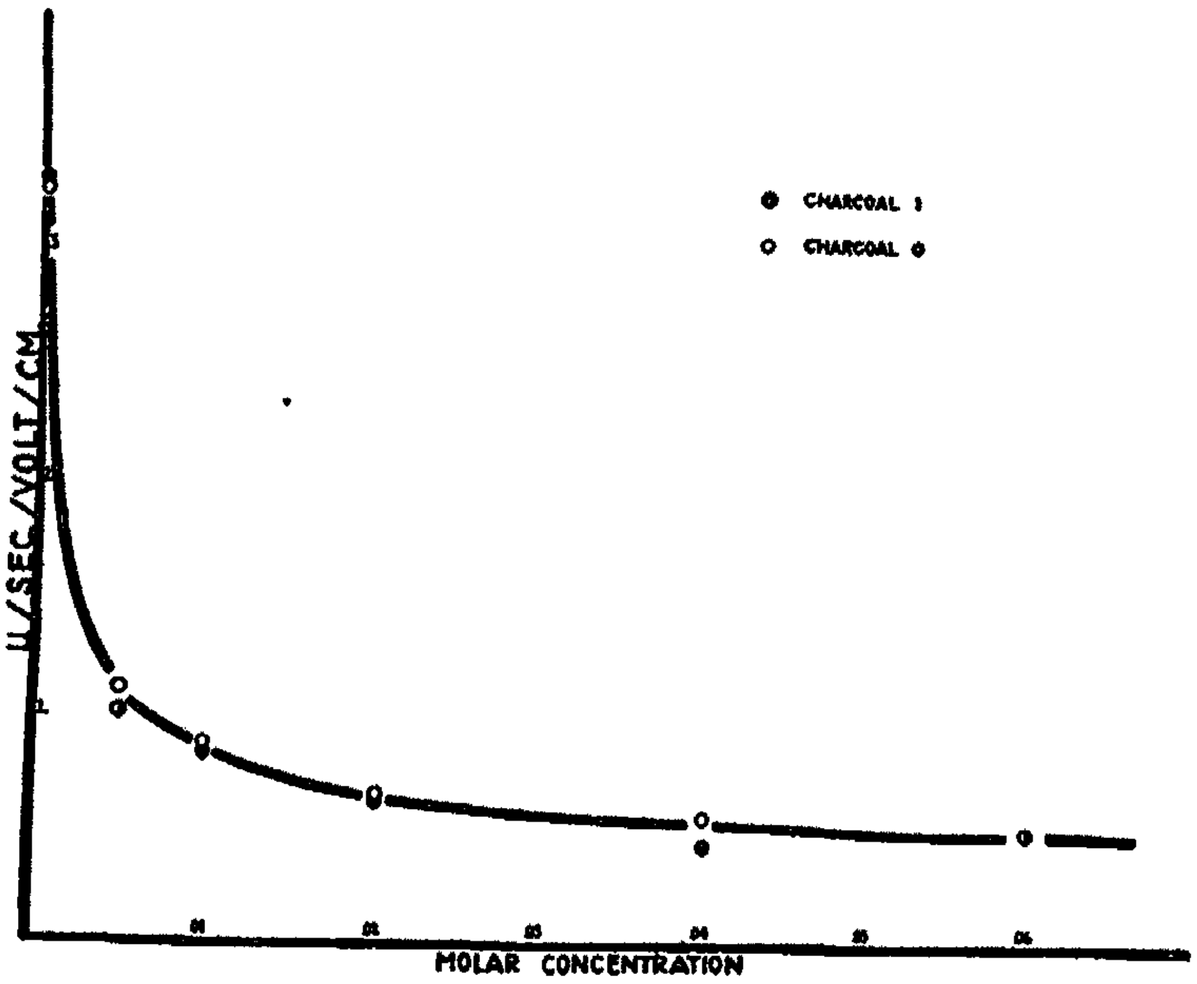

Fig. 2. The concentration–electrokinetic mobility curve for charcoals No. 0 and No. 1 in solutions of formic acid.

TABLE 2

Charge on charcoal No. 0 particles suspended in solutions of formic acid

CONCENTRATION OF ACID	CONCENTRATION OF H^+ ION	SQUARE ROOT OF H^+ ION CONCENTRATION	SPEED OF PARTICLE	CHARGE PER UNIT AREA
normality	$\times 10^4$	$\times 10^2$	*μ/sec./volt/cm.*	*e.s.u.*
0.005	9.25	3.04	1.00	323
0.01	13.4	3.65	0.88	325
0.02	19.6	4.43	0.65	305
0.04	28.2	5.21	0.55	308
0.06	34.8	5.88	0.52	323

The adsorption data for charcoal No. 0 in solutions of sodium hydroxide are shown in figure 5. It will be seen that 1 g. of charcoal No. 0 adsorbs completely from solution 1.70 milliequivalents of sodium hydroxide, leaving the solution neutral. Table 3 shows that charcoal No. 1, Norite, and the

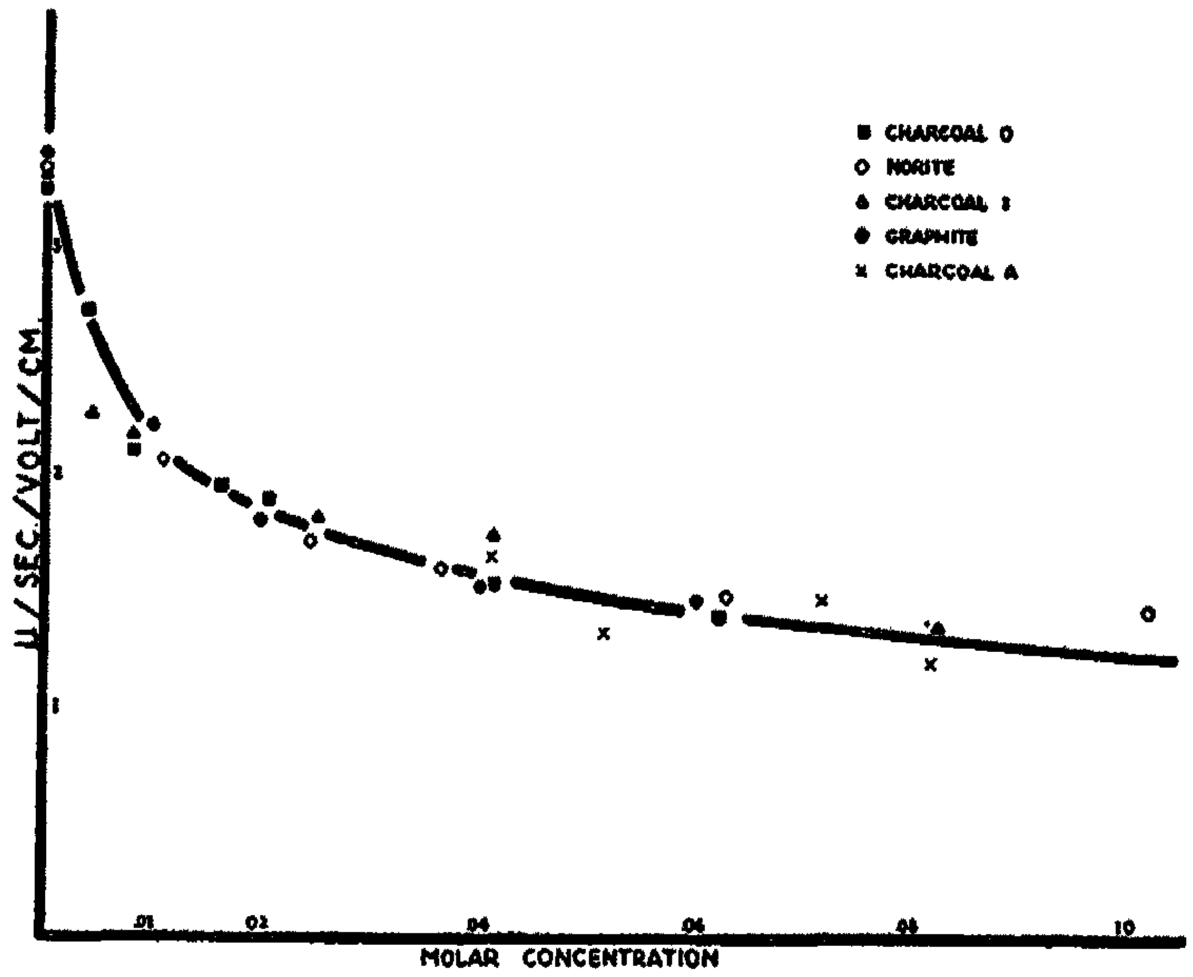

FIG. 3. Electrokinetic mobility of various carbons in solutions of acetic acid

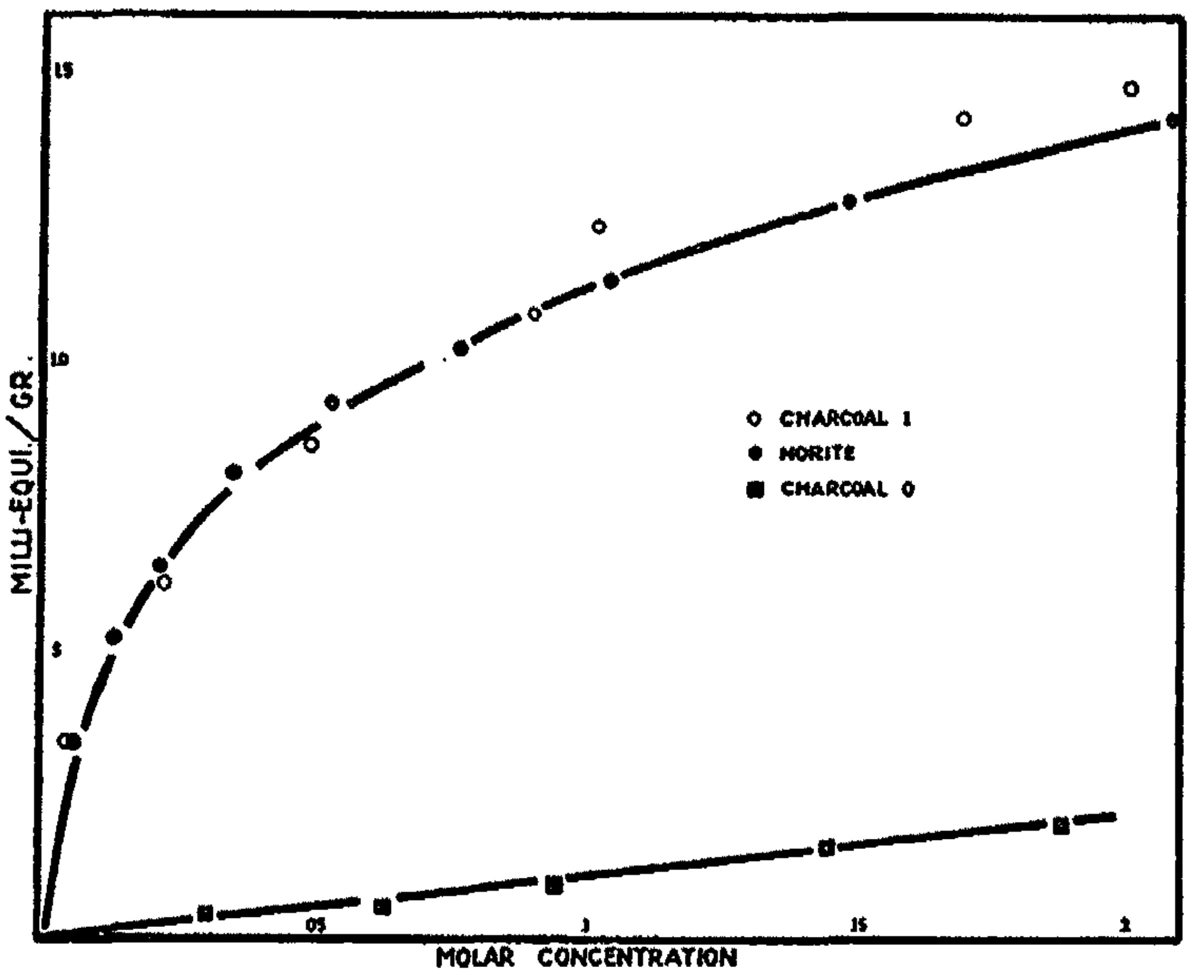

FIG. 4. The adsorption of acetic acid on charcoals No. 0 and No. 1 and Norite. (The data for Norite are those of Linner and Gortner (9).)

graphite adsorb considerably less base. Charcoal No. 0 is definitely more "acid" than are the other carbons, but this difference in acidity is not reflected in the mobility studies of these charcoal preparations either in solutions of acetic acid or in water.

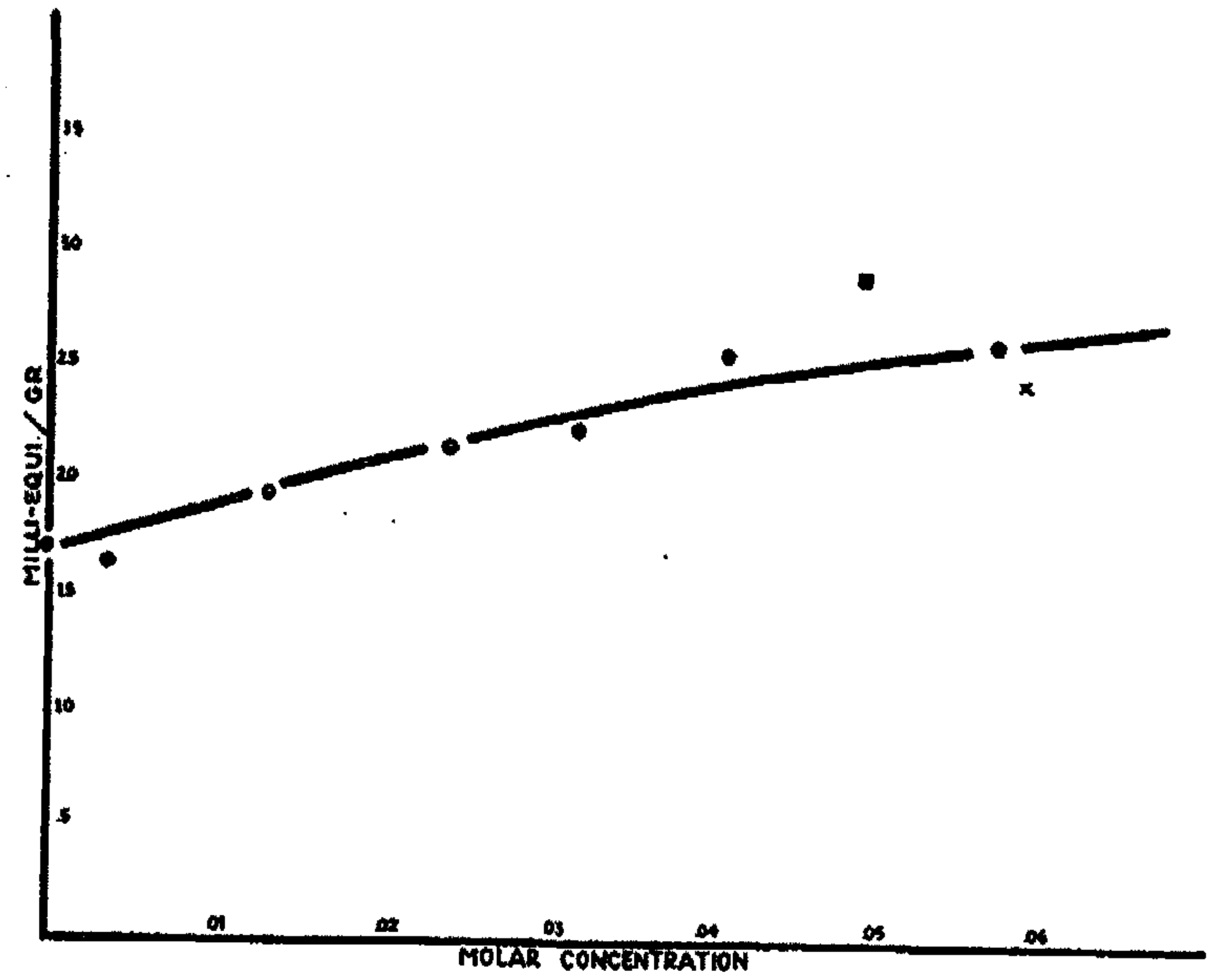

Fig. 5. Adsorption of sodium hydroxide on charcoal No. 0

TABLE 3

Quantity of sodium hydroxide adsorbed by various chars

CHARCOAL NO.	NaOH ADSORBED PER GRAM	EQUILIBRIUM CONCENTRATION OF NaOH
	milliequivalents	*normality*
1	0.582	0.083
10	0.198	0.092
6	2.90	0.049
7	2.49	0.059
Norite	0.269	0.087
Graphite	0.194	0.090

The ability of charcoal No. 0 to adsorb sodium hydroxide is not destroyed by procedures that should remove adsorbed acids. In the first place, this char was electrodialyzed at 220 volts across parchment paper for a week. The dialyzed char was then continuously extracted with water for five days, using a Soxhlet extractor. The square point in figure 5 indicates the adsorptive capacity of this char (charcoal No. 6) for sodium hydroxide, in comparison with that of charcoal No. 0. When charcoal No. 0 was first boiled with a sodium hydroxide solution, and then extracted with water until no further base was removed (charcoal No. 7), and then its behavior toward sodium hydroxide observed, the cross in figure 5 was obtained. The effect of these treatments on the mobility of the char is slight (cf. table 5).

One must accordingly conclude that the adsorption of weak electrolytes on charcoal is apolar, as evidenced by the electrokinetic data. The adsorption of hydrochloric acid on charcoal, however, does not appear to be apolar. The mobility curves for charcoals No. 0 and No. 1 in solutions of hydrochloric acid are shown in figure 6. The data for the mobilities of these charcoals in hydrochloric acid are of particular interest, inasmuch as they give essentially the same curve as was obtained by Kruyt and deKadt (8) with one of their "positive" charcoal preparations. The data they give to indicate how the speeds of the particles vary with the depth of the cell were the ones used in obtaining the points (open circles) in figure 6.

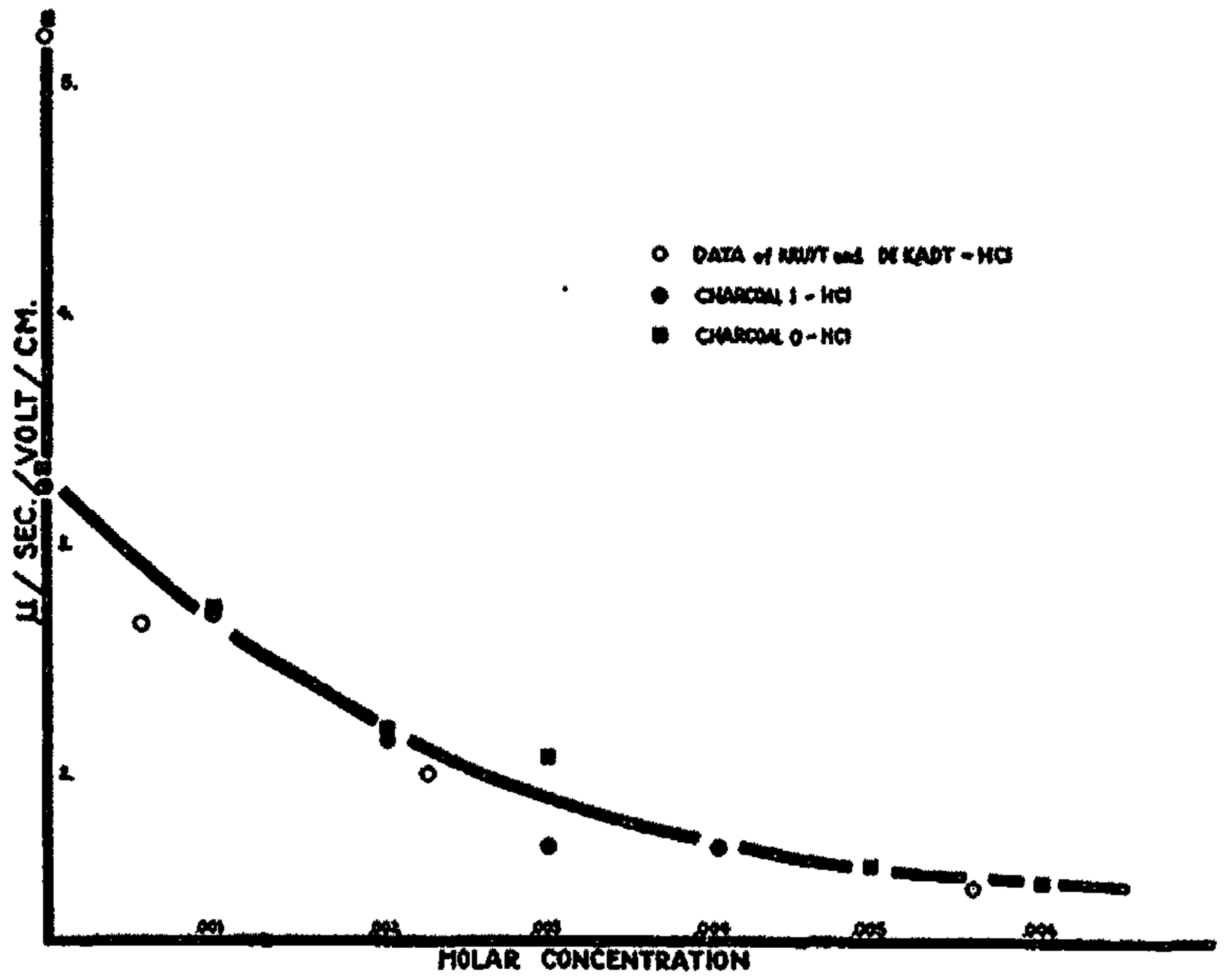

Fig. 6. Mobility–concentration curves for charcoals in solutions of hydrochloric acid

The calculations for the charge per unit area on charcoal No. 0 in solutions of hydrochloric acid are given in table 4. It will be noted that the charge per unit area increases with the concentration of electrolyte, which is typical of inert surfaces in solutions of salts not reversing the sign of the charge.

A study of the speeds of various charcoal preparations in water (specific conductivity *ca.* 3×10^{-6} mhos) indicated that there were no differences in the surface electrical properties of the char induced by the activation. The data are shown in table 5. There is a remarkable constancy in the speeds of these various charcoals suspended in water. No essential difference could be observed in the speeds of charcoals Nos. 0 and 1 suspended in ordinary distilled water and in water which had been carefully redistilled from an all-Pyrex still.

TABLE 4

Charge on charcoal No. 0 suspended in solutions of hydrochloric acid

ACID	SPEED	CHARGE PER UNIT AREA
normality	*μ/sec./volt/cm.*	*e.s.u.*
0.0010	2.79	949
0.0020	2.20	1040
0.0030	2.07	1200
0.0040	1.79	1220
0.0050	1.60	1190
0.0090	1.36	1340

TABLE 5

The electrophoretic mobility of various charcoals including graphite and diamond dust

CHARCOAL NO.	SPEED IN WATER	CHARCOAL NO.	SPEED IN WATER
	μ/sec./volt/cm.		*μ/sec./volt/cm.*
0	−3.32	10	−3.34
1	−3.29	11	−3.35
2	−3.25	12	−3.33
3	−3.47	13	−3.47
4	−3.26	14	−3.56
5*	−3.27	Graphite	−3.39
	−3.41	Norite	−3.31
6	−3.57	Diamond dust	−3.31
7	−4.09		
8	−3.28		
9	−3.33		

* Red hot char from "activation" dropped into water without previously cooling in air.

DISCUSSION

Apparently the adsorption of weak electrolytes from aqueous solution on charcoal is molecular rather than ionic, since the charge per unit area on the char particles suspended in solutions of these electrolytes is independent of the quantity adsorbed and of the concentration in solution. The calculations of the charge are based on the assumption that the limiting law of Debye and Hückel is valid.

One would anticipate that there is something more to the ability or inability of a char to adsorb alkali hydroxides than the presence of "acidic" or "basic" oxides of carbon on the surface of the charcoal preparation. The hypothesis of the existence of oxides of carbon, other than carbon monoxide and carbon dioxide, on the surface of charcoal arose as a consequence of adsorption studies of strong inorganic acids and bases on charcoal, and the theory fits in well with those adsorption data: "basic" oxides of carbon on charcoal enhance the adsorption of acids; "acidic" oxides of carbon enhance the adsorption of bases. The theory does not fit in well with the adsorption data of other species of molecules on charcoal. Lepin (10), for example, in studying charcoals having on their surfaces oxides A and B, respectively, of Schilow *et al.* (15) found the adsorption of aliphatic acids above butyric acid to be the same on the two chars. One would expect that a charcoal which had a basic oxide of carbon on its surface would consistently adsorb more acid than a char having an acidic oxide on its surface. Lepin found that the charcoal having on its surface "oxide B" adsorbed 3.8 times as much hydrochloric acid as did the charcoal having the "oxide A" on its surface. The ratio of valeric acid adsorbed on charcoals "A" and "B", respectively, was 88.2 to 88.1, whereas the ratio for acetic acid on the same charcoals was 1 to 1.7. Sodium hydroxide is only very slightly adsorbed on charcoal which is said to have on its surface a "basic oxide" of carbon. The equally strong base, tetraethylammonium hydroxide, is strongly adsorbed on the same carbon. On the other hand, ammonium hydroxide is not adsorbed at all (12). The electrokinetic data do not indicate a difference between "basic" and "acidic" charcoal, nor do they support the report of Kruyt and deKadt (8) that charcoal which has been heated to 900°C. in an atmosphere of carbon dioxide is positively charged. Dubinin (4) reports that if a charcoal is heated to 800°C. or above, irrespective of whether the heating has been in the presence of carbon dioxide or not, it will adsorb little or no alkali hydroxide. A difference between chars which have been heated to temperatures less than 800°C. and those which have been heated to temperatures more than 800°C. is not revealed by electrokinetic studies.

