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The Rôle of the Physicist in the Development of Chemical Theory.

At a time when the commerce between nations has emerged from the obscurity of custom and assumed paramount importance in the general mind, a scientific man may perhaps be pardoned if his thoughts take a commercial turn and incline to the consideration of the traffic between the sciences. As each country has its imports and exports with respect to other countries, so each science has its imports and exports with respect to other sciences. That there is a liquidated balance of trade can scarcely be maintained: one science remains a lasting debtor, another a lasting creditor. The commodities exchanged are ideas, with occasionally a method or an invention, and their value is not to be measured in depreciated sterling or more depreciated marks: what payment there is must be by way of barter. The general capital of ideas, methods, and inventions is ever increasing, and the accumulated stock is free to all who are capable of using it.

In this exchange the concrete sciences in general profit more than the abstract sciences. The pure mathematician is free from the trammels of matter or ether, and like the chimæra of old, bombinates joyously in a vacuum of n dimensions, shedding functions and operators in his gambols, which to the theoretical physicist may prove of incalculable value. The physicist in turn exports largely to the chemist, to whom the biological sciences, chiefly on their physiological side, are next indebted, and so on.

Since science is one, and is only split into separate disciplines to meet human dispositions and human limitations, the rise of borderland sciences becomes inevitable with the growth of knowledge. The practitioners of these sciences are middlemen in the exchanges; the mathematical physicist, the physical chemist, the biochemist, the physiological psychologist, and the like, facilitate the interchange of ideas and methods between the neighbouring scientific groups. A characteristic of contemporary science is the cultivation of these borderlands. Physical chemistry, if judged by the number of

researches it produces, or by the time devoted to it in academic instruction, now occupies a place almost coequal with the traditional subdivisions of chemistry proper. Since in what follows I shall have to distinguish as sharply as possible between physicists and chemists, I propose to divide physical chemists into two classes, according as their outlook is primarily chemical or primarily physical. For instance, Ostwald and van't Hoff belong to the first group, and these I shall call chemists; whilst Arrhenius and Nernst belong to the second group—these I shall call physicists.

We chemists are, I think, somewhat oblivious of the debt which we owe to physicists in the development of our science, particularly on its theoretical side. At the present time, the existence of the debt can scarcely be denied. The physicist is the scientific *conquistador* of to-day. He has crossed the interatomic ocean, he has skirted or explored the archipelago of electrons that fringe the atom, and has at last invaded the tiny continent of the nucleus. Invasion may seem too mild a term for his operations: he has hurled continent against continent with results that leave us aghast and filled "with a wild surmise" as to his future exploits. Such things are prominently before us, but we tend to ignore the less startling contributions of physicists to the advance of chemical theory during the last century, and these I propose to pass in brief review. We shall find the indebtedness to our physical colleagues so great, that it is no small consolation to know that a chemist and not a physicist laid the foundation of our modern science. As Bacon says, "There is an unavoidable necessity for men, if they will walk consistently, to have recourse to atoms, which are real, material, figurative, measurable things, having situation, resistance, appetite, motion, emanation, and remaining for ever unshaken and the same amid the destruction and change of all natural bodies." This philosophical necessity was supplied by the atomic theory of Dalton, which welded the conceptions of atom and element into a coherent scientific system, and provided a simple quantitative symbolisation of even greater immediate value for the progress of chemistry than the parent theory itself. Indeed for many decades the atom, which the quantitative symbol originally represented, was practically forgotten, and only regained its significance in comparatively recent times.

Whilst the modern notion of the atom is due to a chemist, we owe to physicists the notion of the gaseous molecule as ultimate physically independent unit of chemical substances. Gay-Lussac, who may be regarded with equal right as chemist or physicist, since he was Professor of Chemistry at the *École polytechnique* and Professor of Physics at the Sorbonne, made a contribution of prime

