tions. For instance, in one case, by ordinary assays of the ore, the mill showed to be extracting 87 per cent. of the silver in the ore, which was considered good work. Corrected assays of the ore showed, however, that the extraction was only 79.3 per cent. This led to an investigation, which showed that there was a volatilization loss of 10.9 per cent. in roasting the ore. This has been cut down to 5 per cent., with the expectation of reducing it still more.

In another case the extraction plus the tailings silver was 102.7 per cent., but corrected assays showed it to be only 87.1 per cent. This was brought up to 97 per cent.

These figures show that the commercial assays of ores are too unreliable if accurate mill statistics are desired.

THE ACHIEVEMENTS AND AIMS OF PHYSICAL CHEMISTRY.[1]

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CHEMICAL changes, in common with all other natural processes, are in their ultimate nature transformations of energy. The study of chemical processes is therefore a study of the energy phenomena which they involve. Chemical reactions may absorb or take up heat, changes of density may occur whereby work is done, electrical energy and radiant energy may be produced. But the mutual relations of heat, work, electricity, and the like, involving the characteristic factors, temperature, pressure, tension, force, potential, etc., form the subject-matter of the science of Physics, and hence it is that the study of chemical processes as such has come to be known as the *Physical Chemistry*. The object of this branch oi science is to discover the simple relations connecting the various types of chemical phenomena, and to make of these relations a coherent whole.

The Physical Chemistry is a new science. Up to eight years ago nothing serious had been attempted in the way of generalization. Very important discoveries had been made before that time it is true, yet they where of a wholly disconnected character and their bearing upon a general theory of chemical processes

[1] Read before the Midwinter Fair Congress of Chemists at San Francisco. June 7, 1894.

was not seen. Prominent among these achievements of a generation whose efforts have now become history stand the experimental work of Thomsen and Berthelot in thermo-chemistry, the investigations of Kopp in stoichiometry, the dissociation theory of Horstmann and of Gibbs, the brilliant researches of Helmholtz in electro-chemistry, and that flash of insight which led to the discovery of the law of mass action. Nor is the present generation proving itself unworthy of this inheritance of scientific achievement; the chemical equilibrium, the electro-chemistry, and the thermodynamical generalizations of to-day are supplying a fit sequel to this story of the past.

In 1886 appeared van't Hoff's first paper upon the theory of solutions. It was immediately followed by that extended series of monographs, written by such men as Ostwald, Nernst, Arrhenius, Planck, Riecke, and many others, which has made the thermodynamical theory of solutions one of the most remarkable conquests of the science of chemistry. Van't Hoff's discovery that the inner energy of a dissolved substance when dilute is independent of the volume of its solution led at once to the discovery of simple relations between the physical properties of solutions and their molecular concentrations, *i. e.*, to a series of novel methods for the determination of molecular weights; it brought about an unforeseen extension of the law of mass action to the solution-equilibria of both homogeneous and heterogeneous systems; it led to a strict formulation of the influence of temperature upon chemical equilibrium and the velocities of reactions, to a mathematical theory of hydrodiffusion, to a comprehensive theory of concentration currents and of the voltaic cell, and to an unexpected culmination of Ostwald's exhaustive investigations upon the chemical affinities of aqueous acids and bases. This breathless succession of advances constitutes one of the most interesting and exciting chapters of the history of chemical theory.

It is being succeeded at the present time by work of a more general and wide-reaching character. The great generalizations of thermodynamics are hastening the day when chemistry shall become a deductive science. Planck, of Berlin, has recently directed especial attention to the following course of reasoning.

There are certain processes, such as the conduction of heat from a hot to a cold body, or the diffusion of a dissolved substance from a high concentration to a lower one, which are irreversible—they take place only in one direction. This fact may be shown to require the conclusion that the general trend of natural processes is in an assignable direction: the general state of things tends all one way. If this were not so it would be possible to reverse history, to make trees grow down into seeds, and to awaken fossils to quivering, pulsating life.

The strict formulation which represents this general tendency furnishes, therefore, a means of determining definitely the direction which any given natural process, chemical or otherwise, must pursue; and it leads in consequence to an exact relation between the energy factors upon which the final state of the material system concerned is made to depend, a relation which combines in one expression every law of chemical equilibrium. From it can be derived in order all the laws of isothermal chemical equilibrium in homogeneous and in heterogeneous systems, and those which represent the effect of changes of temperature and of pressure in displacing such equilibria; it yields further the laws relating to the many physico-chemical properties of solutions which depend upon the vapor pressures; and it furnishes, finally, the almost numberless theorems of electro-chemistry. Thus it is seen that from the assumption of a simple fact of experience, the irreversibility of heat conduction, a mathematical theory of chemical changes is obtained which organizes into a coherent and logically connected whole all the exact relations of chemical science. The deductive value of this theory is enormous, in that it clearly points out the limits of our knowledge in every direction. And for the reason that the system is uniform and falls into a logical order it becomes of the greatest service in aiding the conception of chemical theory as a whole and in fixing in the mind the relations between its parts.