The data reported for the adsorption of sodium hydroxide on the various charcoals are within the limits found by other workers, although some workers state that charcoal heated to high temperatures will adsorb no alkali hydroxides. Miller (13) has found that if the char is left in contact with the sodium hydroxide for a short time, the adsorption may be negative. If, however, the char is left in contact with the sodium hydroxide for longer periods, the adsorption may be positive. In our adsorption studies the charcoal was left in contact with the sodium hydroxide solution for twenty-four hours.

SUMMARY

1. It is not possible to distinguish between various aliphatic acids by mobility studies of charcoal suspended in their aqueous solutions.
2. Calculations of the charge per unit area on charcoal particles suspended in solutions of propionic acid indicate that the charge is constant, and is independent of the concentration of the acid or the quantity of acid adsorbed on the char. The interpretation is that the adsorption is apolar.
3. Mobility studies of various carbons suspended in solutions of acetic acid indicate that there is no difference in the surface electrical properties of the carbons such as may be detected by electrokinetic studies.
4. Mobility studies of charcoal suspended in solutions of formic acid indicate that adsorption of formic acid on charcoal is apolar.
5. Adsorption of hydrochloric acid on charcoal is polar, since the charge on the surface of the char suspended in aqueous solutions of this acid increases with an increased concentration of acid, as is typical of inert surfaces in solutions of electrolytes not reversing the sign of the charge.
6. "Activation" apparently does not affect the electrokinetic properties of charcoal, since the migration velocity of various charcoals suspended in water is remarkably constant. Even graphite and diamond dust showed speeds of the same order of magnitude as the more highly "activated" carbons.
7. No electrokinetic data were obtained that would support the theory that adsorption of acids and alkali hydroxides on carbon is associated with "acidic" and "basic" oxides of carbon on the surface of the charcoal.
8. No evidence was found that activating charcoal at higher temperatures in the presence of carbon dioxide resulted in a "positively charged" carbon.

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IONIC EXCHANGE IN RELATION TO HYDROGEN-ION CONCENTRATION AND RIGIDITY OF SILICIC ACID JELLIES

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Silicic acid jellies have been employed for a number of years as solidifying agents in the preparation of culture media for lower plants and bacteria. However, the extent of such usage has been limited by unsatisfactory results, apparently due to the difficulties involved in the preparation of gels of the desired pH, containing the required nutrients, of suitable osmotic concentration, and permitting of sterilization in the autoclave. It seemed desirable, therefore, to study the changes in the hydrogen-ion concentration and the rigidity of silica gels as influenced by time, temperature, dialysis, and autoclaving.

METHODS

Silica gels were made from 7 per cent sodium silicate solution (prepared by dilution of Baker's 40 per cent solution) and 0.6 *N* hydrochloric acid. The method of preparation of the gels differed from the classical procedure by the incorporation of a color indicator in the acid and silicate solutions, i.e., 5 cc. of 0.04 per cent bromothymol blue or bromocresol purple per liter of acid and of silicate. Mixtures of these solutions were prepared at the desired pH, without preliminary titration, by adding the silicate to the acid in a flask until the proper color had apparently been produced. The pH of a small sample of the mixture was then determined colorimetrically or potentiometrically and further additions of acid or silicate were made as required. In the case of mixtures with a short hardening time jelling was delayed by previously chilling the reagents to 4°C. The mixture was distributed among the number of Petri dishes (30 cc. per plate) required for duplicate samples. By this method of preparation it was possible to reproduce any desired batch of gel.

Inasmuch as the pH drift in the gels was beyond the range of the indicators used, the colorimetric method was employed only in adjusting the initial hydrogen-ion concentration. The calomel half-cell and quinhydrone electrode were used to check the pH of the original mixtures and for all subsequent determinations. All measurements were made at 25°C. The temperature of the chilled mixtures was quickly adjusted by shaking 3 cc. of the acid–silicate mixture with excess quinhydrone in 5 cc. of distilled water at 32°C. The pH of the gels was ascertained by rubbing approximately 2 cc. of the jelly with a glass stirring rod, in a short tube containing solid quinhydrone, until a smooth paste was formed. The gel paste was then diluted to a volume of 8 cc. with distilled water and the suspension was shaken. Jellies which had been covered with liquid of syneresis, or with a dialyzing solution, were rinsed in distilled water before samples were removed.

The gels were dialyzed, at 40°C., by immersion in ten times their volume of distilled water, phosphate buffer, and buffer + NH_4^+ solution. The buffer solution had the following composition: KH_2PO_4, 0.25 g.; K_2HPO_4, 0.75 g.; distilled water, 1 liter.

The buffer + NH_4^+ solution contained, in addition to the phosphates, 1 g. of ammonium sulfate per liter. Dialysis was carried out by placing the plates of gel (without lids) on edge in the fluid with the exposed surface of the gel facing slightly downward.

Following dialysis, the gels were autoclaved in a small pressure-cooker at 15 pounds of steam pressure for 15 minutes. In order to avoid bubbles or cracks, even in the most rigid gels, it was necessary to prevent any sudden decrease in the pressure. An alternate to the usual method of autoclave heating was occasionally employed by sealing the autoclave tightly at the start and slowly exchanging the air for steam (pressure held constant) after the desired pressure had been reached.

EXPERIMENTAL RESULTS

Thirty-six batches of gel have been prepared and studied by the methods outlined. The data will be presented under two headings, dealing separately with gels made from mixtures of acid and silicate only and with gels in which the salts of the buffer or buffer + NH_4^+ solutions were incorporated. In each case, one batch of gel has been chosen to exemplify the results.

Gels without incorporated salts

Batch XIII was prepared at pH 6.3, using 300 cc. of 6 per cent hydrochloric acid by volume (0.612 *N*), and slightly less than 300 cc. of 7 per cent sodium silicate ($Na_2O:SiO_2$ ratio of 1 to 3.22 and a sodium hydroxide equivalent of 0.622 *N*). Groups of two or three plates were combined in lots numbered from 1 to 6.

The gels of lot No. 1 were autoclaved immediately after setting and were then stored at 30°C. The three plates of lot No. 2 were stored at 30°C., while those of lot No. 3 were kept at 4°C. The results (figure 1) show that the hydrogen-ion concentration in the jellies of lot No. 1 immediately after autoclaving was pH 7.4 and did not change during the subsequent storage. The pH of the gels in lot No. 2 rose rapidly during the first six hours and slowly but continuously during the remainder of the experiment. Gels stored at this temperature usually required fourteen to twenty-one days to attain the pH of the autoclaved jellies, after which the pH did not change further. In lot No. 3 the process of alkalinization was much slower and more prolonged than in gels subjected to higher temperatures. The time required to establish equilibrium in gels stored at 4°C. has not been determined.

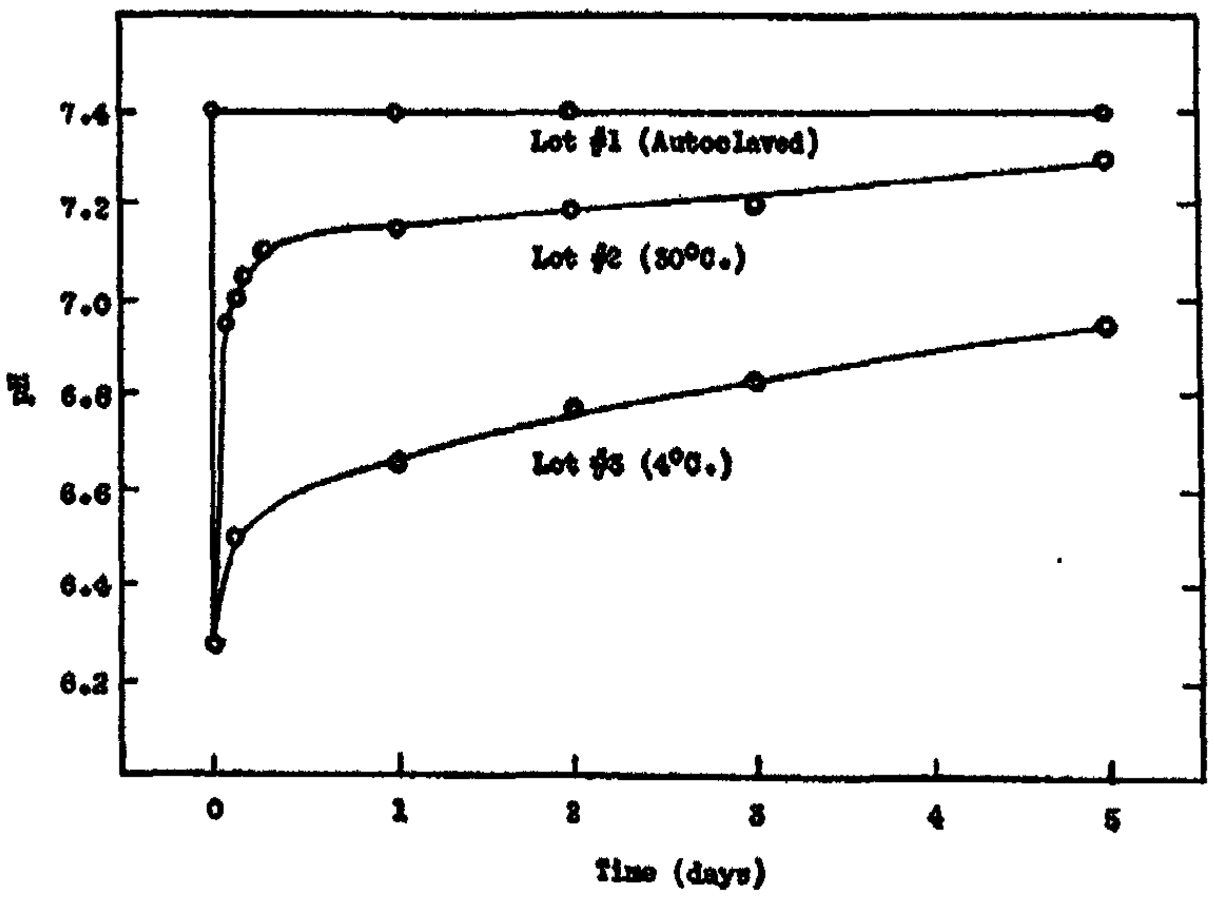

FIG. 1. The pH changes in silica gels as influenced by temperature

Measurements were made also of the pH of the liquid of syneresis collected from each of the three lots of plates at various ages. These liquids also showed a slow alkaline drift, but were always more acid than the corresponding gels.

Inasmuch as the jellies in the three lots possessed differing hydrogen-ion concentrations at the end of forty-eight hours, one plate from each lot was autoclaved at that time. As shown in figure 2, the pH of the previously autoclaved gel from lot No. 1 was not changed, while that of the No. 2 and No. 3 jellies was promptly brought to pH 7.4.

The hydrogen-ion equilibrium attained by any gel under the influence of time and temperature was found to depend on the assortment and concentration of ions in the gel and was changed markedly by dialysis.

Three lots of the batch XIII jelly, immediately following setting, were dialyzed against ten times their volume of distilled water (lot No. 4), of buffer solution (lot No. 5), and of the buffer + NH_4^+ solution (lot No. 6). Figure 3 shows the hydrogen-ion concentrations of the gels and the dialyzing fluids at 3, 6, 9, 21, 30 and 48 hours, as well as the pH and the condition of the jellies following a terminal autoclaving. The gels of lot No. 4 with an initial pH of 6.3 and the distilled water of pH approximately 5.7 rapidly became alkaline.[1] The jelly softened during dialysis and no equilibrium between the pH of these gels and of the dialyzing fluid was established. On autoclaving, the gels were alkalinized further and peptized completely. The gels dialyzed in buffer solution of pH 7.4 (lot No. 5) alkalinized rapidly while the solution was acidified temporarily (Donnan's effect?). Although the gels and the dialyzing solution reached a nearly constant pH relation, the gels were alkalinized and softened on autoclaving. Similar pH changes occurred during dialysis of the gels in the buffer + NH_4^+ solution at pH 7.4

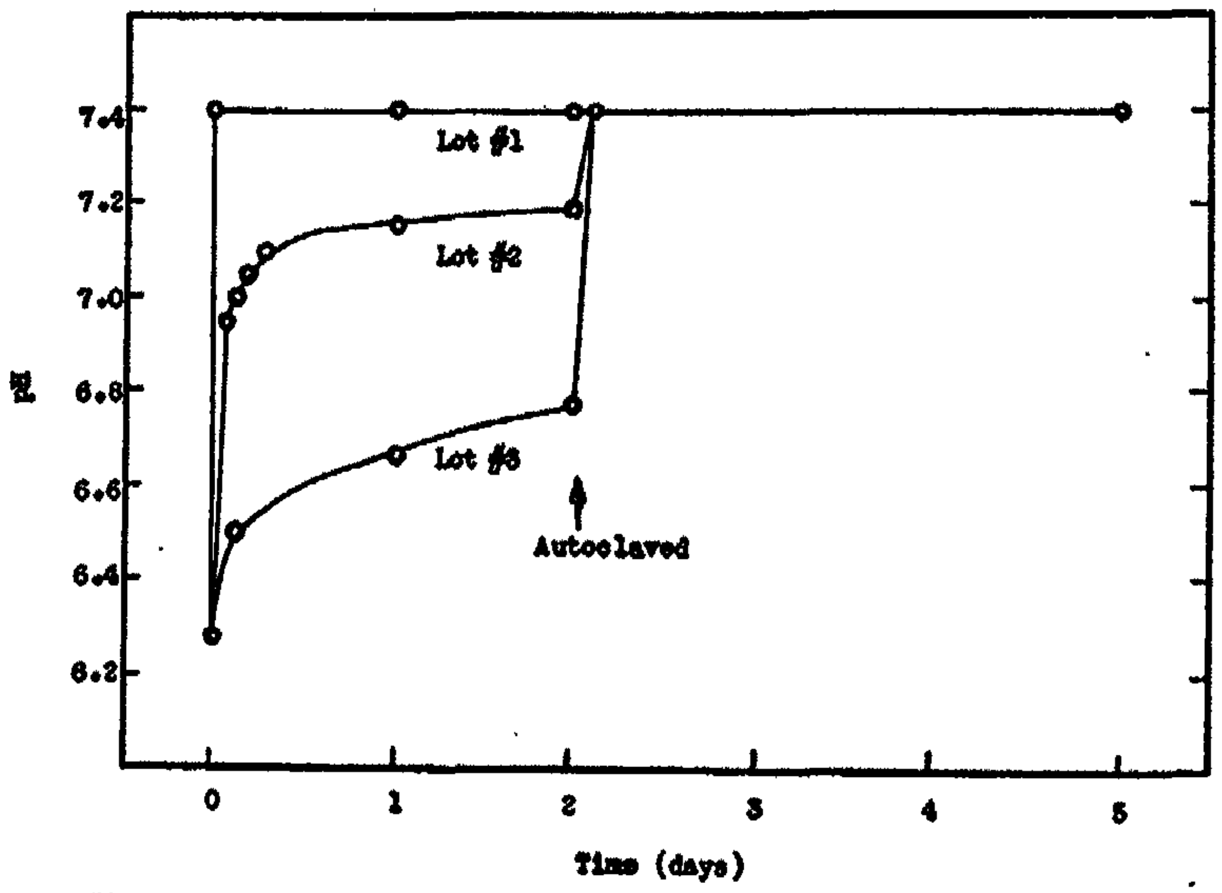

FIG. 2. The effect of temperature in stabilizing the pH of silica gels

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[1] Since the distilled water to be used in dialysis was stored in contact with air and because its initial reaction was difficult to measure accurately, the value was assumed to be approximately pH 5.7. The hydrogen-ion concentrations in this fluid were readily measured after dialysis had proceeded for a few hours.

(lot No. 6). In this case, however, the gels were autoclaved without appreciable change in rigidity or in hydrogen-ion concentration.

Further experiments showed that the pH and rigidity of the gels were stabilized by dialysis in solutions without phosphate buffer but containing 1 g. of ammonium sulfate per liter (or an equivalent amount of ammonium chloride). Dialysis in equivalent concentrations of sodium chloride was not satisfactory. On the other hand, dialysis of the gels in phosphate buffer at pH 6.3 produced firm gels with a stable pH. The stabilizing effect of this slight increase in hydrogen-ion concentration demonstrated that the hydrogen ion greatly exceeds the ammonium ion in effectiveness.

The possibility was considered that the alkalinization of the non-dialyzed gels during storage might influence the firmness and pH of these gels at the end of dialysis. Plates of lots No. 1, No. 2, and No. 3, which

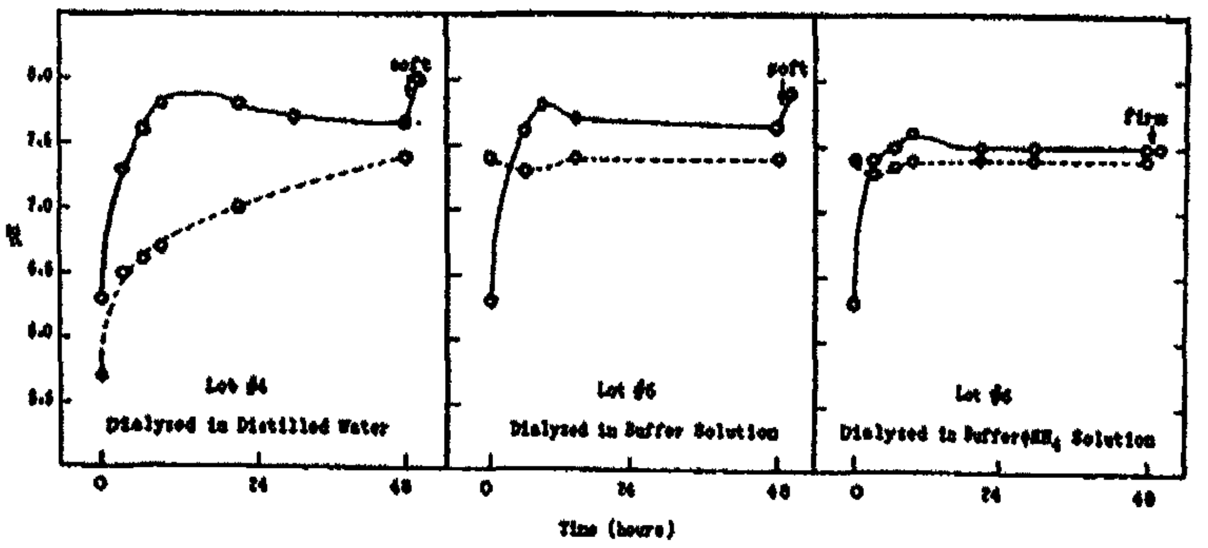

FIG. 3. pH changes during dialysis of silica jellies in distilled water, phosphate buffer, and buffer + NH_4^+ solution. ———, gels; - - - - -, dialyzing solutions; ↓ autoclaved.

had different hydrogen-ion concentrations at the end of five days, were dialyzed separately in the buffer + NH_4^+ solution in order to learn what influence their previous history might have on the pH following dialysis. The gels from all three lots attained the same pH by the end of nine hours of dialysis, and throughout the remainder of their treatment behaved like freshly prepared gels dialyzed in this solution (see lot No. 6).

Gels with incorporated salts

Since approximately equal volumes of the acid and silicate solutions were required, various salts were incorporated in the jellies by adding to the acid a double amount of the desired compounds.

Batch XVIII was prepared at pH 7.1 in three separate lots which differed from each other only in their ammonium sulfate content. Lot No. 1 (minus-NH_4^+ gel) resembled batch XIII and contained no added salt.

Lot No. 2 (1 g.-NH_4^+ gel) contained 1 g. of ammonium sulfate and lot No. 3 (3 g.-NH_4^+ gel) contained 3 g. of ammonium sulfate per liter of gel.

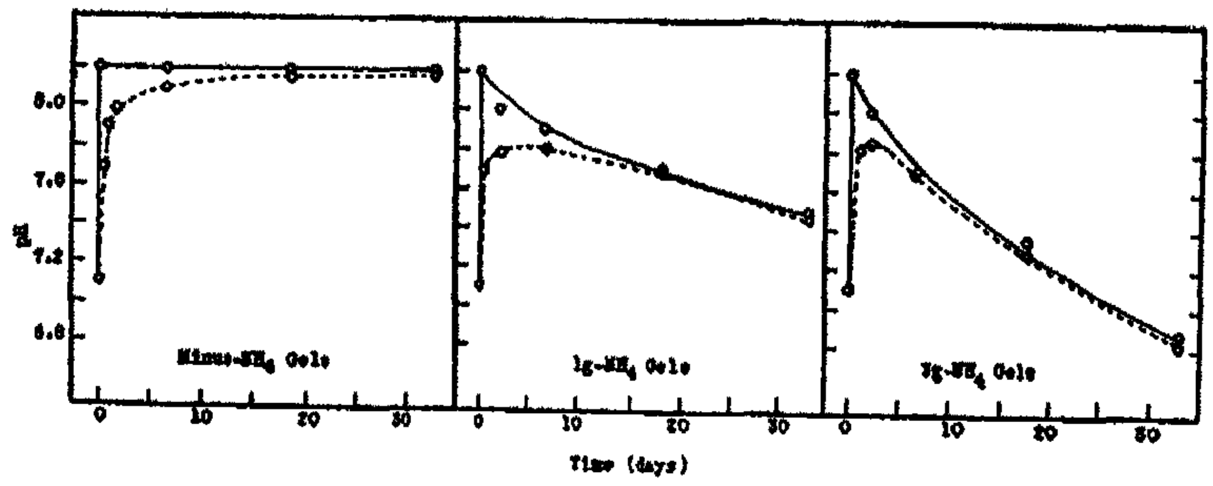

FIG. 4. The influence of incorporated ammonium sulfate on the pH changes in non-dialyzed silica jellies. ———, autoclaved gels, stored at 30°C.; - - - - - -, non-autoclaved gels, stored at 30°C.

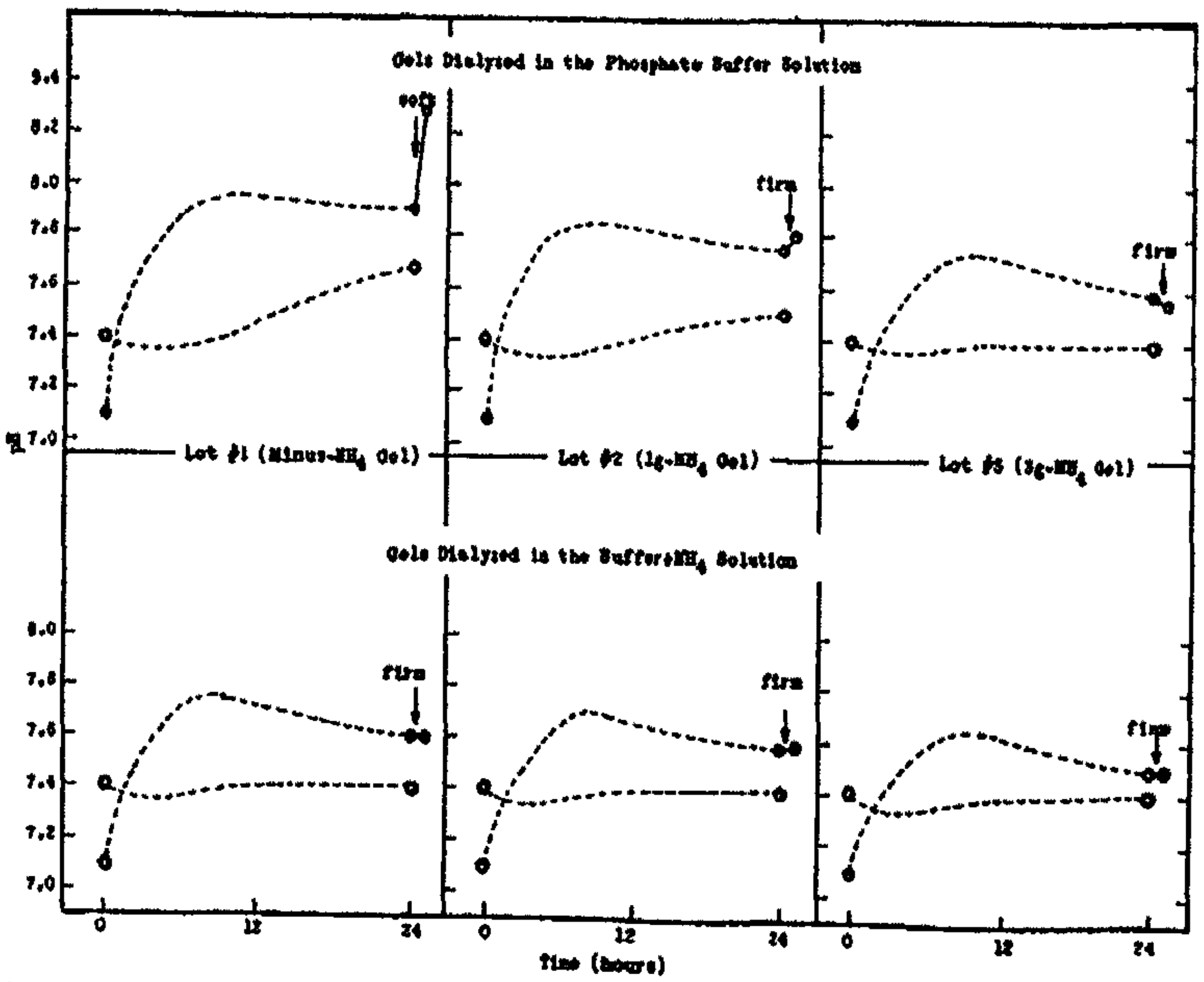

FIG. 5. Gels containing various amounts of ammonium sulfate, dialyzed in the phosphate buffer solution and in the buffer + NH_4^+ solution. ↓ indicates autoclaving; ●, gels; ○, dialyzing fluids; - - - - - -, probable course of the pH curves.

