SCIENCE

CONTENTS

THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE

THE PAST AND FUTURE OF THE STUDY OF SOLUTIONS [1]

Solutions have been known since earliest times, and the problems which they represent have been studied by a long line of very able investigators. All of the early work on solutions has been inseparably linked with the study of chemical phenomena. Indeed, up to the year 1887 chemical views of solutions have predominated. So for example, in his lectures delivered at Yale College in 1837, Benjamin Silliman, Sr., considered solutions as chemical compounds; and in his memorable work on theoretical chemistry which appeared in 1863, Herman Kopp treated solutions as chemical compounds that exhibit variable proportions, which mode of treatment was retained by A. Horstmann when in 1883 he wrote the second volume of the new edition of Kopp's work, now known as Graham-Otto's "Lehrbuch der physikalischen und theoretischen Chemie." Ever since the days of Lavoisier, when the so-called law of definite proportions was first recognized, a distinction has been drawn between compounds which follow that law and combinations that do not. Chemical combinations which exhibit definite qualitative and quantitative composition that can not be varied gradually by small increments arbitrarily chosen were soon termed definite chemical compounds, whereas solutions, whose composition may be varied gradually, quite arbitrarily—at least

[1] Address of the vice-president and chairman of Section C—Chemistry—American Association for the Advancement of Science, Boston, 1909.

within certain limits—were regarded as indefinite chemical compounds, or compounds according to variable proportions. So Robert Bunsen used to teach that we may have compounds according to definite proportions and also compounds according to variable proportions, the latter compounds being the group known as solutions.

The careful quantitative investigation of solutions really dates from the time of Lavoisier, who, as is well known, introduced the balance into the chemical laboratory. Before this the observations made were generally only qualitative in character; at any rate they were often crude and faulty. The very fact that solutions were regarded as chemical compounds led to their study by much the same methods adopted for the investigation of definite chemical compounds, i. e., chemical compounds in the narrower sense in which the term is at present commonly used. So the qualitative composition and the quantitative composition of solutions were carefully studied. The density, the color, the boiling point, the specific heat, the optical activity, the thermal accompaniment of the formation of solutions and of their reactions with other substances, as well as their other physical, chemical and physiological properties, were studied in much the same way that these various properties were determined for definite chemical compounds. And yet, the fact that the composition of solutions may be varied gradually and arbitrarily within certain limits and that this can not be done in the case of definite chemical compounds, has for nearly a whole century been considered to be the vital difference between a solution and a definite chemical compound, and this is quite proper.

To obtain a definite chemical compound in the pure state usually requires a con-

siderable amount of work. The usual operations of purification as in vogue at present are crystallization, solution and precipitation, sublimation and distillation. By means of the so-called purification process a product is finally obtained whose composition does not change further, though the substance be subjected to further similar treatment. As F. Wald states it, a chemical compound is a phase whose composition remains constant though temperature, pressure and contact with other phases be varied within certain limits inside of which the substance in question is stable. In a sense then the so-called definite chemical compounds are really obtained in certain cases as the more resistant cleavage pieces resulting when the purification processes are applied. That the latter processes after all frequently represent rather violent treatment will probably not be gainsaid by any one.

The law of definite proportions was considered by Ostwald in his Faraday lecture, which in turn was discussed by others, among whom Benedicks voiced the sentiment that after all when closely scrutinized it becomes evident that there is an arbitrary element in judging as to when we really have a pure, definite compound before us, and that the matter of definite proportions is to some extent one of definition. As to the law of multiple proportions, this has been directly challenged by P. Duhem as a tenet that can neither be proved nor disproved, though I must frankly confess my inability to agree completely with him in his argument.

The year 1887 is noteworthy, for it brought both the van't Hoff theory of dilute solutions and the theory of electrolytic dissociation of Arrhenius. These theories really supplement each other, as is well known. They may well be called physical theories of solutions as distinct from the chemical views of solutions al-

ready mentioned. It is quite unnecessary to rehearse here the great activity that has resulted in the study of dilute solutions during the last two decades as a direct consequence of the theories of van't Hoff and Arrhenius. The pages of the history of chemistry that record this experimental work on dilute solutions will ever maintain their brilliant luster, for they reflect the enthusiastic efforts of scores of active young hands and minds that were urged on by a most inspiring leader, an able teacher and experimenter, and a most lovable man —Wilhelm Ostwald. Without him the theories of van't Hoff and Arrhenius would scarcely have gained a foothold.

