THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE

SECTION C—CHEMISTRY

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Secretary, W. D. Harkins, University of Chicago, Chicago, Ill.

(Report by W. D. Harkins)

The general opinion expressed by the chemists in attendance at the Boston meeting was that the program gave an extremely interesting and important summary of progress in this science, particularly with reference to a number of topics which are of great interest to other scientists and to the public.

The four principal topics considered were atomic structure, photochemistry and photochemical synthesis, colloids and colloidal behavior, and the ionization of salts in solution. In addition the chemists were invited to attend a symposium arranged by the physics section, upon a subject of extreme importance to chemistry, that of ionization potentials and atomic radiation.

Symposium on Atomic Structure

One of the most interesting subjects presented at the symposium on atomic structure was that of the size of atoms, especially as they exist in solids. Only a few years ago it was believed that the atoms in solids occupy only one fourth to one half the total volume at any instant, but that each atom vibrates with a high frequency in the space between the adjacent atoms available for this purpose. It was supposed that in the compression of the solid the atoms are merely forced closer together, without any distortion of the atoms themselves. About fifteen years ago Professor T. W. Richards of Harvard University began to develop the distinctly novel idea that the atoms occupy most of the space in a solid and that in any considerable decrease of volume the atoms themselves are diminished in size. This gave rise to his celebrated theory of "compressible atoms." In 1921 Professor Richards showed that the dimensions of atoms could be calculated from the compressibilities of the solids in which they exist, provided data are available for a set of compounds related to each other chemically in a sufficiently simple way. For example, he obtained such data for the fluorides, chlorides, bromides and iodides of lithium, sodium, potassium, rubidium and caesium. Using an ingenious extrapolation to zero compressibility he was able to show that the values correspond to a diameter of 2.8 Ångstrom units (ten-millionths of a millimeter) for the chlorine atom in common salt and other similar compounds. The interesting feature of the results is that the diameters of the atoms, especially those of the metals, proved to vary with the nature of the compound in which they are found. Thus the sodium atom is smaller when combined with chlorine (as it is in common salt) for which it has a high affinity, than when it is united to bromine or iodine for which its affinity is less. Professor Richards's most recent work, as described in his paper, has been to devise a new and more directly experimental method for calculating the dimensions of atoms, with the remarkable result that the values obtained are the same, within the limits of error, as those given by the older method. The new method depends upon the idea that the element sodium acts under compression exactly as potassium would act under high pressure. The attractive forces between the atoms is such that the internal pressure in sodium under ordinary conditions is 20,000 atmospheres higher than that in potassium. By using the data on these two elements, he is able to show how the contraction which occurs in the formation of a salt from the elements may be distributed between them. The results throw much light upon the mechanism of chemical combination, the magnitude of the internal pressures involved and many allied phenomena.

It is found that the contraction which occurs in the formation of a salt from the elements involved is of the order of magnitude to be expected from a consideration of the compressibilities and the internal pressures believed to exist in them. The fact that the thus computed order of magnitude of the compressibility of the salt is the same as that of the actual compressibility determined by measurement, seems to show conclusively that the internal pressure is the cause which determines the volumes of liquids and solids.

A closely related topic, that of the changes of volume which occur in the formation of solid salts from the elements which constitute them, and the further volume changes when these salts are dissolved in water, was discussed by Professor Gregory P. Baxter, of Harvard University. It is well known that his results are the most accurate of those obtained in this field, and they have been used as the basis of a number of interesting volume relations developed recently in connection with the development of the Born and Landé theory of atomic structure. Professor Baxter demonstrated that the changes of volume which occur either in ordinary chemical combination or in the process of solution are the result of several factors, the compressibility of the material and the chemical affinity being the principal properties involved. It was found that the volume of salt in a solution is an additive property of the volumes of the ions which constitute it even in concentrated solutions (up to 5 normal) and at all temperatures. This is of importance in connection with the application of the theory of electrolytic dissociation.