Figure 4 shows the pH of autoclaved and non-autoclaved batch XVIII gels during thirty-three days of storage at 30°C. All the autoclaved gels showed the usual alkalinization (1.1 on the pH scale). The pH of the minus-NH_4^+ gel did not change further. On the other hand, the pH of the gels containing ammonium sulfate was not stable but decreased throughout the storage period. The reacidification was greater in the 3 g.-NH_4^+ gel.

Gels containing equivalent amounts of ammonium chloride gave similar results. However, reversals of the pH curves were not observed when ionic equivalents of aluminum, calcium, or sodium (as chlorides) were substituted for ammonium.

The gels of each lot of batch XVIII were dialyzed in the buffer solution and in the buffer + NH_4^+ solution (see figure 5). The final pH of the buffer solution was influenced by the pH changes in the jellies. The buffer solution alone did not bring about stabilization of the minus-NH_4^+ gels. These gels were alkalinized and peptized on autoclaving. It is noteworthy that the 1 g.-NH_4^+ gels and 3 g.-NH_4^+ gels which contributed only 1 g. and 3 g., respectively, of ammonium sulfate to dialyzing systems of 11 liters, attained a fairly stable hydrogen-ion equilibrium and were autoclaved without softening.

The hydrogen-ion concentration of each lot of gels dialyzed in the buffer + NH_4^+ solution was controlled, at the end of dialysis, by the pH of the solution. The pH and rigidity of such gels were not changed by final autoclaving. In every case the solution, after a slight acidification, returned to its original pH.

DISCUSSION

Inasmuch as these studies were made in connection with a practical problem in the field of bacteriology it is natural that many points of possible interest to chemists have been overlooked or have not been studied in systems of sufficient simplicity to permit a quantitative analysis of the results.

For three years prior to this investigation, the authors had observed that gels prepared at the grass-green color of bromothymol blue acquired, on standing, a very deep blue color. Because of the limited range of the indicator the full extent of the pH shift was not appreciated, and it was thought that the change in color arose from changes in the opacity of the jelly. It is now clear that this phenomenon is due to the occurrence of marked changes in the hydrogen-ion concentration of non-dialyzed silica gels prepared with hydrochloric acid.

The studies of Hurd and Griffeth (3) on silicic acid jellies formed with acetic acid have not revealed changes in the pH of the mixtures or gels. This result might be explained by the greater buffer capacity of the acetic acid-acetate system. Furthermore, in the low pH range of the gels of Hurd and Griffeth a much greater change in hydrogen-ion concentration is necessary to produce appreciable changes in pH. In this connection it is interesting that Prasad and Hattiangadi (5) observed a pH rise in alkaline gels produced from silicate and acetic acid.

The results of the present study are believed to afford an explanation of several classical observations on silicic acid jellies. It is well known that neutral or slightly alkaline gels have the minimum time of set (5) and begin to synerize more rapidly, although acid gels finally exude a greater volume of liquid (2); that viscosity increases more rapidly in alkaline gels at first, but later the viscosity of acid gels increases at an even greater rate (7); and that the rapid rise in extinction coefficients occurs earlier in alkaline than in acid gels (6). Possibly these phenomena depend on the fact that neutral and alkaline gels are drifting away from the pH zone most favorable for hardening, while acid gels are drifting into the suitable range.

In addition, the pH shift is perhaps an important factor in the so-called "aging" process of gels. It has been shown that autoclaving establishes an equilibrium, the attainment of which requires several weeks at lower temperatures. It is suggested that heating is a useful method for stabilizing gels on which physical measurements are to be made.

It would appear that the results obtained in this study may be interpreted on the basis of ionic exchange. The factors influencing exchange reactions in colloidal aluminum silicates have been discussed admirably by Jenny (4) and are known to be related to the size, charge, and degree of hydration of the ions involved.

The solution of sodium silicate may be regarded as consisting of silica particles surrounded by a firmly adsorbed shell of hydroxyl ions and by a more diffuse outer envelope of sodium ions (8). It is believed that the initial pH of the acid and silicate mixture represents a titration of the hydrogen and hydroxyl ions furnished by these solutions and that the subsequent pH drift in the jelly results from ionic exchange. Observations on diluted acid-silicate mixtures suggest that the rapid pH drift does not occur until gelation is initiated; the hydrogen-ion exchange seems to be intimately related to the process of gel formation. From this point of view, the sodium ions adsorbed on the silica are displaced during gel formation by hydrogen ions from the capillary water until an equilibrium is reached at a pH value which will depend on the relative concentration of the two ions. The extent of the drift might vary from the observed value of 1.1 on the pH scale when gels are prepared in other ranges of hydrogen-ion concentration. In the pH range studied, variations in the SiO_2 content of the jellies, or in the $Na_2O:SiO_2$ ratio of the silicates, should not modify this value because the relative numbers of hydrogen and sodium ions will be constant.

The gradual reacidification of the gels with incorporated ammonium sulfate or ammonium chloride is not explained readily. That loss of ammonia was responsible for this phenomenon appeared unlikely from the results of semiquantitative tests with Nessler's reagent. Furthermore, the most favorable conditions for driving off ammonia occurred in gels which were alkalinized to pH 8.2 during heating in the autoclave. Had ammonia been lost during heating, the usual pH rise should not have been observed. It would be interesting to repeat the experiment at a lower pH. From the standpoint of ionic exchange, the reacidification would be explained as due to a slow replacement of adsorbed hydrogen by ammonium ions, following the initial substitution of sodium by hydrogen ions.

The results of dialysis also are explained by ionic exchange involving sodium, potassium, ammonium, and hydrogen ions. It was found that low concentrations of the hydrogen ion or moderate concentrations of the ammonium ion produced stabilization of the pH and the firmness of the jellies, while comparable concentrations of the sodium or potassium ion were ineffective. According to Jenny (4) the ease and tightness of adsorption of these ions on clays and permutits is given by the series: $Na^+ < K^+ < NH_4^+ < H^+$. The relative replaceability of each ion may be expressed by arranging the series in reverse order. The results of the present investigation are in agreement with the demonstration that the viscosity, degree of hydration, and general stability of colloidal clays are greatly affected by the nature of the adsorbed ions (1, 9).

It is well known that alkalinity is largely responsible for the peptization of silica gels. In this study it was found that the pH of non-dialyzed gels might rise to 8.4 without undue softening of the gel; a similar pH rise in dialyzed gels was always accompanied by peptization. It would appear, therefore, that the concentration of electrolyte in a gel, as well as the degree of alkalinity, controls its stability on heating. It is assumed that the non-dialyzed jellies remain stable because their OH groups (inner Helmholtz layer) are covered with sodium and hydrogen ions in sufficient number to protect the gel structure.

SUMMARY

1. A method is described for preparing silica jellies at any pH desired.
2. The pH of gels, prepared from silicates and hydrochloric acid, rises during and following setting. A constant pH value is reached.
3. The time required for the gels to attain pH equilibrium depends on the temperature.
4. The pH of gels containing ammonium salts does not reach a constant value. The alkalinization of these gels is followed by reacidification.
5. The effect of dialysis in solutions containing various ions may be studied by determining the rigidity and pH stability of the gels during subsequent heating.
6. Gels dialyzed in phosphate buffer, in buffered sodium chloride solu-

tion, or in distilled water are alkalinized on heating and are softened or peptized.

7. The pH of gels dialyzed in buffered ammonium chloride or ammonium sulfate solutions does not change on heating and these gels remain firm.

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CONTINUITY OF THE METASTABLE STATE

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INTRODUCTION

There is no reason to expect a discontinuity of properties of a system on passing through the limit of complete equilibrium into the metastable equilibrium state. Ostwald (1883), Roozeboom (1889), Rothmund (1907), and most recently Liesegang (4) have discussed this behavior in general, while numerous workers have offered abundant experimental evidence, mostly on the change of properties in the supersaturated region. In addition, the density, vapor pressure, and viscosity of supercooled water, the viscosity of superheated water, and the flow properties of fluids have been reported as continuous from the "stable" region, so that voluminous data indicate the truth of the above statement.

A lone exception to this principle has been interpreted (4) in the work of Nayar (6), who claims a variation in volume of ammonium oxalate, oxalic acid, and potassium nitrate solutions on passing through the saturation point. It was the purpose of this investigation to repeat and extend Nayar's work. He (7) confirms the results of this paper, and states that his object was not to question the principle of continuity of properties, but "to study the behavior of solutions before and during crystallization (and not to prevent crystallization)."

EXPERIMENTAL

Dilatometers, of about 75-ml. capacity with thermometers centrally located, were employed. Sixty to 70 ml. of solution was added and the remaining volume and capillary completely filled with a deaërated mineral oil which was proven to be immiscible, even in the case of the alcoholic solution. The whole was brought to a steady state at a temperature 10° to 15°C. above the saturation temperature, and cooled slowly over the course of one and one-half to three hours in a large well-stirred water bath.

Recrystallized solutes of reagent quality were used.

An amount of solute and water proper to saturation at the chosen temperature was heated for an hour in a closed vessel with agitation at a temperature far in excess of saturation, brought to a boil, and filtered directly into the scrupulously clean and warmed dilatometer. In almost all cases the first portion of filtrate served as wash liquid. The solution was covered immediately with oil, and the saturation temperature determined.

This was accomplished by slowly cooling the vigorously agitated solution, when, in most cases, a spontaneous crystallization occurred at the saturation temperature. This point was confirmed by supercooling the solution to 0.25° to 0.5°C. without stirring, and seeding. In all cases an immediate crystallization occurred. As a further guarantee of the correctness of the accepted values for the saturation temperature, the solutions were seeded while at a temperature 0.25° to 0.5°C. above this temperature. In no case did crystal growth occur.

DISCUSSION

The results are presented in figures 1, 2, and 3. A blank with the oil (figure 2) demonstrates that the cooling curve of oil and apparatus is regular, and equilibrates with the bath temperature within 0.3°C. Therefore any irregularity must be due to the cooling properties of the solution.

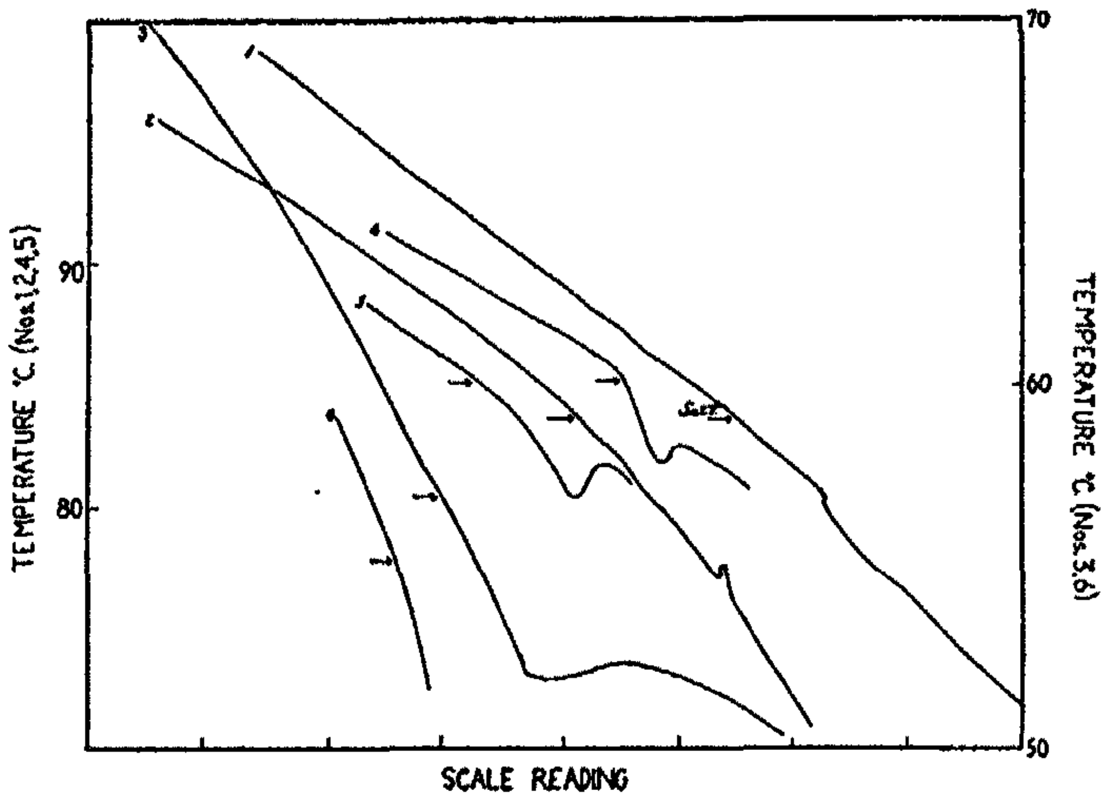

Fig. 1. Cooling curves

	van Hook	Nayar
Potassium nitrate....................	No. 1 83.5°C.	No. 4 85°C.
Ammonium oxalate..................	No. 2 83.5°C.	No. 5 85°C.
Oxalic acid..........................	No. 3 57.0°C.	No. 6 55°C.

All the curves representing this work are smooth and continuous from well above saturation to the crystallization temperature. No indication of change in direction at the saturation point, such as reported by Nayar (6) and presented schematically for comparison in figure 1, is apparent.

The results are in accord with the scant data available on the values of density of supersaturated solutions. The values reported by Scott and Badger (8) for calcium nitrate, sucrose solutions (3), potassium chlorate solutions (1), and supercooled water (2) are all continuous without marked change in slope at the saturation point.

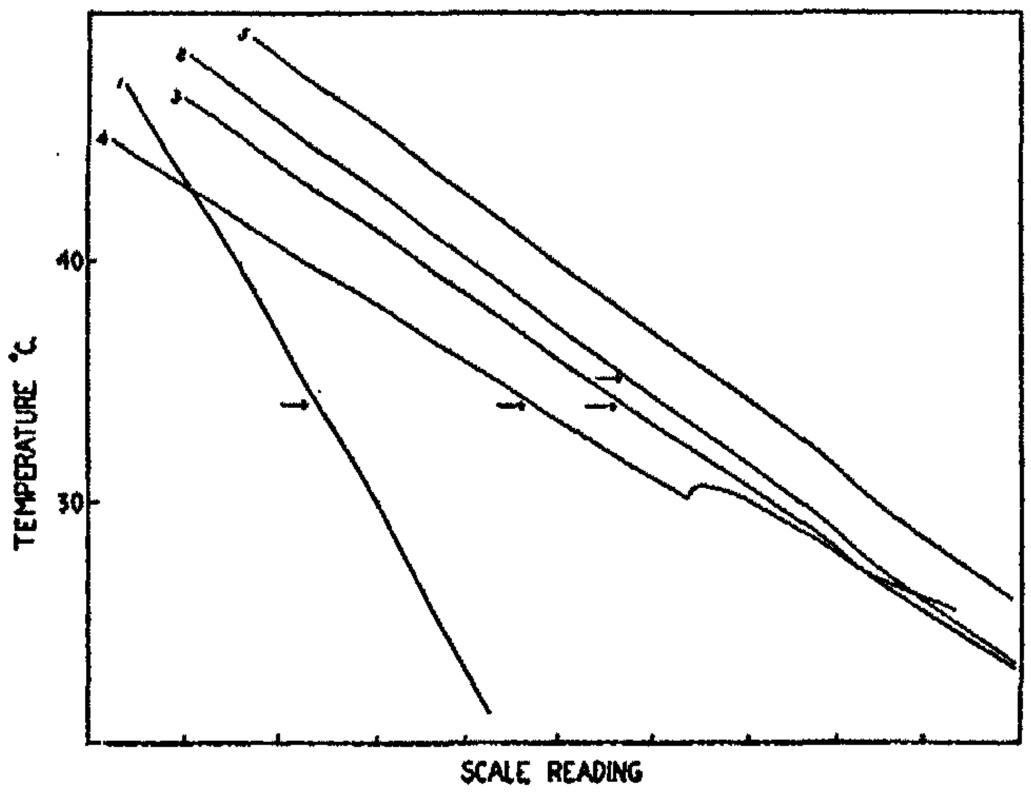

Fig. 2. Cooling curves. 1, calcium nitrate, 34°C.; 2, acetamide in water, 35°C.; 3, acetamide in 95 per cent ethyl alcohol, 34°C.; 4, urea, 34°C.; 5, oil blank.

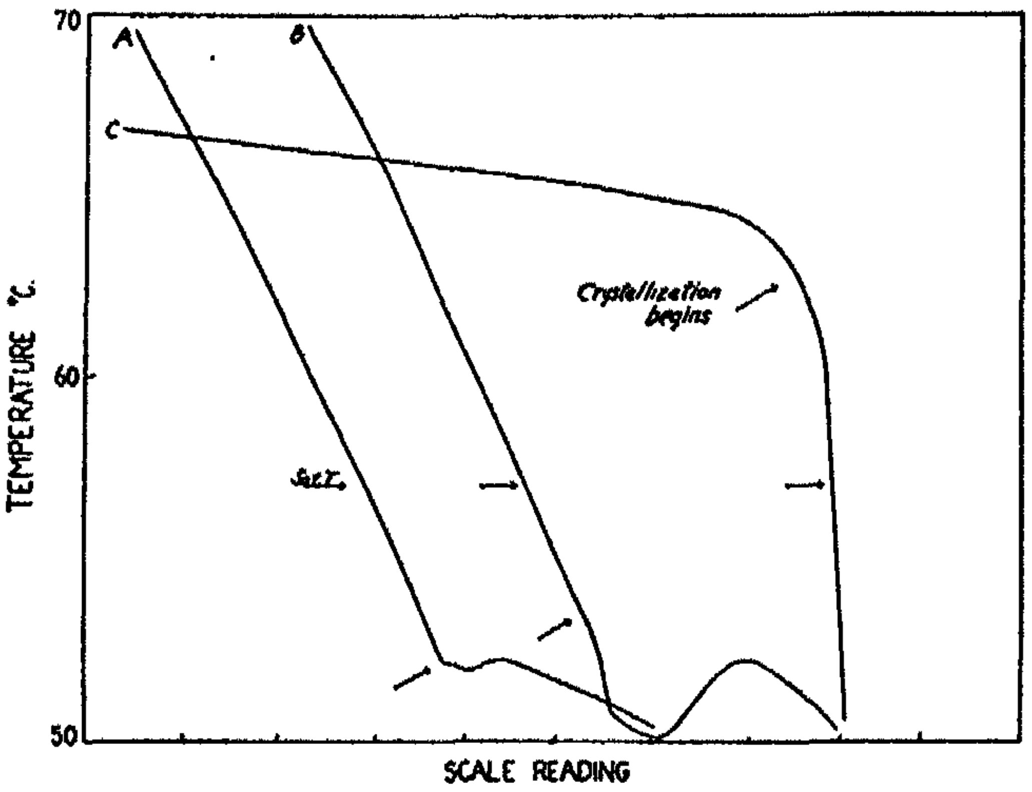

Fig. 3. Oxalic acid, 57°C. A, cooled very slowly, three hours; B, cooled in air, 30 minutes; C, cooled in ice, 3 minutes.

The results presented in figure 3 are all for the same solution in the same dilatometer. The indications are that very rapid cooling induces crystallization, due to localized undercooling, at a point closer to the saturation temperature, thus causing a depression in the cooling curve. The same apparent behavior would result from thermometric lag. Or, what is more likely, accidental inoculation with crystallization nuclei may have caused Nayar's observed results (5). The fact that Nayar's first inflection generally corresponded with the first appearance of a thin shower of crystals is strongly suggestive of this. In this work no such thin shower of crystals was observed.

SUMMARY

The temperature–dilation curves for supersaturated solutions of potassium nitrate, ammonium oxalate, oxalic acid, calcium nitrate, acetamide, and urea show no non-uniformity at the saturation point.

This uniformity is confirmed by the scant data available in the literature.

The principle of continuity of properties into the metastable state is generally valid.

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THE THERMODYNAMICS OF THE ELECTRIC FIELD WITH SPECIAL REFERENCE TO CHEMICAL EQUILIBRIUM

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I. INTRODUCTION

The object of this paper is to obtain the general thermodynamic equations for dielectrics of variable composition in external electric fields, and from these equations to deduce the laws of chemical equilibrium in such systems. Recently E. A. Guggenheim (4) has published a theoretical account of the thermodynamics of the electric and the magnetic field, which so far surpasses all previous ones in accuracy and thoroughness that it will not be necessary for us to discuss the older treatments in detail. Guggenheim starts by showing from Maxwell's equations that for any system of fixed configuration the electrostatic and magnetic energies are given respectively by

$$\frac{1}{4\pi}\int \mathrm{d}V \int_0^D E\mathrm{d}D \tag{1.1}$$

and

$$\frac{1}{4\pi}\int \mathrm{d}V \int_0^B H\mathrm{d}B \tag{1.2}$$

where V, E, D, H, and B denote volume, electric field strength, displacement, magnetic field strength, and induction. These formulae hold no matter what the functional relationship between D and E or B and H may be. By combining equation 1.2 with the two laws of thermodynamics Guggenheim then deduces all the important thermodynamic laws for magnetic systems of constant composition. From equations 1.1 and 1.2 it is evident that the corresponding laws for electrostatic systems are obtainable by substituting E for H and D for B. By the same token any results that, like those of the present paper, are derived from electrostatic considerations, hold also for the magnetic case. The only entirely new results of the present paper are therefore the extension of the treatment to systems of variable composition and the laws of chemical equilibrium thereby obtained.

There are, however, between the approach to the problem here adopted and that of Guggenheim, some differences of which the following should be pointed out. (*i*) In our derivation we make use of no electrostatic system more complicated than a plane condenser, and start from the principle that, if ψ is the absolute value of the potential difference between the plates, the work done by infinitesimally changing the absolute value q of the plate charge is ψdq, no matter what other infinitesimal changes the condenser may simultaneously undergo. This principle, although lacking the generality of equation 1.1, has advantages of concreteness in dealing with variations of volume and composition. (*ii*) The general thermodynamic equations here taken as the source of all the special laws of immediate interest contain only quantities referring to a homogeneous mass of dielectric permeated by a uniform field, whereas the corresponding equations of Guggenheim contain additional terms belonging to the field by which the matter in question is surrounded. Our equations therefore have a form slightly simpler than those of Guggenheim, and are closely parallel to the Gibbsian equations for ordinary systems, in which all quantities refer to a single phase. For the latter reason we shall henceforth refer to a homogeneous mass of dielectric permeated by a uniform field as a *dielectric phase*. (*iii*) For convenience we take the dielectric "constant" of the vacuum to be a constant equal to unity.

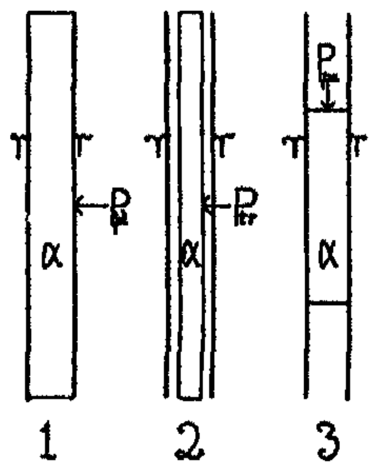

FIG. 1. Three ways of varying the volume of a dielectric phase, α, by action of a uniform pressure.

