loids, upon which life phenomena so largely depend. In a recent volume on "Proteins and the Theory of Colloidal Behavior" (1922) he contends that the behavior of colloids may be explained by the ordinary laws of chemistry without recourse to theories based on adsorption. As in earlier researches he had found a clue to the solution of many problems by applying the theories of electrolytic dissociation and osmosis, so in the work of his later years he discovered a guiding principle in the theory of the Donnan equilibrium. By applying this he was able to give quantitative explanations of some of the most important properties of proteins and to reduce them to simple mathematical laws. These studies, important for chemistry as well as for biology, form a fitting termination of his activity.

Thus closed a career rich in the joy of pioneer adventure in fresh fields of thought, abounding in brilliant discoveries, and splendidly stimulating far beyond the boundaries of biology. It will always stand out as a poriment feature of the progress of biology toward the status of an exact science. It is a career which reveals everywhere a creative imagination and capacity found only in minds of the highest order.

W. J. V. OSTERHOUT

# THE SUBJECT-MATTER OF A COURSE IN PHYSICAL CHEMISTRY<sup>1</sup>

THIS is not intended to be a pedagogical paper. Rather, it is proposed to review briefly the recent progress in theoretical chemistry with the idea of suggesting how the content of the more or less classical course in physical chemistry should be altered. It is quite likely that recent progress will indicate that the emphasis should be shifted from some subjects to others, and it is not unlikely that some of the ideas we have been imparting to the students in the past may in the light of recent developments prove erroneous.

Some instructors in political science, I believe, are wont to present to students the various theories of applied government, old and new, without prejudice, leaving the student to choose for himself those which appear the more logical or feasible. The student thus occasionally becomes infatuated with some highly ingenious theory such as the single tax, to the great disgust of conservative tax-payers who proceed to denounce the university for the inculcation of radical ideas. Now such procedure may be entirely justifiable in the more controversial sciences, but it does not appear desirable in the teaching of theoretical chemistry. In the first place, theories in chemistry are

<sup>1</sup> Paper presented at the Cincinnati meeting of the American Association for the Advancement of Science, Section C. subject to immediate experimental verification and while the results are sometimes ambiguous, if a theory has failed to establish itself after years of experimental test, we may conclude that it is badly conceived, or at least not likely to prove fruitful as a guide to new facts. In the second place, in the limited time available, we can scarcely make the undergraduate familiar with the well-established fundamental principles of theoretical chemistry, and we certainly have little time to spend upon matters of speculation and controversy.

The logical although perhaps not the best psychological way to begin a course in physical chemistry is to develop the concept of the atom and its structure. If we begin this way, the laws of combining weights and multiple proportions become mere axioms, while the experimental work in radio-activity. X-ray study of crystallography and positive rays become exhibit A in proving the case for the existence of the atom. To begin the structure of the atom, we have the Rutherford nucleus, although recent work is said to show that the experiments which Rutherford used to demonstrate the existence of a small nucleus might equally well be used to prove that the atom had the constitution originally assumed by J. J. Thomson. Nevertheless, the work of Bohr and Lewis has given us a picture of the structure of the atom which is sufficiently definite and which explains the necessary and important properties of the atom. While this picture leaves many things to be desired, the evidence for its validity is as direct and abundant as was the evidence thirty years ago for the existence of the atom itself. And one of the greatest mistakes that the physical chemist has made was his adoption under the leadership of Ostwald of an agnostic attitude toward the existence of the atom.

One of the most important things that we can do is to give the student an up-to-date model of the periodic table. The old Mendeleieff table attempted to show only the chemical relationships of the elements and it did that rather badly as its author himself realized. An improved periodic table ought (1) to be based upon atomic number instead of atomic weight, (2) it ought to show the number of valence electrons, (3) it ought to show the number of shells of electrons, (4) it ought to show the real chemical resemblances, (5) it ought to indicate the degree to which the element possesses the property whose presence is variously designated as electronegativity or acidity and whose absence is termed electropositivity or basicity. Now in the nature of things it is not possible to arrange a table which will comply completely with all these requirements. If anything is to be sacrificed. I should prefer it to be some of the far-fetched chemical resemblances.

