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PHYSICAL CHEMISTRY: RETROSPECT AND PROSPECT[1]

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THE Kansas City meeting of the American Chemical Society happens to divide into two halves the expected professional life of one of the members devoting his major activities to the pursuit of knowledge in the field of physical chemistry. It is this fact which has prompted a retrospect of the subject over a period of twenty-two years and some thoughts on the prospects of the science in the subsequent two decades.

To gain a perspective of physical chemistry in those apparently far-off days prior to 1914 resort may be made to the most advanced text-book of physical chemistry of that time, the text-book by Nernst, which, fortunately for our purposes, was issued in a seventh edition in 1913. Whilst one turns its pages, the omissions, in terms of our science of to-day, come readily to mind. In respect to the gaseous state of matter it is evident that kinetic theory was by them in an advanced state of development. Interest was beginning to center in the theoretical treatment of heat capacity vital to the problem of equilibria. The liquid state of aggregation has not shared in the rapid changes of these decades, although recently there has been a change of view-point whereby the analogies between the liquid and solid states is stressed in contrast with the former association of gaseous and liquid states. The study of the solid state was, in 1914, in the initial stages of an activity which has continued to the present. The limitations of the Dulong and Petit Law were known, and heat capacity data over wide ranges of temperature had led to a theoretical

1 An address to the ninety-first meeting of the American Chemical Society at Kansas City, April 13, 1936.

treatment of the specific heats of crystals. But, at that time, crystallography was still empirical, ready to yield to the scientific approach, based on x-ray analysis. How great have been these contributions in two decades to inorganic, organic, stereo-chemistry and metallurgy from the x-ray studies!

The fundamentals of chemical equilibrium had been developed prior to 1914, though much of two decades has been devoted to enlarging the details. Of especial note in this field are the theoretical developments which permit an approach to the problems of equilibrium on the basis of statistical mechanics and the data of spectroscopy. It is now almost true to say that the theoretical calculation of gaseous equilibria, in both homogeneous and heterogeneous systems, is, in many cases, superior to the experimental determination. The range of capacity in this matter is continuously extending.

The application of classical thermodynamics, the first and second laws, to chemical equilibria in gases and solutions has been systematized, largely through the pioneering work of Lewis and his pupils, which made Gibbs practical to the working chemist. Others build continuously on their solid foundations. Nernst's Heat Theorem extended the rôle of thermodynamics in equilibria. Its utility and its limitations have been explored, and it has provided a rational approach to the problem of equilibria in organic reactions with consequent wide applicability in modern industrial chemistry.

Electrolytic equilibria had received, by 1914, an intensive development, but the problem of strong and weak electrolytes was not rationalized until the Debye-Hückel Theory laid the foundations for a resolution of the problem. Salt effects of uni- and polyvalent ions obtained thereby a lucid interpretation. The intensive study, with exact technique, of cell reactions has contributed greatly to these developments and we owe to such measurements much of our new knowledge of thermodynamic concentrations in ionized media. In passing, let us thank electrochemistry for providing the first separation of pure isotopes of the element hydrogen.

It is difficult for the student of physical chemistry to-day to visualize the situation in 1914 in respect to chemical kinetics. In that field alone are to be found some of the most spectacular developments in theory and in major industrial applications. In the field of homogeneous gas reactions, in rapid succession, came the kinetic theory treatment of bimolecular gas reactions and the first modern concept of the old active molecule of the Arrhenius treatment. Next came unimolecular decomposition processes, the basic reactions of the modern petroleum cracking industry, chain reactions, fundamental in the oxidation of gaseous fuels, in processes of chlorination and quite recently in technically important processes of polymerization to yield synthetic rubbers, resins and gasoline. With the concept of reaction chains came a full realization of the scope of inhibitor action and possible technical application in anti-knock materials, and inhibitors of deterioration in fats, oils, rubber, essential oils, pharmaceuticals and foods. The resolution of complex reactions into the simpler components, involving atom-molecule reactions, paved the way not only for the induction of reactions at lower temperatures but also for an entirely new theoretical treatment of the problem of reaction speed and activation. This recent development, which already, in the simpler processes, permits a quantitative theoretical calculation of the absolute rates of chemical reaction, has opened up to the theoretical chemist of the coming generation a rich field to cultivate. I plead with those in charge of large departments of chemistry or chemical research, here and abroad, to include in their personnel at least one who can bring to the problems of chemistry the rich assistance of statistical and quantum mechanical theory.

In the field of heterogeneous reaction kinetics, of contact catalysis, the development of fundamental principles has been equally pronounced. The progress prior to 1914 which produced such important technical developments as contact sulfuric acid, hydrogenation of oils, catalytic hydrogen manufacture and, lastly, ammonia synthesis can not be minimized. But the developments of the science of surface action, in the researches of Langumir, in the demonstration of surface heterogeneity, in the elucidation of the mechanism of poisons and promoter action, have given to the subject a scientific technique which is in large measure responsible for the rapidity of technical development, as illustrated in the synthesis of alcohols and esters, catalytic hydrogenations and dehydrogenations. To the future in this field let us return a few moments later.