II. DERIVATION OF THE GENERAL EQUATIONS

1. Variation of volume under uniform pressure

Figure 1 shows three ways in which the volume V^{α} of a fluid dielectric phase, α, can be varied by movement of a surface the pressure over which is uniform. In each case the area of the condenser plates is so great in comparison with the plate separation that the non-uniformity at the rims is negligible. In system 1 the dielectric α fills the entire space between the plates and is so constrained that volume variations are possible only by movement of the plates, the pressure on which will be denoted by P_{pl}. In system 2, α is in the form of a slab parallel to plates rr and separated from them by spaces having the dielectric properties of the vacuum. V^{α} is varied only by movement of the surfaces lying transverse to the field, the pressure on which surfaces will be denoted by P_{tr}. In system 3 all the space not filled by α again has the dielectric properties of the vacuum and V^{α} is varied only by movement of the surfaces lying parallel to the field, the corresponding pressure being P_{pa}. In system 1 the field strength and the displacement both have uniform values, E and D, respectively, everywhere between the plates. In system 2 the displacement has the same value D throughout, and is related to the field strengths E^{α}, E^{vac} in α and in the vacuum, respectively, by

$$D = \epsilon^{\alpha}E^{\alpha} = E^{\mathrm{vac}}$$

where ϵ^{α} is the dielectric "constant" of α. In system 3 the field strength has the same value throughout and is related to the displacements D^{α}, D^{vac} by

$$E = \frac{D^{\alpha}}{\epsilon^{\alpha}} = D^{\mathrm{vac}}$$

Systems 2 and 3 are the electrostatic analogues of the magnetic "systems of simple symmetry" S2 and S3 considered by Guggenheim (reference 4, page 86 ff.), and it is to him that we owe the definitions of P_{tr} and P_{pa}. The magnetic analogue of system 1 is difficult to realize in practice and therefore P_{pl} does not have the same importance for magnetic as for electrostatic systems. P_{pl} may nevertheless be regarded as defined at every point of a magnetic system by its relations to P_{tr} or P_{pa}, which are deduced below (equation 16).

2. Three equations for the energy change of a dielectric phase

For a given state of the dielectric phase α, characterized, say, by its volume V^{α}, its entropy S^{α}, the field strength E^{α} permeating it, and the number of moles n_i^{α} of its components, the quantities P_{pl}, P_{tr}, and P_{pa} evidently have definite values. These values are in general not equal to each other—for P_{tr} and P_{pa} this has been shown by Guggenheim (reference 4, page 97)—and therefore, for a given state, the work due to a volume change $\mathrm{d}V^{\alpha}$ is not the same in the three systems of figure 1. From this it follows that each of these three systems leads to a different equation for the energy change $\mathrm{d}U^{\alpha}$ corresponding to the most general change of state of a dielectric phase. We proceed to deduce these three equations for $\mathrm{d}U^{\alpha}$.

(*i*). *dU^{α} from system 1.* The total energy included between the plates is here U^{α}. This energy can be infinitesimally varied by the following independent processes: (*i*) the absorption or evolution of heat contributing to U^α an amount $T^\alpha \mathrm{d}S^\alpha$, a change of volume contributing $-P_{\mathrm{pl}}\mathrm{d}V^\alpha$, the transfer of electricity from one of the plates to the other contributing $\psi \mathrm{d}q$, the variation of the chemical content of α, contributing $\sum_i \mu_i^\alpha \mathrm{d}n_i^\alpha$ where μ_i^α is merely an abbreviation for

$$\left(\frac{\partial U^\alpha}{\partial n_i^\alpha}\right)_{S^\alpha, V^\alpha, q, n_i'^\alpha}$$

the subscript $n_i'^\alpha$ denoting the constancy of all the n_i^α save the one with respect to which the differentiation is carried out. It follows that the most general variation of U^α is given by

$$\mathrm{d}U^\alpha = T^\alpha \mathrm{d}S^\alpha - P_{\mathrm{pl}}\mathrm{d}V^\alpha + \psi \mathrm{d}q + \sum_i \mu_i^\alpha \mathrm{d}n_i^\alpha \qquad (2)$$

From elementary electrostatics the term $\psi \mathrm{d}q$ is seen to transform as follows

$$\psi \mathrm{d}q = \frac{EV^\alpha}{4\pi}\mathrm{d}D$$

so that we obtain

$$\mathrm{d}U^\alpha = T^\alpha \mathrm{d}S^\alpha - P_{\mathrm{pl}}\mathrm{d}V^\alpha + \frac{EV^\alpha}{4\pi}\mathrm{d}D + \sum_i \mu_i^\alpha \mathrm{d}n_i^\alpha \qquad (3)$$

(*ii*). *$\mathrm{d}U^\alpha$ from system 2.* Let the total energy included between the plates be denoted by U^{con}. Then by reasoning parallel to that for system 1 the most general variation of U^{con} is found to be[1]

$$\mathrm{d}U^{\mathrm{con}} = T^\alpha \mathrm{d}S^\alpha - P_{\mathrm{tr}}\mathrm{d}V^\alpha + \psi \mathrm{d}q + \sum_i \mu_i^{\alpha\prime} \mathrm{d}n_i^\alpha \qquad (4)$$

where

$$\mu_i^{\alpha\prime} \equiv \left(\frac{\partial U^{\mathrm{con}}}{\partial n_i^\alpha}\right)_{S^\alpha, V^\alpha, q, n_i'^\alpha}$$

For system 2 the term $\psi \mathrm{d}q$ is readily shown to transform as follows

$$\psi \mathrm{d}q = \frac{1}{4\pi}(E^\alpha V^\alpha + E^{\mathrm{vac}} V^{\mathrm{vac}})\mathrm{d}D$$

so that

$$\mathrm{d}U^{\mathrm{con}} = T^\alpha \mathrm{d}S^\alpha - P_{\mathrm{tr}}\mathrm{d}V^\alpha + \frac{1}{4\pi}(E^\alpha V^\alpha + E^{\mathrm{vac}} V^{\mathrm{vac}})\mathrm{d}D + \sum_i \mu_i^{\alpha\prime} \mathrm{d}n_i^\alpha \qquad (5)$$

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[1] In equation 4 and the following equations the entropy of the radiation present is neglected.

This equation is equivalent to that given by Guggenheim for the magnetic analogue of this case at constant composition (reference 4, page 91, equation 8.1), his function F being, in our notation, $U^{\text{con}} - T^{\alpha}S^{\alpha}$. In order to obtain from equation 5 an equation for $\mathrm{d}U^{\alpha}$, we apply the usual convention regarding the localization of energy, according to which

$$\begin{aligned} U^{\text{con}} &= U^{\alpha} + U^{\text{vac}} \\ \mathrm{d}U^{\alpha} &= \mathrm{d}U^{\text{con}} - \mathrm{d}U^{\text{vac}} \end{aligned} \tag{6}$$

where U^{vac} is the energy belonging to the vacuum included between the plates. Now U^{vac} is given by

$$U^{\text{vac}} = \frac{(E^{\text{vac}})^2 V^{\text{vac}}}{8\pi} \tag{7}$$

a familiar formula, deducible from the assumptions of this paper by calculating $\int_0^q \psi dq$ for an empty condenser at constant volume. Since in system 2

$$\begin{aligned} E^{\text{vac}} &= D \\ \mathrm{d}V^{\text{vac}} &= -\mathrm{d}V^{\alpha} \end{aligned} \tag{8}$$

$\mathrm{d}U^{\text{vac}}$ is found from equation 7 to be

$$\mathrm{d}U^{\text{vac}} = -\frac{D^2}{8\pi}\mathrm{d}V^{\alpha} + \frac{DV^{\text{vac}}}{4\pi}\mathrm{d}D \tag{9}$$

Substitution of equation 8 into equation 5 and combination of the result with equations 6 and 9 yields the desired equation for $\mathrm{d}U^{\alpha}$ corresponding to system 2

$$\mathrm{d}U^{\alpha} = T^{\alpha}\mathrm{d}S^{\alpha} - \left[P_{\text{tr}} - \frac{(D^{\alpha})^2}{8\pi}\right]\mathrm{d}V^{\alpha} + \frac{E^{\alpha}V^{\alpha}}{4\pi}\mathrm{d}D^{\alpha} + \sum_i \mu_i^{\alpha\prime}\,\mathrm{d}n_i^{\alpha} \tag{10}$$

To emphasize the fact that equation 10 contains only quantities referring to the dielectric phase α we have in this equation written D^{α} instead of D.

(*iii*). $\mathrm{d}U^{\alpha}$ *from system 3.* Here evidently

$$\mathrm{d}U^{\text{con}} = T^{\alpha}\mathrm{d}S^{\alpha} - P_{\text{ps}}\mathrm{d}V^{\alpha} + \psi\mathrm{d}q + \sum_i \mu_i^{\alpha\prime\prime}\,\mathrm{d}n_i^{\alpha} \tag{11}$$

where

$$\mu_i^{\alpha\prime\prime} \equiv \left(\frac{\partial U^{\text{con}}}{\partial n_i^{\alpha}}\right)_{S^{\alpha}, V^{\alpha}, q, n_j^{\alpha}}$$

The term $\psi \mathrm{d}q$ is readily shown to transform as follows

$$\psi \mathrm{d}q = \frac{E}{4\pi} \mathrm{d}(D^{\alpha} V^{\alpha} + D^{\mathrm{vac}} V^{\mathrm{vac}})$$

so that

$$\mathrm{d}U^{\mathrm{con}} = T^{\alpha} \mathrm{d}S^{\alpha} - P_{\mathrm{pa}} \mathrm{d}V^{\alpha} + \frac{E}{4\pi} \mathrm{d}(D^{\alpha} V^{\alpha} + D^{\mathrm{vac}} V^{\mathrm{vac}}) + \sum_i \mu_i^{\alpha''} \mathrm{d}n_i^{\alpha} \tag{12}$$

This formula is equivalent to that given by Guggenheim for the magnetic analogue of this case at constant composition (reference 4, page 93, equation 9.1), his function $\mathcal{A}$ for system 3 being related to our U^{con} by

$$\mathcal{A} = U^{\mathrm{con}} - T^{\alpha} S^{\alpha} - \frac{E}{4\pi} (D^{\alpha} V^{\alpha} + D^{\mathrm{vac}} V^{\mathrm{vac}})$$

To obtain $\mathrm{d}U^{\alpha}$ we write as for system 2

$$\mathrm{d}U^{\alpha} = \mathrm{d}U^{\mathrm{con}} - \mathrm{d}U^{\mathrm{vac}} \tag{13}$$

and note that for system 3

$$U^{\mathrm{vac}} = \frac{E^2 V^{\mathrm{vac}}}{8\pi} \tag{14}$$

The combination of equations 12, 13, and 14 yields, after simplification with the help of

$$\begin{aligned} D^{\mathrm{vac}} &= E \\ \mathrm{d}V^{\mathrm{vac}} &= -\mathrm{d}V^{\alpha} \end{aligned}$$

the desired equation for $\mathrm{d}U^{\alpha}$ corresponding to system 3

$$\begin{aligned} \mathrm{d}U^{\alpha} = T^{\alpha} \mathrm{d}S^{\alpha} - \left[P_{\mathrm{pa}} - \frac{E^{\alpha} D^{\alpha}}{4\pi} + \frac{(E^{\alpha})^2}{8\pi} \right] \mathrm{d}V^{\alpha} \\ + \frac{E^{\alpha} V^{\alpha}}{4\pi} \mathrm{d}D^{\alpha} + \sum_i \mu_i^{\alpha''} \mathrm{d}n_i^{\alpha} \end{aligned} \tag{15}$$

in which we have written E^{α} instead of E.

3. Remark on the pressures P_{pl}, P_{tr}, P_{pa}

Since all the quantities occurring in the three equations 3, 10, and 15 refer only to the dielectric phase α, these quantities may be regarded as variables of state, of which the intensive ones are defined at every point within a dielectric. The pressures P_{pl}, P_{tr}, P_{pa} consequently have an existence independent of the methods, involving auxiliary surfaces, which must be used to measure them directly, but are in this respect not different from the pressure in ordinary systems, which, though defined at every point in a phase interior, can be directly measured only by introduction of a suitable surface such as that of a manometric fluid or of a piston equipped with a spring.

4. Comparison of the three equations for dU^α

Since all the quantities in equations 3, 10, and 15 are variables of state, these equations can be freely applied to *any* dielectric phase, *regardless* of the nature of the total system of which that phase happens to form a part. Equations 3, 10, and 15 are thus more general than their respective parent equations 2, 4, and 11, for the latter are true only for the particular systems 1, 2, 3, respectively, and then only if the areas of the condenser plates are fixed.

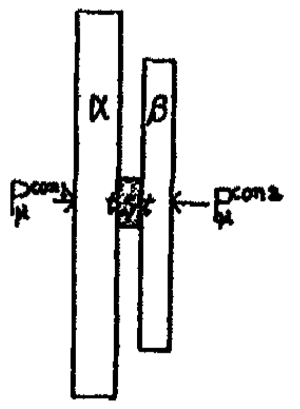

FIG. 2. Two dielectric phases, α and β, in equilibrium with respect to a component

Equations 3, 10, and 15 may therefore be taken as referring simultaneously to a single given dielectric phase. Comparison of equations 3, 10, and 15 then shows that

$$P_{\mathrm{pl}} = P_{\mathrm{tr}} - \frac{(D^\alpha)^2}{8\pi} = P_{\mathrm{pa}} - \frac{E^\alpha D^\alpha}{4\pi} + \frac{(E^\alpha)^2}{8\pi} \tag{16}$$

$$\mu_i^\alpha = \mu_i^{\alpha'} = \mu_i^{\alpha''} \tag{17}$$

The relation between P_{tr} and P_{pa} contained in equation 16 is in agreement with the result of Guggenheim (reference 4, page 97, equation 12.4).

5. General conditions for chemical equilibrium

We shall now show that the coefficients μ_i^α have the same significance for the chemical equilibrium of dielectric phases as do the chemical potentials for that of ordinary systems. Figure 2 represents two systems of the type 1 (figure 1) united through a plug *tst* which is permeable only to one of the components, say the i^{th}, with respect to which the phases α and β are supposed to be in equilibrium. In order that the plug may not disturb the uniformity of the field its faces *tt* are assumed to be electrically conducting, and in order that the plate charges $q_q^{\mathrm{con}\,1}$ and $q_q^{\mathrm{con}\,2}$ may be independently controlled the body s of the plug is assumed to be non-conducting. The amount of the i^{th} component dissolved in the plug is assumed to be negligibly small. The temperature T is taken as the same throughout; the pressures $P_{\text{pl}}^{\text{con}\,1}$, $P_{\text{pl}}^{\text{con}\,2}$ will then in general be different. The total energy and the total entropy of the system in figure 2 are respectively

$$U^{\text{tot}} = U^{\alpha} + U^{\beta} \tag{18.1}$$

$$S^{\text{tot}} = S^{\alpha} + S^{\beta} \tag{18.2}$$

From equations 2, 18.1, and 18.2 it follows that the complete differential of the function A^{tot}, defined as

$$A^{\text{tot}} \equiv U^{\text{tot}} - TS^{\text{tot}} \tag{19}$$

is given by

$$\mathrm{d}A^{\text{tot}} = -S^{\text{tot}}\mathrm{d}T - P_{\text{pl}}^{\text{con}\,1}\mathrm{d}V^{\alpha} - P_{\text{pl}}^{\text{con}\,2}\mathrm{d}V^{\beta} + [\psi\mathrm{d}q]^{\text{con}\,1} + [\psi\mathrm{d}q]^{\text{con}\,2} + \sum_i \mu_i^{\alpha}\mathrm{d}n_i^{\alpha} + \sum_i \mu_i^{\beta}\mathrm{d}n_i^{\beta} \tag{20}$$

On the other hand it follows from the two laws of thermodynamics and the definition (19) that for reversible processes at constant T and $n_i^{\text{tot}}(= n_i^{\alpha} + n_i^{\beta})$

$$\mathrm{d}A^{\text{tot}} = w \tag{21}$$

where w is the work done upon the system in the process. As an example of such a process consider the isothermal passage of an infinitesimal amount, $\mathrm{d}n_i$, of the i^{th} component from α to β, brought about by a suitable movement of the condenser plates. Since $q^{\text{con}\,1}$ and $q^{\text{con}\,2}$ remain constant, the only work done is that of the plates, so that, by equation 21

$$\mathrm{d}A^{\text{tot}} = -P_{\text{pl}}^{\text{con}\,1}\mathrm{d}V^{\alpha} - P_{\text{pl}}^{\text{con}\,2}\mathrm{d}V^{\beta} \tag{22}$$

But equation 20 demands that for the process in question

$$\mathrm{d}A^{\text{tot}} = -P_{\text{pl}}^{\text{con}\,1}\mathrm{d}V^{\alpha} - P_{\text{pl}}^{\text{con}\,2}\mathrm{d}V^{\beta} - \mu_i^{\alpha}\mathrm{d}n_i + \mu_i^{\beta}\mathrm{d}n_i \tag{23}$$

For equations 22 and 23 to be true simultaneously, it is necessary and sufficient that

$$\mu_i^{\alpha} = \mu_i^{\beta} \tag{24}$$

This is therefore the condition for heterogeneous chemical equilibrium in the electric field.

By a similar proof, omitted for brevity, it can be shown that if a chemical reaction has come to equilibrium in a dielectric phase, then

$$\sum_i \nu_i^{\alpha}\mu_i^{\alpha} = 0 \tag{25}$$

where ν_i denotes the coefficient of the i^{th} substance in the *chemical* equation describing the reaction, taken with negative sign if the substance is a reactant, with positive sign if it is a product.

Finally by making use of the extension of the second law of thermodynamics to irreversible processes, according to which, at constant T and n_i^{tot}, $\mathrm{d}A^{tot} < w$, it can be shown in the same way that if the component i tends to pass from α to β, then $\mu_i^\alpha > \mu_i^\beta$, and if a homogeneous chemical reaction tends to take place, then $\sum_i \nu_i^\alpha \mu_i^\alpha > 0$.

Because of this parallelism with ordinary systems the coefficients μ_i^α will be called chemical potentials.

6. Characteristic functions and Gibbsian equations

The mathematical consequences of the equations 3, 10, and 15 and of the conditions 24 and 25 include all the physically interesting thermodynamic relations of dielectrics. Before starting the deduction it is expedient (*i*) to introduce equation 17 into equations 10 and 15, (*ii*) to dispense with the superscript α, since henceforth, unless the contrary is indicated, all quantities shall refer to a single dielectric phase, and (*iii*) to set

$$\frac{EV}{4\pi} \equiv J \tag{26}$$

Equations 3, 10, and 15 then become

$$\mathrm{d}U = T\mathrm{d}S - P_{\mathrm{pl}}\mathrm{d}V + J\mathrm{d}D + \sum_i \mu_i \mathrm{d}n_i \tag{27}$$

$$= T\mathrm{d}S - \left(P_{\mathrm{tr}} - \frac{D^2}{8\pi}\right)\mathrm{d}V + J\mathrm{d}D + \sum_i \mu_i \mathrm{d}n_i \tag{28}$$

$$= T\mathrm{d}S - \left(P_{\mathrm{pa}} - \frac{ED}{4\pi} + \frac{E^2}{8\pi}\right)\mathrm{d}V + J\mathrm{d}D + \sum_i \mu_i \mathrm{d}n_i \tag{29}$$

The simplest method of deducing the consequences of equations 27, 28, and 29, that of Gibbs, depends upon the use of characteristic functions. The mathematical theory of such characteristic functions has recently been elaborated in an interesting paper by H. A. C. McKay (9), whose terminology we adopt. Characteristic functions owe their usefulness to the fact that they summarize the relations corresponding to given "canonical sets" (reference 9, page 715) of independent variables. Equation 27 shows that it is expedient to choose canonical sets of independent variables out of the set

$$P_{\mathrm{pl}},\ V,\ T,\ S,\ D,\ J,\ \mu_i,\ n_i \tag{30}$$

If k denotes the number of components, the total number of such canonical sets is, as McKay has shown, 2^{k+3}. Most of the familiar equations of physical interest, however, correspond to those canonical sets which contain all the n_i and therefore we shall here, in accordance with the procedure of Gibbs for ordinary systems, define explicitly only the characteristic functions for such sets. Of such sets there are $2^3 = 8$ contained in the variables (30), and the corresponding eight characteristic functions are

$$\begin{array}{ll} U & \mathfrak{U} \equiv U - DJ \\ H \equiv U + P_{\text{pl}}V & \mathfrak{H} \equiv H - DJ \\ F \equiv H - TS & \mathfrak{F} \equiv F - DJ \\ A \equiv F - P_{\text{pl}}V & \mathfrak{A} \equiv A - DJ \end{array} \qquad (31)$$

The corresponding Gibbsian equations are

$$dU = -P_{\text{pl}}dV + TdS + JdD + \sum_i \mu_i dn_i \qquad (32.1)$$

$$dH = TdS + VdP_{\text{pl}} + JdD + \sum_i \mu_i dn_i \qquad (32.2)$$

$$dF = VdP_{\text{pl}} - SdT + JdD + \sum_i \mu_i dn_i \qquad (32.3)$$

$$dA = -SdT - P_{\text{pl}}dV + JdD + \sum_i \mu_i dn_i \qquad (32.4)$$

$$d\mathfrak{A} = -SdT - P_{\text{pl}}dV - DdJ + \sum_i \mu_i dn_i \qquad (32.5)$$

$$d\mathfrak{F} = VdP_{\text{pl}} - SdT - DdJ + \sum_i \mu_i dn_i \qquad (32.6)$$

$$d\mathfrak{H} = TdS + VdP_{\text{pl}} - DdJ + \sum_i \mu_i dn_i \qquad (32.7)$$

$$d\mathfrak{U} = -P_{\text{pl}}dV + TdS - DdJ + \sum_i \mu_i dn_i \qquad (32.8)$$

There are, however, many useful results not included among those deducible from the equations 32, because these equations do not contain P_{tr} or P_{ps}. From the relations containing P_{pl} which are deducible from equations 32, it would of course be possible, by means of equation 16, eventually to obtain any desired relations involving P_{tr} or P_{ps}. But it would be simpler if the latter relations could be derived from sets of characteristic functions in which the "conjugates" (reference 9, page 715) of V are P_{tr} or P_{ps} instead of P_{pl}. Actually such functions exist.

For P_{tr} a set of eight functions of the type desired is given by

$$\begin{array}{ll} U' \equiv U - \dfrac{D^2V}{8\pi} & \mathfrak{U}' \equiv U' + DI \\ H' \equiv U' + P_{\text{tr}}V & \mathfrak{H}' \equiv H' + DI \\ F' \equiv H' - TS & \mathfrak{F}' \equiv F' + DI \\ A' \equiv F' - P_{\text{tr}}V & \mathfrak{A}' \equiv A' + DI \end{array} \qquad (33)$$

where I is defined by

$$I \equiv \frac{(\epsilon - 1)EV}{4\pi} = (\epsilon - 1)J \qquad (34)$$

Physically I is familiar as the total macroscopic electric moment of the dielectric phase. The Gibbsian equations corresponding to equations 33 are found by combination of equations 33 with equations 28 and 34 to be

$$dU' = -P_{tr}dV + TdS - IdD + \sum_i \mu_i dn_i \tag{35.1}$$

$$dH' = TdS + VdP_{tr} - IdD + \sum_i \mu_i dn_i \tag{35.2}$$

$$dF' = VdP_{tr} - SdT - IdD + \sum_i \mu_i dn_i \tag{35.3}$$

$$dA' = -SdT - P_{tr}dV - IdD + \sum_i \mu_i dn_i \tag{35.4}$$

$$d\mathfrak{A}' = -SdT - P_{tr}dV + DdI + \sum_i \mu_i dn_i \tag{35.5}$$

$$d\mathfrak{F}' = VdP_{tr} - SdT + DdI + \sum_i \mu_i dn_i \tag{35.6}$$

$$d\mathfrak{H}' = TdS + VdP_{tr} + DdI + \sum_i \mu_i dn_i \tag{35.7}$$

$$d\mathfrak{U}' = -P_{tr}dV + TdS + DdI + \sum_i \mu_i dn_i \tag{35.8}$$

Finally, for P_{ps} there are eight convenient functions defined by

$$\begin{aligned} U'' &\equiv U - \frac{E^2V}{8\pi} & \mathfrak{U}'' &\equiv U'' - EI \\ H'' &\equiv U'' + P_{ps}V & \mathfrak{H}'' &\equiv H'' - EI \\ F'' &\equiv H'' - TS & \mathfrak{F}'' &\equiv F'' - EI \\ A'' &\equiv F'' - P_{ps}V & \mathfrak{A}'' &\equiv A'' - EI \end{aligned} \tag{36}$$

The corresponding Gibbsian equations are found by combination of equations 36 with equations 29 and 34 to be

$$dU'' = -P_{ps}dV + TdS + EdI + \sum_i \mu_i dn_i \tag{37.1}$$

$$dH'' = TdS + VdP_{ps} + EdI + \sum_i \mu_i dn_i \tag{37.2}$$

$$dF'' = VdP_{ps} - SdT + EdI + \sum_i \mu_i dn_i \tag{37.3}$$

$$dA'' = -SdT - P_{ps}dV + EdI + \sum_i \mu_i dn_i \tag{37.4}$$

$$d\mathfrak{A}'' = -SdT - P_{ps}dV - IdE + \sum_i \mu_i dn_i \tag{37.5}$$

$$d\mathfrak{F}'' = VdP_{ps} - SdT - IdE + \sum_i \mu_i dn_i \tag{37.6}$$

$$d\mathfrak{H}'' = TdS + VdP_{ps} - IdE + \sum_i \mu_i dn_i \tag{37.7}$$

$$d\mathfrak{U}'' = -P_{ps}dV + TdS - IdE + \sum_i \mu_i dn_i \tag{37.8}$$

It is to be noted that in the three sets of Gibbsian equations 32, 35, and 37, corresponding to P_{pl}, P_{tr}, P_{ps}, respectively, the conjugate pairs of electric variables are different. Of the total of twenty-four equations, the eight containing dD and the four containing dE lead to results of greater interest than the four containing dJ and the eight containing dI.