Another form of the same fundamental idea has been employed by the eminent French mathematical physicist, Duhem, in developing a systematic treatment of the theory of chemistry. From the properties of his *thermodynamical potential* (taken from the thermodynamical studies of Willard Gibbs) he has evolved an orderly discussion of the theory of dissociation, the continuity of the liquid and gaseous states, and the general theory of the chemical and physical equilibria of fluid mixtures, all of which is characterized throughout by strict uniformity of method and an unusual elegance of mathematical style.

These two methods of research are essentially identical, for they are based upon the same principle, and they both refer the solution of every problem to the properties of a single function of quantities which fix the state of the system concerned. In this respect they mark a distinct advance in the study of the science of chemistry.

The eminent fruitfulness of these thermodynamical methods has led to a fuller appreciation of the bearing and significance of the great energy generalization which they involve, and upon which, indeed, the entire framework of modern physical science really rests. If chemistry be in its ultimate nature, an energy science, chemists obviously must study those energy transformations which constitute its phenomena. In a chemical change different energies come into play, and the change continues until they hold one another exactly in balance. This balance determines, therefore, what the final state of the system in question shall be. Two energy forms are in equilibrium when a possible variation of one is exactly compensated by the corresponding variation of the other. All that is necessary then to determine the final state which any given material system must assume is to represent mathematically the possible variations of its opposed energies and to set these variations equal. This procedure is identical with that which is employed in Statics to investigate the equilibria of mechanical systems. When applied systematically to the different types of chemical action it yields a rational classification of chemical processes, and, in a logical sequence, all of the known elements of the modern physical chemistry. This reconstruction of theoretical chemistry upon the basis of the Energy Theory is one of the most brilliant of Ostwald's many splendid contributions to science.

It is important to observe that the great advances of recent years in the theory of chemical action have not been made with the aid of the kinetic-molecular hypothesis. The assumption of atoms and molecules has been a constant hindrance to the progress of rational chemical theory. The "Kinetic Theory of Gases" has been able to account for the behavior of gases only in an imperfect manner, and it has not been able to account at all for the laws of chemical equilibrium and the properties of solutions. The fact that gases react in simple volume relations justifies the selection of a definite volume as the chemical unit, the relative weight of this volume becoming then the so-called molecular weight, but it justifies in no wise the conclusion that gases are composed of discrete particles. This unwarranted assumption was made because of a desire to "explain" from the behavior of a purely mechanical system the observed characteristics of gases. Yet the behavior of the model is, after all, only approximately that of the gas. And, moreover, it is not the province of science to "explain" anything, certainly not to explain phenomena by reference to irrealizable mechanical constructions. It is becoming more and more clearly seen, day by day, that the business of science is to *describe* phenomena in a simple manner, to seek actual relations between measurable quantities, to deal only with things which can be handled and observed. Hypotheses must be employed, if at all, only provisionally and as analogies.

There is no desire to deny that the molecular hypothesis has been fruitful of results; any hypothesis may lead to work whereby knowledge is gained. Yet this one has nearly outlived its usefulness, and it will be employed less and less in the future by those chemists who refuse to believe upon insufficient evidence. As an accepted hypothesis its days are numbered. In the place of the Molecule appears the Molecular Weight, a sharply defined quantity whose conception does not transcend experience.

The average student of chemistry is trained to confuse the real with the hypothetical. He believes molecular formulas and molecules to involve each other, whereas, the former represent facts while the latter are creations of fancy. The molecular formulas of our chemical equations possess a very real and important signification, and this is no less true of the structural formulas which form at the present time so important a feature of the technical apparatus of organic chemistry. These structural formulas are valuable mnemonic expressions for the individual chemical character of the substances in question, and when employed for what they represent their value is not to be underestimated. Yet one must not for a moment suppose that they supply a picture of the mechanical structure of small particles of the substances; this idea is a purely hypothetical one, and at the best represents nothing more than the original facts. The symbols, properly used, represent the facts and not the hypothesis.

