SCIENCE

A WEEKLY JOURNAL DEVOTED TO THE ADVANCEMENT OF SCIENCE, PUBLISHING THE OFFICIAL NOTICES AND PROCEEDINGS OF THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

FRIDAY, NOVEMBER 24, 1905.

CONTENTS.

MSS. intended for publication and books, etc., intended for review should be sent to the Editor of SCIENCE, Garrison-on-Hudson, N. Y.

THE RELATION OF PHYSICAL CHEMISTRY TO PHYSICS AND CHEMISTRY.[1]

ACCORDING to the program, I have to consider the 'General Principles and Fundamental Conceptions which connect Physical Chemistry with the Related Sciences, reviewing in this Way the Development of the Science in Question itself.'

Let me begin by defining physical chemistry as the science devoted to the introduction of physical knowledge into chemistry, with the aim of being useful to the latter. On this basis I can limit my task to the relations of physical chemistry to the two sciences it unites, chemistry and physics.

But even if I limit myself to these relations, which are not the only two,[2] I wish to restrict myself yet more, in order, in the spirit of this congress, to call your attention to broad views. So I shall follow up only two lines, in answering two questions regarding two fundamental problems in chemistry: (1) What has physical chemistry done for our ideas concerning matter? (2) What has it done for our ideas concerning affinity?

The small table which I have the honor to put before you will enable us to answer these questions by appeal to the scientific development of our science, which also I have to review:

I. IDEAS CONCERNING MATTER.

1. Lavoisier, Dalton (1808).
2. Gay-Lussac, Avogadro (1811).

---

[1] Read before the International Congress of Arts and Science.

[2] In Chicago I devoted to this subject eight lectures, which have since appeared in the Decennial Publications under the title 'Physical Chemistry in the Service of the Sciences,' Chicago, 1903.

3. Dulong, Petit, Mitscherlich (1820).
4. Faraday (1832).
5. Bunsen, Kirchhoff (1861).
6. Periodic System (1869).
7. Pasteur (1853), Stereochemistry (1874).
8. Raoult, Arrhenius (1886–7).
9. Radioactivity (Becquerel, Curies).

II. IDEAS CONCERNING AFFINITY.

1. Berthollet, Guldberg, Waage (1867).
2. Berzelius, Helmholtz (1887).
3. Mitscherlich, Spring (1904).
4. Deville, Debray, Berthelot.
5. Thomsen, Berthelot (1865).
6. Horstmann, Gibbs, Helmholtz.

I. PHYSICAL CHEMISTRY AND OUR IDEAS CONCERNING MATTER.

The Concepts of Atoms and Molecules.—Regarded as a whole, we may say that the initial application of physical knowledge for the purpose of developing our ideas of matter consisted chiefly in the employment of physical methods and instruments in the study of the properties of matter. This stood foremost in physical chemistry in the first period of its existence.

Reviewing the history of chemistry, we must acknowledge that one of the first fundamental steps was made by the study of the physical property of weight, and the introduction of a physical instrument, the balance, for this purpose. It was, in large part, on this basis that Lavoisier was the great innovator of chemistry; and it was due solely to the following of chemical change with the balance that chemistry got its fundamental laws of constant weight and of constant and multiple proportions. These were summarized by Dalton in the fruitful though hypothetical conception of atoms, which, as is well known to you all, asserts that every element exists in the form of small unchangeable particles, identical for a given element, but differing with the latter.

As the study of weight led to the idea of atoms, so the study of another physical property, that of volume and density, led to our idea of molecules. These molecules, which might be described as constellations of atoms, were a necessity with Dalton's conception; but, in a binary compound, for instance, they might consist of two atoms or of twenty. Now, it hardly needs to be recalled that Gay-Lussac, and especially Avogadro, in following the volume relations of gases in chemical action, drew the conclusion that the molecules of gases occupy equal volumes under identical conditions. Thenceforward we had a reliable method for determining the relative weights of such molecules.