The set of equations 37 is furthermore of particular interest because it is its first member without the chemical term that many previous writers on this subject, especially P. Debye (1) and E. C. Stoner (10), have used as a starting point for obtaining useful relations. In doing so they have not specified what sort of pressure is meant and have usually referred to the function here denoted by U'' as the energy or internal energy of the dielectric (or the magnetic matter). That this terminology is inexact has been made amply clear by Guggenheim (4) and should be evident also from the present paper. What we wish to emphasize is that all equations, such as those for electrostriction or for thermal effects, deduced by the authors in question merely from the assumption that dU'' is an exact differential, are true if under the P of these authors one understands P_{ps}.

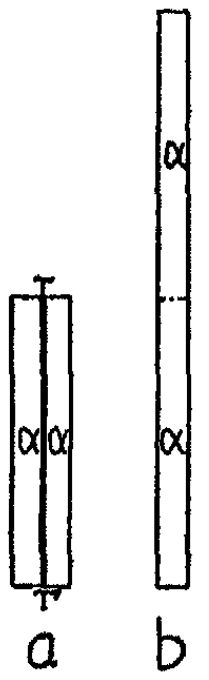

FIG. 3. To show the homogeneity of the characteristic functions of a dielectric phase

Finally we point out that each of the sets of equations 32, 35, and 37 has cubic or octahedral symmetry in the sense that it is invariant under a certain substitution group derivable from the cube or the octahedron, in the same way as the Gibbsian equations for ordinary systems are invariant under a group derivable from the square (6). A detailed account of this relationship is about to be published elsewhere.

7. *The homogeneity of the characteristic functions*

The energy and the twenty-three other characteristic functions defined in equations 31, 33, and 36 are homogeneous of the first order in the extensive variables V, S, J or I, n_i. This is readily evident from the following consideration. Let two identical systems of type 1 (figure 1) be united as shown in figure 3a. Then, neglecting effects due to the inhomogeneous field at the rims, the work required to remove the pair of superposed plates, $\pi\pi'$, is zero. In the resulting system the energy U, therefore, and also the extensive variables V, S, J, I, n_i have values twice as great as in either of the original systems, whereas the intensive variables P_{pl}, P_{tr}, P_{pa}, T, E, D, μ_i have the same values as before. It follows from the definitions 31, 33, and 36 that the twenty-three other characteristic functions have also doubled their values. The same result is achieved by uniting the two original systems at their rims, as shown in figure 3b. Similar considerations, here omitted for brevity, can obviously be applied to systems 2 and 3. It is to be noted that the plate charge q *cannot* be included among the variables in which the characteristic functions in question are homogeneous, for in figure 3a q remains constant (while ψ is doubled) and in figure 3b q is doubled (while ψ remains constant). This difference between q on the one hand and J or I on the other is related to the fact (see section 4 above) that equations 3, 10, and 15 are more general than equations 2, 4, and 11.

8. The explicit expression for the energy of a dielectric phase

Because of the homogeneity of the characteristic functions, equations 27, 28, 29, 32, 35, and 37 can be integrated by means of Euler's theorem. It is unnecessary to write down all the resulting equations, which are interrelated in an obvious manner through the definitions 31, 33, and 36. The equations for the energy U, as derived from equations 27, 28, and 29, are

$$U = TS - P_{\mathrm{pl}}V + \sum_i \mu_i n_i \tag{38}$$

$$= TS - \left(P_{\mathrm{tr}} - \frac{D^2}{8\pi}\right)V + \sum_i \mu_i n_i \tag{39}$$

$$= TS - \left(P_{\mathrm{pa}} - \frac{ED}{4\pi} + \frac{E^2}{8\pi}\right)V + \sum_i \mu_i n_i \tag{40}$$

9. The Gibbs–Duhem equations

From the homogeneity of the characteristic functions it follows further that corresponding to each of the three sets of Gibbsian equations 32, 35, and 37 there is one equation of the Gibbs–Duhem type. The three Gibbs–Duhem equations are readily seen to be

$$0 = SdT - VdP_{\mathrm{pl}} - JdD + \sum_i n_i d\mu_i \tag{41}$$

$$0 = SdT - VdP_{\mathrm{tr}} + IdD + \sum_i n_i d\mu_i \tag{42}$$

$$0 = SdT - VdP_{\mathrm{pa}} + IdE + \sum_i n_i d\mu_i \tag{43}$$

As shown below, these equations are useful for the treatment of the nonuniform field.

III. EFFECT OF THE FIELD ON CHEMICAL POTENTIAL

1. Derivatives of μ_i with respect to E

Since practically all the important formulae for electrocaloric or electrostriction effects deducible from the equations 32, 35, and 37 have been given by previous authors, we shall confine ourselves to the study of the effect of the field upon the μ_i. The field variable most useful for this purpose is E, since E is readily measured in electrostatic experiments. We shall accordingly calculate $\frac{\partial \mu_i}{\partial E}$ at constant

$V,\ T,\ n_i$
$P_{\text{pl}},\ T,\ n_i$
$P_{\text{tr}},\ T,\ n_i$
$P_{\text{pa}},\ T,\ n_i$

(*i*). *At constant V, T, n_i.* Equation 37.5 yields

$$\begin{aligned}\left(\frac{\partial \mu_i}{\partial E}\right)_{V,T,n_i} &= -\left(\frac{\partial I}{\partial n_i}\right)_{V,T,E,n_i'} \\ &= -J\left(\frac{\partial \epsilon}{\partial n_i}\right)_{V,T,E,n_i'}\end{aligned} \tag{44}$$

(*ii*). *At constant P_{pl}, T, n_i.* Equation 32.5 yields

$$\left(\frac{\partial \mu_i}{\partial D}\right)_{P_{\text{pl}},T,n_i} = \left(\frac{\partial J}{\partial n_i}\right)_{P_{\text{pl}},T,D,n_i'}$$

$$\begin{aligned}\left(\frac{\partial \mu_i}{\partial E}\right)_{P_{\text{pl}},T,n_i} &= \left(\frac{\partial D}{\partial E}\right)_{P_{\text{pl}},T,n_i} \cdot \left(\frac{\partial J}{\partial n_i}\right)_{P_{\text{pl}},T,D,n_i'} \\ &= \left(\frac{\partial D}{\partial E}\right)_{P_{\text{pl}},T,n_i} \cdot \left[\left(\frac{\partial J}{\partial n_i}\right)_{P_{\text{pl}},T,E,n_i'} + \left(\frac{\partial J}{\partial E}\right)_{P_{\text{pl}},T,n_i} \cdot \left(\frac{\partial E}{\partial n_i}\right)_{P_{\text{pl}},T,D,n_i'}\right] \\ &= \left(\frac{\partial J}{\partial n_i}\right)_{P_{\text{pl}},T,E,n_i'} \cdot \left(\frac{\partial D}{\partial E}\right)_{P_{\text{pl}},T,n_i} - \left(\frac{\partial J}{\partial E}\right)_{P_{\text{pl}},T,n_i} \cdot \left(\frac{\partial D}{\partial n_i}\right)_{P_{\text{pl}},T,E,n_i'}\end{aligned} \tag{45}$$

(*iii*). *At constant P_{tr}, T, n_i.* Equation 35.3 yields

$$\left(\frac{\partial \mu_i}{\partial D}\right)_{P_{\text{tr}},T,n_i} = -\left(\frac{\partial I}{\partial n_i}\right)_{P_{\text{tr}},T,D,n_i'}$$

whence by calculation parallel to that for equation 45

$$\left(\frac{\partial \mu_i}{\partial E}\right)_{P_{\text{tr}},T,n_i} = \left(\frac{\partial I}{\partial E}\right)_{P_{\text{tr}},T,n_i} \cdot \left(\frac{\partial D}{\partial n_i}\right)_{P_{\text{tr}},T,E,n_i'} - \left(\frac{\partial I}{\partial n_i}\right)_{P_{\text{tr}},T,E,n_i'} \cdot \left(\frac{\partial D}{\partial E}\right)_{P_{\text{tr}},T,n_i} \tag{46}$$

(*iv*). *At constant* P_{pa}, T, n_i. Equation 37.6 yields

$$\left(\frac{\partial \mu_i}{\partial E}\right)_{P_{pa},T,n_i} = -\left(\frac{\partial I}{\partial n_i}\right)_{P_{pa},T,E,n_j'} = -E\left(\frac{\partial \chi}{\partial n_i}\right)_{P_{pa},T,E,n_j'} \tag{47}$$

where χ is defined by

$$\chi \equiv \frac{(\epsilon - 1)V}{4\pi} = \frac{I}{E} \tag{48}$$

and may be called the "total susceptibility," since it is the product of the volume by the quantity usually called the susceptibility.

2. The special case: $\chi = \sum_i n_i \chi_i(T)$ (49)

This case is of interest because from statistical mechanics it follows that equation 49 is the law obeyed by systems whose molecules do not polarize each other appreciably. It is therefore obeyed to a high degree of accuracy by all gases. Debye, following Langevin, has shown that for such systems at ordinary temperatures and not too high field strengths χ_i is of the form

$$\chi_i = L\left(a_i + \frac{m_i^2}{3kT}\right)$$

where L is Avogadro's number, a_i is the polarizability by distortion of the molecule of the component i by the applied field, m_i is the permanent moment of the molecule, and k is Boltzmann's constant.

For systems obeying equation 49 the chemical potential can be calculated as an explicit function of the field strength. From equation 49 it follows that

$$\left(\frac{\partial \chi}{\partial n_i}\right)_{P_{pa},T,E,n_j'} = \chi_i(T)$$

and hence by integration of equation 47 that

$$\mu_i = \mu_i^*(P_{pa}, T, n_i) - \tfrac{1}{2}\chi_i E^2 \tag{50}$$

where μ_i^* is the value of μ_i for $E = 0$ in a system of the same temperature and composition as the system considered and a pressure equal to P_{pa}.

Equation 50 leads to an extended form of the law of mass action because it can be written as

$$\mu_i = \mu_i^0(P_{pa}, T) + RT \log N_i f_i - \tfrac{1}{2}\chi_i E^2 \tag{51}$$

where N_i is the mole fraction of i and f_i its activity coefficient, i.e., a function of P_{pa}, T and composition equal to unity at infinite dilution. The substitution of equation 51 into the general condition (25) for homogeneous chemical equilibrium yields the law of mass action for the systems in question

$$\prod_i (N_i f_i)^{\nu_i} = K(P_{pa}, T) \exp \frac{E^2}{2RT} \sum_i \nu_i \chi_i \tag{52}$$

where K is the equilibrium constant in the absence of a field, i.e.

$$K \equiv \exp\left(-\frac{1}{RT} \sum_i \nu_i \mu_i^0\right)$$

The sum $\sum_i \nu_i \chi_i$ is evidently the change in χ produced when at constant temperature ν_i moles are transformed, and is therefore conveniently denoted by $\Delta\chi$. At temperatures and field strengths for which equation 52 is valid, $\frac{E^2}{2RT} \Delta\chi \ll 1$, so that instead of equation 52 it is sufficient to write

$$\prod_i (N_i f_i)^{\nu_i} = K\left(1 + \frac{E^2}{2RT} \Delta\chi\right) \tag{53}$$

and since in practice the systems in question are all very nearly ideal, equation 53 simplifies to

$$\prod_i N_i^{\nu_i} = K\left(1 + \frac{E^2}{2RT} \Delta\chi\right) \tag{54}$$

from which it appears that in a closed system an increase in E at constant P_{pa} and T shifts the equilibrium in such a direction as to cause an increase in χ.

3. *Perfect gaseous mixture*

If the system not only obeys equation 49 but is also (in the absence of a field) a perfect gas, we can go a step further because for perfect gases the f_i are unity and the μ_i^0 in equation 51 is of the form

$$\mu_i^0(P_{pa}, T) = \mu_i^{0'}(T) + RT \log P_{pa}$$

so that the chemical potential becomes

$$\mu_i = \mu_i^{0'} + RT \log P_{pa} + RT \log N_i - \tfrac{1}{2} \chi_i E^2 \tag{55}$$

The equation of state for a perfect gaseous mixture permeated by an electric field may now be deduced as follows. Equation 37.6 gives

$$\left(\frac{\partial \mu_i}{\partial P_{pa}}\right)_{T,E,n_i} = \left(\frac{\partial V}{\partial n_i}\right)_{P_{pa},T,E,n_i'}; \tag{56}$$

whence, because of equation 55,

$$\left(\frac{\partial V}{\partial n_i}\right)_{P_{\text{pa}},T,E,n_i'} = \frac{RT}{P_{\text{pa}}} \tag{57}$$

But since V is an extensive quantity we have in general that

$$V = \sum_i n_i \left(\frac{\partial V}{\partial n_i}\right)_{P_{\text{pa}},T,E,n_i'} \tag{58}$$

The substitution of equation 57 into equation 58 gives

$$P_{\text{pa}}V = \sum_i n_i RT = nRT \tag{59}$$

where n is the total number of moles. In terms of P_{pa}, therefore, the equation of state is not affected by the field. The more complicated equations in terms of P_{tr} or P_{pl} are immediately obtained by combining equation 59 with equation 16.

For perfect gases the law of mass action (equation 54) is replaced by two simpler expressions as follows. In analogy to the partial pressure in the absence of a field, we define the partial pressure $p_{i,\text{pa}}$ by

$$p_{i,\text{pa}} \equiv N_i P_{\text{pa}} \tag{60}$$

Equation 59 then yields

$$p_{i,\text{pa}} = c_i RT \tag{61}$$

where c_i is the volume concentration, and equation 55 gives

$$\mu_i = \mu_i^{0'} + RT \log p_{i,\text{pa}} - \tfrac{1}{2}\chi_i E^2 \tag{62}$$

$$= \mu_i^{0'} + RT \log RT + RT \log c_i - \tfrac{1}{2}\chi_i E^2 \tag{63}$$

Equations 62 and 63 give as laws of mass action, respectively,

$$\prod_i p_{i,\text{pa}}^{\nu_i} = K'(T)\left(1 + \frac{E^2}{2RT}\Delta\chi\right) \tag{64}$$

$$\prod_i c_i^{\nu_i} = K''(T)\left(1 + \frac{E^2}{2RT}\Delta\chi\right) \tag{65}$$

where K' and K'' are the familiar "K_p" and "K_c" of perfect gas equilibria. From equation 65 it is clear that in a closed system an increase in E at constant T and V shifts the equilibrium so as to increase χ.

IV. EQUILIBRIUM IN A NON-UNIFORM FIELD

The general equations for dielectric phases can be applied to dielectrics permeated by non-uniform fields by considering the matter to be divided into infinitesimal regions, called subphases, in which the field may be taken as uniform. The fact that all extensive variables thereby become infinitesimals and their differentials infinitesimals of higher order causes no inconvenience, because it is only the relations between intensive variables that are of physical interest in the non-uniform field. Formally the treatment is closely analogous (7) to that of the gravitational field, the electric variables E and D playing parts similar to that of the gravitational potential.

1. Pressure gradient

From equations 41, 42, and 43 it follows that for a given independent phase or subphase

$$\left(\frac{\partial P_{\mathrm{pl}}}{\partial D}\right)_{T,\mu_i} = -\frac{J}{V} = -\frac{1}{4\pi}E \qquad (66.1)$$

$$\left(\frac{\partial P_{\mathrm{tr}}}{\partial D}\right)_{T,\mu_i} = \frac{I}{V} = \frac{\epsilon - 1}{4\pi}E \qquad (66.2)$$

$$\left(\frac{\partial P_{\mathrm{pa}}}{\partial E}\right)_{T,\mu_i} = \frac{I}{V} = \frac{\epsilon - 1}{4\pi}E \qquad (66.3)$$

Since all the subphases of a fluid in complete equilibrium in a non-uniform field have the same values of T and the μ_i, it follows that in such a fluid there exist the following pressure gradients

$$\mathrm{d}P_{\mathrm{pl}} = -\frac{1}{4\pi}E\mathrm{d}D \qquad (67.1)$$

$$\mathrm{d}P_{\mathrm{tr}} = \frac{\epsilon - 1}{4\pi}E\mathrm{d}D \qquad (67.2)$$

$$\mathrm{d}P_{\mathrm{pa}} = \frac{\epsilon - 1}{4\pi}E\mathrm{d}E \qquad (67.3)$$

The magnetic analogues of equations 67.2 and 67.3 for a one-component system have been obtained by Guggenheim (reference 4, page 97). For the special case that the gradient of ϵ with E can be neglected, equations 67 integrate to

$$P_{\mathrm{pl}} - P_0 = -\frac{\epsilon}{8\pi}E^2 \qquad (68.1)$$

$$P_{\mathrm{tr}} - P_0 = \frac{\epsilon(\epsilon - 1)}{8\pi}E^2 \qquad (68.2)$$

$$P_{\mathrm{pa}} - P_0 = \frac{\epsilon - 1}{8\pi}E^2 \qquad (68.3)$$

where P_0 is the pressure at all points where $E = 0$.

2. *Concentration gradient*

We shall now show that besides a pressure gradient there is also a concentration gradient in a non-uniform field. Since the chemical potential of any component, say the j^{th}, is completely determined by P_{pa}, T, E and the mole fractions $N_{j'}$ of all the components except the j^{th}, we have

$$-\mathrm{d}\mu_j + \left(\frac{\partial \mu_j}{\partial P_{\text{pa}}}\right)_{T,E,N_{j'}} \mathrm{d}P_{\text{pa}} + \left(\frac{\partial \mu_j}{\partial T}\right)_{P_{\text{pa}},E,N_{j'}} \mathrm{d}T + \left(\frac{\partial \mu_j}{\partial E}\right)_{P_{\text{pa}},T,N_{j'}} \mathrm{d}E + \sum_{j'} \left(\frac{\partial \mu_j}{\partial N_{j'}}\right)_{P_{\text{pa}},T,E,N_{j''}} \mathrm{d}N_{j'} = 0 \tag{69}$$

where the subscript $N_{j''}$ denotes the constancy of all the $N_{j'}$ except the one with respect to which the differentiation is carried out. Taking E, T, and μ_i as independent variables of which T and μ_i are kept constant, it follows from equation 69 that

$$\sum_{j'} \left(\frac{\partial \mu_j}{\partial N_{j'}}\right)_{P_{\text{pa}},T,E,N_{j''}} \cdot \left(\frac{\partial N_{j'}}{\partial E}\right)_{T,\mu_i} + \left(\frac{\partial \mu_j}{\partial P_{\text{pa}}}\right)_{T,E,N_{j'}} \cdot \left(\frac{\partial P_{\text{pa}}}{\partial E}\right)_{T,\mu_i} + \left(\frac{\partial \mu_j}{\partial E}\right)_{P_{\text{pa}},T,N_{j'}} = 0 \tag{70}$$

Recalling equations 56 and 47, we have

$$\left(\frac{\partial \mu_j}{\partial P_{\text{pa}}}\right)_{T,E,N_{j'}} = \left(\frac{\partial \mu_j}{\partial P_{\text{pa}}}\right)_{T,E,n_j} = \left(\frac{\partial V}{\partial n_j}\right)_{P_{\text{pa}},T,E,n_{j'}} \tag{71}$$

$$\left(\frac{\partial \mu_j}{\partial E}\right)_{P_{\text{pa}},T,N_{j'}} = \left(\frac{\partial \mu_j}{\partial E}\right)_{P_{\text{pa}},T,n_j} = -E\left(\frac{\partial \chi}{\partial n_j}\right)_{P_{\text{pa}},T,E,n_{j'}} = -\frac{\epsilon - 1}{4\pi} E\left(\frac{\partial V}{\partial n_j}\right)_{P_{\text{pa}},T,E,n_{j'}} - \frac{EV}{4\pi}\left(\frac{\partial \epsilon}{\partial n_j}\right)_{P_{\text{pa}},T,E,n_{j'}} \tag{72}$$

The substitution of equations 71, 72, and 66.3 into equation 70 gives

$$\sum_{j'} \left(\frac{\partial \mu_j}{\partial N_{j'}}\right)_{P_{\text{pa}},T,E,N_{j''}} \cdot \left(\frac{\partial N_{j'}}{\partial E}\right)_{T,\mu_i} = \frac{EV}{4\pi}\left(\frac{\partial \epsilon}{\partial n_j}\right)_{P_{\text{pa}},T,E,n_{j'}} \tag{73}$$

In order to apply equation 73 to non-uniform fields it is necessary to express the quantity on the right in terms of intensive variables alone. Since the $N_{j'}$ are functions of the n_j we have

$$\left(\frac{\partial \epsilon}{\partial n_j}\right)_{P_{\text{pa}},T,E,n_{j'}} = \sum_{j'} \left(\frac{\partial \epsilon}{\partial N_{j'}}\right)_{P_{\text{pa}},T,E,N_{j''}} \cdot \left(\frac{\partial N_{j'}}{\partial n_j}\right)_{n_{j'}} \tag{74}$$

but

$$N_{j'} = \frac{n_{j'}}{n}$$

$$\left(\frac{\partial N_{j'}}{\partial n_j}\right)_{n_{j'}} = -\frac{n_{j'}}{n^2} = -\frac{N_{j'}}{n}$$

where n is $\sum_j n_j$, so that equation 74 becomes

$$\left(\frac{\partial\epsilon}{\partial n_j}\right)_{P_{pa},T,E,n_{j'}} = -\frac{1}{n}\sum_{j'} N_{j'}\left(\frac{\partial\epsilon}{\partial N_{j'}}\right)_{P_{pa},T,E,N_{j''}}$$

$$= -\frac{1}{n}\sum_{j'}\left(\frac{\partial\epsilon}{\partial \log N_{j'}}\right)_{P_{pa},T,E,N_{j''}} \tag{75}$$

The introduction of equation 75 into equation 73 gives

$$\sum\left(\frac{\partial\mu_j}{\partial N_{j'}}\right)_{P_{pa},T,E,N_{j''}}\cdot\left(\frac{\partial N_j}{\partial E}\right)_{T,\mu_i} = -\frac{E\bar{V}}{4\pi}\sum_{j'}\left(\frac{\partial\epsilon}{\partial \log N_{j'}}\right)_{P_{pa},T,E,N_{j''}} \tag{76}$$

where $\bar{V}$ is the mean molar volume of the phase or subphase. From equation 76 it follows that the mole fractions $N_{j'}$ are subject to gradients such that

$$\sum_{j'}\left(\frac{\partial\mu_j}{\partial N_{j'}}\right)_{P_{pa},T,E,N_{j''}}\cdot dN_{j'} = -\frac{E\bar{V}}{4\pi}\sum_{j'}\left(\frac{\partial\epsilon}{\partial \log N_{j'}}\right)_{P_{pa},T,E,N_{j''}}\cdot dE \tag{77}$$

Among the factors governing the concentration gradient is thus seen to be the variation of dielectric constant with composition.

3. The immersed condenser

This system consists of a fixed plane condenser immersed in a mass of dielectric fluid so large that the field at the free surfaces of the dielectric is negligible. It is conveniently discussed in connection with the nonuniform field because it reveals the physical significance of equation 68.1. P_0 is the pressure at the free surface of the fluid and is therefore also the *hydrostatic* pressure acting on the outside of the condenser plates. Since the *total* pressure on the outside of the plates at equilibrium is P_{pl}, equation 68.1 shows that the plates are not in equilibrium under the fluid forces alone, but must be prevented from moving towards each other by an additional force, which, if ϵ is constant everywhere, is equal to $\frac{\epsilon}{8\pi}E^2$ per unit area. Equation 68.1 is therefore merely the familiar electrostatic formula, valid for constant ϵ, for the "pull on a condenser plate."

The immersed condenser is further of interest because it represents a convenient experimental arrangement for the study of the electrostriction of liquids. The magnetic analogue of this system (at constant composition) has been discussed in detail by Guggenheim (reference 4, page 88) as the first one of his "systems of simple symmetry." His general result can be obtained from our equations for the energy of a dielectric phase as follows. The system is treated as if the field strength were uniform of value E^α between the plates and zero everywhere else. If α refers to the matter between the plates then, since the latter are fixed, dV^α is zero and equation 32.1 gives for the energy of α

$$dU^\alpha = T^\alpha dS^\alpha + J^\alpha dD^\alpha + \sum_i \mu_i^\alpha dn_i^\alpha \tag{78}$$

For the part outside the plates, referred to by the subscript 0,

$$dU_0 = T_0 dS_0 - P_0 dV_0 + \sum_i \mu_{i0} dn_{i0} \tag{79}$$

Since

$$T_0 = T^\alpha = T$$
$$\mu_{i0} = \mu_i^\alpha = \mu_i$$
$$dV_0 = dV$$

where the quantities without superscript α or subscript 0 refer to the entire system, we have for the latter, by addition of equations 78 and 79,

$$dU = TdS - P_0 dV + J^\alpha dD^\alpha + \sum_i \mu_i dn_i \tag{80}$$

which agrees with the result of Guggenheim, his function F being our $U - TS$.

Equation 80 closely resembles equation 32.1 for the energy of a dielectric phase, and it is worth noting that the introduction of the functions

$$U^* \equiv U - \frac{(D^\alpha)^2 V^\alpha}{8\pi}$$

$$U^{**} \equiv U - \frac{(E^\alpha)^2 V^\alpha}{8\pi}$$

leads to the equations

$$dU^* = TdS - P_0 dV - I^\alpha dD^\alpha + \sum_i \mu_i dn_i \tag{81}$$

$$dU^{**} = TdS - P_0 dV + E^\alpha dI^\alpha + \sum_i \mu_i dn_i \tag{82}$$

which closely resemble equations 35.1 and 37.1 for a dielectric phase. The difference between equations 80, 81, and 82 on the one hand and equations 32.1, 35.1, and 37.1 on the other lies of course not only in the nature of the pressure variable but also in the relation of J and I to V. As mentioned above, it is an equation of the form of equation 37.1 that has generally been used by previous authors as a starting point for their deductions, and thus from the similarity of equations 82 and 37.1 arises the fact, pointed out by Guggenheim (reference 4, page 100), that many of these deductions are applicable to the immersed condenser, the P of these authors then being interpreted as P_0.