An interesting and important paper on the relation between X-rays and atomic structure, and on the application of X-rays in the determination of crystal structure, was presented by Professor William Duane of Harvard, the leading American authority upon this subject. He showed in a simple way the relations exhibited between the emission and absorption of X-rays and the structure of the atoms as interpreted in the light of the quantum theory. Two kinds of X-radiation have been discovered: The general or continuous spectrum, and the characteristic X-ray spectrum. The wave lengths of the latter depend upon the atomic number of the chemical element used as a target in the X-ray tube, while the former contains all wave lengths down to a well-defined minimum, the value of which depends upon the difference in potential (V) applied to the X-ray tube. The relationship supposed to hold in this connection is the quantum relation of Planck as expressed by the equation of Einstein:

$$Ve = h\upsilon = h\frac{c}{\lambda}$$

in which c is the charge on the electron, υ is the frequency of the radiation, λ is its wave length, and h is the quantum constant.

In 1914 Professor Duane tested this quantum law, using the limit of the general radiation, and found that it holds with great exactness, so that this method gives one of the most precise methods for the determination of the value of the quantum constant (h). This equation has recently been used by Clark and Duane as the theoretical basis of the most precise method yet devised for determining the distance between the atomic planes in a crystal, in which case the equation is most simply applied in the form:

$$V\lambda = h\frac{c}{e} = 12{,}354$$

in which V is in volts and λ in Ångstroms.

In the experiments the crystal is so set that the X-rays reflected by the planes whose distance apart it is desired to measure enter an ionization chamber filled with ethyl bromide vapor. The voltage is then reduced gradually, and at a certain definite voltage it is found that the ionization in the chamber disappears. This is the voltage corresponding to the limit of the general radiation described above. The distance d between the atomic planes is obtained by the use of the general equation for a grating,

$$d = \frac{n\lambda}{2\sin\theta} = \frac{12{,}354}{2V\sin\theta}$$

in which n is a whole number and θ is the angle corresponding to the proper peak in the ionization current diagram obtained by rotating the crystal. In the case of potassium iodide this was found to be 3.534 Ångstrom units, which corresponds almost exactly to the density of the same salt as determined by Baxter.

Dr. George L. Clark, of the same laboratory, discussed the application of this method to the determination of the crystal structure of caesium tri-iodide. This work is remarkable in that it represents the first successful attempt to determine the structure of a rhombic crystal, all crystal structures heretofore investigated being of a simpler type. It is found that the atoms of caesium lie at the corners of a rhombohedron, and that diagonally across this solid figure three iodine atoms are distributed in such a way as to divide the distance equally between them. The completion of this work, together with the determination of the structure of potassium tri-iodide, marks an important step in the study of the structure of complex inorganic compounds. The most interesting feature of the experimental work on caesium tri-iodide is the discovery of a method of fixing the positions of atoms of different elements which have practically the same atomic weight, as is the case with caesium and iodine. This was done by causing each atom to register its own spectrum.

The University of Chicago was represented by two general papers, one on ionization and resonance potentials and their importance to chemistry, by W. Albert Noyes, Jr., and the other on the separation of isotopes, particularly as carried out in the Chicago laboratory, by R. S. Mulliken. In addition to a general treatment of his subject Dr. Noyes discussed the idea of Gibson and Noyes that in most cases the potential required to produce luminosity in a gas, when a heated cathode is used, is an integral multiple of the ionization potential. At the request of the chairman, and in answer to numerous questions from the floor, Dr. Irving Langmuir discussed this paper at some length.

Dr. Mulliken showed very clearly that many of the methods proposed for the separation of an element into different types of atoms or "isotopes" have failed thus far. All of the methods which have proved successful may be classified under the one term "diffusion methods," whether the diffusion takes place through a membrane as in the experiments of Harkins and his collaborators, Broeker, Hayes and Liggett, using chlorine in the form of hydrogen chloride, or through the surface used as a membrane, as in the work of Broensted and Hevesy, Mulliken and Harkins, and Harkins and Madorsky, in which mercury has been separated by vaporization at low pressures. Dr. Mulliken described a very rapid apparatus which he has recently constructed, in which mercury, separated to some extent by vaporization, is further separated by diffusion of the vapor through a membrane of filter paper. The centrifugal method, which has thus far failed, seems to give promise of becoming the most rapid of all methods thus far proposed, provided the structural problems of the centrifuge are properly solved. Dr. Langmuir suggests that Hertz has devised a method of applying the diffusion method which might lead to a rapid separation, but a later consideration of this method by Dr. Mulliken seems to indicate that the method is unlikely to show any marked superiority over other diffusion methods, and *may* be decidedly inferior.