But excellent as were many of the experimental acquisitions that were thus obtained as a result of these working hypotheses, time has shown that the latter have long since served their purpose, and that mere physical conceptions of solutions are untenable as an explanation of the phenomena actually observed. Furthermore, a theory which applies merely to very dilute solutions, and then only in an imperfect way, is quite untenable in the long run, even as a working hypothesis. It is not my purpose to enter upon a discussion of the numerous experimental researches which have made the theories of van't Hoff and Arrhenius untenable. These investigations have been published at various times during the last decade, and I have dwelt upon them in detail on previous occasions. It is quite safe to assume that they are sufficiently well known to all. Moreover, I frankly confess that I am glad to escape the task of recounting again the weaknesses of these views of solutions as exhibited by experimental facts, for in my younger days I was quite enthused with these hypotheses, and it was to me a great disappointment to find later that they were contradicted by so many experimental truths. It is rather my pur-

pose to point out the direction in which experimental investigations made thus far have led us, and to attempt to indicate the line of attack which must be followed to insure success in the future, so far as this can at present be foreseen.

The data collected since 1887 in studying the various properties of solutions, though frequently gathered with the aid of the physical hypotheses already named, have nevertheless gradually and unerringly demonstrated that the chemical view of solutions is far nearer to the truth, than is the idea that a solution is a mere physical mixture. In this connection permit me to call attention to a few experimental illustrations.

When antimony trichloride and camphor are brought together the two solids liquefy each other, forming a thick syrupy solution, the proportions of the two ingredients of which may be varied within certain limits. Antimony trichloride and chloral hydrate similarly liquefy each other, though less readily. Again, camphor and chloral hydrate when in intimate contact with each other form a liquid. If now cane sugar or paraffine be treated with antimony trichloride or with camphor or chloral hydrate no change will be observed. The question arises, why do antimony trichloride and camphor liquefy each other and cane sugar and camphor not? It is perfectly clear that all that we can say is that this is because of the specific nature of the substances themselves. In other words, antimony trichloride and camphor liquefy each other and sugar and camphor do not for reasons that are similar to those which we give as to why charcoal will burn and platinum will not. We may say that the mutual attraction, *i. e.*, the affinity of antimony trichloride for camphor, is sufficient to overcome their cohesions, and so they unite and form the solution. Now as to whether the antimony trichloride dis-

solves the camphor or the camphor the antimony trichloride is clearly an idle question. We may regard either the one or the other as the solvent, for this is obviously a purely arbitrary matter. Let us now raise the following question: In the syrupy liquid that has been formed by the action of antimony trichloride and camphor on each other, how much of the camphor present is combined with the antimony trichloride that has been employed? The answer is perfectly obvious, for clearly all of the antimony trichloride is combined with all of the camphor in the syrupy liquid that has been formed. One might as well ask the question: When mercury and oxygen unite to form mercuric oxide, how much of the oxygen present is united with the mercury that the oxide contains? Clearly here too all of the oxygen is united with all of the mercury present. When the solution of antimony trichloride and camphor is heated, the vapor obtained contains both of the ingredients. Similarly when we heat mercuric oxide the vapor contains mercury and oxygen. We see thus that the cases are essentially similar in character, the only difference being that in the case of the solution in question we have a compound according to variable proportions, whereas in the mercuric oxide we have a compound according to definite proportions.