4. Perfect gaseous mixture in non-uniform field

For this case formulae analogous to the "barometer formulae" in a gravitational field are very simply derived from equations 62 and 63 for the chemical potential. Denoting any two points in the gas by α and β, respectively, we obtain, because of $\mu_i^\alpha = \mu_i^\beta$ and $T^\alpha = T^\beta = T$.

$$p_{i,\mathrm{pa}}^\alpha = p_{i,\mathrm{pa}}^\beta \exp \frac{(E^\alpha)^2 - (E^\beta)^2}{2RT} \chi_i \tag{83}$$

$$c_i^\alpha = c_i^\beta \exp \frac{(E^\alpha)^2 - (E^\beta)^2}{2RT} \chi_i \tag{84}$$

Further, because of

$$p_{i,\mathrm{pa}}^\beta = N_i^\beta P_{\mathrm{pa}}^\beta$$

$$\sum_i p_{i,\mathrm{pa}}^\alpha = P_{\mathrm{pa}}^\alpha$$

we obtain from equation 83

$$P_{\mathrm{pa}}^\alpha = P_{\mathrm{pa}}^\beta \sum_i N_i^\beta \exp \frac{(E^\alpha)^2 - (E^\beta)^2}{2RT} \chi_i \tag{85}$$

For the special case of one component this formula has been derived from statistical considerations by O. E. Frivold (2).

The introduction of the approximation

$$\exp \frac{(E^\alpha)^2 - (E^\beta)^2}{2RT} \chi_i = 1 + \frac{(E^\alpha)^2 - (E^\beta)^2}{2RT} \chi_i$$

into equation 85 leads to the so called "electrostriction formulae for gases," which have been known for a long time. For the special case that $E^\beta = 0$, for which we set

$$E^\alpha = E, \qquad P_{\mathrm{pa}}^\alpha = P_{\mathrm{pa}}, \qquad P_{\mathrm{pa}}^\beta = P_0, \qquad N_i^\beta = N_{i0}$$

we obtain

$$P_{\mathrm{pa}} = P_0 + \frac{P_0}{RT} \cdot \frac{E^2}{2} \sum_i N_{i0} \chi_i \tag{86}$$

But, recalling equations 49, 48, and 59, we have

$$\sum_i N_{i0} \chi_i = \tilde{\chi}_0 = \frac{\epsilon_0 - 1}{4\pi} \tilde{V}_0 = \frac{\epsilon - 1}{4\pi} \cdot \frac{RT}{P_0}$$

where $\bar{\chi}_0$ is the mean molar susceptibility, $\bar{V}_0$ the mean molar volume, and ϵ_0 the dielectric constant at points where $E = 0$. Hence equation 86 reduces to

$$P_{pa} - P_0 = \frac{\epsilon_0 - 1}{8\pi} E^2 \tag{87}$$

For the special case of one component this well-known formula was first obtained by G. Lippmann (8) in 1881. It is not identical with equation 68.3 because it implies that the dielectric constant may vary throughout the system, whereas equation 68.3 assumes ϵ constant everywhere.

If the interior of a closed fixed condenser is connected with a reservoir of volume very large compared with that between the condenser plates, then, when a field is applied, gas moves from the reservoir into the condenser. The volume ΔV of the gas moved, measured at the pressure P_0 of the reservoir, which remains practically constant, is found from equations 87 and 59 to be

$$\Delta V = \frac{V^\alpha}{P_0} \cdot \frac{\epsilon_0 - 1}{8\pi} E^2 \tag{88}$$

where V^α is the volume between the plates. This equation has been verified experimentally for sufficiently low field strengths by various authors (2, 3, 5).

SUMMARY

The general thermodynamic equations for dielectrics permeated by electric fields are extended to include the case of variable composition. The derivation is based on the elementary laws of the plane condenser. Chemical equilibrium is shown to depend upon a chemical potential, μ_i, as in ordinary systems. It is shown that for a "dielectric phase" (homogeneous mass of dielectric permeated by a uniform field) there exist three convenient sets of characteristic functions corresponding to three kinds of pressure measurement. The effect of the field upon chemical potential is considered. The chief laws of equilibrium in a non-uniform field are derived. Among the new results of physical interest are (*i*) explicit formulae for the energy of a dielectric phase (equations 38, 39, and 40), (*ii*) the equations of state and the law of mass action for perfect gases in the electric field (equations 59, 64, and 65), (*iii*) thermodynamic proof of the existence of a concentration gradient at equilibrium in a non-uniform field (equation 77), and (*iv*) the extension of the Lippman electrostriction formula for perfect gases to mixtures (equation 87).

It gives me great pleasure to thank Mr. E. A. Guggenheim for his kind and helpful advice.

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COLLOIDS IN GLACIAL ACETIC ACID. I

ELEMENTS, CHLORIDES, SULFIDES, AND SULFATES

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Most of the recent work done using glacial acetic acid has dealt largely with salt solubilities (1, 2), phase studies (3, 6), electrometric work (8), and activity coefficients of salts (4, 5, 7, 10). Weiser and Mack (13) list numerous examples of colloidal dispersions in other organic solvents. Voet (11, 12) discusses colloidal solutions in concentrated electrolytes and he has prepared some sols in mixtures of concentrated sulfuric and acetic acids. Since the completion of this investigation Ostwald and Wannow (9) have reported the preparation of arsenic trisulfide in glacial acetic acid and have noted its very great stability.

COLLOIDAL ELEMENTS

Arsenic

The yellow, metastable form of arsenic is slightly soluble in carbon disulfide. Some of this solution was added to glacial acetic acid and the arsenic was dispersed in the colloidal state. The glacial acetic acid was prepared in a pure and anhydrous condition by refluxing with 1–2 per cent chromic oxide and the calculated amount of acetic anhydride and then carefully distilled. Only that acid with melting point of 16.5°C. or above was used in the experimental work. The yellow sols which formed varied in intensity according to the concentration of arsenic present.

One stable arsenic sol was prepared by dissolving 0.120 g. of arsenic in 333 ml. of carbon disulfide and then pouring this solution into 667 ml. of glacial acetic acid. Somewhat higher concentrations of arsenic can be used. Attempts were made to stabilize arsenic sols further by the use of gum mastic and gum dammar in concentrations of approximately 0.1 g. per liter. Instead of stabilizing the sols, the opposite effect was noted. Attempts were made to remove the carbon disulfide by dialysis and by heating, but each resulted in decreasing the stability of the sol.

Selenium

Red selenium was dissolved in carbon disulfide and this solution was added in varying amounts to glacial acetic acid. The color of the sol depended upon the concentration of selenium present, some being red, others pink, and some having a yellowish tinge. By transmitted light all the sols were nearly colorless. These sols were stable for about three days. No satisfactory protective agents were found. Sixteen sols were prepared varying in selenium concentration per liter from 0.00179 to 0.4470 g. The carbon disulfide concentration was varied from 0.2 to 50.0 per cent by volume.

Sulfur

White to yellow sulfur sols, depending upon the amount of sulfur dissolved in carbon disulfide, were prepared by adding the glacial acetic acid slowly from a buret to the sulfur dissolved in carbon disulfide. These sols were not very stable. A sol containing 0.0762 g. of sulfur, 0.0452 g. of gum mastic, 168 ml. of carbon disulfide, and 832 ml. of glacial acetic acid contained no precipitate after seven hours, but had precipitated in one day.

Sulfur sols were also prepared by dissolving sulfur monochloride in glacial acetic acid and passing dry hydrogen sulfide into this solution. The yellow sols which formed were not very stable. It is interesting to note that these sols, immediately after formation, could be poured into large volumes of water without the sulfur precipitating.

Phosphorus

Better phosphorus sols were prepared by dissolving yellow phosphorus in benzene than in carbon disulfide. If glacial acetic acid is added very slowly to the benzene containing the phosphorus, very stable sols are formed. In some instances it was necessary to seed with a small amount of another phosphorus sol. Dialysis through cellophane to remove the benzene eventually caused complete precipitation of the sol. If the phosphorus sol is poured into water, the sol fumes and smells strongly of burning phosphorus.

Two typical stable phosphorus sols were prepared as follows: (1) 0.02995 g. of phosphorus was dissolved in 2 ml. of benzene and 998 ml. of glacial acetic acid was added and (2) 2.96 g. of phosphorus was dissolved in 200 ml. of benzene and 800 ml. of glacial acetic acid was added. Many phosphorus sols of other ratios of phosphorus:benzene:acetic acid have been prepared.

Gold, platinum, silver, and copper

Platinic and auric chlorides are not soluble in acetic acid. If dry hydrogen chloride gas is passed into suspensions of these salts in glacial acetic acid, the soluble complexes H_2PtCl_6 and $HAuCl_4$ form. Small amounts of phosphorus dissolved in benzene added to the solution of chloroauric acid in glacial acetic acid produced a beautiful change in color from a pale yellow to red and finally brown. A precipitate soon forms, so these sols cannot be considered as being very stable. With chloroplatinic acid a similar reaction took place, the final product being a black precipitate. It was found possible to reduce chloroplatinic acid with gum dammar. No satisfactory stabilizing agent was found.

Silver nitrate and silver acetate dissolved in glacial acetic acid were immediately reduced to unstable red sols by the addition of yellow phosphorus dissolved in benzene.

Copper acetate dissolved in glacial acetic acid was slowly reduced by phosphorus, but it always precipitated as a reddish brown deposit.

SULFIDES

Many elements which form insoluble sulfides in water also form insoluble sulfides in glacial acetic acid. Soluble acetates are very desirable for the preparation of sulfide sols, because the secondary product is acetic acid. Oxides are not desirable because water is formed. Some sulfides, such as arsenious sulfide, antimony trisulfide, and nickel monosulfide in the presence of a large excess of ammonium ion, tend to be colloidal in acetic acid as well as in water.

Colloidal sulfides containing Pb^{++}, Hg^{++}, Cu^{++}, Ni^{++}, Co^{++}, As^{+++}, Sn^{++++}, and Ag^{+} have been prepared by bubbling hydrogen sulfide into acetic acid solutions of lead acetate, mercuric chloride, cupric acetate and ammonium acetate, nickel acetate and ammonium acetate, cobaltous chloride, arsenic trichloride, stannic chloride, and silver nitrate, respectively. Arsenic, cobalt, and copper sols have been prepared which have been stable for about a month. The others were not as stable. Gum mastic was a satisfactory stabilizing agent.

Very stable arsenic trisulfide and antimony trisulfide sols were prepared by bubbling hydrogen sulfide into acetic acid solutions containing arsenic trioxide and antimony trioxide. Since water is a product of this reaction, the system is no longer non-aqueous.

COLLOIDAL CHLORIDES

Attempts were made to prepare colloidal silver, lead, mercurous, and thallous chlorides by passing dry hydrogen chloride gas into silver nitrate, lead acetate, and thallous nitrate. None of these sols was stable for more than a few hours. Mercuric chloride was dissolved in glacial acetic acid and a small amount of yellow phosphorus in benzene added. A colloidal solution of mercurous chloride formed, which was stable for about two days.

COLLOIDAL SULFATES

Since nearly all of the inorganic sulfates are insoluble in glacial acetic acid, it is possible to precipitate the sulfates by adding 100 per cent sulfuric acid to a solution of a soluble salt in glacial acetic acid. Barium sulfate formed by adding sulfuric acid to a solution of barium chloride in glacial acetic acid showed a slight tendency to be colloidal. Lead sulfate formed from lead acetate dissolved in glacial acetic acid tended to precipitate immediately. The reaction between copper acetate and sulfuric acid in glacial acetic acid forms a thick gel-like solution when first mixed. Upon standing, the white copper sulfate precipitates, leaving a clear solution. The most stable sulfate sol was prepared from strontium acetate dissolved in glacial acetic acid. A sol which was stable for four days contained 0.62 g. of strontium acetate and 0.376 g. of sulfuric acid per liter.

SUMMARY

Colloidal elements, sulfides, chlorides, and sulfates have been prepared in glacial acetic acid.

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A CALCULATION OF THE CHANGE IN FREE ENERGY IN THE FORMATION OF TRICALCIUM SILICATE FROM CALCIUM OXIDE AND β-DICALCIUM SILICATE

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INTRODUCTION

The studies of Thorvaldson and his coworkers (6) and of von Gronow and Schwiete (3) permit a preliminary calculation of the change in free energy occurring when calcium oxide and β-dicalcium silicate combine to form tricalcium silicate. This reaction is well established by the work of Rankin and Wright (10) and of Bogue and his staff (1).

The change of free energy of reaction may be found by substituting the proper values in the equation

$$\Delta F = \Delta H - T\Delta S$$

The values of ΔH were obtained by means of the equation

$$\Delta H_T = \Delta H_{293^\circ} + \int_{293^\circ}^{T} \Delta Cp dT$$

The data used were taken from the work of Thorvaldson (6) and von Gronow and Schwiete (3). The integrations were carried out graphically except that for the temperature interval from 20° to 300°C., which was obtained by subtraction. The values of ΔS were found by means of the equation

$$\Delta S = 2.303 \int_{293^\circ}^{T} \Delta Cp d \log T$$

The graphical method of Lewis and Randall (8) was utilized. The instantaneous specific heats were also determined graphically from the values for the average specific heats given by von Gronow and Schwiete.

RESULTS

The results of the calculations are given in table 1 and figure 1. The values for the change in free energy are expressed in tenths of kilocalories, as it is felt that the accuracy of the calculations is probably not much better than this. The difference between 20°- and 15°-calories as a basis is also smaller than the estimated accuracy of the results. It is evident that the calculated change of free energy for the reaction is small and becomes negative at about 900°C.

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TABLE 1

TEMPERATURE IN	C_p CaO	C_p $(CaO)_2(SiO_2)$	C_p $(CaO)_3(SiO_2)$	ΔH	$-T\Delta S$	ΔF
	20°-cal. per mole per °C.			In kilocalories (20°C.)		
°C.						
20				+0.470	0	+0.5
300	11.71	γ38.71	49.25			
500	12.12	γ41.57	56.25			
675	12.37	γ44.63*	58.00			
675	12.37	β46.77*	58.00			
700	12.37	β46.77	58.16	+0.602	−0.396	+0.2
900	12.50	β46.77	59.33	+0.517	−0.521	0.0
1100	12.72	β48.90	60.61	+0.357	−0.575	−0.2
1300	12.76	β48.90	61.46	+0.252	−0.601	−0.4
1400	12.76		61.76	+0.252*	−0.670*	−0.4*

* Extrapolated value.

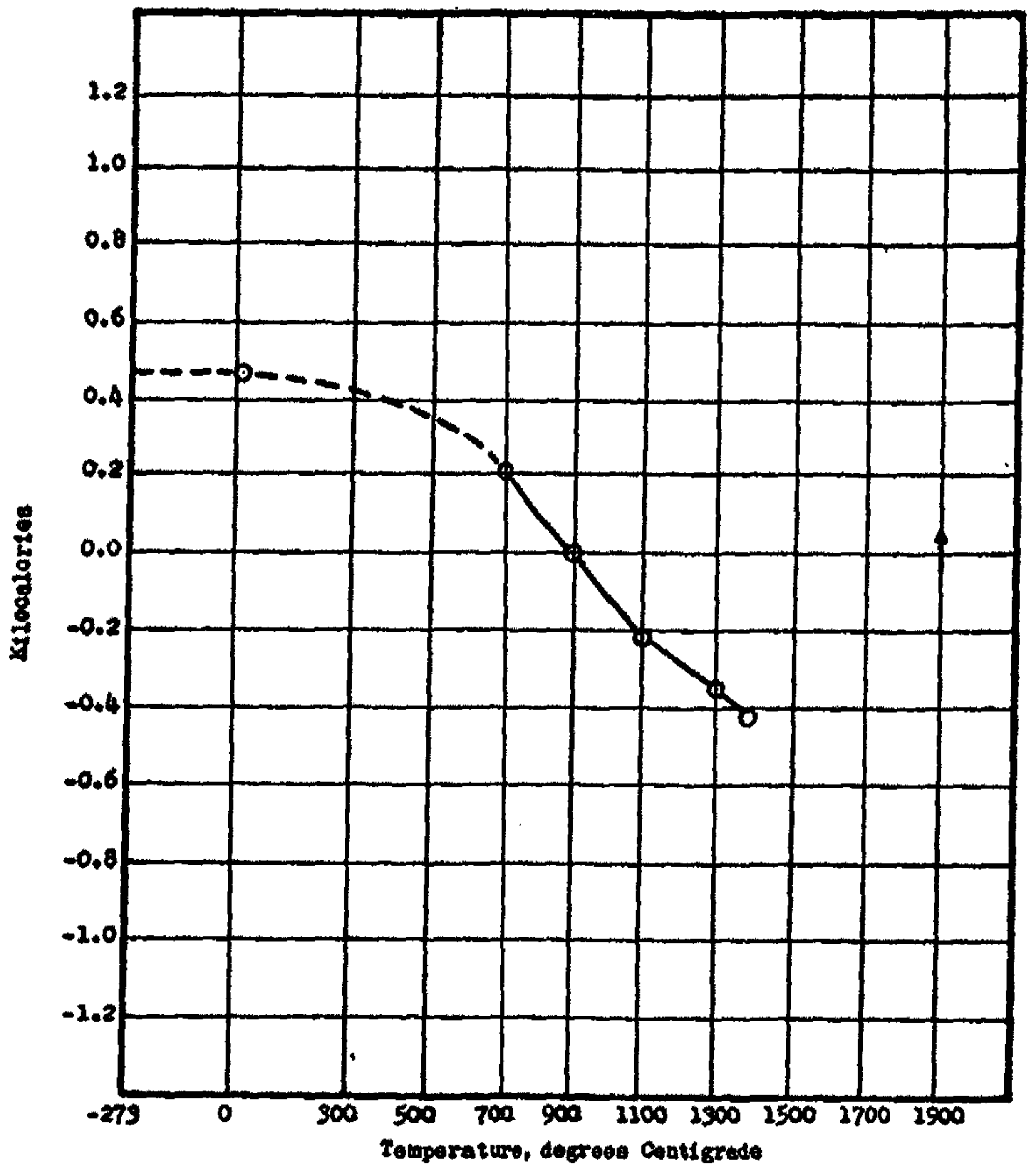

FIG. 1. The calculated change of free energy for the formation of tricalcium silicate from calcium oxide and β-dicalcium silicate.

DISCUSSION

Since the data on the average specific heats of dicalcium silicate and tricalcium silicate below 20–300°C. have not yet been reported, it was necessary to assume values for them in order to carry out the calculation. It was finally decided to assume that between 0°K. and 293°K. (20°C.) the instantaneous molal heat of tricalcium silicate was equal to the sum of the instantaneous molal heats of calcium oxide and β-dicalcium silicate, and that they all equaled zero at absolute zero. The assumption leads to the further assumptions that

$$\Delta H_{0^\circ\mathrm{K.}} = \Delta H_{20^\circ\mathrm{C.}}$$

$$\Delta S_{0^\circ\mathrm{K.}} = \Delta S_{20^\circ\mathrm{C.}} = 0$$

Although the assumption of the identity of these values was somewhat arbitrary, observations have been published (5, 9) that seem to give some support to the results of the calculations. However, these results are subject to revision as more extensive data appear, especially for specific heats from near absolute zero to ordinary temperatures, and also for certain high temperatures.

According to these calculations, crystalline tricalcium silicate has a tendency to form from calcium oxide and β-dicalcium silicate crystals above about 900°C., but below that temperature tends to decompose into calcium oxide and β-dicalcium silicate. This is indicated by the change of sign of the change of free energy of the reaction from minus to plus at 900°C., and is a qualitative check of the experimental results reported by Carlson (2) and Lea and Parker (7), namely, that tricalcium silicate decomposes at 1000–1300°C. These authors, however, give the probable temperature of decomposition as about 1175–1250°C. On the other hand, Nagai and Kosacki (9) report that tricalcium silicate may be formed to some extent at 1000–1300°C. Jander and Hoffmann (5) also give data supporting this observation, although they point out that other observations seem to conflict with it. The point is still under discussion.

Rankin and Wright (10) state that tricalcium silicate decomposes at 1900 ± 20°C. into calcium oxide and α-dicalcium silicate, as shown by experiment. It appears then that crystalline tricalcium silicate is stable under ordinary conditions only between about 1100 ± 200°C. and 1900°C., and decomposes at each limiting temperature into the same two chemical compounds, although the dicalcium silicate may be in different crystalline states, alpha at the higher and beta at the lower limiting temperature. Lea and Parker (7) have already pointed out that this is unusual. We may write

$$\left.\mathrm{CaO(c)} + (\mathrm{CaO})_2(\mathrm{SiO}_2)\,(\mathrm{c}) \rightarrow (\mathrm{CaO})_3(\mathrm{SiO}_2)(\mathrm{c});\ \Delta F\right] \begin{array}{l} 1900^\circ\mathrm{C.} \\ = \text{negative} \\ 1100^\circ\mathrm{C.}\pm \end{array}$$

I am indebted to Prof. T. F. Young of the Department of Chemistry of the University of Chicago for several helpful suggestions.

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STUDIES ON COPRECIPITATION AND AGING. XI

Adsorption of Ammonio Copper Ion on and Coprecipitation with Hydrous Ferric Oxide. Aging of the Precipitate

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Various studies have been published on the coprecipitation of copper and other ions with hydrous ferric oxide, when the latter is precipitated with an excess of ammonia. Toporescu (12) studied the adsorption (actually coprecipitation) of copper from ammoniacal medium, but he did not investigate the effect of a large number of variables upon the coprecipitation. Geloso and Levy (4) added ferric chloride to a mixture of ammonium and copper sulfates (or ammonium chloride) in more or less concentrated ammonia at room temperature and analyzed after three hours of standing. They found relatively large amounts of copper coprecipitated at small ammonia concentrations, the amount decreasing with increasing ammonia concentration. A similar effect was found in the present study, and is attributed by us not to an adsorption but to a chemical precipitation of the copper at very low ammonia concentrations. With further increase of the ammonia concentration the above authors found that the amount of coprecipitated copper decreased only slightly. They obtained inconclusive evidence that in the adsorption of the metal ions no ammonia was adsorbed, indicating that the ions are adsorbed or coprecipitated as aquo ions and not as ammonio ions. Levy (9) continued the studies at various temperatures and concentrations, confirming the fact that no ammonia was adsorbed, and concluding that the effect of the ammonia concentration upon the adsorption is explained mainly by its effect upon the stability of the complex cations and partly by its effect upon the pH of the solution. In a discussion of the coprecipitation of calcium with hydrous ferric oxide, Charriou (3) found a maximum adsorption at a certain ammonia concentration. His explanation of this fact has been found unwarranted by Kolthoff and Stenger (7), who noticed a similar relation between the adsorption of lime on silica gel and the ammonia concentration, but who gave a different interpretation. Hamence

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[1] From the experimental work intended to constitute part of the doctor's thesis of the late Benjamin Moskovitz, who died on October 17, 1935.

(5) studied the coprecipitation of small amounts of copper with hydrous ferric oxide at room temperature. At constant ammonia concentration the adsorption followed the Freundlich adsorption isotherm: $x = ac^{1/n}$, n being 1.7, in agreement with the value found by Toporescu (13). The same amount of copper was found in the filtrate when filtration was made immediately or three hours after the precipitation. A similar result was obtained in the present work with larger amounts of copper. Ammonium salts were found to decrease the coprecipitation materially, a fact well known for a long time to analytical chemists (1, 2, 6). From the analytical viewpoint it is also of interest to mention that Lundell and Knowles (11) precipitate hot and boil 1 to 2 minutes after precipitation. Excess of ammonia and ammonium chloride were found to be favorable in a separation of iron and aluminum from copper and zinc, but less satisfactory from manganese, nickel and cobalt, whereas the precipitation of aluminum was found to be incomplete.

From the above condensed review it is evident that most data obtained are of direct analytical interest. However, from a physicochemical viewpoint no systematic study has been made of the various factors which affect aging and coprecipitation, and no distinction has been made between adsorption and coprecipitation. The present study, and those to be communicated in subsequent papers, deal with these problems and reveal new and unexpected results when hydrous ferric oxide is aged in the presence of various divalent cations in ammoniacal medium.

MATERIALS USED

Ferric chloride, $FeCl_3 \cdot 6H_2O$. A C. P. product was used, which did not contain foreign constituents or basic ferric chloride. The iron and chloride contents were determined gravimetrically and volumetrically, a stoichiometric relation within 0.1 per cent between the iron and chloride being found. In the earlier part of the work a standard solution was made up every fourteen days; later it appeared that it made no difference whether an older solution was used.

Copper chloride and copper sulfate. C. P. products were recrystallized twice and dried at the proper humidity in hygrostats.

Copper bromate. A solution of this salt was prepared by shaking precipitated hydrous copper oxide with a solution of bromic acid. The latter was prepared from a suspension of barium bromate in slightly less than the equivalent amount of sulfuric acid.