consequence in the development of chemical theory by his discovery of the law of gaseous volumes. According to Dalton, all bodies, including gaseous bodies, enter into chemical action in simple multiples of their characteristic combining weights: according to Gay-Lussac gaseous bodies enter into chemical action in simple multiples by volume. There must then exist some simple relation between the volumes occupied by the combining weights of different gases. Dalton attempted to state the relation in the form that equal volumes of different gases contained the same number of atoms. This immediately led to contradictory results, and Dalton was induced to doubt the accuracy of Gay-Lussac's experiments. The reconciliation of theory with experiment was effected in 1811 by Amedeo Avogadro, Professor of Physics at the University of Turin, and independently a few years later by Ampère, also a physicist. Avogadro defined in effect the gaseous molecule and stated the principle that equal volumes of all gases under the same conditions contained the same number of molecules. These physicists were, however, so far in advance of the chemical thought of their time that their work, fundamental and simplifying as it was, fell into utter neglect. The reason is, no doubt, that volatile compounds were then comparatively few in number, that accurate methods of vapour density determination were not available, and that organic chemistry was not sufficiently advanced for the necessity of the precise definition of the molecule to be felt. The work of the great organic chemists of the forty years succeeding the announcement of Avogadro's principle led only slowly to the recognition of its significance. The French school of chemists, and Williamson in this country, saw the advantage of comparing equal volumes of gaseous compounds, but the systematic application of Avogadro's principle to organic and inorganic compounds alike was not made until 1858 by Cannizzaro, who first appreciated its full scope and bearing. By its use the present system of atomic weights was practically fixed, recourse being had in some cases, where volatile compounds were wanting, to the principle of the constancy of atomic heats, due to the collaboration of the physicist Petit with the chemist Dulong.

The next great principle, which we also owe to a physicist, is the law of the identity of the chemical and electrochemical equivalents. This law summarises the electrochemical work of Faraday, dating from the thirties of last century. The beginnings of electrochemistry are due to chemists—the practical side largely to Davy, the theoretical application of electropositive and electronegative in systematic chemistry to Berzelius. It was Faraday, however, who stated the quantitative laws of electrolysis and invented the nomen-

clature used at the present day. The quantitative association of matter with electricity is fundamental, and Faraday first gave precision to the ratio of charge to mass, of which so much has been heard in recent years.

By the end of the fifties the consideration of the organic molecule had led to the recognition of the essential quadrivalence of the carbon atom and its expression in graphic formulæ as we now use them. The molecule, from one point of view a mere gaseous particle, has now a definite structure assigned to it, a structure which can be represented by an easily grasped symbolism, dependent on the general notion of valency. In the next decade, progress was made in various directions, chiefly by chemists alone, but sometimes in association with physicists. First there was the development of the formulation of the carbon compounds which led eventually to the conception of the asymmetric carbon atom as put forward by Le Bel and van't Hoff, and to stereochemistry generally. Then there was the foundation of spectrum analysis by the collaboration of the chemist Bunsen with the physicist Kirchhoff. Here we have an example of the importance of a new instrument of investigation. The spectroscope of the physicist gave the chemist a method of detecting with ease and certainty quantities of chemical elements so small as to be beyond the reach of the finest balance. In its modern development, spectroscopy helps the astronomer on the one hand to state what substances are in the remotest stars, to measure their proper motion, and in general to determine the nature of the stellar universe, whilst, on the other, it enables us to peer into the structure of the atom. In the early sixties the spectroscope found its most striking use in promoting the discovery of new elements, for example, cæsium, rubidium, thallium, which without its aid would scarcely have been detected. In later times, the discovery of helium and all that it implies may likewise be attributed to the spectroscope.

With the definite establishment of atomic weights by the recognition of Avogadro's principle and the discovery of new elements it was only natural that a system of the elements based on atomic weights should be sought, and at the end of the sixties this received definite expression in the Periodic Law of Mendeléeff and Lothar Meyer. Almost simultaneously, the fundamental chemical law of mass-action regulating chemical velocities and chemical equilibria was laid down in a general manner by Guldberg and Waage, once more a co-operation between a chemist and a practitioner of a more abstract science.

The great contribution of the seventies to theoretical chemistry is to be found in the Phase Rule of the mathematical physicist, Willard Gibbs. It is a principle of the widest scope, applicable to

heterogeneous equilibrium, both physical and chemical. Being published in the Transactions of a minor academy and being, in addition, unattractive in form, it was only in the nineties that its vast importance was realised. Like Avogadro's principle, it was in advance of its time. Gibbs defined clearly the phases or mechanically separable constituents of a system, and the components of which the phases were constituted. By proofs based on thermodynamical principles, he showed that the number of phases in equilibrium could never exceed the number of components by more than 2, and that the system gained an additional degree of freedom for each phase short of this maximum number. The rule finds its most important application to solutions, which had only been investigated sporadically at the time of its inception. As instances of its utility on the great scale may be cited its application to the Stassfurt salt deposits by van't Hoff, and to the production during the war of ammonium nitrate from sodium nitrate and ammonium chloride.