Now when ice acts on sodium chloride is not the case quite similar to that of camphor and antimony trichloride? Suppose we knew of no temperature above 0° C., would any one argue that the solid ice dissolved the solid salt in the process of forming the brine? Certainly not, we should say that the brine has been formed by the union of the ice with the salt. And here similarly the question as to how much of the salt in the brine is united with how much of the water in the latter is quite idle, for obviously all of the salt used has united with all of the ice. The case would clearly not be altered if we started with liquid water and solid salt and formed the brine by the interaction of the two substances. This view, that in a solution all of the substances present are united with one another just as all of the elements in a definite compound are combined with one another, is to my mind the only rational view we can take of the matter. It is not new; on the contrary, it is quite old. It has been held quite generally by scientists prior to 1887, when the physical theories came upon the stage and diverted attention into other channels, as already stated, with the result that the true nature of solutions has been thoroughly obscured. If now we dilute the brine with more water, does the water added combine further with the salt present? Most assuredly, for is not the vapor tension of a brine, however dilute, lower than that of pure water, and does not this show that the water in the brine experiences greater difficulty in evaporating because of the mutual attraction between the salt and the water? Were any of the latter uncombined with the salt of the brine, this uncombined water would show the same vapor tension as pure water; but a brine of the same vapor tension as pure water of the same temperature does not exist.

The phase rule of Willard Gibbs marks a great advance in the study of heterogeneous equilibrium. Through the practical work of Bancroft, Roozeboom and numerous other able chemists, the phase rule has borne rich fruits. In all of this work the composition of the phases that are in equilibrium with one another under given conditions of temperature and pressure was carefully determined. This work has revolutionized solubility determinations, placing them upon an accurate scientific footing. Nowadays when the solubility of a compound is to be thor-

oughly investigated nothing less than the complete equilibrium curves of the compounds in question will suffice; but once the work is carefully done, it is final for all time. This is not the place to dwell upon all the various questions that have been cleared up by the application of the phase rule. It should here be emphasized, however, that the latter deals with the equilibrium of the various phases whose qualitative and quantitative composition is of course ascertained. As to the inner structure of any one of the phases the phase rule is able to tell us nothing. Indeed, in the study of single-phase chemistry, the phase rule is no help whatever. We may consider the investigation of the constitution of definite chemical compounds a part of single-phase chemistry, and we may similarly consider the question as to the inner nature of a solution (*i. e.*, of a compound according to variable proportions) as a problem of single-phase chemistry. In the investigation of the constitution of single phases it is quite impossible to get along without hypotheses. While the phase rule does not involve even the atomic and molecular theories, these are at present indispensable tools in prying into the inner nature of any one phase. But in the study of solutions, interest centers not so much in the equilibrium between phases as in the inner structure of the latter themselves.

Our methods of ascertaining the structure of chemical compounds are quite numerous, but they readily fall into a few categories. So we argue as to the structure of a compound from its synthesis, from its analysis, from its behavior toward various other chemical agents, from alteration by the application of pressure, heat, electricity, light and kindred agencies, and also from its various physical and physiological properties. Thus, for example, it

has always been considered as sound reasoning that because red precipitate can be formed from mercury and oxygen, these substances are in red precipitate, which conclusion is verified by the fact that the latter compound may be decomposed into oxygen and mercury. There has never been any objection to the argument that if one of the elements actually enters into a compound during the latter's formation, or can be obtained from the compound either in the free state or in combination with other elements, that element is actually in the compound. So since calcium carbonate may be made from calcium, carbon and oxygen, we argue that these elements and these only are contained in calcium carbonate. Again, when calcium carbonate is heated, calcium oxide and carbon dioxide, and these only, are obtained; and conversely calcium carbonate may be formed by the union of calcium oxide and carbon dioxide. These facts were duly expressed by the old dualistic formula for calcium carbonate $CaO.CO_2$ which consequently had much to commend it. Yet while we thus hold that the elements calcium, carbon and oxygen are in calcium carbonate, we do not argue that this compound contains calcium oxide and carbon dioxide, even though the last two substances will unite and thus form calcium carbonate, or though they may be obtained as decomposition products of the latter compound. We write our formula for calcium carbonate $CaCO_3$ because of the precipitation methods by which the compound may be prepared, and because of the formulæ that we assign to soluble carbonates on the basis of the products that they yield by electrolysis. We consequently hold that the carbon dioxide and lime that form when calcium carbonate is heated result from the rearrangement of the atoms and splitting of the compound on account

of the violence to which it has been subjected by heating it very highly. Similarly, while we recognize that carbon, hydrogen and oxygen are contained in cane sugar, we do not argue that the latter consists of water and carbon, though these products may among others be obtained by heating sugar. Likewise we are loath to conclude that proteins contain amino acids, simply because these result as cleavage products when the proteins are subjected to certain rather drastic treatment.