As the study of the physical properties weight and volume led to the concepts of atoms and molecules, so sharply defined that the relative weights of these entities form the fundamental constants of chemistry, so a further study of physical properties has led to broad generalizations concerning the nature of atoms and molecules, which we shall now outline.

Properties of Atoms.—As to atoms, I would call your attention to four peculiarities which seem to me of fundamental importance. First, Dulong and Petit found that the physical property called heat capacity is nearly the same for different atoms, *i. e.*, that the quantity of heat requisite to produce a given rise of temperature does not vary greatly for atomic quantities, for 7 parts of lithium and for 240 parts of uranium.

Second, Faraday, in studying the electrical conductivity of electrolytes, *e. g.*, of aqueous solutions of salts, found that the quantity of electricity which atoms can transport varies as the whole numbers,—from one in potassium to two in zinc. This fundamental property, which gives the sharpest expression to our notion of valency, was brought by Helmholtz into a very clear form by the assumption that electricity as well as matter consists of atoms, either negative or positive, and that material atoms are able to combine with them—potassium with one of the positive kind, zinc with two, chlorine with a negative one,—and so transport them in electrolysis.

The third great step was made by the study of light, a physical property again. Bunsen and Kirchhoff found that, heated in the gaseous state, every atom emits a definite set of light waves, producing a characteristic line-spectrum which is yet the sharpest test of the kind of atoms one is dealing with, and which so became the most fruitful guide in the detection of new kinds.

The last generalization that I have to mention, and which we owe to Newlands, Mendeléeff and Lothar Meyer, includes physical properties in general, and asserts that they vary with increasing atomic weight in a periodic way. This shows itself most sharply in the atomic volume, which passes through maximum values in lithium (7), sodium (23), potassium (39), rubidium (85) and cæsium (133). A corresponding periodicity is observed in other properties, as, for example, that of combining with electrical atoms or valency, which in the said elements passes through unity. Analogous behavior is exhibited by the melting points and boiling points, which for these metals are exceptionally low.

If my program did not to a certain extent exclude quite recent investigations, confining me to a view of past history, I should like to consider one more physical property, that of radioactivity, which also seems to be a property of atoms. I can only insist on the fact that it was physical properties again, the making the air conductive for electricity, and the spectrum, which revealed radium.

Properties of Molecules.—Turning to molecules, I have three predominant generalizations to outline. The first is Mitscherlich's discovery of the fact that analogous molecular constitution corresponds to analogous outer crystalline form, to so-called isomorphism. Let me add that there is hardly any more satisfactory proof of the soundness of our concept of the internal structure of matter than, *e. g.*, the identity of the crystalline forms of the alums, which we consider to have corresponding internal structure.

A second step, to a certain extent a similar one, was made by Pasteur when he deduced disymmetry of molecular constitution from disymmetry in behavior, optically as well as crystallographically. For instance, the dextrorotatory ordinary tartaric acid and its lævorotatory antipode showed this disymmetry both in optical rotation and in the particular so-called enantiomorphous crystalline form. The molecules were supposed to have analogous structures differing from each other as the right hand from the left. As is well known, it was only later that the probable molecular structure was sharply defined, and stereochemistry was founded.

The third great step was the opening of a way to determine the molecular weights of dissolved substances. It was chiefly the application of Avogadro's law to osmotic pressures, in connection with Raoult's measurements of freezing points and vapor pressures, that opened the way. We may now assert that the liquid state is not characterized by high molecular complexity. But the great innovation, introduced by Arrhenius and immediately brought into relation with the achievement in question, was the admission of the existence of ions in electrolytes—for example, the presence of negatively charged chlorine atoms and positively charged sodium atoms in an ordinary salt solution. Once more it was a physical property, the electrical conductivity, that led to this extremely fruitful supposition.