Ammonia. Concentrated ammonia was distilled over barium hydroxide. The carbonate-free distillate was stored in large paraffined containers protected from the carbon dioxide of the air.

ANALYTICAL PROCEDURES

Copper was determined iodometrically. Other methods used were standard procedures, the accuracy of which was tested by appropriate blanks.

EXPERIMENTS AT ROOM TEMPERATURE

Coprecipitation

Procedure a: The entire amount of ammonia given in table 1 was added quickly with constant stirring to a mixture of 25 ml. of 0.1 *M* ferric chloride and 25 ml. of 0.1 *M* copper chloride, and the mixture made up with distilled water to a volume of 100 ml. at 25°C. The suspension was shaken thoroughly and filtered after the time indicated, and the filtrate was analyzed for copper. In these experiments the amount of ammonium chloride formed as a result of the precipitation of iron and copper corresponded to a concentration of 0.115 molar. The excess of ammonia indicated in the table was calculated by subtracting from the amount added the amount necessary to precipitate the iron and copper and that required to keep the copper in solution as complex ammonio ion. In the latter case it was assumed that 1 Cu combined with 4 NH_3 to give $Cu(NH_3)_4^{++}$,

TABLE 1

Coprecipitation of copper with hydrous ferric oxide at 25°C.

Final total concentration of copper 0.025 molar

EXCESS OF AMMONIA	TIME OF STANDING BEFORE FILTRATION	COPPER REMOVED BY 1 G. OF Fe_2O_3 (METHOD A)	COPPER REMOVED FROM SOLUTION		
			Method a	Method b	Method c
molar		*millimoles*	*per cent*	*per cent*	*per cent*
0.165	9 minutes	3.38	27.3		
0.165	13 minutes	3.34	27.0	26.2	29
0.165	20 hours	3.01	24.2		
0.165	69 hours	2.86	23.0		
0.335	6 minutes	2.39	19.3		
0.335	9 minutes	2.34	18.8	17.5	19.1
0.335	20 hours	1.97	15.9		
0.335	70 hours	1.90	15.4		
0.676	6 minutes	1.53	12.4		
0.676	9 minutes	1.45	12.0	10.9	12.2
0.676	20 hours	1.25	10.0		
0.676	70 hours	1.17	9.5		
1.696	9 minutes	0.95	7.6	5.0	5.2
1.696	20 hours	0.52	4.2		
1.696	69 hours	0.52	4.2		
1.696	70 hours	0.57	4.5		

although the actual composition of the ion varies somewhat with the concentration of ammonia in solution.

Procedure b: 25 ml. of 0.1 *M* ferric chloride was added to a mixture of 25 ml. of 0.1 *M* copper chloride in an excess of ammonia, and the suspension made up to a volume of 100 ml. The excess of ammonia indicated in table 1 was calculated as described under procedure a.

Procedure c: A mixture of 25 ml. of 0.1 *M* ferric chloride and 25 ml. of 0.1 *M* copper chloride was added to an excess of ammonia and the suspension made up to a volume of 100 ml. The excess of ammonia was calculated as above.

TABLE 2

Coprecipitation of copper at 25°C.

25 ml. of 0.1 *M* $FeCl_3$ + 25 ml. of 0.0364 *M* $CuSO_4$ + salt (if added) + ammonia. Procedure a; filtered after 2 to 2.5 hours. Concentration of salt added refers to volume of 100 ml.

EXCESS OF AMMONIA	CONCENTRATION OF AMMONIUM CHLORIDE	CONCENTRATION OF POTASSIUM CHLORIDE	Cu COPRECIPITATED PER 1 G. OF Fe_2O_3	Cu REMOVED
molar	*molar*	*molar*	*millimoles*	*per cent*
0.182			2.20	48
0.363			1.50	32
0.727			0.95	21
1.454			0.53	11.7
2.18			0.27	6.0
0.182	0.1		1.55	33.4
0.182	0.5		0.58	12.6
0.182	1		0.31	6.7
0.182	2		0.10	1.9
0.182		0.1	2.15	47
0.182		0.5	1.83	40
0.182		1	1.54	34
0.182		2	1.17	26

Coprecipitation experiments were also carried out with copper bromate instead of copper chloride, and the amounts of copper and bromate were determined in the filtrate (procedure a). The total concentration of copper bromate was 0.0091 *M*, that of ammonia 0.182 *M* or greater. At this or larger concentrations of ammonia all the bromate was found in the filtrate, hence there was no coprecipitation of bromate. The percentage of copper coprecipitated from this dilute solution was 49.0 per cent; if filtered after 4 hours it was 45 per cent, and after 25 hours 41 per cent. Similar experiments were carried out with copper sulfate instead of bromate and about the same amounts of copper were found coprecipitated (53 per cent after 10 to 20 minutes; 50 per cent after 3 hours; 45 per cent after 20 to 26 hours).

It should be mentioned that in all experiments described above (including table 1) and in those reported below it was immaterial whether the suspensions were shaken during the aging or allowed to stand quietly after thorough mixing.

In table 2, results are reported to the effect of the concentration of ammonia upon the coprecipitation of copper from dilute solution (procedure a; total concentration of copper 0.0091 *M*). Again it was found that the coprecipitation of copper decreases with increasing ammonia concentration. Moreover the effect of different concentrations of ammonium and potassium chloride was investigated. Other alkali salts, such as potassium nitrate and sodium chloride, had an effect similar to potassium chloride and the results are not reported.

TABLE 3

Adsorption of copper on hydrous ferric oxide (25°C.)

EXCESS OF AMMONIA	TIME OF STANDING OF ENTIRE MIXTURE BEFORE FILTRATION	Cu ADSORBED PER 1 G. OF Fe_2O_3 (a)	Cu REMOVED FROM SOLUTION		
			Method a	Method b	Method c
molar		*millimoles*	*per cent*	*per cent*	*per cent*
0.165	9 minutes	2.49	20.0	18.8–20.6	25.5
0.165	21 hours	2.65	21.3		
0.165	69 hours			21.3	
0.335	9 minutes	1.74	14.0	14.0	18.5
0.335	21 hours	1.74	14.0		
0.335	69 hours			14.4	
0.676	9 minutes	1.16	9.3		
0.676	21 hours	1.07	8.6	9.7	
1.676	9 minutes	0.52	4.2	5.2	5.4

Adsorption and coprecipitation of copper

(*a*) An excess of ammonia was added to 25 ml. of 0.1 *M* ferric chloride, then 25 ml. of 0.1 *M* copper chloride was added and the suspension was made up with water to a volume of 100 ml., mixed thoroughly, and filtered after standing for the indicated periods of time (table 3). Again it was found immaterial whether the suspension was allowed to stand or was shaken continuously.

(*b*) Ammonia was added to a mixture of 25 ml. of 0.1 *M* ferric chloride and 25 ml. of 0.1 *M* copper chloride until complete precipitation of both metal ions. Then an excess of ammonia was added and the experiment continued as above.

(*c*) 25 ml. of 0.1 *M* ferric chloride was added to a mixture of 25 ml. of 0.1 *M* copper chloride and 1.72 ml. of 4.362 *M* ammonia (equivalent to amount of iron). Then an excess of ammonia was added, etc., as above. The results are given in table 3.

Adsorption isotherm

Twenty-five milliliters of 0.1 *M* ferric chloride was precipitated at room temperature with ammonia, the excess of the latter after filling up to 100 ml. being 1 molar, then a measured volume of copper sulfate was added and the suspension made up to 100 ml.; it was allowed to stand for 40 minutes, filtered, and the filtrate analyzed for copper. The results are given in table 4. The figures given in the last column were calculated from the equation of the Freundlich adsorption isotherm

$$\frac{x}{m} = ac^{1/n}$$

in which x/m is the number of millimoles of copper adsorbed per gram of Fe_2O_3, whereas a and $1/n$ were found to be equal to 5.63 and 0.46, respectively. At the two highest copper concentrations the calculated amounts adsorbed were found to be larger than the experimental amounts. This difference is explained by the fact that the relatively large amounts of ammonium sulfate formed by the interaction of copper sulfate and ammonia in these cases repress the adsorption.

TABLE 4

Adsorption isotherm of copper in 1 N ammonia (25°C.)

INITIAL CONCENTRATION OF COPPER SULFATE	FINAL CONCENTRATION OF COPPER SULFATE	Cu ADSORBED	MILLIMOLES OF Cu ADSORBED PER 1 G. OF Fe_2O_3	
			Found	Calculated
molar	*molar*	*per cent*		
0.005	0.004	19.7	0.50	0.044
0.010	0.00877	12.5	0.63	0.63
0.020	0.0182	9.0	0.91	0.89
0.035	0.0327	6.6	1.17	1.17
0.050	0.0473	5.4	1.36	1.38
0.070	0.0669	4.2	1.48	1.62
0.100	0.0961	3.5	1.74	1.93

In a few instances the coprecipitation of copper was determined under the above conditions. With an initial copper sulfate concentration of 0.01 *M*, 16.5 per cent of the copper was found coprecipitated (adsorbed 12.5 per cent); with an initial concentration of 0.02 *M*, 10.0 per cent Cu was coprecipitated (adsorbed 9.0 per cent).

Aging experiments at room temperature

Fresh precipitates of hydrous ferric oxide were aged under various conditions in the absence and sometimes in the presence of copper. With the exception of the first two experiments in table 5, in which the aging and the adsorption medium (without copper) were identical, the fresh precipitate of hydrous oxide was filtered after the precipitation, washed with water until the washings were chloride free (after about three hours continuous washing), and transferred into the aging medium given in the first column of table 5. When the aging medium was alkaline the suspension was kept in a paraffined bottle. After the indicated periods of aging the precipitate was collected, filtered, and the adsorption of copper determined in a medium that was 1 M in ammonia and 0.115 M in ammonium chloride and 0.01 M in copper sulfate. In some cases the aging occurred in the presence of the copper. The results are reported in table 5.

TABLE 5

Adsorption of copper after aging of fresh hydrous ferric oxide in the absence and presence of copper (25°C.)

COMPOSITION OF AGING MEDIUM	TIME OF AGING	Cu ADSORBED	
		Fe_2O_3 aged in absence of copper	Fe_2O_3 aged in presence of copper
		per cent	*per cent*
1 N NH_3 + 0.12 N NH_4Cl	0	10.4	(10.4)
	26 hours	9.4	11.0
	31 days	4.0	
1 N NH_3	26 hours	9.4	
	13 days	4.0	11.2
	31 days	2.7	11.9
	60 days	1.4	
1.66 N NH_3	13 days	3.2	
Conductivity water	13 days	7.8	
	31 days	7.5	
0.01 N HCl	2 days	8.2	
	13 days	8.2	
0.01 N H_2SO_4	5 days	7.7	9.0
	31 days	7.4	9.2

EXPERIMENTS AT 98°C.

Adsorption of copper on precipitate formed at 98°C.

Twenty-five ml. of 0.1 M ferric chloride was heated for five minutes in a water bath at 98–99°C. and enough ammonia was added to precipitate the iron at this temperature. After aging for one minute, the suspension was cooled and sufficient ammonia added to make the solution 1 N to ammonia after making up to 100 ml. After addition of ammonia a measured volume of copper sulfate solution was added and the volume made up to 100 ml. in a volumetric flask. The suspension was thoroughly shaken, allowed to stand for 50 minutes, and filtered. The copper was determined iodometrically in an aliquot part of the filtrate. The results are reported in table 6. For comparison, the percentages of copper adsorbed on a precipitate formed at room temperature are given in the last column.

The hydrous ferric oxide precipitated at 98°C. already shows a crystalline structure, whereas the precipitate formed at room temperature is amorphous. Therefore, the surface of the former is smaller than that of the latter. The precipitate formed at 98°C. adsorbs three and one-half to four times less copper than that formed at room temperature.

TABLE 6

Adsorption of copper on hydrous ferric oxide formed at 98°C. and at room temperature

INITIAL $CuSO_4$ CONCENTRATION	FINAL $CuSO_4$ CONCENTRATION	Cu ADSORBED PER 1 G. OF Fe_2O_3	Cu ADSORBED	
			Pptd. at 98°C.	Pptd. at room temperature
molar	*molar*	*millimoles*	*per cent*	*per cent*
0.005	0.00472	0.147	5.9	19.7
0.010	0.00964	0.18	3.6	12.5
0.020	0.01946	0.26	2.6	9.0
0.035	0.03430	0.32	1.8	6.6
0.050	0.04922	0.33	1.3	5.4
0.070	0.06912	0.38	1.1	4.2

Coprecipitation of copper with precipitate formed at 98°C.

Whereas the amount of copper coprecipitated with a precipitate formed at room temperature was found to be only slightly greater than the amount of copper adsorbed after its formation, pronounced differences were observed between the amounts adsorbed and coprecipitated with a precipitate formed at 98°C. A mixture of 25 ml. of 0.1 *M* ferric chloride and a measured volume of copper sulfate was heated to 98–99°C. and sufficient ammonia added to make the concentration of the latter 0.5 *N*. After the time of heating indicated in table 7 the suspension was cooled to room temperature and more ammonia added so that the final concentration of the latter was 1 *N* after making up to 100 ml. After shaking and standing the copper was determined in the filtrate. The results are given in table 7. For comparison the amounts of copper adsorbed by a precipitate formed at 98–99°C. and those coprecipitated with the hydrous oxide formed at room temperature are reported in the last two columns.

The amounts of copper coprecipitated with the hydrous oxide at 98°C. are about four times greater than the amounts adsorbed after the formation. Qualitatively, such a difference was to be expected as the precipitate, although imperfect, separates in a crystalline form; therefore adsorption occurs on the internal surface during the formation and also on the external surface after the formation. From the results reported in table 7 and those in tables 1 and 2 it appears that the amount of coprecipitated copper at 98°C. is of the same order of magnitude as that at room temperature.

TABLE 7

Coprecipitation of copper with precipitate formed at 98-99°C.

INITIAL $CuSO_4$ CONCENTRATION (IN 100 ML.)	TIME OF HEATING OF SUSPENSION AT 98°C.	COPPER COPRECIPITATED	COPPER ADSORBED	COPPER COPRECIPITATED BY PRECIPITATE FORMED AT 25°C.
molar	*minutes*	*per cent*	*per cen*	*per cent*
0.01	1	17.9; 16.4	3.6	16.5
0.01	30	20.0		
0.01	60	20.6		
0.025	1	8.8; 7.7	2.3	6.8
0.025	30	9.8		

TABLE 8

Aging at 98°C. of hydrous oxide formed at room temperature

TIME OF AGING AT 98°C.	EXCESS OF AMMONIA DURING AGING	CONCENTRATION OF NH_4Cl DURING AGING	Cu ADSORBED	Cu ADSORBED BY UNAGED PRECIPITATE
minutes		*N*	*per cent*	*per cent*
6*	0	0	17.9	23.3
60*	0	0	15.1	23.5
6	0	0.1	11.0	12.5
60	0	0.12	9.3; 10.3	12.5
60	1		7.9	12.5
70	1	0.1	3.6	12.5

* Aged in conductivity water; no ammonium chloride present in adsorption experiment.

Aging of the hydrous oxide at 98°C. in the absence of copper. Precipitate formed at room temperature

The precipitate was aged under various conditions and for various periods of time at 98°C. in pressure bottles in order to prevent the escape of ammonia. After heating, the suspension was cooled to room temperature, transferred to a volumetric flask of 100 ml., and enough ammonia, ammonium chloride, and copper sulfate solution were added to make the concentrations 1 *M*, 0.1 *M*, and 0.01 *M*, respectively, after making up to volume. The adsorption of copper was then determined in the usual way. The results are found in table 8.

From the results it is seen that there is only a slight aging after heating for 1 hour in conductivity water or in 0.1 *N* ammonium chloride. A pronounced aging occurs after 1 hour of heating in a mixture 1 *N* in ammonia and 0.1 *N* in ammonium chloride, the adsorptive properties of the precipitate approaching that of the hydrous oxide formed at 98°C. It is peculiar that the aging as measured by the copper adsorption was found to be more pronounced in a mixture 1 *N* in ammonia and 0.1 *N* in ammonium chloride than in 1 *N* ammonia alone. A precipitate formed at 98°C. and aged at this temperature for 1 hour in 1 *N* ammonia and 0.1 *N* ammonium chloride showed relatively little change, the fresh precipitate adsorbing 3.6 per cent copper, the 1-hour old precipitate 2.6 per cent copper.

Aging of the hydrous oxide at 98°C. in the presence of copper. Precipitate formed at room temperature

Hydrous ferric oxide precipitated at room temperature was washed chloride-free and aged for 1 hour at 99°C. in 0.1 *N* ammonium chloride. Under the final conditions, given before table 8, the precipitate adsorbed from 9.3 to 10.3 per cent copper at room temperature. The experiment was repeated, but after the hour of aging the precipitate was heated at 98°C. for another hour in a pressure bottle in a medium 1 *N* in ammonia, 0.1 *N* in ammonium chloride, and 0.01 *M* in copper sulfate. At the end of the experiment the suspension was cooled to room temperature, etc. The amount of copper removed corresponded to 13.8 per cent. Hence upon the further heating of the precipitate in the presence of dissolved copper more of the latter was taken up by the precipitate. This entrance of the copper into the aging precipitate was more striking with precipitates formed at 98°C. The precipitate (98°C.) immediately after its formation adsorbed 3.6 per cent copper (from 0.01 *M* solution; conditions as in table 8) at room temperature; after aging for 1 hour at 98°C. in 1 *N* ammonia and 0.1 *N* ammonium chloride *without copper it adsorbed 2.6 per cent copper; aged with copper it adsorbed 12.4 per cent copper.* The precipitate (98°C.) was aged for 1 hour in water at 98°C., and then heated for 4 and 60 minutes respectively in 1 *N* ammonia, 0.1 *N* ammonium chloride, and 0.01 *M* copper sulfate. The percentages of copper removed corresponded to 4.4 and 5.4 per cent, respectively. All these experiments indicate that copper enters the precipitate upon aging of the hydrous oxide at 98°C. in ammoniacal medium in the presence of copper.

Aging at 98°C. of the precipitate formed in the presence of copper in ammoniacal medium

Hydrous ferric oxide was precipitated in the presence of copper (0.01 *M*; 100 ml.) at room temperature and heated at 98°C. in ammoniacal medium

(1 *N* in ammonia and 0.1 *N* in ammonium chloride) in pressure bottles. The suspension was cooled afterwards and the percentage of copper removed determined at room temperature. The results are given in table 9. Experiments have also been carried out in which the copper was coprecipitated with the hydrous oxide at 98°C. and the suspension aged at this temperature in ammoniacal medium in pressure bottles. Again it was found that the amount of coprecipitated copper increased with increasing time of heating. A few figures are given in table 7, but more data could be added.

TABLE 9

Hydrous ferric oxide formed in the presence of copper at 25°C. and aged at 98°C.

Time of heating in minutes	10	30	60	70
Cu removed in per cent	11.7	12.7	13.7	14.2

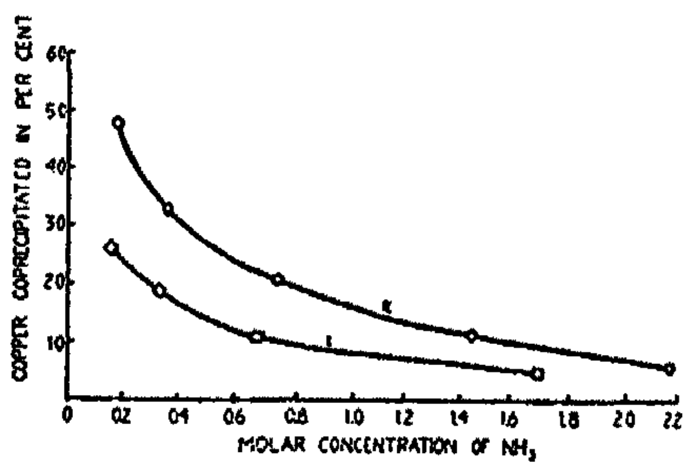


FIG. 1

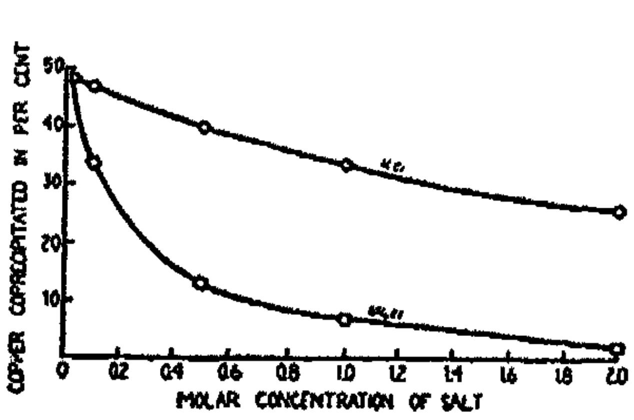


FIG. 2

FIG. 1. Effect of concentration of ammonia upon coprecipitation of copper. I, total concentration of copper, 0.025 *M*; II, total concentration of copper, 0.0091 *M*.

FIG. 2. Effect of ammonium chloride and potassium chloride upon coprecipitation of copper. Concentration of NH_3 = 0.182 *M*.

DISCUSSION

1. From tables 1, 2, and 3, as well as from figure 1, it is seen that the adsorption or coprecipitation of copper on or with hydrous ferric oxide decreases with increasing concentration of ammonia. The depressing effect of ammonium chloride upon the adsorption of copper (figure 2) is much greater than that of potassium chloride (figures 1 and 2) or other alkali salts. Primarily the adsorption of copper or other cations on hydrous ferric oxide is attributed to an adsorption of hydroxyl ions, the cations functioning as "counter ions." In correspondence with the Hardy-Schultze rule it is found that divalent cations are more strongly adsorbed than monovalent cations; hence it was to be expected that potassium would exert only a relatively slight replacing effect upon the ad-

sorption of copper (figure 2). The much greater effect of ammonium salts is explained by their replacing effect upon the adsorption of copper, but in addition by their materially lowering the hydroxyl-ion concentration of the solution. Consequently, the primary adsorption of hydroxyl ions decreases and that of the counter ions as well. Although with increasing concentration of ammonia the hydroxyl-ion concentration of the solution increases, the adsorption of copper decreases, this effect of ammonia being relatively independent of the copper concentration in the solution. This is explained by the fact that the stability of copper ammonio ion increases with increasing ammonia concentration and that the copper is not adsorbed as the ammonio complex (Geloso and Levy (4)). In studies carried out by L. Overholser in this laboratory, which will be reported later, it was shown by chemical analysis that zinc is not adsorbed as ammonio zinc ion from ammoniacal medium and that qualitatively in all respects the adsorption of zinc is comparable to that of copper. Thus it may be concluded that the replacing effect of ammonium upon the adsorption of copper by hydrous ferric oxide increases with increasing stability of the copper ammonio complex.

2. From the results in table 1 it is seen that the coprecipitation of copper at room temperature is practically independent of the method of precipitation of the iron. Almost the same amounts of copper were found in the precipitates, whether the ammonia was added to a mixture of iron and copper salt, or the precipitation was made in the reverse way, or the iron solution was added to the ammoniacal copper solution.

3. In aging experiments in the presence or absence of copper it was found immaterial whether the suspension was allowed to stand quietly or was shaken.

4. In agreement with Hamence (5) it was found that the adsorption of copper from ammoniacal medium is determined quantitatively by the Freundlich adsorption isotherm,

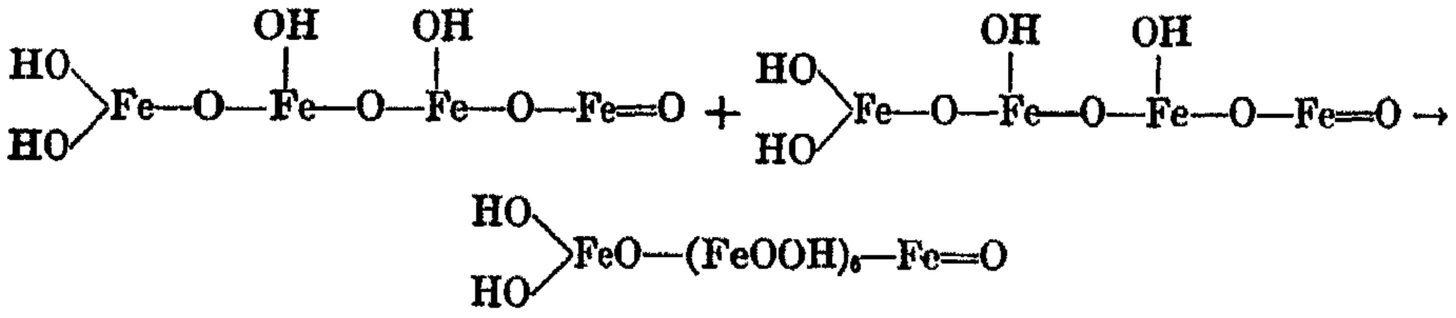
$$\frac{x}{m} = ac^{1/n}$$

a being found equal to 5.63 and $1/n$ to 0.46 ($n = 2.17$) at room temperature.