Although much scattered work had been done on solutions in the seventies and eighties, it was only towards the end of the latter decade that a theory of any generality was reached. Van't Hoff, founding on experiments by the botanist Pfeffer, developed his osmotic pressure theory, according to which there is for dilute solutions a formal analogy between the dissolved substance in the solution and the same substance in the state of a gas. For gaseous pressure we substitute osmotic pressure, and find for dilute solutions the same simple laws as regulate the behaviour of gases. Although the principle is only a first approximation to exact statement, it opened the door to experimental and theoretical investigations which are still in progress. Amongst other things, it gave the theoretical basis for the determination of molecular weights of substances in solution by the freezing-point and boiling-point methods.

At first sight, electrolytic solutions could not be brought immediately under the osmotic pressure generalisation. The physicist, Arrhenius, however, by putting forward the theory of electrolytic dissociation almost simultaneously with the osmotic pressure theory, accounted for the exceptional behaviour of electrolytes in a simple manner. According to Faraday's theoretical conception, salts, acids, and bases in aqueous solution conduct electricity in virtue of their being split up into ions: Arrhenius gave a quantitative precision to this notion by showing how the actual conducting power was related to the number and speed of the ions (the relative speeds having been previously measured by the physicists Hittorf and Kohlrausch). Whilst the theory together with the law of mass-

action gives an accurate picture of the behaviour of aqueous solutions of feeble electrolytes, the treatment of strong electrolytes still offers difficulties which have not been overcome. Taking the theory of electrolytic dissociation as starting point, the physicist Nernst developed a comprehensive treatment of electromotive force, which to the chemist is not only useful in its application to determining very small ionic concentrations, but is indispensable in determining the affinities of certain systems. To Nernst also we owe a new thermodynamical rule of much use in calculating chemical equilibria and the affinities of the substances concerned in them.

We now come to a branch of chemistry the development of which has been almost exclusively in the hands of physicists. The phenomena of the discharge tube have always attracted the attention of investigators. Crookes considered that in high vacua the matter present was so tenuous and different in its properties from ordinary matter as to deserve the special name of radiant matter. The thought was a happy one, and the study of the passage of electricity through matter of such tenuity, where the effects of the electric strain on separate particles are not immediately wiped out by collisions, has led to discoveries which have revolutionised our notions both of atoms and of elements. Amongst physicists who studied such phenomena at the beginning of the productive period may be named Lenard Röntgen and J. J. Thomson. Not only was their work of great importance in itself, but it led to the development of experimental methods which accelerated the advance of knowledge to a marvellous degree. The electroscope here plays the part which was played half a century earlier by the spectroscope. Without this delicate instrument the quantitative study of radioactivity would have been practically impossible. The linking up of the investigation of X-rays, cathode rays, and radioactivity is one of the most interesting concatenations in the history of physical science.

The discovery of radioactivity we owe to the physicist Becquerel, and its successful prosecution to the combined activities of a physicist and chemist, Pieuad Curie and his wife. The further development of the subject has been carried on by physicists and by chemists, either working separately or together, as in the instance of Rutherford and Soddy. The theory of atomic disintegration due to these workers breaks new ground in our conception of elements and atoms. The element is no longer an unchangeable ground material; the atom of Dalton is no longer an ultimate indivisible unit. The problem of the composition and structure of the atom assumes an insistent form : it ceases to be merely speculative, and demands a definite answer.

