CHAPTER VII

PHYSICAL CHEMISTRY

BY WILDER D. BANCROFT[1]

Early History

The period of physical chemistry in America really began with J. P. Cooke, who lectured at Harvard on the New Chemistry over fifty years ago. He seems to have been the first man to include the concept of the absolute temperature in lectures to chemists. Cooke called his subject "chemical physics" and he labored alone so long that, when the physical chemistry of Ostwald, van't Hoff, and Arrhenius appeared, he did not recognize it as the normal development of his viewpoint. That was a pity; but it is a fate that comes often to pioneers.

The famous monograph on equilibrium in heterogeneous systems by J. Willard Gibbs is in some respects one of the most remarkable scientific articles that has ever been written. Gibbs was possessed of marvelous and apparently unerring insight; but the gift of expression was denied to him. It is not too much to say that Gibbs wrote in hieroglyphics and that a great part of his manuscript is still undeciphered. We know now that we can find in it the chemical potential, the phase rule, and the theory of osmotic pressure; the theory of electromotive forces, the Donnan equilibrium, and the theory of emulsification. We feel certain that some day we shall find in it theories in regard to all sorts of other things; but we do not know when we shall find them. It used to be popular to ascribe the negligible influence which Gibbs had then had on the development of physical chemistry to the fact that his monograph was published in the *Transactions of the Connecticut Academy;* but that fiction cannot be maintained. Everybody knows about Gibbs now; but the only way that one

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[1] There will usually be differences of opinion as to the relative or absolute value of almost any piece of scientific work, and the physical chemists of America are, fortunately for us, extremely individualistic. The opinions expressed in this article are my own and are not necessarily those of the AMERICAN CHEMICAL SOCIETY or of any of its other members.

can find anything new in Gibbs is to discover it independently oneself and then to look it up in Gibbs.

Carey Lea was another pioneer who had no immediate followers. His work on colloidal silver and on the photohalides was remarkable for those days; but the time was not ripe for it. The same thing is true of the work of Barus on the two-phase nature of colloidal solutions. R. B. Warder published work on the rate of saponification of the esters by alkali before Reicher did; but he was not a van't Hoff and he did not have van't Hoff behind him as Reicher did, so the real development was done in Holland and not in America.

The continuous development of physical chemistry in America began in the late eighties when the American students started studying with Ostwald. Morris Loeb was the first to come back; A. A. Noyes was a little later; and the first chair in physical chemistry was founded at Cornell in 1895. The early work consisted in the development of the ideas of van't Hoff, Arrhenius, and Nernst, as expounded by Ostwald; and of the phase rule theory of Gibbs, as expounded by Roozeboom.

Electrolytic Dissociation Theory

While the American physical chemists have, with a few exceptions, been enthusiastic adherents of the electrolytic dissociation theory, the exact measurements and the theoretical developments by A. A. Noyes and his collaborators have changed it to such an extent that there is practically nothing left of Arrhenius' original theory except the conception of ions as independently existing substances. The study of solubilities soon presented such difficulties that Noyes advocated what he called "the dismemberment of the mass law." He threw over the calculation of the dissociation from the molecular conductance and clung to the constancy of the solubility product. Arrhenius showed that the concentration of the undissociated salt is not always constant, which played havoc with the positive part of Noyes' program; but the calculation of electrolytic dissociation presupposes that the migration velocities of the ions are independent of the concentrations, a state of things which we know not to be true in many cases and which may not be true in any case. The carefully made experiments of Noyes, Coolidge, and others on the conductance of salt solutions at different temperatures showed conclusively that the Ostwald dilution law described the facts only for moderate dilutions and then only for weak acids and weak bases. A number of empirical modifications of the dilution law have been suggested—many of them by Americans; but not one is really satisfactory. Making use of the van der Waals formula or of the Keyes equation of state merely adds to the complexity.

Different people have tried different ways of getting at a more exact theory. Morse showed that mass concentrations were better than volume concentrations for calculating osmotic pressures, unfortunately without referring to what van't Hoff had said previously on this point, and thereby missing that the important thing is the volume occupied by the solvent in the solution and not the volume of a given mass of the pure solvent. Jones developed a hydrate theory on the explicit assumption that the van't Hoff-Raoult formula holds absolutely when one chooses the constituents properly. At Cornell we emphasized the statement by van't Hoff that the formula cannot hold if the heat of dilution is not zero. Hildebrand, at the University of California, discards the van't Hoff part of the formula completely. The question of compounds in solution has been considered by Kendall, at Columbia, with reference to freezing points, and by Bingham, at Lafayette, with reference to fluidity. Morgan, at Columbia, has followed the lead of Ramsay and Shields, specializing in associated liquids. The Ostwald theory of indicators has been shown to be inadequate in detail, though sound in principle, and Stieglitz has been influential in developing the chromophoric theory.

Kahlenberg in America, H. E. Armstrong in England, and Traube in Germany are the three irreconcilables, who do not believe at all in the electrolytic dissociation theory. While they have not accomplished what they set out to do and are not likely to, it is interesting to note what Walden has said on this point.

> Both Traube and Kahlenberg have helped along the electrolytic dissociation theory by their criticism of it. The deliberate emphasis on the overhasty generalizations (for instance that all reactions are ion reactions), the logical criticism of the insufficiently explained causes for the dissociation into ions, and the contradictions in the enormous fields of non-aqueous solutions which often rested on inaccurate observations, the planning and carrying out of his own clever experiments on instantaneous reactions in non-conducting solutions, all these can be considered as positive achievements by Kahlenberg because they made it necessary for the upholders of the dissociation theory to make new experiments to clear up their own views, to make limitations, to reconsider their assumptions.* * * Quite irrespective of whether Kahlenberg succeeds in accumulating enough dynamite to destroy the osmotic and electrolytic solution theories, his experimental work is full of interest, because it calls attention to a neglected field, which one can consider as a borderland between organic chemistry and physical chemistry.

The work of Franklin, Cady, and Kraus on solutions in non-aqueous solvents shows that there are many cases where the electrolytic dissociation theory has much harder sledding than in aqueous solutions.

Sutherland was the first to suggest that electrolytes are really dissociated completely at all concentrations, and this view has been adopted by A. A. Noyes, Debye, Brönsted, Bjerrum, and others since the X-ray study of sodium chloride crystals has made it plausible that there are no molecules in these crystals. Harkins recognizes at least three types of dissociation, for he says that a tenth-normal solution of sodium chloride is 100 per cent polarized or ionized, 85 per cent electrolytically dissociated, and 68 per cent thermodynamically dissociated. This is an epigrammatic way of saying something else. If sodium chloride crystals are 100 per cent polarized or ionized, Harkins asserts that they must be the same in solution, though this seems to prove too much because the reasoning would seem to apply equally well to non-aqueous solutions. With regard to the other two dissociations, Harkins merely means that the apparent dissociation, as calculated from the conductance, is 85 per cent, while it is 68 per cent when calculated from solubility determinations, electromotive force measurements, etc.

Lewis has gone one step farther and considers ionic concentration as a rather meaningless phrase.