Professor Kraus, of Clark University, gave a valuable review of his extensive work upon the characteristics of the metals, salts and non-metals, or of metals, electrolytes and non-electrolytes. Professor Kraus has made extensive studies of the behavior of substances when dissolved in solvents other than water, such as ammonia, sulphur dioxide, etc. He has been able to show that a substance which is usually considered as a metal, such as sodium, may act as a salt when dissolved in the proper solvent. Thus this is the case when sodium is dissolved in liquid ammonia.

Professor Kraus presented a new classification of substances in four groups, as follows: (1) Electrolytes, which conduct even in the pure state; (2) non-electrolytes, which conduct neither when pure nor when in solution; (3) meso-electrolytes, which show a slight conducting power both in solution and when pure; (4) pseudo-electrolytes (like the acids), which are non-conductors when pure, but ionize in solution because they combine with the solvent.

The address of the retiring vice-president of the section was on the subject of atomic structure and the general periodic system of the isotopes,[1] and will be published in a later issue of SCIENCE. Many interesting photographs of the tracks of helium atoms (α-particles) in gases, as obtained by R. W. Ryan and the speaker, were exhibited.

Colloids

One of the features of the meeting was an illustrated address on "Proteins and the theory of colloidal behavior," in which Dr. Jacques Loeb, of the Rockefeller Institute for Medical Research outlined the theory presented in his recent book of the same title. He discards the older idea that the swelling of protein gels is due to the preferential absorption of certain ions, notably of hydrogen and hydroxyl,

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[1] See a paper entitled "The Stability of Atom Nuclei, the Separation of Isotopes, and the Whole Number Rule," by William D. Harkins, *J. Franklin Institute,* Vol. 194, August to December (1922), and Vol. 195, January to March (1923).

since his experiments indicate that proteins behave as definite chemical compounds of an amphoteric nature, that is, in the presence of acids they act as bases, and in the presence of bases they act as acids. Dr. Loeb considers that the erroneous older view has held sway so long only on account of the general failure to measure the hydrogen ion concentration of the solutions used in the investigations.

It is concluded that the basis of colloidal behavior is to be found in Donnan's theory (1910) of membrane equilibria. Donnan found that when a membrane separates two solutions of electrolytes, one of which contains an ion which cannot diffuse through the membrane which is penetrable to the other ions, the result will be an unequal distribution of the diffusible ions on the opposite sides of the membrane. Thus if there is a solution of NaR (where R^- is the ion which does not pass through the membrane) on one side, and NaCl on the other of the membrane represented by the vertical line below

$$\begin{array}{r|l} Na^+ & Na^+ \\ R^- & Cl^- \end{array}$$

there will follow a diffusion of NaCl from left to right as represented below

$$\begin{array}{r|l} Na^+ & Na^+ \\ R^- & \\ Cl^- & Cl^- \end{array}$$

until the product of the concentrations of the sodium and chlorine ions on the right becomes as great as the similar product on the left, which represents the attainment of a state of equilibrium. This reminds the reviewer of very similar relations worked out even earlier by Haber (in 1909). In any event, Dr. Loeb makes a very strong case for the importance of this relation in the interpretation of the action of proteins. He considers that the famous Hofmeister series of ions has been obtained on the basis of erroneous reasoning.

The chemistry of the photographic process was discussed in an illustrated address by Dr. C. E. K. Mees of the Eastman Kodak Company, who described the methods of investigation in use in the laboratories of his own company and in those of various European investigators.[2] One of the most interesting of the recent results is concerned with the application of the quantum theory to the theory of development of the photographic plate. The silver chloride in a photographic plate exists as small crystals belonging to the regular system and imbedded in the gelatin. Each of these crystals is commonly called a grain. These grains often gather into clumps, which tend to develop together, so that there seems to be a process of "infection." In the early applications of the quantum theory it was considered that one quantum of energy should make a single grain developable, but it has recently been demonstrated in the laboratories of the Eastman Kodak Company that it is necessary to supply several hundred quanta per grain. It is found that a grain may be more or less exposed, and that the development depends upon the reduction potential of the developer which is used. Dr. Mees showed that if the number of grains developed per 1,000 grains present is plotted on the Y-axis, and the wave lengths of the light used upon the X-axis, a Gaussian type of curve is obtained in the case of par-speed portrait film, and a very different type of curve when standard slow speed lantern slides are used, at least for the wave lengths so far investigated.