Turning now, for example, to a compound like blue vitriol whose composition we are wont to express by the formula $CuSO_4.5H_2O$, to indicate that it consists of copper sulphate plus water, we find that the water may be driven off by heat properly applied and that the dehydrated copper sulphate remains behind. On heating the copper sulphate further it is decomposed into copper oxide and sulphur trioxide. If it were intended to express these changes by means of a formula, surely the old dualistic formula $CuO.SO_3.5H_2O$ would best indicate what has been observed. But here again we have departed from the idea that copper sulphate contains copper oxide and sulphur trioxide because upon electrolysis of an aqueous solution of copper sulphate, metallic copper, sulphuric acid and oxygen are obtained; while upon adding zinc or iron to a copper sulphate solution metallic copper is thrown out, and the sulphate of the more basic metal results. So far as the water content of blue vitriol crystals is concerned, we only know its relative amount and that it can be driven off by heat, higher temperatures being required to secure complete dehydration, while relatively lower temperatures will suffice to remove a large portion of the water. As to how this so-called water of crystallization is held, whether it is united with the copper sulphate simply as water molecules adhering to the copper sulphate molecule, or whether, like the oxygen and hydrogen content of the cane-sugar molecules, the oxygen and hydrogen in blue vitriol are united with the sulphur and copper in some more complicated way, is an open question. So far as the facts known are concerned, they are expressed by the formula $CuSO_4.5H_2O$, just as at one time the formula $CaO.CO_2$ expressed what was known about calcium carbonate. To me it would seem very probable that the hydrogen and oxygen content in blue vitriol is not present as water molecules clinging to the copper sulphate molecule, but some subtle experimental method, as yet quite unknown, is required to elucidate this matter, and until such a method is found we shall continue to write our formula for blue vitriol as we are wont to do. It is perhaps well in this connection to allude to the well-known fact that many salts containing water of crystallization can not be dehydrated by heating them, for when this is attempted not only water, but other ingredients as well, are driven off, in other words further deep-seated decomposition occurs.

If crystals of blue vitriol be placed in water, a blue liquid is formed as a result of the action of the crystals and water on each other. This liquid we call a solution. The amount of water and blue vitriol used in its preparation may be varied arbitrarily within certain limits. For reasons already stated, this blue liquid contains no water that is not in combination with the salt present, and also no salt that is uncombined with the water. The fact is that this blue liquid is found to be perfectly homogeneous by all tests that we are able to apply. If we add more water to it, this additional water also combines with all of the salt present and the liquid is again

homogeneous; and this dilution may be carried on indefinitely. If, on the other hand, we permit the blue liquid to evaporate, we thus decompose it by abstracting water from it. We say that the solution is becoming more concentrated. This change is a perfectly reversible one, and like all chemical changes it follows the law of mass action. The abstraction of water from a solution of copper sulphate by means of heat is just as truly an act of decomposing that liquid as is the abstraction of carbon dioxide from limestone when the latter is heated.

Blue vitriol is formed by the addition of water to anhydrous copper sulphate. The compound thus produced is quite stable at room temperature. If now we add anhydrous copper sulphate to crystals of blue vitriol, the latter lose part of their water content, which is taken up by the anhydrous salt till equilibrium is established. If, on the other hand, we treat the blue vitriol crystals with water, it is clear that we can not thus dehydrate the crystals. On the contrary, this added water will, because of mass action, tend to increase the stability of the complex which we represent by the formula $CuSO_4.5H_2O$, and to this complex all of the additional water present in the solution adds itself. What then is the formula of the hydrate contained in an aqueous copper sulphate solution at known temperature? This question is really an idle one, for since all of the copper sulphate present is combined with all of the water of the solution, the composition of the hydrate is clearly expressed by $CuSO_4.xH_2O$, where x represents the number of water molecules which the entire solution contains per each copper sulphate molecule; and so x increases as we dilute the solution and diminishes as we concentrate it. But this must not be taken as meaning that all of