> It may be of interest to view for a moment the logical implications of such a term as "degree of dissociation." Let us consider the equilibrium in the vapor phase between diatomic and monatomic iodine, and at such a temperature that, on the average, each molecule of I_2, after it has been formed by combination of two atoms, remains in the diatomic condition one minute before it redissociates. During this minute such a molecule will traverse several miles in a zigzag path; and, after its dissociation, each of its constituents will traverse a similar path before it combines once more with another atom. If we imagine an instantaneous photograph of such a gaseous mixture, with such an enormous magnifying power as to show us the molecules as they actually exist at any instant, then by counting the single and double molecules we should doubtless find the same degree of dissociation which is actually determined by physicochemical methods.
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> On the other hand, if we should choose a condition in which the dissociation and reassociation occur 10^{13} or 10^{14} times as frequently, the atoms of the dissociated molecules would hardly emerge from one another's sphere of influence before they would combine once more with each other or with new atoms. In such a case the time required in the process of dissociation would be comparable with the total time during which the atoms would remain free, and even our imaginary instantaneous photograph would not suffice to tell us the degree of dissociation. For, first, it would be necessary to know how far apart the constituent atoms of a molecule must be to warrant our calling the molecule dissociated. But such a decision would be arbitrary; and according to our choice of this limiting distance, we should find one or another degree of dissociation.
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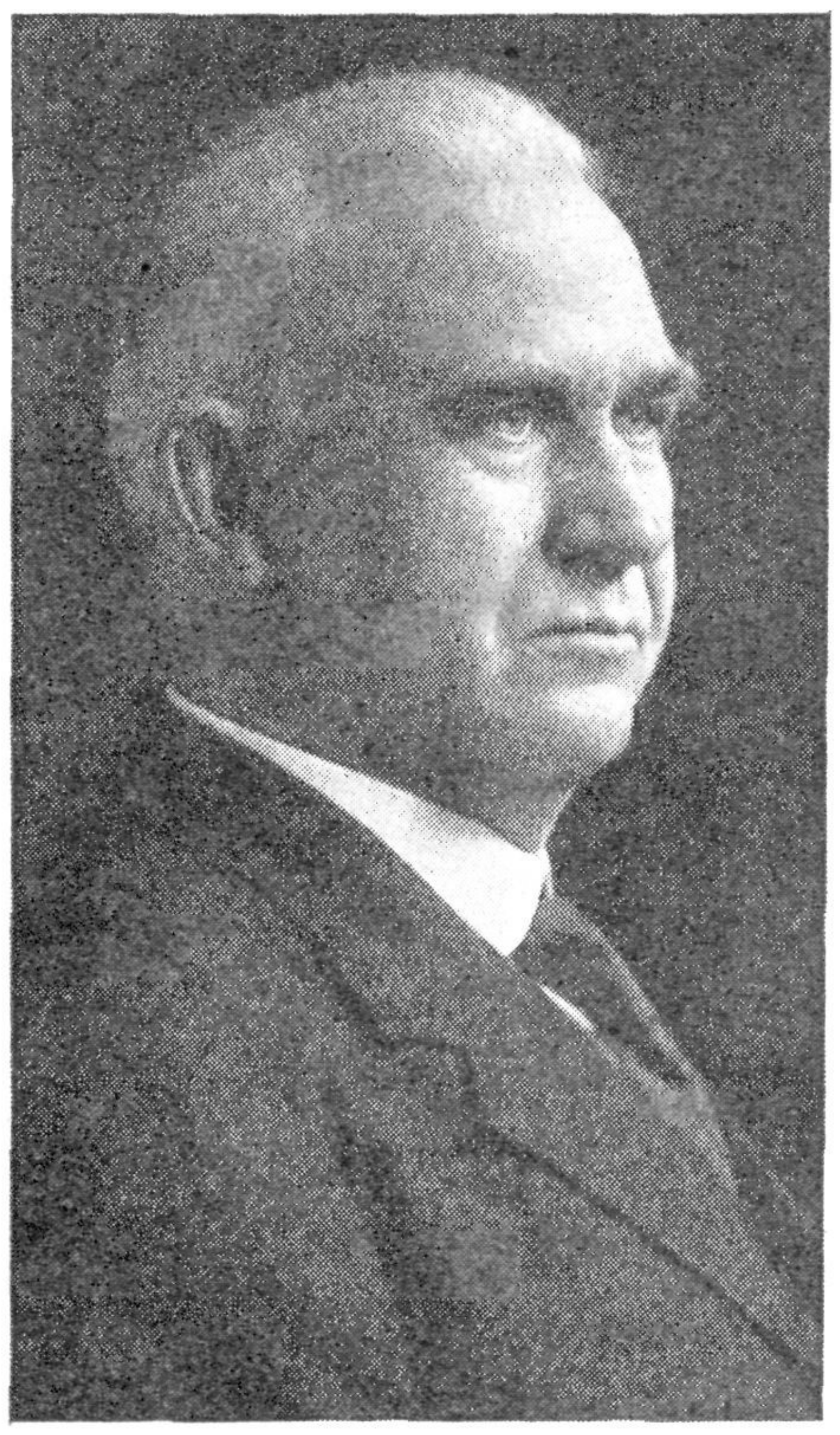
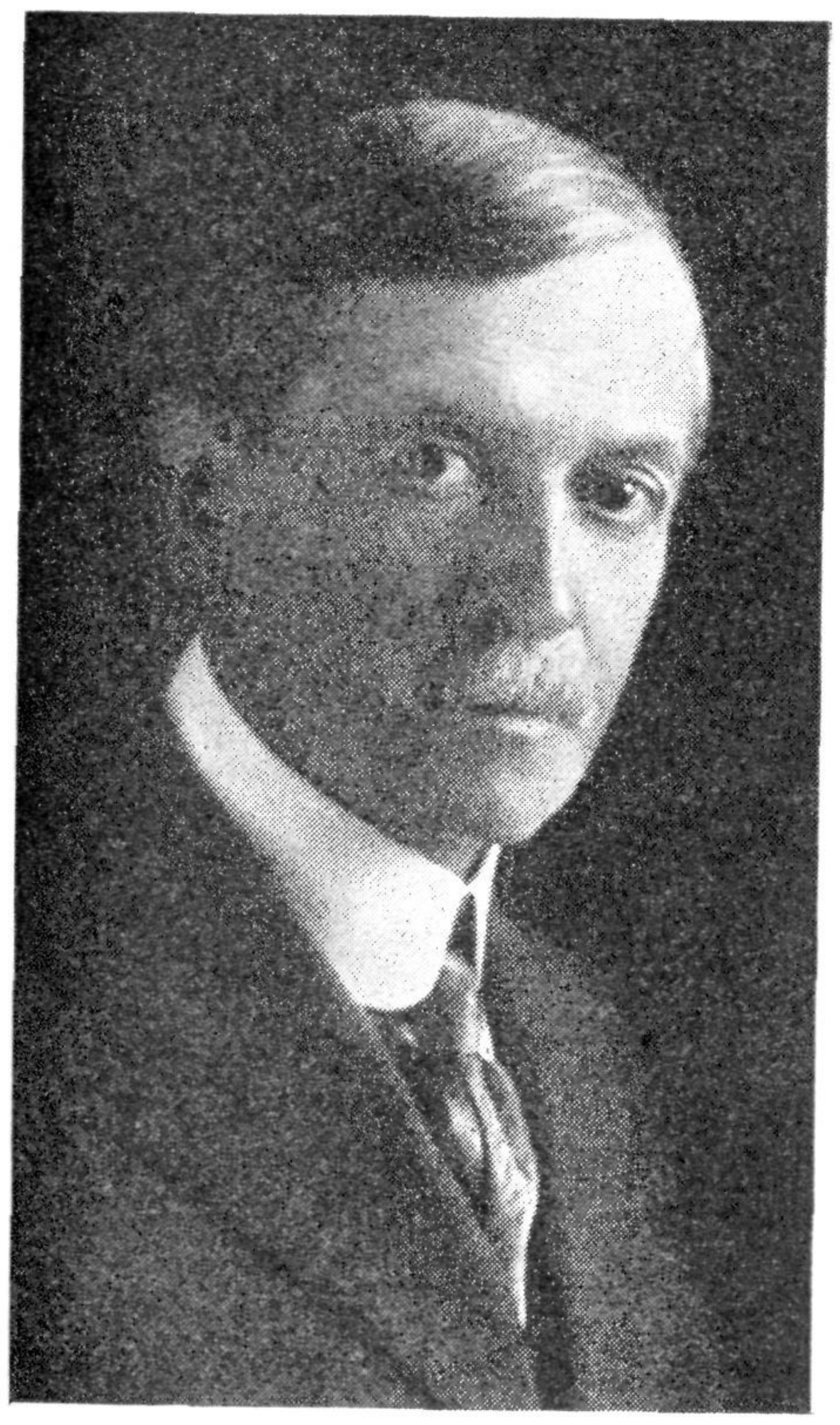
> Until a problem has been defined logically, it cannot be solved experimentally; and it seems evident in such a case as we are now considering that, just as we should obtain different degrees of dissociation by different choices of the limiting distance, so we should expect to find different degrees of dissociation when we come to interpret different experimental methods. Now it is generally agreed that ionic reactions are among the most rapid of chemical processes, and it is in just such reactions that we should expect to find difficulty in determining, either logically or experimentally, a really significant value of the degree of dissociation.