Ionization of Salts in Solution

Much interest was excited by the program of the symposium on the ionization of salts in solution, in which Dr. D. A. MacInnes of the Massachusetts Institute of Technology presented the argument for the newer theory, which is that strong electrolytes are practically 100 per cent. ionized in aqueous solutions, and in other solvents similar to water. The viewpoint of the classical or Arrhenius theory was to have been presented by Dr. James Kendall of Columbia University, but on account of a severe New England snow storm he did not arrive until shortly after the meeting was over. This made it necessary for Dr. MacInnes to present both sides of the question, which he did very ably.[3] The subject was discussed by W. Lash Miller, Charles A. Kraus, E. W. Wash-

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[2] See "Recent Advances in Photographic Theory," by C. E. K. Mees, *J. Franklin Inst.*, 195, 1-21 (1923).

[3] It is hoped that the paper of Dr. MacInnes may be secured for publication in a later issue, so what is presented here represents the point of view of the discussion rather than that of his paper.

burn, W. D. Harkins, and a few others whose names were not recorded. There seemed to be a general agreement that the general question at issue is not at all the relative value of the newer theory as opposed to the original form of the Arrhenius theory, but rather its merits in contrast to those of the most recent form of the classical theory. Thus practically all of the upholders of the classical theory no longer think of the existence of molecules of sodium chloride ($NaCl$) as such in an aqueous solution, but they assume that *at any instant* a part of the salt is less ionized than the rest in the sense that the ions of opposite charge are closer together, and are therefore less independent as carriers of the current. Unfortunately, from the standpoint of a clear presentation of the subject, the meaning of the term "ionized" has been entirely changed in later years by its use in a different sense from the original one by workers in physics. It is now customary to say that in solid sodium chloride there is complete ionization, and the upholders of the classical theory of ionization in solution have always assumed that the ionization in aqueous solution is more marked than in the solid state. It therefore becomes necessary to devise another term to replace the word ionization. Several years ago it was suggested that the term "electrolytic dissociation" might well be used in all discussions of the theory in place of the word "ionization."

On the whole the impression gained from the meeting was that the upholders of the two theories have the same ideas, but talk about them in different words. However, it would seem that in so far as the 100 per cent. theory assumes independent migration of the ions, and the independent influences of the ions in connection with solubility effects, it is in error, since these assumptions are contrary to the facts as represented in the work of Braley on the transference of sodium in a 0.01 normal sodium chloride with 0.1 normal potassium chloride present. In this case the sodium is not transferred at all, which is a result wholly unexpected from the point of view of the 100 per cent. theory. The solubility relations of salts of the type of calcium and magnesium sulphates also give evidence of the formation of complexes.

The principal support for the 100 per cent. theory lies in the additive nature of the properties of salt solutions, but this is a fact well known to the upholders of the older theory. One of the principal arguments of the newer theory is based upon the fact that the thermodynamic potential or the activity of the salt in solution varies in quite a different way from the conductivity ratio. No one at the meeting seemed to defend the present values of the percentage dissociation listed in text-books, such as the value 86 per cent. given for potassium chloride at 0.1 normal concentration. Thus the value of the newer idea may be that it indicates that the classical theory has been expressed in too dogmatic a way. What seems to be most needed in connection with this subject is a new terminology. It is probable that ion aggregates of the type $Cl^-Na^+Cl^-$ exist, at least for a very minute interval of time, in aqueous solutions. These were formerly designated as "intermediate ions" since the term complex ions, better in many respects, was reserved by custom for more stable aggregates. If it is to be assumed that these aggregates are completely ionized it would seem that the term "ion aggregate" would serve as well as any other. The new theory seems to give its greatest promise along the line partly developed by Milner—that of working out the general kinetic theory of electrolytic solutions on the basis that the ions preserve their charges, but that they unite more or less with ions of the opposite charge to form aggregates which are less affected in their motion by the applied potential. It is apparent that much of the work now appearing in support of the newer theory is related specifically to neither theory, since it simply involves the finding of equations containing enough constants to enable them to represent the facts. While this is a very valuable method of progress, it is well known that such equations can be developed in the case of almost any type of related phenomena, so the existence of such equations is not evidence in favor of any specific theory until it is shown that the theory is a necessary basis for the equations. The above discussion of the symposium on ionization does not properly represent the discussions presented, since they embodied a great deal of detail, but it represents simply one view of the situation as suggested to the mind of the individual asked to report on the present status of the theories as brought out by the symposium.