Conclusion.—If, after this short summary of its properties, we try to look into the nature of matter, we conclude that matter is not continuous, but that there are centers of action which seem to have an eternal existence, changing only in the place that they occupy—these are the atoms. They keep together in some way and form the molecule; how, it is pretty hard to say. The planetary constellation, with ordinary attraction and centrifugal force in equilibrium, is excluded by the consideration that at the absolute zero there is no movement at all. The repulsive force that we want might be of electrical nature; and so we come to our combination of material and electrical atoms. There is indeed something fascinating here, and when we admit for carbon that it may unite to four equally charged electrical atoms and hold them by a force of the nature of elasticity, we have at once a possible equilibrium and the tetrahedral grouping. My only difficulty is that an uncharged atom of carbon, coming into contact with the ions just described, would take away half the electric charge, and so the valency of any element might be reduced to unity. The latest supposition, that matter is built up of electricity alone, lies again beyond the scope of this address.

Let me now turn to the second part of my subject, and touch upon the problem of affinity; indeed, the action that keeps atoms together must be closely related to affinity.

II. PHYSICAL CHEMISTRY AND OUR NOTIONS CONCERNING AFFINITY.

While physical chemistry, in the first period of its development, was chiefly devoted to the study of the physical properties of matter, the second and present period is characterized by the predominant place of the problem of affinity.

This change in the general aspect of our science goes hand in hand with a different way of working: in the development of our ideas of matter, physical chemistry introduced physical methods and instruments for the study of physical properties; in the development of our ideas of affinity, physical chemistry has introduced physical principles.

Affinity Considered as Force.—The first line of thought considered affinity as a force, and in this direction it was natural to think of the Newtonian attraction as the chemical agent. So it was that Berthollet, and with far more success Guldberg and Waage, applied the laws of mass action to problems of affinity, formulating a relation still known as the mass law, according to which affinity is proportional to the weight in the unit of volume.

Now, as we all know, affinity is of a specific nature, and does not depend on weight merely; on the contrary, the least heavy elements are generally the most active. So Berzelius built up his system founded on the notion that elements have a specific electrical character, either positive or negative, and, in combining, act by electrical attraction. In this direction Helmholtz made a further step in taking into account the quantitative side. Considering the electrical charges involved in Faraday's law, he pointed out as very important that the attraction due, for instance, to the negative charge in chlorine and the positive one in hydrogen far exceeds the gravitational attraction of the masses. Yet a satisfying notion of affinity was not obtained in this way.

Affinity Measured as Work.—A second line of thought took into consideration not the force but the work that affinity represents; and it seemed a decisive step when Thomsen and Berthelot declared that the heat developed in chemical change corresponds to the work that affinity can produce. Indeed, it was in this way that in many cases an *à priori* calculation of the heat development of a reaction permitted prediction of the direction in which the process would proceed, the direction being that of the evolution of heat. Yet, this principle, however weighty, is not absolutely reliable. The chemical actions that produce cold, as that of hydrochloric acid on sodium sulphate, are objections not to be overcome.

The step really leading to a clear and unobjectionable notion of affinity was made in the study of the so-called reversible chemical changes. This reversible character perhaps needs some explanation, easily to be provided by an illustration. Kill a chicken and prepare chicken soup; it would then be very difficult to get your chicken again. This is because preparing chicken soup is not reversible. On the contrary, let water evaporate or freeze; it will be easy to reproduce the water.

Now, at first sight, chemical change does not seem reversible; and indeed it often is not, as in the explosion of gunpowder. But investigations of Berthelot and Péan de St. Gilles on the mutual action of acids and alcohols, and those of Deville and Debray on high temperature action, which even splits up water, have shown that many chemical changes can be reversed. Indeed, we have types corresponding absolutely to evaporation, as the loss of water vapor from hydrates; and others corresponding as well to freezing and melting, as the splitting of double salts into their components at definite temperatures, *e. g.*, copper calcium acetate at 77° C. Also in analogy with physical phenomena, we have in these reversible chemical changes the possibility of equilibrium, the two chemically different forms of matter coexisting, as do water and its vapor at a maximum pressure.