In the second edition of the "Treatise on Physical Chemistry" published in 1931 there is a solid block of some 375 pages, representing more than one fifth of the total work, which is practically entirely absent in the physical chemistry of Nernst in 1913. These sections treat of the applications of quantum theory to atomic and molecular structure and the science of photochemistry in its newer aspects based upon the quantum concept. It is in this portion of the subject that the most fundamental advances have been made, with consequences in thermochemistry, equilibria, energetics of molecular assemblies to which brief allusion has already been made. Developments in this field have made possible conclusions concerning the initial stages in excitation of molecules by radiation of various types and a more penetrating approach to the problems of reaction mechanism. The later developments in quantum mechanics have indicated the methods of theoretical approach to the chemist's problems of valency, stereochemical properties, homo-polar and ionic types of binding as well as to the phenomenon of activation energy, the controlling factor in rates of reaction. The new mechanics also has taught us the phenomenon of spin isomerization involving spins of the electrons and nuclei of symmetrical molecules, with important practical consequences in the case of hydrogen and conclusions that can not be avoided in the computation of equilibrium conditions involving other molecules. The discovery of Raman spectra, the more intensive study of infra-red and ultra-violet absorption spectra, dipole moments, x-ray and electron diffraction have provided us with further possibilities in the eludication of molecular structure. The spectral studies as well as the development of the mass spectrograph have enormously expanded our concept of isotopes which first came to our consciousness through the discoveries in the chemistry of radioactive substances in the early days of 1914. The closing years of these two decades of change have brought the isolation of two isotopes of hydrogen with all the consequences in chemical kinetics, in nuclear transmutations and biological research which resulted. Other isotope separations are within reach. Nuclear transmutations, whether with deuterium, as conspicuously developed by Lawrence, Cockcroft and Walton or with neutrons as discovered by the Curie-Joliots and developed by Fermi, have provided the chemist of the next two decades with radioactive isotopes with which to multiply the spectacular achievements attained with deuterium. A beginning in this field has already been made and the years immediately ahead will be significant.

If the gains in the field of surface chemistry have been substantial in the decades just concluded, the gains yet to be achieved are no less attractive. Excellent as are the results of studies of surface action already completed we still are far from an ideal which everywhere around us compels our attention. We can achieve a certain chastening of spirit if we contemplate the perfection of chemical action that is attained in vital processes. The enzymatic processes of digestion, synthesis sensitized by chlorophyll, the multi-functional activities possessed by the hormones indicate a level of reaction technique far above that of the most delicate of our reaction processes *in vitro*. We shall need to learn much more in these coming years of the adaptation of the catalyst, whether in a surface or a large molecule, to the particular process to be achieved. We need, to borrow once more the analogy from Fischer, a key more exactly fashioned to the lock to be opened than is usual in our present contact catalysts. We need for this purpose a more penetrating knowledge of complex organic structures. We need also to know more concerning the coupling of two or more chemical processes, the energy available from the one to supply the energetic needs of the other. In this field, it is probable indeed that the organic chemist will need the most energetic assistance of the physical chemist. The wonderful recent achievements in the organic chemistry of biologically important compounds such as the vitamins and the hormones must not be allowed to obscure the fact that these are problems intrinsically much simpler than those which involve carbohydrates, glucosides and proteins, largely because of the greater molecular complexity of the latter. We do not yet see how the synthetic and analytic studies so successful with the simpler biological molecules can be transferred to the more complex molecules. In the meantime the physical chemist can be of assistance, helping towards a solution of the problem by kinetic, colloidal and stereo-analytical studies. The physico-chemical technique which is even now being developed for the analysis of problems in the synthetic polymer field is so much gained in the approach to the problem of complex biological structures.

The last decade has seen the development of our knowledge and control of reactions involving atoms and molecule fragments. We are beginning to learn something of the individualities of the free radicals whose lifetime is measured in small fractions of a second. We are learning how to manipulate these fragments of high reactivity into patterns more suited to our needs. Any one who knows the differences, in fuel value, for example, between a straight chain octane and iso-octane, standard of anti-knock rating, must recognize the importance of such controlled rearrangements. We can no longer be content to take our molecules "as we find them," as Kipling once said of the British soldier, but rather, in the words of the older poet, we must be ready "to shatter them to bits and then remould them nearer to the heart's desire."