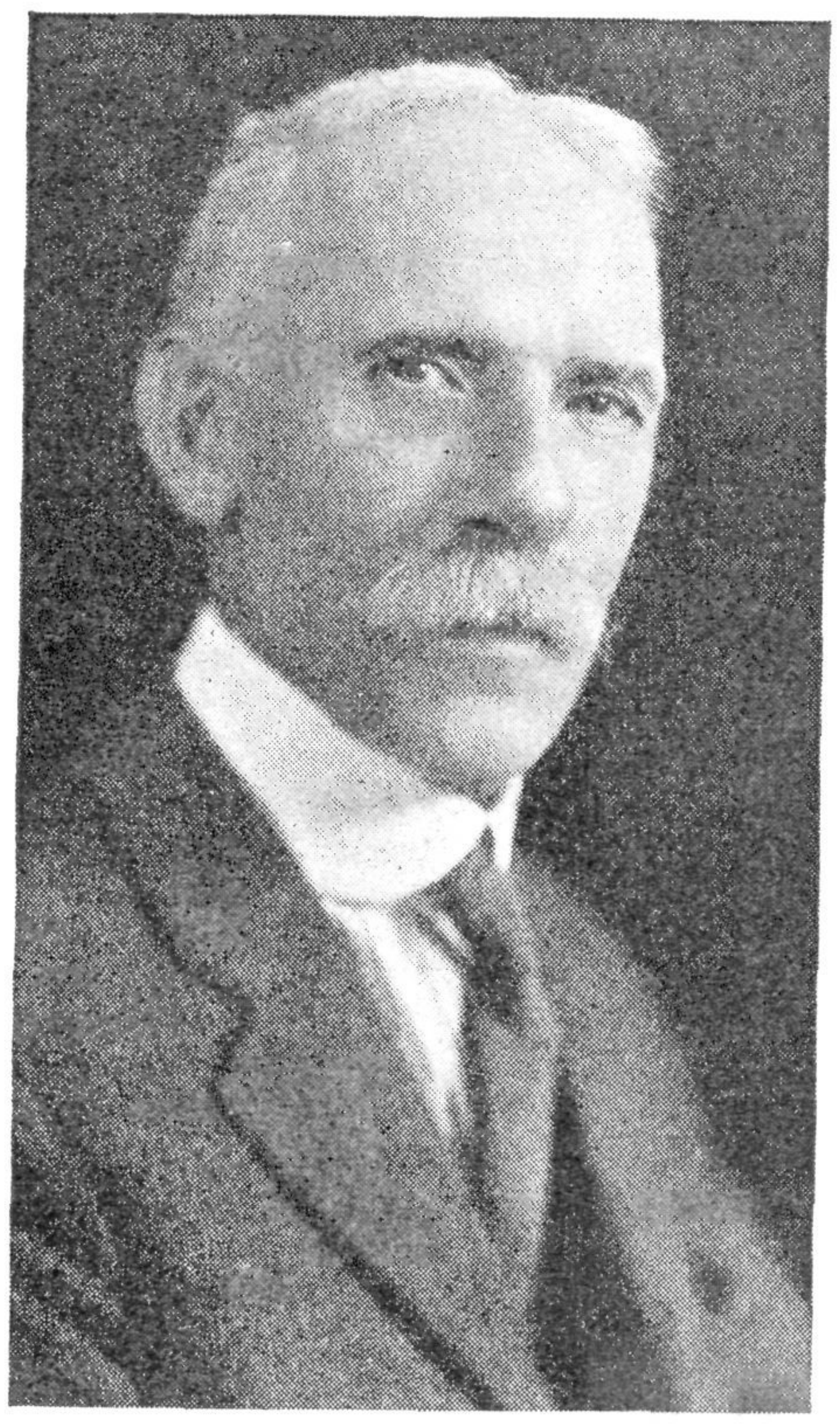
Ira Remsen
(1846–   )
President 1902



John H. Long
(1856–1918)
President 1903



Arthur A. Noyes
(1866–   )
President 1904



Underwood & Underwood

Francis P. Venable
(1856–   )
President 1905

> On the whole, we must conclude that the degree of dissociation and the concentration of the ions are quantities which we cannot determine by existing methods, and which perhaps cannot be defined without some degree of arbitrariness. The question is one which should be left open, especially as its answer is of no immediate concern to those who employ purely thermodynamic methods.

Gibbs has gone to the other extreme and has deduced Henry's law for the case where there is only one molecule of the solute, even though it cannot, by definition, be in both phases simultaneously.

A phenomenon which appears to bear out Lewis' contention is the so-called neutral salt effect. If we take a tenth-normal hydrochloric acid solution and add enough sodium chloride or bromide, it is a simple matter to bring the apparent concentration of hydrogen ion up to half-normal or more, which is absurd whether we consider tenth-normal hydrochloric acid as 100, 85, or 68 per cent dissociated. Lewis has got round this difficulty, as well as others, by introducing the conceptions of fugacity, activity, activity coefficients, etc., working with activities instead of concentrations. Speaking roughly, the activities are the values which the formulas under consideration do give, and consequently they satisfy the formulas with any desired degree of accuracy.

For a while the concepts of fugacity and activity did not appeal to the chemists; but the lack of any more satisfactory explanation has led people to take up this viewpoint. Debye in Switzerland and Brönsted and Bjerrum in Copenhagen are strong for it. In America a number of the younger chemists are spending most of their time measuring activity coefficients.

It must be admitted that the electrolytic dissociation theory has suffered much more from its friends than from its foes. Forty years of intensive development have brought us to the point where we cannot determine any electrolytic dissociation with any degree of accuracy and where we question the significance of the term "electrolytic dissociation." The range over which our formulas apply has decreased and it is not much of an exaggeration to say that the really orthodox physical chemist now looks upon a hundredth-normal solution as a moderately concentrated one. A situation like this cannot last, because physical chemistry must deal with actual solutions and not limit itself to a study of slightly polluted water. Water analysis deals with parts per million; but physical chemistry should not be restricted to this. It is probable that the Semicentennial of the AMERICAN CHEMICAL SOCIETY will mark the beginning of a new period.