If the answer is to be more than qualitative we must attain a

knowledge of the magnitude of the atom. The beginnings of this knowledge were made in the middle of last century in the determination of a limit of continuity, for example, in gold leaf, in soap-bubbles, etc. The kinetic theory of gases, too, afforded information as to the probable magnitude of molecules, the relation of which to that of the atoms was definitely known. The study of the Brownian movement of suspended particles and the settling of suspensions enabled Perrin to estimate molecular and atomic magnitudes with some precision. The most accurate methods, however, depend on our knowledge of the fundamental electrical magnitude, the charge of the electron. In his Faraday Lecture, Helmholtz said: "If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid the conclusion that electricity, positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity." This conclusion follows from Faraday's laws of electrolysis, which show that "electricity" may be added to the list of chemical elements, obeying in its combination with other elements the laws of fixed and multiple proportions. If the elements of the ions are atomic, the electricity with which they are charged must be atomic likewise. We know accurately the ratio of charge to mass—say in the case of hydrogen, 1.0076 grams of which are associated in solution with 96,540 coulombs of electricity. If we could only learn then how many atoms of electricity it takes to make up 96,540 coulombs, we should know that there is the same number of atoms of hydrogen in 1.0076 grams of that element. To ascertain the magnitude of the charge of the electron or "atom" of electricity is of prime importance to chemists. The researches of J. J. Thomson, C. T. R. Wilson, Millikan, and other physicists have supplied the answer. We now know the absolute weights of the atoms with an error not exceeding 1 per cent.

Since the electron may be generated from any kind of matter, it was only natural that it should be regarded as a universal constituent of atoms. But as the electron is essentially negative, the atom must also contain positive electricity in order that it should be electrically neutral, and since likewise the mass of an electron is minute compared with that of the lightest atom, the main mass of the atom is in all probability associated with positive electricity. It remained then to determine, first, how the electrons were related to the positive part of the atom, secondly, how many electrons were contained in an atom. J. J. Thomson's first hypothesis that the electrons were distributed through a sphere of positive electricity uniformly occupying the whole bulk of the atom has been discarded in favour of Rutherford's theory that the positive electricity

is condensed in a single nucleus surrounded by electrons, the sum of the negative charges of which is equal to the positive charge in the nucleus. It was soon discovered from a study of the scattering of α -rays by the atom and the intensity of scattered X-rays that the number of electrons in an atom was comparatively small, being indeed about equal to half the atomic weight. The admirable work of Moseley on the characteristic X-radiation of the elements defined with certainty what we know as the atomic number of the elements, and it was an easy step to recognise in this essentially integral number the number of electrons surrounding the nucleus. Here we have definite material for the construction of an atomic model. For a given atom we know the nuclear charge and the number of electrons corresponding with it, and it only remains to find an arrangement of the electrons about the nucleus which shall correspond with known chemical and physical data.

In the atomic model of Bohr, the electrons move in orbits round the nucleus much as planets move round the sun; and on certain assumptions regarding these orbits Bohr has been able to calculate the wave-lengths of the spectral lines of the simpler elements with an almost uncanny accuracy. This type of atomic model satisfies the physicist, but it offers to the chemist no adequate account of valence. The chemist therefore naturally turns to the Lewis-Langmuir model, in which the electrons are ranged round the nucleus in successive shells and are regarded for schematic purposes as being at rest. That the electrons tend to form stable octets is taken as the fundamental principle in atom-building, and on this principle the main facts of valency may be accounted for. Only the electrons of the outermost shell are affected in chemical actions, and by suppositions as to the transference of such electrons from atom to atom, or the sharing of electrons between atoms, a moderately satisfactory picture of chemical combination and chemical compounds may be formed.

These two models, each satisfactory in its own sphere, are, however, irreconcilable: in one, the electrons move in orbits round the nucleus; in the other, they are fixed, or move about fixed points external to the nucleus. In science there can be no compromise in the strict sense, but only compromise in the sense in which a baby may be regarded as a compromise between its parents. It is to be hoped that these two apparently antagonistic atomic models may be the progenitors of a new atomic model which will satisfy physicists and chemists alike.

As has been said, it is only the electrons of the outermost shell that interest the chemist for his everyday purposes: they alone play a part in chemical reactions. The nucleus and kernel of the

atom are beyond the reach of his reagents. But the philosophical inquirer must not be limited to commonplace reactions. The nucleus is all-important for the explanation of radioactive disintegration. It is the nucleus which expels a charged atom of helium as α -particle, it is the nucleus which primarily expels an electron as β -particle, although in the end the outer electrons are thereby affected, with consequent changes in valence and chemical properties in accordance with the well-known scheme of Soddy and Fajans. As Sir Ernest Rutherford showed in a recent lecture to the Society, the nucleus of ordinary atoms is not immune from external attack, vigorous bombardment by fast α -particles leading in some cases to its disintegration.