It is not, however, the rôle of the physical chemist to sketch out the many consequences in applied science which will certainly follow from the more intensive development of the theoretical aspects of the subject. To others the glory and the plaudits that come for obvious and spectacular benefits of science to human society. Ours the humbler and yet more satisfying task—to reveal the origins of things—to order our knowledge even more scientifically, ever less empirically. For it is of our faith that the less empirical the science becomes, the more assured do we become in its application. The years ahead will reveal the men to carry on the glorious traditions of Dalton and Faraday, of Helmholz and Gibbs, of van't Hoff and

Arrhenius, of Ostwald and Nernst, of Einstein, Debye and Langmuir, the men who, by their contributions to theoretical chemistry, their new laws, their new generalizations, will provide the broader foundations upon which may be built a more satisfying scientific superstructure.

THE HARVARD TERCENTENARY

HARVARD UNIVERSITY will confer on September 18 honorary degrees on sixty-six of the principal speakers at the Tercentenary Conference of Arts and Sciences, which will be held from August 31 to September 19.

Those selected do not include those who have received honorary degrees from Harvard in the past. Among these are Albert Einstein, Robert A. Millikan, John Dewey, Henry N. Russell and William B. Scott.

Fourteen of the scholars to be honored are from the United States, twelve from England, ten from Germany, six from France, five from Switzerland, three from Italy, two each from Japan, Denmark, Scotland and Sweden and one each from the Netherlands, Argentina, Norway, Canada, Czechoslovakia, Austria, China and Australia.

The scientific men who will receive degrees with the descriptive statements sent to SCIENCE by the Harvard University News Office is as follows:

Edgar Douglas Adrian, Foulerton professor of the Royal Society and fellow of Trinity College, University of Cambridge, Nobel Prize winner in physiology and medicine, is an acknowledged leader of the modern school of neuro-physiologists, and has elucidated the neurological basis of sensation, the action of the various sense organs and the activity of nervous centers.

Edward Battersby Bailey, professor of geology at the University of Glasgow, Scotland, is a world leader among geologists, and has made important contributions dealing with the origin of mountains and the nature of volcanic and intrusive rocks.

Sir Joseph Barcroft, professor of physiology at the University of Cambridge, is a leading member of the group of British physiologists who have contributed largely during the past quarter of a century to knowledge of the blood as a carrier of oxygen and carbon dioxide.

Friedrich Bergius, of the Deutsche Bergin-Aktiengesellschaft, Heidelberg, Nobel Prize winner in chemistry, has developed processes in fuel technology which rank among the most important advances in chemical technology since the development of the method of making synthetic ammonia.

Niels Bohr, professor of physics at the University of Copenhagen, Nobel Prize winner in physics, is one of the world's outstanding figures in theoretical physics, and has pioneered in the study of atomic structure and the quantum theory.

Norman Levi Bowen, petrologist in the Geophysical Laboratory of the Carnegie Institution in Washington, is one of the world's leaders in the application of physical chemistry to problems in geology, having done notable work on igneous rock.

Elie Joseph Cartan, professor of mathematics at the University of Paris, one of the leading European mathematicians, has made important contributions to hypercomplex numbers and the theory of groups in the field of algebra, differential geometry and complex geometry in the field of geometry, integral invariants in the field of analysis and the theory of finite continuous groups.

James Bertram Collip, professor of biochemistry at McGill University, collaborated in the isolation of insulin and has done other important research in the chemistry of the blood, internal secretions, insulin, the parathyroid hormone and placental hormones.

Arthur Holly Compton, professor of physics at the University of Chicago, Nobel Prize winner in physics, is one of the world's outstanding figures in the study of cosmic rays and x-rays.

Peter Debye, professor of physics at the University of Leipzig, is one of the world's leading authorities in the field of polar molecules and has made many important contributions to physics.

Leonard Eugene Dickson, professor of mathematics at the University of Chicago, is one of the foremost algebraists and number theorists in the United States.

Sir Arthur Stanley Eddington, professor of astronomy and director of the observatory at the University of Cambridge, is one of the world's outstanding astronomers, and one of the great elucidators of modern astronomy and physics.

Hans Fischer, professor of chemistry at the Technische Hochschule in Munich, Nobel Prize winner in chemistry, is a world leader in the study of the structures of haemin and of chlorophyll, substances of extreme complexity and of the utmost importance in the understanding of animal and plant life.

Ronald Aylmer Fisher, professor of eugenics at the University of London, has made major contributions to the theory of statistics, has designed improved layouts for agricultural experimentation and has made a notable contribution to the genetical theory of natural selection.

Corrado Gini, professor of statistics and sociology at the University of Rome, is one of the most prominent sociologists, statisticians and demographers in the world.

Godfrey Harold Hardy, professor of mathematics at the University of Cambridge, is one of the most outstanding figures in mathematics, his principal contributions having been made in the fields of analysis and the analytic theory of numbers.

Ross Granville Harrison, professor of biology at Yale University, developed the method of embryonic transplantation which led to great advances in experimental biology, and has made important contributions to knowledge of the nervous system, symmetry and development after heteroplastic transplantation in the amphibia.

Werner Heisenberg, professor of theoretical physics at