It is easy enough to point to one factor which has been neglected practically completely and which may be the one which has caused most—and perhaps all—of our difficulties. For years H. E. Armstrong in England has chided the physical chemists for considering water only as water, whereas it is a complex and variable mixture. This criticism seems well founded; but, unfortunately, Armstrong has never succeeded in showing what could be done with his idea and consequently the idea has been valueless hitherto. Everybody admits that water is a polymerized liquid and that the degree of polymerization may change on the addition of electrolytes. This is the orthodox way of accounting for the displacement by salts of the temperature at which the maximum density of water occurs. Sutherland, Lewis, McBain, and others have suggested such a displacement of equilibrium as a possible source of error in our physical chemistry calculations; but nobody seems to have made a serious attempt to see how adequate this suggestion really is.

In the case of the dilution law, a change in the degree of polymerization of water with the concentration means a change in the solvent or in what Washburn calls "the thermodynamic environment." This carries with it a change in the dissociation constant. We do not know to what extent this hypothetical displacement of equilibrium will account for the discrepancies between theory and experiment; but it is a factor which has not been taken into account quantitatively. In the electrometric determination of hydrogen-ion concentration, we are really measuring the difference of chemical potential and we calculate the data into concentrations on the explicit assumption that there has been no change in what Nernst calls "the solution pressure" and which is really the difference in the free energy levels for unit concentration. Increasing the chemical potential of the hydrogen ion is equivalent to decreasing the solution pressure of hydrogen. It is possible theoretically to increase the chemical potential of the hydrogen ion without necessarily increasing its concentration. Lash Miller has shown that adding alcohol to a sugar solution increases the chemical potential of the sugar because it decreases the solubility of the sugar. Consequently, the measured pH of a solution does not necessarily show anything about the actual concentration of the hydrogen ion. We usually say that the color change of an indicator, phenolphthalein for instance, occurs at a definite hydrogen-ion concentration. This is a careless, and sometimes an inaccurate, way of speaking. What we really mean is that the color change occurs at a definite chemical potential of the hydrogen ion, when there is no salt error.

For this case Lewis' activity is another form of Gibbs' chemical potential, and the Gibbsian way of putting it is better because we know that there is another term in the chemical potential beside the concentration term, and consequently we realize that the two must be studied separately. In other words, there are two independent variables jumbled together and hidden in the activity concept but kept clearly distinct when we speak in terms of the chemical potential.

There is no reason for despondency about the electrolytic dissociation theory and about concentrated solutions until after we have determined the effect of the changing polymerization of water on our formulas; and by that time there may be no cause for despondency. It is worth noting that McBain suggested, seven years ago, that the effect of a neutral salt upon the volatility of acetic acid was due to a change in the chemical potential; but it is clear that he did not realize the tremendous significance of that remark.

In two cases which have been studied recently, the importance of the liquid equilibrium stands out clearly. It seems practically certain that the peptization of gelatin by potassium iodide solution is due to the displacement of the water equilibrium by the potassium iodide. Since the action of the potassium iodide can be duplicated by raising the temperature, the peptization is due to depolymerized water. The reverse case is to be found in the ether-alcohol peptization of pyroxylin, where the ether changes the degree of polymerization of the alcohol. Since alcohol does not peptize pyroxylin when heated and does when cooled way down, it must be the polymerized alcohol which peptizes the pyroxylin. A sol which is quite fluid at low temperatures becomes a soft, flowing jelly at room temperature, and a stiff jelly at 120° C.

An important contribution to the study of reaction velocity was made by A. A. Noyes. Wilhelmy had determined the order of reaction by seeing whether a good constant is obtained over the whole run or nearly so, and this is the method which is used ordinarily. Harcourt and Esson adopted the plan of making all concentrations but one relatively large so that only one component changed appreciably in concentration and they then determined the order of the reaction for that component. This was afterwards formulated a little more definitely by Ostwald and is often credited to him. For gas reactions van't Hoff determined the order of the reaction direct from the differential coefficients; but nobody realized the value of this method until it was resurrected by Noyes, who showed that the time necessary for a reaction to run half-way is proportional to log 2 for a monomolecular reaction (i. e., independent of the initial concentration); $1/A$ for a bimolecular reaction (i. e., inversely proportional to the initial concentration); and $3/2A^2$ for a trimolecular reaction (i. e., inversely proportional to the square of the initial concentration). By varying the initial concentration sufficiently, differences were obtained which quite overbalanced the secondary disturbances that are liable to vitiate the conclusions based on the other two methods. This method, that Noyes adapted from van't Hoff, changed our views completely in regard to many reactions which had been studied prior to that time. At the Toronto laboratory under Lash Miller work was done for several years on reaction velocities in systems containing oxidizing and reducing agents and on systems involving coupled reactions. Miller showed the inadequacy of Luther's classification of coupled reactions, without being able, however, to substitute a clear and workable classification of his own. That particular problem is one which will be solved long before the Centennial celebration.

It was A. A. Noyes, this time in collaboration with Whitney, who wrote the first satisfactory formula for the rate of solution of a solid; but unfortunately their treatment was purely formal and it was left to Nernst to discover that the important factor was the rate of diffusion, both in this case and in many others of reaction velocities in heterogeneous systems. This covers such apparently different things as the rate of solution of iodine in potassium iodide solutions, the action of benzoic acid solutions on magnesia, and the catalytic decomposition of hydrogen peroxide solutions by platinum black.

Catalysis

Great progress has been made in this country in the theory of contact catalysis since the importance of adsorption has been recognized. The very mysterious phenomenon of the poisoning of the catalyst has been cleared up so far as the general theory is concerned, though there is still some question why a given amount of the poison is necessary in any given case rather than some other amount. Langmuir's conception of oriented adsorption has already proved its value and is going to be of increasing importance. In Taylor's laboratory, at Princeton, it has been shown experimentally that nickel splits hydrogen into monatomic, electrically neutral hydrogen, as previously postulated by Langmuir. Bancroft has pointed out that ultra-violet light will do many of the things that a catalyst will do and that consequently the activation of a substance consists fundamentally in the opening of some bond or contravalence, one of the problems then becoming the determination of what bond it is in any given case. This is Baly's hypothesis made a little more definite; it really inaugurates a new organic chemistry, the chemistry of radicals instead of the chemistry of molecules. The statement that reactions are always between ions was never taken seriously because it was known to be inaccurate. It seems probable, however, that most reactions involve activated molecules, the ions being one class of active substances, and the active forms of the organic molecules not necessarily being charged.

Stress has been laid upon the importance of differentiating between the two possible types of contact catalysis. In one case there is an intermediate formation of a definite chemical compound, meaning thereby one which is described by the law of definite and multiple proportions. In the other case there is an intermediate formation of an adsorption complex, or indefinite chemical compound if one prefers that term. Bray believes that these two types merge insensibly, one into the other, and that there are cases which it is impossible to classify under either head. An example of this is the cupric chloride used as a catalyst in the Deacon chlorine process. It is not necessary to assume that a definite oxychloride of copper is produced.

> It is only necessary to assume that an exchange of oxide and chloride ions occurs at various points in the solid cupric chloride lattice. The extent to which such an exchange will occur will obviously depend on experimental conditions, such as oxygen and chlorine concentrations, temperature, and the like. It will only be a fortuitous circumstance if these are such that, on the average, half the chloride ions are replaced by oxide ions; nor, in rapid reactions, can the change be expected to extend much beyond the surface.