The subject of isotopy is also primarily concerned with the atomic nucleus. The conception first arose in connexion with the radioactive elements, the scheme of disintegration leading to the necessity of acknowledging elements which differed in their radioactive properties (that is, in the behaviour of their nuclei) and were yet chemically identical. The powerful positive-ray method of Thomson, since modified by Aston and others, has shown that isotopy is far from being restricted to the radioactive elements, at least half the ordinary elements so far studied being, not simple, but mixtures of isotopes of different atomic weights. The atoms of such mixtures differ in their nuclei, but are identical in their outer electrons, and therefore in their chemical properties.

Theories of the structure of the nucleus are now based on the assumption that the nucleus of each atom is composed of hydrogen nuclei closely packed together with electrons. The weight of the atom is essentially determined by the number of hydrogen nuclei it contains, the positive charge of the nucleus (or the number of external electrons) is equal to the excess of hydrogen nuclei over electrons in the atomic nucleus. We have thus reverted to the hypothesis of Prout, promulgated more than a century ago, that all atoms are composed of hydrogen atoms, or rather of hydrogen nuclei. The "philosophical" atoms are therefore no longer the atoms of Dalton, but the electron, and the hydrogen nucleus or proton. Whether in these two there will be revealed an ultimate unity, we may leave without too much anxiety to the future.

We chemists have looked into the structure of the atom, not merely with the instruments, but with the eyes of the physicists, and to them again we are indebted for our knowledge of the structure of crystals. The work of Laue and of the Braggs on the refraction and reflection of X -rays by crystals has already yielded results of the greatest import. We know definitely how certain atoms and groups of atoms are arranged in crystals, and even the

arrangement of electrons in atoms does not seem beyond the scope of the method. An interesting side-light too has been thrown on colloidal solutions, it having been shown, for example, that the colloidal particle of gold is crystalline and has the same crystal structure as massive gold.

When we turn from the structure of the atom to the source of its activities we find another physical conception indispensable for its comprehension—the quantum theory of Max Planck. Originally proposed to account for the facts of radiation, this theory has proved a most powerful weapon of attack in physico-chemical problems of the most varied description : nothing seems beyond its range. It can be applied to the discussion of physical and chemical equilibria, to the atomic heats of solids, the molecular heats of gases, the absorption spectra of liquids, photochemical reactions, catalysis, and chemical action in general. It seems indeed to be a key which can open all doors, although the nature of the key is itself obscure.

Finally, we owe to the all-pervading theory of relativity the interesting suggestion that the difference between the mass of the hydrogen nucleus as found in other nuclei, namely 1.000, and the mass of the hydrogen atom, 1.0076, is due to the close packing of nuclei, the vanished mass having assumed the form of energy.

I fear that this recital of our obligations must have proved somewhat depressing to a chemical audience. Can we do nothing theoretical for ourselves? Within our special province we can and do. The chemist's chief concern is, after all, with material change. He has built up and is still elaborating a theory of the molecule, particularly of the organic molecule, which gives expression to the changes that occur when the molecule is being formed from other matter, or is being converted into other matter. But if the analysis of properties and phenomena is to be carried back to pure dynamics or electromagnetics, he is in the end dependent on the physicist, who is a specialist in these matters. This being so, are we content with acknowledging the obligation? Can we not in some measure repay it? One humble means of repayment is to provide the physicist with a variety of materials—pure materials—which he may study. But there is another of a much more fundamental character. By placing our theoretical requirements before the physicist we suggest to him new fields for cultivation, and provide a fresh stimulus to his research. This is a general method of repayment of the more concrete to the more abstract sciences. A firm insistence on the fact that no atomic model can be regarded as satisfactory by the chemist unless it accounts in a simple way for the phenomena of valency may guide the physicist to altogether new conceptions.

This repayment may strike even us as inadequate, but we have the satisfaction to know that if our wares are of comparatively little utility to the physicist, they are highly prized by the physiologist. The modern physiologist revels in colloids, osmotic pressure, and hydrogen-ion concentration, and thereby increases our activities by setting us problems which we feel bound to solve. Thus the exchanges between the sciences, although often one-sided, are always beneficial and foster the growth of science as a whole.