5. Comparison of the results in tables 1 and 3 reveals that the amount of copper coprecipitated with hydrous ferric oxide at room temperature is only slightly greater than the amount of copper which is adsorbed when the copper is added to the suspension immediately after precipitation. This behavior is in agreement with the coprecipitation rule derived for substances which precipitate in amorphous form (Kolthoff (8)). The fresh amorphous hydrous oxide consists mainly of surface, and the copre-

cipitated copper is mainly present on the surface. The relatively small differences between the results reported in tables 1 and 3 may be attributed to an agglomeration of primary particles of $Fe_2O_3 \cdot xH_2O$. If the copper is present during the precipitation it can be adsorbed on the entire surface (external and internal); if added after the precipitation the internal surface is less easily accessible to the copper. It is of interest to notice that the amount of coprecipitated copper decreases slightly during the earlier stages of aging, whereas the amount adsorbed increases slightly when the copper is left in contact with the precipitate for longer periods of time. After twenty to seventy hours of standing the amount of coprecipitated copper is virtually the same as the amount of adsorbed copper.

6. From the data in tables 1 and 3 one is inclined to infer that the aging of the hydrous oxide at room temperature is negligibly small. It is the most interesting part of this study that we have shown this conclusion to be unwarranted. From the results in table 5 (third column) it is seen that the speed of aging of hydrous ferric oxide depends greatly upon the degree of alkalinity of the solution. A slow but pronounced aging occurs in 1 *N* ammonia (aged in the absence of copper). Although not reported in the table, it was found that the aging occurs much faster in 0.01 *N* sodium hydroxide than in 1 *N* ammonia. Krause (9) and his coworkers, who have carried out extensive investigations on the mechanism of the aging of hydrous ferric oxide, showed that in the earlier stages of the aging a polymerization occurs. First two molecules of the "ortho hydroxide" react to form a polymerization product containing eight atoms of iron;



$$\mathrm{\begin{smallmatrix}HO\\HO\end{smallmatrix}{>}Fe{-}O{-}\overset{OH}{\overset{|}{Fe}}{-}O{-}\overset{OH}{\overset{|}{Fe}}{-}O{-}Fe{=}O + \begin{smallmatrix}HO\\HO\end{smallmatrix}{>}Fe{-}O{-}\overset{OH}{\overset{|}{Fe}}{-}O{-}\overset{OH}{\overset{|}{Fe}}{-}O{-}Fe{=}O \rightarrow \begin{smallmatrix}HO\\HO\end{smallmatrix}{>}FeO{-}(FeOOH)_6{-}Fe{=}O}$$

More molecules of the ortho hydroxide can be added, and finally chain-like conglomerates can be formed containing from forty to fifty atoms of iron; in these conglomerates there is a definite ordering but they are not yet crystalline. Finally a ring closure may occur which will not be discussed here. The speed and even the kind of aging depends upon the composition of the aging medium. We found that hardly any aging, as measured by the adsorption of copper, is noticed in conductivity water or in dilute hydrochloric or sulfuric acid.

The most striking result of this study is that when the fresh precipitate was allowed to age in ammoniacal medium in the presence of copper (last column of table 5) no desorption of copper was found, but actually a slight increase of the amount of copper removed from the solution was found upon standing at room temperature. On aging in 1 *N* ammonia in the absence of copper the adsorption of copper decreased from 10.4 per cent to 2.7 per cent after thirty-one days of aging; when aged in the presence of copper the amount removed from solution increased from 10.4 per cent to 11.9 per cent. One might explain this phenomenon by assuming that the adsorbed copper prevents the aging of the hydrous oxide, and might attribute the slight increase in the adsorption to a slow penetration of the copper to the internal surface. However, there is also a possibility that the amorphous fresh hydrous oxide is subject to a slow crystallization when aged at room temperature, and that the copper is incorporated in the crystals in the form of copper ferrite, or that both inhibited aging and incorporation occur. In order to get an indication as to which of the views was correct, the extractibility of the copper from the precipitates aged in the presence of copper (table 5) was investigated. After the periods of time indicated in table 5 the precipitates were washed with 1 *N* ammonia or a solution 1 *N* in ammonia and 1 *N* in ammonium chloride until the filtrates did not give a reaction with hydrogen sulfide or a xanthate solution. A great number of washings were required to obtain a copper-free filtrate. The residue left on the filter was dissolved and analyzed for copper. It was found that from 5 to 20 per cent of the original amount of copper adsorbed was present after the efficient washing. These results might be attributed to an incorporation of the copper in the aging hydrous oxide, but also to the fact that the copper adsorbed on the internal surface was not removed completely by the washings. Further experiments were made in which the fresh precipitate was aged in the presence of copper in 1 *N* ammonia at room temperature, and after various periods of time ammonium chloride was added. The suspension, 2 *N* in ammonium salt, was then shaken for 1 hour, and the copper determined in the supernatant liquid. With a fresh precipitate all of the copper was extracted by the ammonium chloride; when aged for one day 0.3 per cent of the copper originally adsorbed remained in the precipitate; when aged for fifty days 2 per cent was not extracted. When the precipitate was allowed to age in the presence of copper (0.01 *M*) in a medium 1 *N* in ammonia and 2 *N* in ammonium chloride no copper was found removed from the solution after twenty days, and only 0.4 per cent after fifty days of standing. The effect of the ammonium salt upon the adsorption of copper has been explained above (replacement of copper by ammonium, and decrease of hydroxyl-ion concentration); at the low hydroxyl-ion concentration the formation of copper ferrite is also less probable. Although the above experiments are not entirely conclusive they indicate that an aging of the hydrous oxide occurs at room temperature in the presence of copper and that the latter is incorporated into the aging hydrous oxide. Moreover, evidence is ob-

tained that the polymerization is inhibited by the adsorbed copper. More work is being carried out to substantiate these conclusions. The results in tables 7 and 9 show conclusively that copper is incorporated in a hydrous oxide formed at room temperature or at 98°C. when the precipitate is allowed to age at 98°C. in an ammoniacal copper solution. The increase of the amount of coprecipitated copper with aging is contrary to one of the coprecipitation rules (8), and is attributed to a chemical reaction between the hydrous ferric oxide and the copper in ammoniacal medium with the formation of copper ferrite. Finally it may be mentioned that blanks consisting of ammoniacal copper solutions were heated at 98°C. for various periods of time in the pressure bottles. Although the walls were etched after longer periods of heating no copper was found to be lost from the solution.

SUMMARY

1. The effect of the concentration of ammonia and of ammonium and alkali salts upon the adsorption of copper on and coprecipitation with hydrous ferric oxide at room temperature has been determined. The results agree with those reported in the literature. An interpretation of the various effects has been presented.

2. The coprecipitation of copper with hydrous ferric oxide at room temperature is negligibly small when the concentration of ammonia in the supernatant liquid is at least 1 *N* and that of ammonium chloride 1 to 2 *N*.

3. In agreement with the coprecipitation rule it was found that the coprecipitation of copper with hydrous ferric oxide at room temperature is only slightly greater than the adsorption of copper when the latter is added after the precipitation, which is explained by the amorphous character of the primary precipitate.

4. The adsorption of copper follows the Freundlich adsorption isotherm.

5. Hydrous ferric oxide precipitated at 98°C. adsorbs three and one-half to four times less copper from ammoniacal medium than a precipitate formed at room temperature. The amount of copper coprecipitated at 98°C. is about four times greater than the amount adsorbed at room temperature by a precipitate formed at 98°C. The coprecipitation of copper at 98°C. is of the same order of magnitude as that at room temperature.

6. The speed of aging of hydrous ferric oxide depends greatly upon the alkalinity of the aging medium. The fastest aging at room temperature was found in 0.01 *N* sodium hydroxide, then in 1 *N* ammonia, but hardly any aging was noticed in conductivity water or in dilute hydrochloric or sulfuric acid. *A precipitate formed at room temperature and aged at 98°C.* showed the most pronounced aging in a mixture 1 *N* in ammonia and 0.1 *N* in ammonium chloride, less aging in 1 *N* ammonia, and relatively little aging in conductivity water or in 0.1 *N* ammonium chloride as indicated by

the copper adsorption. A precipitate formed at 98°C. aged very slowly only on heating for 1 hour in a mixture 1 *N* in ammonia and 0.1 *N* in ammonium chloride.

7. When hydrous ferric oxide precipitated at room temperature or at 98°C. is aged at room temperature or at 98°C. in ammoniacal medium in the presence of copper, a slow entrance of the latter into the precipitate occurs. When the hydrous oxide formed at room temperature or at 98°C. in the presence of copper is heated in ammoniacal medium, the amount of coprecipitated copper increases with increasing time of heating. This contradiction of one of the coprecipitation rules is attributed to a slow copper ferrite formation.

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THE INFRA-RED ABSORPTION OF MIXTURES OF WATER AND ORGANIC LIQUIDS

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Previous studies of the infra-red absorption of acetone–water and ethyl alcohol–water mixtures have revealed the presence of certain bands which are not characteristic of either component of the mixtures (9, 10). In the spectra of the acetone–water mixtures intense bands appear near 2.7μ, where absorption is not to be expected in a simple mechanical mixture of these components. In the case of the ethyl alcohol–water mixtures, similar absorption bands are present near 2.8μ. The origin of these bands was attributed to an interaction between the molecules of the components of the liquid mixture, resulting either in the distortion of the water molecules or in an associational bond between the water molecules and the molecules of the other component.

Kinsey and Ellis (7) have measured the infra-red absorption of water in non-polar solvents in the region between 0.9μ and 2.5μ and report that the absorption of small amounts of water in carbon disulfide and carbon tetrachloride is similar to the absorption of water vapor. They are inclined to believe that water in non-polar solvents exists in an unassociated state. Water is only slightly soluble in the solvents used by these authors. It was the purpose of the present investigation to study the absorption spectra of methyl alcohol–water, propyl alcohol–water, and glycerol–water mixtures with the hope of gaining additional information concerning the state in which water exists when dissolved in polar liquids with which it is miscible in all proportions. The changes in specific heat and density which occur in this type of mixture, as well as the large heat of mixing, indicate a type of association which does not occur in mixtures of water and the non-polar solvents used by Ellis.

The absorption of water has been studied by a number of investigators (2, 4, 6). In the spectrum of water vapor absorption maxima have been observed at 2.66μ, 2.78μ, and 6.26μ, while in liquid water intense bands are found at 3μ, 4.70μ, and 6.18μ. The 3μ region of absorption in liquid water is composed of three bands with maxima at 2.78μ, 2.92μ, and 3.10μ. The absorption at 4.70μ has been attributed to the combination of a "hindered rotation" frequency with the frequency giving rise to the 6.18μ band and is characteristic of water in the liquid and solid states. The spectra of methyl alcohol, propyl alcohol, and glycerol have also been studied, and intense bands have been observed at 3.0μ, 3.4μ, and at 7μ (3, 8).

The spectroscopic methods employed in the present work have been described elsewhere (5). A Hilger spectrometer with a fluorite prism was used as a resolving instrument. The organic liquids were dried for several days over anhydrous copper sulfate and were then distilled. The absorption cells used in the study of the 3μ region were 0.01 mm. in thickness. Owing to the extreme viscosity of glycerol it was impossible to reproduce the 0.01 mm. thicknesses of the absorbing layers of this compound very accurately, and, although the results seemed to be in general agreement with the results obtained with mixtures of water and the alcohols, little definite information could be obtained concerning the absorption of glycerol-water mixtures in the 3μ region. In the 4.7μ and 6μ regions, absorbing layers 0.03 mm. in thickness were used satisfactorily in all cases.

In the 3μ region it was found that the addition of small amounts of water produced absorption near 2.8μ. As the intensity of this absorption band increased with increasing water concentration, it was concluded that the 2.8μ band was caused by the water molecules, and curves showing the absorption of the water were plotted. As no changes in characteristic alcohol bands in other spectral regions were observed, it was assumed that the absorption coefficient of the alcohol was unchanged by the presence of the water, and, in determining the absorption produced by the water molecules, the following method was used: If I is the intensity of the radiation transmitted by an alcohol cell and I_0 is the intensity of the incident radiation, then one may determine the absorption per alcohol molecule from the usual type of exponential relation:

$$I = I_0e^{-n\alpha} \tag{1}$$

where n is the number of alcohol molecules per unit area of the absorbing layer and α is the absorption coefficient. After determining α in this way one may determine β, the corresponding coefficient for the water molecules in solution, from the relation for a mixture:

$$I' = I_0e^{-(n_a\alpha + n_w\beta)} \tag{2}$$

where n_a and n_w are the numbers of alcohol molecules per unit area and water molecules per unit area, respectively. If it be assumed that α is unchanged by the presence of the water molecules, the value of β may be determined directly, the proper values of n_a and n_w having been determined from the densities of the mixtures.

After the values of the absorption coefficients had been calculated, the transmission curve for water itself could be plotted for the various mix-

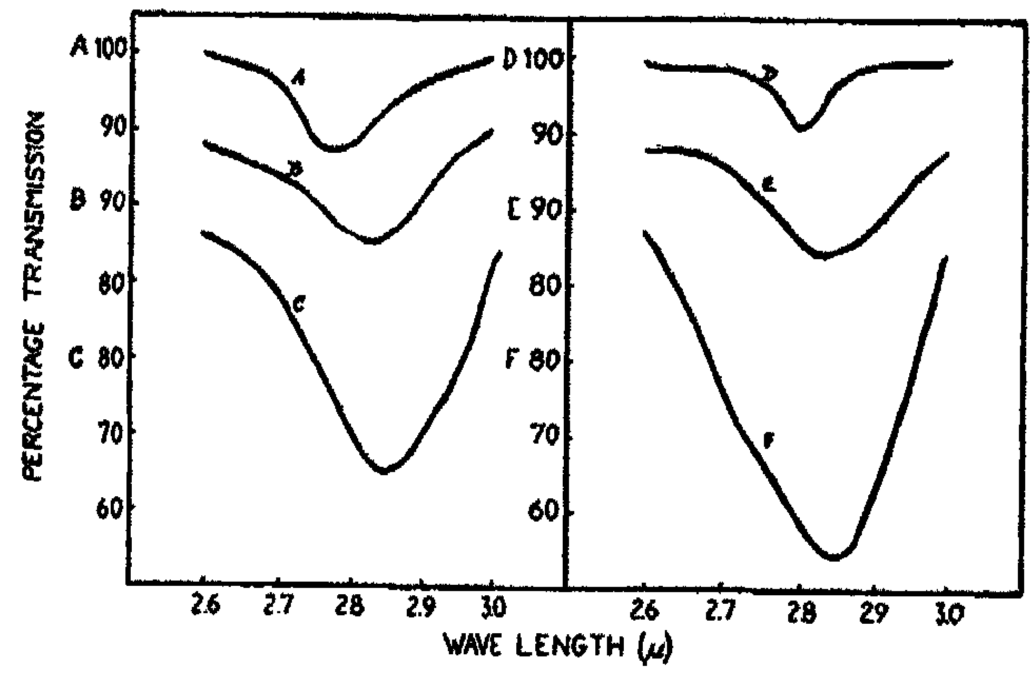

FIG. 1. Percentage transmission of water in organic solvents. A, 5 per cent water in methyl alcohol; B, 10 per cent water in methyl alcohol; C, 20 per cent water in methyl alcohol; D, 5 per cent water in propyl alcohol; E, 10 per cent water in propyl alcohol; F, 20 per cent water in propyl alcohol.

TABLE 1

Absorption of water in various organic solvents

A.

PERCENTAGE CONCENTRATION OF WATER	POSITION OF ABSORPTION MAXIMUM	
	Methyl alcohol	Propyl alcohol
	μ	μ
5	2.77	2.79
10	2.81	2.82
20	2.84	2.86
50	2.92	2.93
70	2.98	2.98
100	3.00	3.00

B.

PERCENTAGE CONCENTRATION OF WATER	POSITION OF ABSORPTION MAXIMUM		
	Methyl alcohol	Propyl alcohol	Glycerol
	μ	μ	μ
5	6.11	6.13	6.12
10	6.13	6.15	6.13
20	6.15	6.17	6.14
50	6.17	6.18	6.16
70	6.18	6.18	6.17
100	6.18	6.18	6.18

tures. In figure 1 is shown the transmission of water in methyl and propyl alcohol solutions. The water concentration is indicated. It will be noted that the maxima for dilute solutions come near 2.8μ and that with increasing concentration the absorption becomes more like that of ordinary liquid water, which is found to have a maximum at 3.0μ when studied with the present spectrometer arrangement. In table 1 are given the positions of absorption maxima for various concentrations. Although mixtures of low alcohol content were studied, no changes were observed for the positions of alcohol maxima. The 2.8μ absorption coefficient of the water in the mixtures is somewhat greater than for water vapor or ordinary liquid water.

As the glycerol and the alcohols have no very intense bands near 6μ, the absorption bands produced by the water are clearly discernible without replotting the curves to show the absorption arising from the water component alone. The curves shown in figure 2 represent the percentage transmission of the mixtures. It is evident from the figure that for low water concentrations the absorption maximum appears at 6.10μ, whereas the maximum for water in the liquid state is at 6.18μ and at 6.26μ in water vapor. The exact positions of maxima for different concentrations as computed in the manner mentioned above are given in table 1.

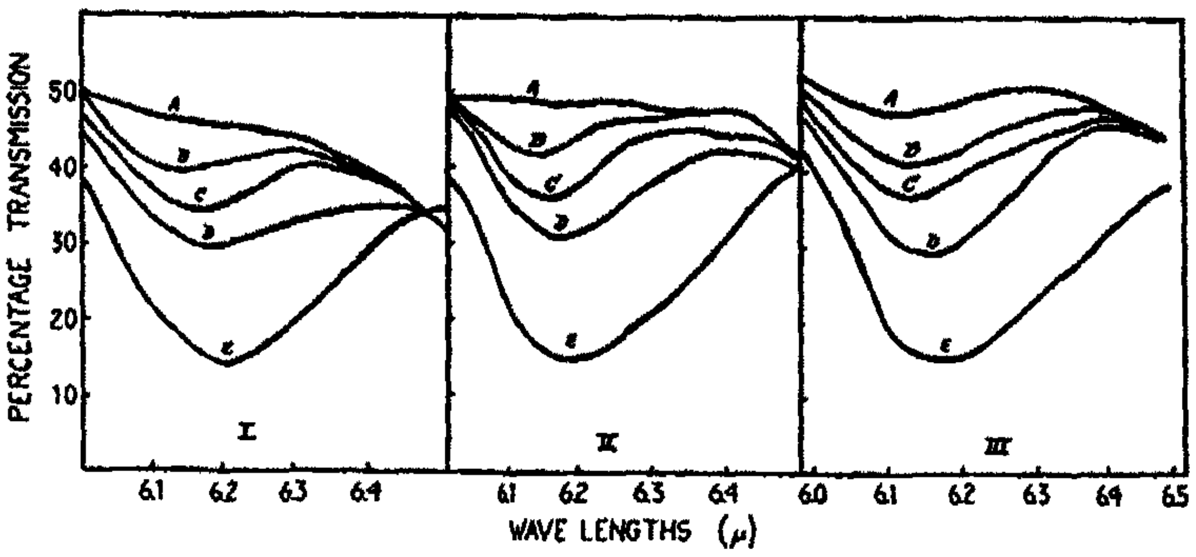

FIG. 2. Transmission of mixtures: I, water and methyl alcohol; II, water-propyl alcohol; and III, water-glycerol. Curve A gives the percentage transmission of the pure solvents. Curves B, C, D, and E give the percentage transmission of mixtures containing 5, 10, 20, and 100 per cent water, respectively.

The associational band characteristic of liquid water is very broad and has its maximum at 4.7μ. As in the case of the mixtures studied previously (9, 10), there is a broad region of absorption with maximum near this point in the spectra of the mixtures under consideration in the present investigation. Although absorption at 4.7μ was present even in the mixtures containing only 5 per cent water and although the intensity of this band increased with increasing water concentration, it is extremely doubtful that all the molecules of the water present were associated in the ordinary way.

In interpreting the results one finds untenable the earlier suggestion of vibration at an associational bond as the origin of the intense absorption near 2.8μ in the spectra of the mixtures, since it is improbable that similar associational bonds would be formed between water and compounds as different as acetone, glycerol, and the alcohols. If associational bonds are formed, it is probably that the absorption bands caused by vibrations at the bonds lie at longer wave lengths than those studied here. It may be suggested that the band at 2.8μ is caused by water existing in an unassociated, vapor-like state in the mixtures, and this would seem quite reasonable since the absorption maxima of water vapor appear at 2.66μ and 2.78μ. However, there are two serious objections to such an explanation: (1) the existence of absorption at 4.7μ where water vapor has no maximum, and (2) the shift of the 6.18μ band of liquid water to 6.10μ instead of toward 6.26μ where the water vapor maximum lies. Thus, it seems doubtful that the water in alcohol and glycerol mixtures exists in an unassociated state as was the case for the non-polar solvents used by Ellis and Kinsey. It is concluded that the intense bands at 2.8μ and the weaker bands at 6.1μ have their origins in water molecules which have been distorted by the solvent molecules and that even in mixtures containing only 5 per cent water a considerable number of these distorted molecules are associated in a manner similar to the association of water molecules in the liquid state, as is evidenced by the existence of the 4.7μ absorption. No evidence of distortion of the alcohol molecules was found in the present work.[1]

The writers wish to express their appreciation to Dr. E. K. Plyler for the use of his laboratory facilities.

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[1] Since the present paper was presented, other evidence has been found which indicates that part of the absorption near 2.9μ may arise from distorted OH groups. However, no other alcohol bands seem to be affected.

COMMUNICATION TO THE EDITOR

THE FORMATION OF BENZENE IN THE RADIOCHEMICAL POLYMERIZATION OF ACETYLENE

In a recent communication Mund and Rosenblum (J. Phys. Chem. **41**, 469 (1937)) reported absorption spectral evidence for the formation of benzene in the radiochemical polymerization of acetylene. The production of benzene appeared to be parallel with the formation of cuprene.

Further measurements, performed manometrically after separation of benzene from acetylene, demonstrated that about 20 per cent of the reacting acetylene yielded benzene. This percentage dropped appreciably during the course of the reaction.

In view of the fact that benzene itself polymerizes (W. Mund and E. Bogaert: Bull. soc. chim. Belg. **34**, 410 (1925)) under the influence of alpha-radiation, the diminishing benzene/cuprene ratio may be due to the succession of polymerizations:

$$3C_2H_2 \rightarrow C_6H_6$$
$$nC_6H_6 \rightarrow (C_6H_6)_n$$

To account for the observed rate of formation of benzene, however, the velocity constant ($k\mu/\lambda$ of Lind) for the benzene polymerization in the presence of acetylene must be assumed to be about twice as great as for the benzene alone. This greater velocity of benzene disappearance may be due to a catalyzing influence on the part of acetylene which, though not inert, is always present in large excess.

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NEW BOOKS

Recent Advances in Physical Chemistry. By S. GLASSTONE. 21 x 13 cm.; viii + 477 pp. London: J. & A. Churchill, Ltd., 1936. Price: 15 s.

Recent Advances in General Chemistry. By S. GLASSTONE. 21 x 13 cm.; ix + 430 pp. London: J. & A. Churchill, Ltd., 1936. Price: 15 s.

Both of these books are to be commended as providing, for the advanced student and for the teacher or worker in other fields of enquiry, comprehensive and well-written introductions to recent progress in the domains of physicochemical science. They may with advantage be read together. The new edition of *Recent Advances in Physical Chemistry* has been well revised, earlier chapters on solubility and acid-base and salt catalysis omitted, and new sections upon the applications of quantum mechanics and the representation of electronic configurations in molecules inserted. Improvements in the treatment of homogeneous gas reactions and of photochemical reactions are welcome, but are capable of extension.

In the second work, Dr. Glasstone has wisely not attempted a critical survey of the latest work upon topics ranging from atomic disintegration, through ortho- and para-hydrogen, deuterium, electron diffraction, solubility, reactions in solution, acid-base and salt catalysis, to a brief excursus upon organic free radicals, confining himself to a lucid presentation of the orthodoxies. The chapter upon statistical methods is particularly to be welcomed, the derivations being based mainly upon Giauque's simpler treatment, and including an excellent exposition of the partition function.

E. J. B. WILLEY.

Reports on Progress in Physics. Vol. 3. 25 x 18 cm.; 394 pp. London: The Physical Society, 1937. Price: 20/-.

The third volume of these excellent reports deals with the following subjects: general physics, fluid motion, the upper atmosphere, atomic physics, the conservation of energy and momentum in elementary processes, sound, the measurement of noise, heat, magnetism, experimental electricity and magnetism (including dielectrics, alloys for permanent magnets, soft magnetic materials and magnetic measurements, and piezo-electricity), electrical methods of counting, superconductivity and the theory of metals, photoelectricity, optics (with eight sections, including theory, instruments, vision, glare and new light sources), x-rays (with nine sections, including production, absorption and scattering, ionization, crystal structures, and radium), and spectroscopy (including atomic spectra, applications to photochemistry and rotation-vibration spectra of lighter hydrocarbons). In each section enough is said of the general background of the subject to make the account intelligible even for those who approach it for the first time, and the bibliographies are very full. It will be seen that many of the subjects dealt with are of particular interest to physical chemists, and the volume may be unreservedly recommended as an excellent and well-balanced survey of certain selected branches of physics of present-day interest. The very commendable feature noticed in previous volumes of avoiding a narrowness of outlook by too much concentration on certain branches of the subject is fully maintained. The paper and printing are excellent, and the volume is strongly bound.

J. R. PARTINGTON.