Whether one can separate the sheep from the goats with accuracy is a debatable point; but the value of the classification does not depend on that. Everybody will agree that it is desirable to distinguish between animals and plants, even though it is not possible to draw a sharp dividing line. Whewell says that:

> Names of *kinds* of things (*genera*) associate them according to total resemblances, not partial characters. The principle which connects a group of objects in natural history is not a *definition*, but a *type*. Thus we take as the type of the rose family, it may be the common *wild rose;* all species which resemble this flower more than they resemble any other group of species are also *roses* and form one *genus*. All genera which resemble roses more than they resemble any other groups of genera are of the same *family*. And thus the rose family is collected about some one species which is the type or central point of the group.
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> In such an arrangement, it may readily be conceived that though the nucleus of each group may cohere firmly together, the outskirts of contiguous groups may approach, and may even be intermingled, so that some species may doubtfully adhere to one group or another. Yet this uncertainty does not at all affect the truths which we find ourselves enabled to assert with regard to the general mass of each group. And thus we are taught that there may be very important differences between two groups of objects, although we are unable to tell where the one group ends and the other begins; and that there may be propositions of indisputable truth, in which it is impossible to give unexceptionable definitions in the terms employed.

Taylor believes that the activating atoms (or molecules) of the catalyst usually occupy only a small fraction of the total surface and are those in the surface which are unsaturated—the extra-lattice atoms—which may be held to the mass of the catalyst by perhaps a single bond.

> The X-ray examination of metallic hydrogenation catalysts has shown that these catalysts, even when prepared at low temperatures, possess the definite lattice structure of the crystalline material. A granule of such a catalyst must, therefore, possess, in part, the ordered arrangement of the atoms found in crystalline material. The method of preparation of active material suggests, nevertheless, that the ordered arrangement of the atoms has not been completely attained and that, here and there, on the surface of a partially crystalline material there are groups of atoms in which the process of crystallization is not yet complete.
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> The atoms in the plane surface of any face of the crystal, e. g., a face-centered cubic crystal of nickel, will be practically saturated by the neighboring metal atoms in three dimensions, with the exception that there will be a certain degree of unsaturation towards the gas phase.* * * Atoms in the edges of such a crystal will be one degree less saturated than the atoms in the surface, by reason of the fact that they are surrounded to a less degree by nickel atoms. For this reason they will possess stronger attractive force for impinging atoms. * * * This increased attractive force at an edge will be surpassed by that obtaining at a corner. In the incompletely ordered atoms the attractive force will increase progressively as the degree of saturation by neighboring nickel atoms becomes less and less, until, finally, in atoms which are held to the granule by only one attachment, e. g., Ni-Ni, the unsaturation of the metal atom and the attractive force for impinging molecules will become a maximum. The methods of preparation of active catalysts and the activation of inactive masses all tend to produce arrangements of atoms in which these varying characteristics are multiplied.* * * The attractive force of a surface atom may be adequate to retain one molecule, whereas another gas would suffer a practically completely elastic collision. The less saturated atoms in the catalyst surface will be the preferred positions of attachment of catalyst poisons. Hence the varying ratio of adsorption between poisoned and unpoisoned catalyst.

On Taylor's hypothesis, the simultaneous formation of ethylene and acetaldehyde from ethyl alcohol is due to differently oriented adsorption by atoms of the catalyst held differently on the surface or by differently oriented adsorption at different portions of the crystal. Adkins claims that the difference in product is due to a variation in the spacing of the atoms or molecules of the catalysts, and he apparently obtained different alumina catalysts by decomposing different compounds of aluminum. He says:

> On the basis of Dr. Taylor's hypothesis, a slightly unsaturated surface atom might induce one reaction, a more unsaturated one another reaction, etc. That is to say, an atom of a catalyst produces hydrogenation because it exerts a greater (or lesser) force than does one that produces dehydration. It seems to me more reasonable to believe that there are differences in kind rather than of degree of dislocation of the molecule. Instead of there being four or five kinds of catalyst-ethanol compounds or four or five degrees of unsaturation of catalyst atoms, the various reactions are dependent upon the relationship in space of the catalyst atom which are *simultaneously* exerting their attractive forces upon the organic molecule, thereby distorting it in different ways. It seems probable that differences in the degree of unsaturation of catalyst atoms as well as the geometrical relationship of these active points, are important factors in catalytic reactions.

Emphasis should be placed on the fact that there are two distinct phases to these catalytic reactions, and that these two phases have apparently no relationship to each other. The one phase has to do with *how much* material reacts under a given set of conditions and the other phase has to do with the ratio of the reactions that take place. The first phase may very well have an intimate relationship to the adsorptive capacity of the catalyst. It varies with very slight changes in the method of preparation of the catalyst. In general this behavior of the catalyst is not readily duplicated with different preparations from the same materials. In marked contrast to this is the case of duplication of the characteristics of the second phase; provided the catalyst is made by the same method, i. e., by the ignition of a carbonate, dehydration of a hydroxide, hydrolysis of an alkoxide, etc. Two catalysts made from a butoxide may differ from each other by as much as 100 per cent in the *amount* of material that they will cause to react in unit time, but the proportion of the reactions induced will differ only by a per cent or so. The one characteristic of the catalyst is dependent, I believe, upon the number of active adsorbing centers, the other upon the characteristics of the surface at these active points. The distinctness of these two characteristics of catalysts has never been sufficiently realized.

The Phase Rule

The Cornell laboratory was the first one in this country to do serious work on the phase rule and the Geophysical Laboratory at Washington is a wonderful example of what can be done with the phase rule as an instrument of research. Miller and Kenrick at Toronto University have developed the method of indirect analysis which is most in use in identifying double and basic salts. While we owe much to Heycock and Neville, to Roozeboom, and to Tammann for their work on alloys, there has also been much good work done in this country. Jeffries has worked out what seems to be the best theory of the hardening of duralumin and of steel; and Gillett has done great service in calling attention to the probable bearing of sonims on the fatigue of metals. It is true that the Beilby amorphous-film theory was accepted at one time fairly generally in this country; but we have seen the error of our ways.

Colloid Chemistry

Cameron, at the Bureau of Soils, and Jacques Loeb, at the University of California, did good work on the application of physical chemistry to soils and to biology, respectively. Indeed Loeb's work on the application of physical chemistry to vital phenomena is epoch-making. In both cases the work soon became colloid chemistry. In spite of his brilliancy—or perhaps because of it—Loeb was not able to acquire the new point of view and to the day of his premature death he looked upon colloid chemistry as unmitigated foolishness. Clowes showed that some of Loeb's results on the antagonism of salts could be explained on the assumption that protoplasm acts like an emulsion and that the change from an oil-in-water to a water-in-oil type is favored by certain salts and hindered by others. Some of the cases of antagonism of salts involve osmotic pressure relations rather than emulsification, and Gurchot has shown that salts, alcohols, etc., may cause temporary coagulation or permeability of the semipermeable membrane. This minimizes the difficulty as to the way in which some of the materials get into the cells.

There has been an enormous difference in the lines along which colloid chemistry has developed in Europe and in America. This can be seen clearly by comparing the latest edition of Freundlich's "Kapillarchemie" with Bancroft's "Applied Colloid Chemistry." Freundlich's book—stupendous though it is—is essentially a collection of facts. There is no real attempt and not much desire on Freundlich's part to change colloid chemistry from a descriptive to a deductive science.