Any arrangement of the periodic table should pre-

serve the Rydberg periods. The arrangement which seems to be most instructive is one of 16 columns and 7 rows. Each row represents a shell of electrons and the maximum number of valence electrons is characteristic for each column, starting with 1 for the alkali metal column at the left and running up to 8 for the platinum group, then starting over again with 1 for silver and increasing up to 8 for the rare gases. In such a table the transition groups, such as iron, cobalt, nickel, the platinum metals and the rare earths, are each assigned a single place in the table. Cerium is the one element which might appear twice in the table. Hydrogen is placed with the halogens. The only important chemical resemblances not shown are relations such as that of Mg to Zn and these relations can be very nicely indicated if we draw dotted lines dividing the table into zones of equal electron affinity.

The amount of information presented to the eye by such a table is enormous and it is my opinion that with nothing more than Coulomb's law, the mathematical physicist will some day calculate the chemical properties of every element quantitatively. At any rate, with nothing more than Coulomb's law and the concept of successive electron shells we can predict qualitatively the electronegativity of every element.

I had hoped that we might be able to substitute electron affinity or ionizing potential for the wretched term electronegativity, but these quantities are measured for the gaseous state and our ordinary chemical properties are concerned with the condensed phases. For instance, the electron affinity of the chlorine atom is less than the ionization potential of sodium, so that a chlorine atom should never rob a sodium atom of its electron, and yet nothing is more certain than that it does so in a solution of sodium chloride.

And while we are on the subject the greatest need of the theoretical chemist to-day is a definite concrete language. Some of you have, no doubt, been wondering how we are going to give our students a complete understanding of the chemical properties of the elements in terms of atomic structure, when there is so little agreement among the leaders in thought in chemistry as to the interpretation of the facts. Well, as a matter of fact, the reason that so few chemists agree on anything is that so few chemists talk the same language. The curse of the chemist is the use of indefinite expressions. The so-called chemical intuition about which we hear so much is nothing more than the ability to recognize an obvious experimental generalization even when it is couched in language that is ambiguous and indefinite. Somebody has said that one of the social sciences expresses things that everybody knows in language that nobody can understand, but this statement is dangerously near to being true of the jargon of the theoretical chemist. Such

expressions as polar, negative, electronegativity, residual affinity, partial valency, unsaturation, etc., have been used over and over again with radically different meanings, often in the same article. It is for this reason that most of the speculative articles which have been published regarding the important chemical properties which these words are supposed to represent, will, when translated and analyzed, be found to be the purest nonsense.

The development of the laws of combining weights and multiple proportions by inductive reasoning (assuming that they were arrived at in that way) constitute one of the most difficult achievements of the human mind, and the teachers of chemistry are so impressed with this achievement that, on the one hand, they try to make the freshman repeat it, which is disastrous for the freshman, and, on the other hand, they continue to talk chemical phenomena with inductive vagueness when they should be doing a little deductive reasoning from Coulomb's law of electrostatics.

Recently a book has appeared whose main theme is the beauty of the scientific method as a means of drawing accurate conclusions from existing data and the desirability of extending this method to the political affairs of mankind. Now whether this book be overly enthusiastic or not, the fact remains that the members of this meeting could not agree upon any single fundamental statement of the relation of chemical properties to atomic structure. I believe, however, that the reason is chiefly that no two people would be trying to say the same thing, let alone use the same language. The older generation of chemists in conclave is in the same predicament as the multitude that happened to be present at the raising of the tower of Babel. The only hope is with the vounger generation. If we teach them the electrical nature of matter, make the electron a reality with the fundamental laws of physics as a working rule, then we will have a generation of chemists who will be able to converse with one another. Nor is this ambiguity confined to the chemist. When I hear a physicist speak of a Helmholtz double layer it always gives me a hopeless feeling. In the early stages of science, when investigators were struggling in the dark, it was inevitable that their communication with each other would be difficult, but now that the light has been turned on we should become articulate. Let us hope that the near future will bring us many of the sort of clarifications of meaning that G. N. Lewis achieved when he pointed out that an acidic group was one that was seeking a pair of electrons and a basic group was one that had a pair of electrons that it was willing to share.

The kinetic theory ought to be given a greater emphasis than ever before. The derivation of the perfect gas law from kinetic theory is the most elegant piece of reasoning we have in physical chemistry. The time usually spent on deviations from the perfect gas law and Van der Waal's equation is probably wasted, for we actually treat all gases as perfect in our ordinary work and with reason. I wish that we could say as much for the perfect solution.