The general methods which give to the best modern thought its distinctive character appeal to experience alone. Things other than observable fact do not fall within their province, such things are not objects of human knowledge. It should not need emphasis that this is the only natural and reasonable basis for a science of the facts of nature. And it cannot be denied that our first real insight into the nature of chemical processes has been gained by the application of these straightforward methods.

The age of mechanical hypotheses is of the past. The desire to replace known laws by unproven or unprovable assumptions is passing away. And it can now be clearly recognized that the view which seeks to place mechanics at the base of all departments of physical science is, in its thoughtless exclusion of energies other than mechanical, a prejudice. Now, the thermodynamical systems and the energy doctrine involve only accessible facts. They are built upon no assumption other than the irreversibility of some spontaneous process, or the observed conservation of the energy of an isolated system. Their aim is to increase knowledge, and not representations of knowledge, to seek out the facts of nature and the wonderful and simple relations subsisting among these facts. And in this there are notable instances of what is fittingly termed *Physical Theory*. The distinction between theory and hypothesis can now be sharply drawn, the Hypothesis is a mechanical construction substituted by the imagination for things as they actually are, the Theory is an organized system of logical consequences drawn from the established facts of experience. Mechanical Hypotheses have dimmed the glory of the history of chemistry, Physical Theory endows chemistry with the attributes of an exact science.

The subject of electro-chemistry has become, in recent years, a prominent feature of the physical chemistry. The energy liberated in chemical changes may appear as electrical energy; or electrical energy may, during a chemical process, be transformed into the inner energy of the products of the reaction. Our knowledge of these things has had a contentious and a profoundly interesting history. The strugglings and gropings of a hundred years lie between this time and that in which the first observations of electro-chemical action were made by Galvani and Volta. The intervening years have been largely occupied by a study of the phenomena of electrolysis pure and simple. The insight thereby gained into the nature of this process has led to a clear conception of what takes place in the various types of voltaic cell, and has, in consequence, rendered accessible to immediate calculation all the essential details of the transformation between the free energy of the chemical action in a cell and the electrical energy which is produced. This comprehensive theory of electro-chemistry is one of the greatest results which has followed the introduction of the energy theory into chemistry, it is the fitting close of a century of effort.

And now that such a result has been reached it is a matter for congratulation that the event is to be marked by a great literary monument. This is Ostwald's work on electro-chemistry, at the present moment passing through the press, a book which is to give a full and clear account of the entire development of the subject from its beginnings.

The influence which has been exerted upon physical chemistry by its literature is of the most interesting character. Widespread interest in physical chemistry as an independent subject dates, probably, from the publication of Ostwald's *Lehrbuch der allgemeinen Chemie*, in 1887. The interest thus aroused was immediately intensified by the appearance of van't Hoff's thermodynamical theory of dilute solutions, and the remarkable series of theoretical and experimental discoveries which followed in its train. This period marks, undoubtedly, the beginning of physical chemistry as a connected and organized science. Its development since then, due to no small extent to the efforts of Ostwald and van't Hoff and their pupils, has found a fit channel for expression in the pages of the *Journal of Physical Chemistry*

(*Zeitschrift für physikalische Chemie*), whose first number appeared also in 1887. A systematic account of the present status of the science is now being supplied by a new edition of Ostwald's *Lehrbuch*, which has in the meantime grown to be a monumental work in three volumes, two of which are already in print. And it is well to add that the general desire for a text-book of less exhaustive nature has been well met by the briefer "*Outlines*" by the same author, and the "*Theoretical Chemistry*" of Nernst. Due reference has been already made to Ostwald's magnificent publication upon electro-chemistry.

The great demand now to be made upon the future is for a book upon the *General Theory of Energy;* a work in which the relations of natural phenomena to one another may be brought into a clear light, a work in which we may finally see effaced the artificial distinctions between the subjects of Chemistry, Mechanics, Thermodynamics, Electricity, etc., which, as we have them now, are partly historical, partly physiological, partly conventional, and wholly unsatisfactory.

The science of Physical Chemistry is, at the present moment, in a stage of the most active development. Every month brings to the light some startling experimental discovery, or some broader generalization. The general methods now in use have already begun to furnish a complete thermodynamical theory of solutions for all concentrations, a thorough grasp of the conditions of chemical equilibrium in complex heterogeneous systems, a really adequate comprehension of the phenomena of galvanic polarization, and an exact definition of chemical affinity. These are the things of to-day, what the morrow may bring forth is for no man to say. Yet it is certain that the chemistry of the future will deal with fact and not with fancy, and that its immediate aim will be the establishment of exact relations between those quantities upon which the state of every material system ultimately depends. For it is in this way, and in this way only, that a real insight into the nature of chemical processes will finally be attained.

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