When discussing contact catalysis, reference was made to Langmuir's theory of oriented adsorption. The similar work on oriented adsorption at the surface of a liquid has created more of a sensation than the other, though it is probably not so important a contribution to science. Bingham's work on plasticity and fluidity is of course colloid chemistry, though he is not over-enthusiastic about that side of it because he came into the subject from a study of the fluidity of true solutions.

Electrochemistry

In electrochemistry we start with that part of Gibbs' paper which deals with a reversible cell. In a sense this contains in capsule form about everything which has been done since, though the later work of Helmholtz, Nernst, and others was necessary to show what was in Gibbs and what it meant. There is even to be found in Gibbs the statement that the high chemical potential is at one electrode and the high electrical potential at the other. Goodwin's work on the voltaic cell was done in Germany under Ostwald's direction and should perhaps not be credited to America. Cady showed the effect of the heat of dilution on concentration cells in certain cases and the careful work done in Richards' laboratory proved that this theory accounted for about 75 per cent of the apparent discrepancies. Hulett has done admirable work on standard cells and Lewis obtained the true value of the gas cell to within one one-hundredth of a volt twenty years ago. Ever since then his laboratory has been active in determining free energies by the electrometric method. Lewis was the first to devise a method for measuring the free energy of the alkali metals.

Electrolytic analysis began with Wolcott Gibbs. Although a great deal of the development of this subject was done in Germany, notably in Classen's laboratory, it is to America that we must turn for rapid methods of electrolytic analysis. The University of Pennsylvania laboratory under Edgar F. Smith was for years the headquarters of electrolytic analysis in this country, and it is to Smith that we owe—among so many other things—the ingenious method of determining sodium with a mercury cathode. Electrometric analysis runs back to Behrend in Ostwald's laboratory. Böttger attempted to popularize it; but it was Hildebrand, now of the University of California, who really put the subject across and made the method a regular laboratory one. The definition of pH and the preparation of many indicators we owe to Sörensen of the Carlsberg laboratory in Copenhagen; but Clark and Lubs have done good work in this country in preparing what seems to be the best series of indicators for use over the whole range.

Whitney, now the head of the Research Laboratory of the General Electric Company, was the originator of the electrolytic theory of corrosion, and Walker, of the Massachusetts Institute of Technology, did much to develop it. After a good many vicissitudes, this theory seems now to have weathered the storms and to be the only one worthy of serious consideration so long as we are working under ordinary conditions. Nobody claims that it applies to metals heated in dry air or exposed to an oxyacetylene torch.

It is not possible to claim the electrochemical industries at Niagara Falls for physical chemistry, much as one would like to; because Castner, Acheson, Hall, and Bradley, for instance, were not physical chemists and got no help, so far as we know, from the principles of physical chemistry. On the other hand, the Cottrell process for smoke precipitation and the Betts process for the electrolytic refining of lead are to be credited to physical chemistry, as is also the work on electroplating by Blum, of the Bureau of Standards. The electrolytic restoration of corroded medallions and other objects by Fink of Columbia is a bit of work of which anybody could be proud.

Photochemistry

In photography the Research Laboratory of the Eastman Kodak Company under C. E. K. Mees has been, of course, the center of activity, both in the way of making new sensitizing dyes and in working out problems involving measurement and theory. A most brilliant piece of work is Sheppard's discovery that allyl isothiocyanate or its conversion product, allyl thiocarbamide, is the substance which is responsible primarily for the sensitizing action of gelatin. Somewhat less dramatic are the crystallographic work of Trivelli on the silver bromide grain, the statistical work of Wightman, Trivelli, and Sheppard on the size-frequency distribution of silver halide grains, and the work of Nietz on the electromotive forces of developers. Starting from the premise that any of the photographic developers will reduce unexposed silver bromide when not protected by gelatin, Bancroft worked out a theory of solarization and of development which is based primarily on relative reaction velocities rather than on equilibrium relations. On this basis, selective adsorption and peptization by the developer are of much more importance than the chemical potentials as measured by the electromotive forces.

Over a century ago Grotthuss showed that only that light which is absorbed can produce chemical reaction and that the question whether a photochemical change can occur depends, in many cases, on the presence of a suitable depolarizer. The first of these two propositions was rediscovered by Herschel in England and by Draper in America. It is often called "Draper's law." The second proposition was also forgotten to a great extent and was rediscovered in part by Vogel, in Germany, with his chemical and optical sensitizers. It came fully into its own when it was shown by Bennett, at Cornell, that a copper sulfate solution can be made light-sensitive by the addition of a suitable depolarizer, in this case a solution of phosphorus in ether. A more adequate formulation is that all light which is absorbed raises the chemical potential of the portion of the molecule which absorbs it and thereby makes it less stable. Whether any reaction will take place and what reaction takes place is a question of chemistry. There are, therefore, no chemical rays as such and no oxidizing or reducing rays as such. Since $h\nu$, the Planck constant multiplied by the frequency, has the dimensions of energy, an absorption band in the violet may involve the taking up of more energy than a band in the red, which accounts for the fact that, of two absorption bands, the one corresponding to the shorter wave length and greater frequency is usually the more light-sensitive.

Another important problem in photochemistry is the relation between the amount of light absorbed and the amount of chemical change which occurs—the application of the quantum theory. The lead in this field, so far as America is concerned, is being taken by Taylor, at Princeton. It seems to the outsider as though one should distinguish rather sharply between systems which are in a metastable state, like hydrogen and chlorine, and systems in which the light actually displaces the equilibrium, like oxygen or sulfur trioxide. The interesting cases of so-called chain reactions will probably be found only in the first group.

Porter, at the University of California, has shown that Baly's experiments on the formaldehyde synthesis are by no means conclusive as yet. Spoehr, at Carmel, and Bovie, at Harvard, are studying the photochemistry of the living organism. Langmuir, at Schenectady, has given definite theoretical reasons for rejecting the radiation theory of reaction velocities put forward by W. C. McC. Lewis and by Perrin, while Daniels, at the University of Wisconsin, has made an admirable experimental study of the photochemical decomposition of nitrogen peroxide. Under production of light we have the work of Harvey, at Princeton, on the chemistry of the firefly, and the work, at the Cornell laboratory, by Weiser, Wilkinson, and others on the chemistry both of flame reactions and of cathode ray luminescence.

Exact Measurements

In exact measurements the Harvard laboratories take the lead, whether one considers the atomic weight determinations by Richards and by Baxter, the thermochemical measurements by Richards, the verification of Faraday's law by Richards, or the compressibility measurements by Richards and by Bridgman. Washburn, at the University of Illinois, has developed the technic of measuring electrolytic conductance beyond what anybody else has done, and is now editing the International Critical Tables under the auspices of the National Research Council.

Atomic Structure

Richards has been amply justified in his contention that the atoms cannot consist of incompressible masses; but it is only in the most formal way that one can consider his elastic atoms as standing in any close relation to the modern atom, either of the physicist or of the chemist. Lewis outlined and Langmuir developed what is now known as the octet theory or the Lewis-Langmuir atom. This is sometimes known as the atom of the chemist to differentiate it from the Bohr atom or the atom of the physicist. The essential difference between the two models is that Bohr has the electrons move in orbits around the nuclei of the atoms. Langmuir claims that the facts of stereochemistry prove that the valence forces between atoms act in directions fixed with reference to each other, a point which does not follow obviously from the Bohr model.

In his recent book entitled "Valence," Lewis points out how it is possible, in his opinion, to harmonize the two points of view.