The rapid progress of the quantum theory means that the chemist of the future must study the kinetic theory from the standpoint of statistical mechanics. I should be surprised if there is any process of chemistry to which the quantum theory will not be applied. Processes such as rates of reaction, which we have always supposed to be continuous, are being found on close scrutiny to be discontinuous. The people who a year or two ago became excited over radiation as a cause of chemical action overlooked the fact that the kinetic theory together with the quantum theory will explain any phenomenon so far disclosed in regard to rate of reaction. The mechanism of evaporation is to be explained by the kinetic theory. But the student must be taught the kinetic theory from the standpoint of statistical mechanics. Maxwell's law of distribution for the total kinetic energy of a gas molecule is probably the most useless expression in molecular physics. I believe that shortly we will be teaching juniors the methods of statistical mechanics, which, a few years ago, were buried in the works of Boltzman and Gibbs.

On the other hand, it is a clever teacher who can give an honest presentation of the laws of solutions and retain the respect of his students. The perfect solution is almost a fiction of the imagination. Until we can get some kind of an empirical equation of state for solutions that will serve as an approximation, I suspect we are wasting time on solutions. Perhaps we could lump these doubtful subjects which do so much to discredit chemical theory with the student under a chapter on the "Experimental determination of limiting values." Thus we can show the student that exact molecular weights of gases may be calculated from limiting densities, the exact molecular weights in solution from freezing points of very dilute solutions and accurate percentage ionization for weak electrolytes from conductivities, if the electrolytes are weak enough. Put in this way we are teaching a scientific method of great beauty and usefulness, but we should make a great mistake if we try to pretend to the student that we know anything about solutions.

The next topic that we must consider is the one that monopolized physical chemistry for 30 years to its detriment, I fear, *viz.*, the ionization of electrolytes. The followers of Ostwald talked about the migration of hydrogen ion instead of hydrogen ions because they didn't believe in atoms and it is no wonder that their thinking was rather ineffective. At any rate, omitting mention for lack of time of a number of attempts in this direction, the first successful application of the laws of electrostatics together with the kinetic theory to solutions of strong electrolytes has been made by Debye within the present year. We can not hope to treat concentrated solutions of strong electrolytes until we know the exact dimensions of ions, nor can we hope to calculate irreversible phenomena such as conductivity. But in dilute solution, Debye's theory leads to exactly the same equation for the lowering of freezing points by electrolytes that was deduced empirically by G. N. Lewis from a scrutiny of all existing data. I think Debye's work must revolutionize our treatment of strong electrolytes. Debye assumes the existence of a completely polar electrolyte. Now probably there are no completely polar electrolytes, just as there are no perfect gases, but we have real gases like helium that are very nearly perfect and we must admit that a salt like potassium chloride is very nearly completely polar. Debye's picture of an electrolyte in solution is that the positive and negative ions are not distributed at random, but that there is a tendency for a positive ion to be surrounded by negative ions and vice versa. Thus, even in the most dilute solutions with which we work, the ions are still close enough together to exert appreciable attractions on each other and cause a negative deviation from Rault's law. You see what this does to the concept of dissociation. If we say that an ion is dissociated only when it is out of the sphere of influence of any other ion then a 0.001 molal solution of potassium chloride is completely undissociated. On the other hand, if we say that two ions are dissociated unless they are arranged exactly as in the crystal, then a solution of potassium chloride is practically completely dissociated at any concentration. All this, of course, applies to strong electrolytes. The dissociation of acetic acid is undoubtedly a chemical reaction with a true equilibrium.

Apparently one feature that should receive more emphasis with students is the nature of ionic reactions. The typical ionic reaction is of a radically different behavior from the typically non-ionic reaction and yet many chemists to-day fail to perceive the distinction. We can always detect the presence of ions by conductivity. The forces of an ion are free and an ion is always ready to react. On the other hand, reactions between molecules require that the molecules collide with some critical momentum and a proper orientation. Molecular reactions are slow, ionic reactions are rapid. Typical examples are the precipitation of  $BaSO_4$ , on the one hand, and the hydrolysis of an ester on the other.