Work of the Fixed Nitrogen Laboratory

In an illustrated address on the above subject Dr. F. G. Cottrell, director of the laboratory, discussed in detail the practical and the research methods used in the fixation of nitrogen. So much valuable information was presented that it is impossible to do the subject justice in the space which is available. It was pointed out that catalyzers for such a reaction as the formation of ammonia from nitrogen and hydrogen differ greatly in their relative effectiveness at different temperatures, so that the choice of the proper catalyzer is very difficult. An effective catalyzer must not only take up nitrogen and hydrogen easily, but it must also not hold too strongly to the ammonia which is formed. Many of the most active catalyzers adsorb impurities readily, and thus become much less active than those which are as poor at the start as they ever will be, which is the case with magnetite. The present tendency is to use very dense fused oxides to form the catalyzer. On reduction sufficient porosity is gained. The present tendency in this process is toward higher pressures.

International Critical Tables

Dr. E. W. Washburn, editor of the "International Critical Tables," pointed out that the aim of scientific research is to express its results in the simplest possible form, which is in general attained when they are reduced to numbers. These numbers are then used as the basis of new laws and principles, which help us to attain the scientific ideal—that of describing the universe in as simple a manner as possible. Not only science, but industry as well, is controlled by such numerical data. Up to the present time there has been no world-wide endeavor to collect the available data in such a form that it may be easily consulted, but at the first meeting of the International Union in 1919, it was decided to take up the preparation of a general set of critical tables through international cooperation. The cost of compilation was assigned to America, and the editorship to the National Research Council and the American Chemical and Physical Societies. While the object of the work is to tabulate existing data, it is found that when they are arranged, many easily determined and important data are missing, so the editor is ready to supply investigators with suggestions as to what work will aid most in making the tables as complete as possible.

Professor Kenrick, of the University of Toronto, showed that there are three different causes of the blue color of water: (1) Absorption, as in the water of a swimming tank; (2) scattering of light, which is the cause of the deep blue color seen on looking vertically into the sea in the tropics; and (3) reflection of the blue of the sky, which gives rise to the color of a lake or the sea as seen from the land.

An interesting report on the detection of small amounts of arsenic in plant tissue was presented by Dr. E. R. Schulz, of the U. S. Department of Agriculture, and a paper on gels and the theory of adsorption from solution by Professor Niel E. Gordon of the University of Maryland. A paper on the position of atoms in aliphatic hydrocarbon compounds was prepared by Maurice L. Huggins, of Harvard University.

A large audience was present to hear the joint program with Section G and the Physiological Section of the Botanical Society of America.[4] The general topic was "Photosynthesis in plants and other aspects of photochemistry." The program included the following papers: "Inventory of the world supply of energy," E. E. Slosson; "Analysis of the mechanism of photosynthesis," H. A. Spoehr; "The nature of photochemical reactions," W. T. Bovie; "Photochemical reactions," S. E. Sheppard; "Carbohydrate metabolism," Charles O. Appleman.

Practically all of the papers presented during the three days of the meeting were discussed at length by the chemists present. This discussion was constantly enlivened by the witty and relevant remarks and suggestions of the chairman, Professor W. Lash Miller, of Toronto.

The officers elected by the section were E. W. Washburn, of the National Research Council, Washington, D. C., as chairman and as vice-president of the association, and W. D. Harkins, of the University of Chicago, as secretary.

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[4] The details of this meeting will be presented in a report from Section G.