If we regard as the important thing the orbit as a whole, and not the position of the electron within the orbit, and if each electron is assigned an independent orbit, then we may think of each electron orbit as having a fixed position in space. The average position of the electron in the orbit may be called the position of the electron and will correspond entirely to that fixed position which was assigned in the theory of the static atom.* * * We shall adopt the whole of Bohr's theory in so far as it pertains to a single atom which possesses a single electron. There are no facts of chemistry which are opposed to this part of the theory, and we thus incorporate in the new model all of Bohr's theory which is strictly quantitative. In the case of systems containing more than one nucleus or more than one electron, we shall also assume that the electron possesses orbital motion, for such motion seems to be required to account for the phenomenon of magnetism; and each electron in its orbital motion may be regarded as the equivalent of an elementary magnet or magneton. However, in the case of these complex atoms and molecules we shall not assume that an atomic nucleus is necessarily the center or focus of the orbits. These orbits occupy fixed positions with respect to one another and to the nuclei. When we speak of the position of an electron, we shall refer to the position of the orbit as a whole rather than to the position of the electron within the orbit. With this interpretation, we may state that the change of an electron from one position to another is always accompanied by a finite change of energy. When the positions are such that no change in position of the several parts of the atom will set free energy, we may say that the system is in the most stable state. In a process, which consists merely in the fall of an electron from one position to another more stable position, monochromatic radiant energy is emitted, and the frequency of this radiation multiplied by h, the Planck constant, is equal to the difference in the energy of the system between two states. The electrons of an atom are arranged about the nucleus in concentric shells. The electrons of the outermost shell are spoken of as valence electrons. The valence shell of a free (uncombined) atom never contains more than *eight electrons*. The remainder of the atom, which includes the nucleus and the inner shells, is called the kernel. In the case of the gases it is customary to consider that there is no valence shell and that the whole atom is the kernel.

Lewis has now modified somewhat his conception of what he called the "group of eight" and which Langmuir called the "octet."

The new theory, *which includes the possibility of complete ionization as a special case*, may be given definite expression as follows: Two atoms may conform to the rule of eight or the octet rule, not only by the transfer of electrons from one atom to another, but also by sharing one or more pairs of electrons. These electrons which are held in common by two atoms may be considered to belong to the outer shells of both atoms.

The discovery that those electrons which are held jointly by two atoms always occur in pairs led to the realization that the "rule of two" is even more fundamental than the "rule of eight." We see at the beginning of the periodic table that helium, with its pair of electrons, has the same qualities of stability that characterize the remaining rare gases which possess outer octets. Hydrogen may form hydrogen ion with no electrons, it may form hydride ion by adding one electron and thus completing the stable pair, or finally two hydrogen atoms may unite to form the hydrogen molecule, in which each atom shares with the other this stable pair of electrons. I called particular attention to the remarkable fact that when we count up the electrons which are comprised in the valence shells of various types of molecules, we find that of some hundred thousand known substances all but a handful contain an even number of such electrons. It is, therefore, an almost universal rule that the number of valence electrons in the molecule is a multiple of two.

Crystal Structure

Hull and Davey, at Schenectady, and Wyckoff, at the Geophysical Laboratory, have been active in the field of crystal structure.

Radioactivity

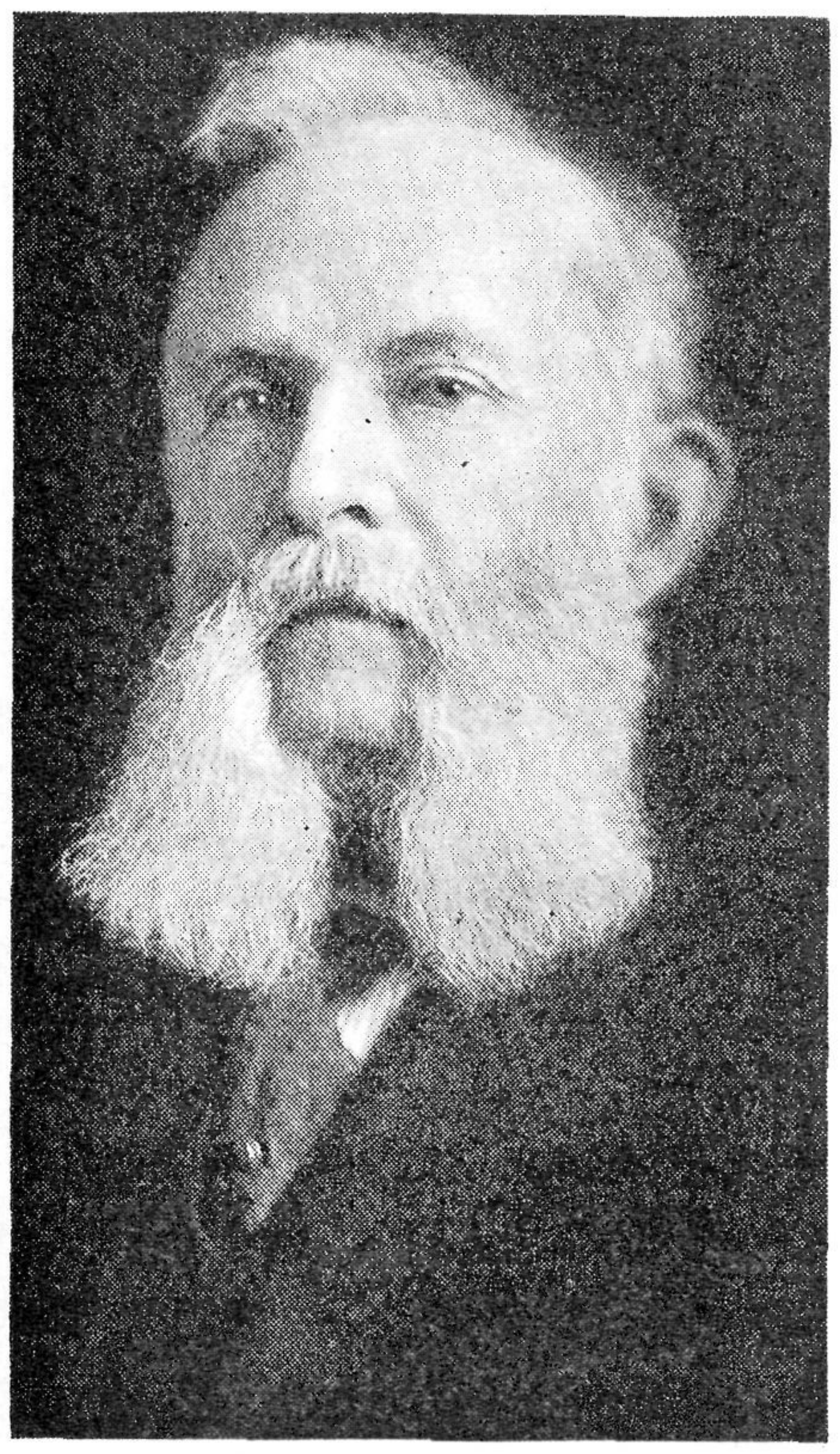
In the field of radioactivity we have the methods of extracting radium from the Colorado ores which were worked out by Parsons and Moore, the discovery of ionium by Boltwood, and the radioactive measurements of Lind. Boltwood mixed ionium and thorium, and showed that the mixture could not then be separated. This was an important preliminary step to the understanding of the behavior of isotopes. Harkins has got actual results on the fractionation of isotopes, and Kendall has developed a method which looks promising. The occurrence of helium in natural gas was discovered by Cady, and the final method of extraction and purification is due to Moore.