the water in a copper sulphate solution is equally strongly bound to the salt molecules. Indeed, in the case under consideration it is extremely probable that at least five molecules of water are more strongly bound to each copper sulphate molecule in the solution, for as the salt separates out, these five molecules remain in combination as a part of the compound. But while in the solution the copper sulphate molecule plus five molecules of water may be present as a nucleus to which the additional water molecules are attached, the force of attraction with which the outlying water molecules are held by the nucleus shades off so gradually as the radius of the sphere of influence increases that there is at no point any very sharp demarcation, and so it would be folly to attempt to ascribe any definite formula whatever to the hydrate existing in the solution. Attempts to deduce the formulæ of hydrates in solutions from the boiling points or freezing points of the latter are very far from the mark, though to be sure boiling-point and freezing-point curves do frequently show maxima and minima which are doubtless due to changes of intensity with which the water and salt molecules are held together as their relative number is changed. Furthermore, it is very significant that such maxima and minima in the boiling-point and freezing-point curves are found in the case of those substances, which, when they crystallize from the solution, do so with one or more molecules of the solvent attached as so-called crystal water. It is well known that at higher temperatures salts separate from solutions with less crystal water than at lower temperatures. Indeed at high temperatures the anhydrous salt is frequently in equilibrium with the saturated solution. So while at ordinary temperatures copper sulphate forms crystals with five molecules of water, at lower

temperatures it may be obtained with seven molecules of crystal water. Now would it then be right to conclude from this that at room temperature the hydrate in the solution is $CuSO_4.5H_2O$ and at lower temperatures $CuSO_4.7H_2O$? Obviously not, but we may say that it is at least that indicated by the composition of the compound that separates. In the solution itself many additional water molecules are combined with the salt molecules, and the force of attraction gradually shades off as the radius of the sphere of attraction from the nucleus outward increases so that it is quite impossible to ascribe any definite formula to the hydrate in the solution. (I should like to add parenthetically here that the recent attempts made to draw conclusions as to how many water molecules are attached to a portion of certain salts, from observations of changes of concentration that occur at the electrodes during electrolysis, are also based upon misapprehensions, but these details can not be taken up here.) It is, moreover, well known that when any physical property of a solution is studied at different temperatures the curve representing the alteration of that property with change of temperature does not show sharp points of inflection, indicating that whatever the internal alterations may be within the solution, they occur gradually rather than suddenly.

In the study of the various physical properties of solutions with changing temperature and changing concentration, it has been absolutely demonstrated that different solutions behave quite differently, and that solutions of compounds that are chemically analogous show an analogous, but by no means an identical, behavior. It is consequently quite impossible to write an equation that will hold for the various known solutions—not even approximately.

Attempts to formulate an equation for a so-called perfect or ideal solution are about as successful as an attempt to write an equation for an ideal or perfect chemical compound would be. In short, such equations are necessarily based upon postulates that are not in accord with experimental facts, and consequently the equations themselves can not and do not agree with what is actually observed. The attempts to parallel solutions with gases in a quantitative way would naturally suggest that there might be an equation for an ideal or perfect solution just as we are wont to write an equation for a so-called ideal gas, but the suggestion is quite misleading, just as all of the efforts at a quantitative study of solutions based upon gas analogies have proved futile. This is true not only of solutions of moderate concentration, but of dilute solutions as well, as a careful unbiased scrutiny of the numerous experimental data that have been collected shows.

The act of solution is accompanied by all of the phenomena that are observed in the case of changes that are regarded as chemical by common consent, and this shows that solutions are chemical in character. We commonly say that whenever substances combine chemically with each other, the new substance formed has properties that are quite different from those possessed by the original substances. While this is true, it is also the case that some of the properties are not changed at all, while others are but slightly modified, and still others are very greatly altered indeed. So, for instance, the weight remains unchanged during chemical action; the specific heat is frequently altered but little, whereas the color, volume and other properties may be very greatly affected. In general, we may say that *when an element or compound enters into combination with other elements or compounds, each of the ingredi-*