Such a reversal of chemical change can take place under the influence of temperature, of electricity, of light, of pressure. And the easiest way to arrive at a measure of affinity is presented in the last case, as was foreseen by Mitscherlich. Let us take gypsum as an example. Burnt commercial gypsum, mixed with water, will combine with the water. We know that this chemical change can produce pressure, and that it may be prevented by sufficient pressure and be reversed by it, as Spring succeeded in pressing out sulphuric acid from sodium bisulphate. And it is possible in such cases exactly to determine the limiting pressure, such that a higher one presses out the sulphuric acid while a lower one is overpowered by the affinity action. If the chemical change takes place under a pressure only slightly less than that which would prevent it, thus practically taking place under the limiting pressure, we get out of affinity the greatest quantity of work that it can possibly produce; and this quantity is the same whatever the nature of the opposing action, be it electricity, light, or anything else. Therefore, in this maximum work we have a sound measure of affinity.

It was a very happy coincidence indeed, that this conception of affinity made possible the application of a physical principle known as the second law of thermodynamics. This principle may be formulated in different ways. For my purpose let me say that it limits the possibility of natural processes to the occurrence of those in which a difference of intensity is diminished. If there is a difference of pressure in two parts of a gas, a movement will occur producing equality; if there is a difference of temperature, heat will be transported so as to produce equality once more. It is curious that such simple necessities, which we all feel as such, can be converted into far-reaching sharply formulated equations, as was done by Carnot and Clausius. These principles were first applied in chemistry by Horstmann. Then, by successive application to chemical problems by Massieu, Gibbs, Helmholtz and others, was won a system of relations touching the problem of affinity, to which I can give only brief attention:

1. Affinity may be defined as the maximum quantity of work that a chemical change can produce. Equilibrium ensues when this quantity is zero.
2. The mass law can be obtained in a well-founded and somewhat modified form, restricted to dilute gases and solutions.
3. The Thomsen-Berthelot principle assumes a modified form in the rule that a fall of temperature induces the formation of that which develops heat. It is, for instance, in accordance with this rule that at ordinary temperatures water is stable in comparison with detonating gas, and that at high temperatures this relation is reversed, as it was found by Deville to be.
4. Lastly, we have the phase rule, indicating, for example, in what cases chemical phenomena will be comparable with melting and freezing, and in what cases they will be comparable with evaporation and condensation.

Most curious of all, we can treat problems of affinity in an absolutely trustworthy way, so that our calculations furnish a check upon experiment, without admitting anything concerning the nature of affinity or of the matter wherein the affinity is supposed to reside.

J. H. VAN 'T HOFF.

THE PROBLEM OF RENAL FUNCTION.[1]

IN my first lecture I touched upon a series of physiological problems that have been elucidated in a pharmacological way. I treated these problems in a merely cursory manner and did not enter upon details of the various investigations. Permit me to-day to discuss more fully a problem which has for a long time claimed my attention and which has for many years been a topic of research in my laboratory, namely, the problem of renal function.

As is well known, there are two leading and opposing theories on the nature of urinary secretion. According to one of these theories, which was developed most fully by Heidenhain, we have to deal with a true secretory process by which water and perhaps the salts pass through the glomerulus, whereas the specific constituents of the urine are liberated from the tubules so that the sum of both secretions is represented by the outflowing urine. According to the other hypothesis, which was first proposed by Ludwig and subsequently modified (in a biological sense) by his successors, there goes on in the kidney, side by side with the glomerular activity, dependent essentially on the mechanical conditions of the circulation, and independently also on the secretion of certain urinary constituents, a process of resorption in the urinary tubules. Through this resorption the slightly concentrated secretion of the glomerulus, corresponding to the water of the blood, undergoes concentration to a point characteristic of the urine.

The output of urine is chiefly conditioned on the largely physical excretory process, which, on account of its dependence on the blood flow, and the blood pressure in the kidneys, one is justified in regarding as a kind of filtration or transudation. On the other hand, the resorption of water through the tubules is not directly dependent on the circulation of the blood. That is, it is in nowise proportional to the abundance of

---

[1] Being the second of the Herter Lectures delivered at the Johns Hopkins Medical School.