Thermodynamics

In thermodynamics Gibbs is, of course, still in a class by himself; but that does not mean that others have not done good work. Trevor set himself the task of presenting chemical thermodynamics in a more accurate and more polished form. This is a dangerous thing to do because it is likely to lead, as it did in his case, to the interest in mathematics superseding the interest in chemistry. Richards just missed deducing the third law of thermodynamics. Washburn introduced the conception of thermodynamic environment; but never carried it beyond the formal stage. Miller has specialized in the zeta function of Gibbs. As has been stated, Lewis developed the conception of activity, which does not seem to be an improvement on Gibbs; he worked out methods of measuring free energy; and, in conjunction with Randall, has written a successful book on "Thermodynamics and the Free Energy of Chemical Substances." Whether it was wise or helpful to break away as completely as he did from the notation of Gibbs is a question which various people have already answered differently. The work of Lewis on relativity is rather out of the field of physical chemistry at present. Among Tolman's contributions are the determination of the mass of the electric carrier in metals and papers on statistical mechanics applied to chemical kinetics and on the similitude principle. Langmuir's work on electron emission, on surface tension, on contact catalysis, and on molecular distribution is extremely brilliant.

Applications

In the applied field the tungsten lamp and the Coolidge tube are two of the striking achievements of the physical chemist. For that matter the whole output of the Research Laboratory of the



Harris & Ewing

WILLIAM F. HILLEBRAND
(1853–1925)
President 1906

MARSTON T. BOGERT
(1868–   )
President 1907, 1908

WILLIS R. WHITNEY
(1868–   )
President 1909

WILDER D. BANCROFT
(1867–   )
President 1910

General Electric Company is to be credited in the last analysis to W. R. Whitney and consequently to physical chemistry.

Journal of Physical Chemistry

The *Journal of Physical Chemistry* was started in 1896 and is now in its thirtieth year. Through the support of the Chemical Foundation it has become an international journal for the English-speaking peoples and is now published under the auspices of the AMERICAN CHEMICAL SOCIETY, the Chemical Society (London), and the Faraday Society. Even this outlet does not relieve appreciably the strain on the *Journal of the American Chemical Society*.

Future Problems

The future of physical chemistry calls for a few words, because we cannot gauge the progress satisfactorily unless we know something about the goal. One of the leading physical chemists of America has said:

> Physical chemistry exists no longer. The men who have been called physical chemists have developed a large number of useful methods by which the concrete problems of inorganic chemistry, organic chemistry, biochemistry, and technical chemistry may be attacked. As the applications of these methods grow more numerous, it becomes increasingly difficult to adhere to our older classification.

According to this, physical chemistry is a technic and not a point of view. The other side is that the physical chemistry of dilute solutions is not in good shape so long as it is possible to speak seriously about sodium chloride being 100 per cent polarized or ionized, 85 per cent electrolytically dissociated, and 60 per cent thermodynamically dissociated. We have made no serious attempt as yet to tackle the theory of concentrated solutions, chiefly because we have assumed that it must be very much more difficult than the theory of dilute solutions. In a sense this is true, because some of the disturbing factors become negligible in very dilute solutions. On the other hand, the place to study these disturbing factors is in the concentrated solutions where their effect is large enough to make the form of the function easy to find.

No one disputes that we are very far from being clear as to the physical chemistry of non-aqueous solvents. We are only just working out a theory of colloid chemistry and it will be a good while before we can say that we really understand about dyeing, paper, leather, paints, rubber, pottery, cement, etc. While the organic chemist does make conductivity determinations and molecular weight measurements, and does study reaction velocities occasionally, it would be a bold man who would claim that anything more than a beginning had been made in the application of physical chemistry to organic chemistry.

There are a number of important developments in physical chemistry which some of us should live to see. We need the development of a more exact thermodynamical theory of chemical statics and dynamics, which will put the electrolytic dissociation theory, the theory of non-aqueous solutions, and the theory of concentrated solutions on a satisfactory basis. This will include a quantitative recognition of the effect of changing the degree of polymerization of the solvent.

We need an extension of Loeb's work on the application of chemistry to vital phenomena and we need, above all, a knowledge of the chemical processes as they go on in the plant and animal. We are not yet really certain of the way in which carbon dioxide is assimilated and one gets no answer if one asks how a shellfish puts bromine into the compound from which we get Tyrian purple.

We are only just starting on a scientific study of photochemistry, and we know almost nothing as yet about the photosynthesis of organic compounds. In the absorption spectrum of any given substance, we must determine which lines or bands belong to the molecule and to what parts of the molecule they belong. If we can then develop an efficient method of producing an intense light of any desired wave length, we have the possibility of an entirely new organic chemistry with perhaps 100 per cent yields. Of course one does not expect the organic chemist to believe this. I am not sure that I believe it myself; but it is a possibility and a fascinating one.

Except for atomic spectra we have made very little progress in the theory of chemiluminescence, though the production of cold light is a problem that we ought to be able to solve and that we probably shall solve as soon as somebody tackles it both systematically and intelligently.

We know that chemical reaction velocity is probably directly proportional to the difference in chemical potential and inversely proportional to the chemical resistance; but we have not yet started on the question of what we mean by chemical resistance and consequently we do not know what really determines the speed of a reaction. We have been satisfied hitherto with a formulation of the laws of chemical kinetics. Now that we are able to calculate the equilibrium constants with some degree of accuracy from the third law of thermodynamics, we must begin the study of the reaction velocity constants, of which we can now predict the ratio.

We must develop a theory of contact catalysis which will enable us to prophesy what catalytic agent will give us a particular result. In the recent synthesis of methanol, we could predict that high pressure would be helpful; but nobody could have said in advance that zinc oxide would be the best catalyst. They had to try one hydrogenating catalyst after another until the right one was found —a slow and unsatisfactory procedure in general. Since the contact catalytic agent activates substances in most cases by opening some bond, we need a study of the organic radicals thus produced, so that we may have a real knowledge of the intermediate steps in organic reactions. The question of contact catalysis and overvoltage in electrochemistry is also one of great interest.

We need two institutes of colloid chemistry. One is already advocated by the Committee on Colloid Chemistry of the National Research Council; it would deal with pure science, would develop the technic, and would render invaluable service by applying colloid chemistry in biology and medicine. The other should deal with the applications to the industries and should develop the scientific foundations of the so-called colloid chemistry industries, such as textiles, paper, leather, dyeing, paints and varnishes, rubber, pottery, cement, photography, etc. At present the practice is far ahead of the theory in these industries. Judging from the past, we are justified in concluding that bringing the theory up to or beyond the present state of the art would be followed very soon by distinct industrial advances.

The real work on the structure of the atom only dates back a few years and we can look forward with confidence to very great advances in this field within the next few years. While most of the work hitherto has been done by physicists, the development will soon reach a point where it will become more and more physical chemistry. That has been the universal experience, as shown strikingly in the theory of the voltaic cell and in the work on electrolytic conduction, to cite two instances out of many.

Another thing that the physical chemist must do, because he is apparently the one with the pioneering spirit, is to develop the borderlands between physical chemistry and the other sciences, such as biology, geology, physics, medicine, engineering, psychology, etc. It should be the aim of all chemists to have chemistry take its place as the fundamental science and that can only be done by and through the physical chemist. The idea that there is no future for physical chemistry is very far from the truth.