Also, if the student is to understand and compre-

hend he must be taught to think in terms of hydrogen ion concentrations. The use of pH is like the use of degrees Beaumé. Specialized industries like to develop their special jargon. It makes numerical details easier to remember and it makes the outsider feel more ignorant. It is all right to use pH if you know what it means. Likewise, one might say for the benefit of our friends in the allied sciences that it is all right to use a hydrogen electrode if you know what you are doing.

There remain only two or three topics to mention. The phase rule is apparently becoming relatively less important in theoretical chemistry. Of rates of reaction and the mass law in solutions we shall have to speak softly. But equilibrium and rate of reaction in the gaseous phase has become of greater interest than ever from recent experimental work, and the student is not likely to get too much of them.

In this paper it is hardly necessary to mention thermodynamics, the faithful handmaiden of physical chemistry. Twenty years ago, we had many branches of exact science, mechanics, electrodynamics, etc. The wave of heresy known as the quantum theory came. Perhaps it will pass. At any rate, to-day the only branch of physical science in which we put an unfaltering trust is thermodynamics.

The early chemists started to develop the idea of chemical affinity. Then they met with the phenomenon of chemical equilibrium and they abandoned the affinity idea in favor of the law of mass action. But each view is partially right. Atomic structure tells us of chemical affinity; statistical mechanics predicts the effect of thermal energy; what happens to matter is the resultant of the action of these two agents. Apparently the theoretical chemistry of the future will consist almost entirely of these two subjects.

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## THE HARVARD BOTANICAL GARDEN IN CUBA

### A TROPICAL STATION FOR GENERAL BIOLOGICAL RESEARCH

Some twenty years ago, Mr. E. F. Atkins set aside a portion of his estate at Soledad near Cienfuegos, Cuba, for development into a tropical botanical garden, with special facilities for plant breeding. At an early date Mr. Atkins secured the cooperation of the late Professor George L. Goodale and of Professor Oakes Ames to help carry out his plans, and since this time the work has progressed continuously.

Mr. R. M. Grey, the superintendent during this period, has been indefatigable. A collection of nearly two thousand species of tropical plants has been

brought together from various parts of the world, including particularly fine aggregations of palms and of tropical fruits. All the important fruits of the tropics are now represented, the varieties of mangos, of citrus fruits and of avocados being especially extensive. In addition, a great many crosses have been raised and tested on a large scale. Mr. Grey has been particularly interested in sugar cane breeding, and his work on this crop has been second to none in the Americas, but his work on citrus fruits, cotton, mangos and guavas is also worthy of mention.

From these statements, it will be seen that the Harvard Botanical Garden in Cuba has long been a going concern, with exceptional facilities for tropical research in botany. Unfortunately, the garden has not been able hitherto to accomplish the purpose for which it was designed by its founder, because of the lack of laboratory and of living quarters.

Through the generosity of Mr. Atkins, this difficulty has now been removed, and it is the hope of both the founder and the corporation of Harvard University that the garden will become one of the centers of tropical research in America. There is a substantial endowment for work, and a handsome brick and stucco building which is to serve both as laboratory and living quarters for investigators.

### LOCATION OF THE GARDEN

The Harvard Botanical Garden is on the southern side of Cuba six miles from Cienfuegos and may be reached by rail from Havana in about nine hours. The land on which it is situated is the rolling plain typical of the sugar estates of Santa Clara province. The garden itself is well watered and furnishes soils of several types upon which almost every sub-tropical plant can be grown to advantage. Near the garden is a second-growth jungle of several acres. Twenty miles to the east lie the Trinidad Mountains rising over 2,000 feet from the surrounding plain, partly untouched by the cultivator and partly planted to coffee. To the south, reached in one hour by boat from Soledad, is Cienfuegos Bay, one of the wonder harbors of the world.

#### FACILITIES FOR INVESTIGATION

The Harvard Botanical Garden in Cuba will be of primary interest to the botanist, but it is really a general biological institution offering extraordinary opportunities to the zoologist and physiologist.

To those interested in land plants and animals, the garden itself will be an inexhaustible source of material. The plant pathologist, the plant breeder, the physiologist and the entomologist need never lack interesting and important problems. The taxonomist, be he zoologist or botanist, will be long in exhausting the possibilities of the surrounding country.