*ents of the new substance formed tends
to retain its original characteristics as
far as the new conditions to which it
has been subjected permit.* In reality
every chemist is well aware of this, though
as far as I know the idea has never before
been stated in so many words. The degree
to which an element loses its original prop-
erties on entering into combination with
other elements depends very largely upon
whether the chemical change involved is
a drastic or a mild one, which in turn is
principally determined by the energy ac-
companiments of the reaction. In the
study of solutions, which in general repre-
sent rather compounds formed by rela-
tively mild changes as compared with
many of the stereotyped chemical reac-
tions, the thought just expressed is particu-
larly helpful. So, for instance, sodium
has a great affinity for the elements of
water, upon which the solubility of sodium
compounds in water largely depends. On
the other hand, sodium is inert toward
hydrocarbons, which fact is at the basis of
the insolubility of sodium salts in hydro-
carbons. An element with pronounced
chemical characteristics like sodium, for
example, will retain to a high degree its
chemical predilections even after it has
entered into combination with other ele-
ments. Thus if we take sodium oleate, in
which the metal is combined with the
large fatty oleic radical, we nevertheless
find that this soap dissolves in water.
Here again the great affinity of sodium for
water manifests itself, and though the
metal is chained to the fatty radical which
of itself exhibits no inclination to unite
with water, yet this radical is dragged
along into solution as it were by the great
chemical attraction which sodium still has
for water. But the combination which
water and sodium oleate form is after all
but a loose one, as one would naturally

expect from what has been stated. The
fact that a solution of sodium oleate boils
but slightly higher than pure water shows
that there is but little affinity between
water and the soap. Again, the insolubil-
ity of sodium oleate in hydrocarbons shows
that the oleic radical, though it is known to
have affinity for hydrocarbons and fats, is
yet unable to drag the sodium with it into
solution. On the other hand, however, the
affinity of the oleic radical for fatty sub-
stances does manifest itself when a strong
aqueous soap solution is brought into con-
tact with greasy matter on clothes, etc., for
by virtue of this affinity the grease is
loosened from the fabrics, and though not
dissolved, it is nevertheless emulsified so
that it can be removed mechanically with
the soap solution. Numerous other ex-
amples illustrating the principles stated
might here be mentioned. I am at present
engaged in the work of collecting these.
Before the advent of the physical theories
of solutions considerable work was done in
ascertaining the chemical relationships
that must exist between solvent and solute
in order that solution may take place;
but during the last two decades this work
has been practically discontinued, which is
particularly unfortunate. It clearly indi-
cates, however, how our so-called modern
conceptions of solutions, which have been
pressed upon the scientific public by a
species of propagandism that is, and it is
to be hoped will remain, quite unrivaled
in the history of chemistry, have really
stood in the way of progress.

In some quarters the idea is still preva-
lent that electrolytes are essentially dif-
ferent from non-electrolytes in their chem-
ical behavior. This is thoroughly fallaci-
ous, for *all chemical changes that occur in
electrolytes can now be reproduced as to
type and as to rapidity in the best of insu-
lators. An electrolytic solution behaves*

like any other solution, except that it has the property of conducting electricity with concomitant chemical decomposition. There is no way known at present by which any one can foretell whether a given solution will conduct the current or not. The only way to find out is by actual trial with the electric current itself. There is also a mis-apprehension that only electrolytes will cause the coagulation of colloids. Such coagulation can be quite as well accomplished by non-electrolytes, so that here too there is no essential difference between electrolytes and non-electrolytes. Upon what electrolytic conduction really depends we are still quite ignorant, just as we do not know why a bar of silver conducts and a stick of sulphur insulates. But upon this matter I have already expressed myself more fully on other occasions.

Again it is necessary to call attention to the fact that there is really no essential difference between colloidal solutions and solutions of crystalline substances. I do not refer to those so-called colloidal solutions which from the very mode of their preparation must be regarded as suspensions, which view has also been confirmed by the use of the ultramicroscope. *We are now able to separate crystalline bodies from each other by dialysis, also crystalline bodies from those that have never been obtained in the crystalline state by having the latter pass through the septum and the crystalloids remain behind; and indeed, even two colloids may be separated from each other by dialysis,* as I have demonstrated experimentally in the course of my researches on osmosis. The matter depends entirely upon the nature of the solutions and the chemical nature of the septum, and from a knowledge of these, what will happen may be foretold.

Water is a great solvent, and because of its abundance and importance to all life on the globe aqueous solutions will ever be studied with the greatest interest. But in obtaining a correct conception of the nature of solutions, aqueous solutions obviously can have no stronger vote than solutions in less abundant and far less readily procurable liquids. Water has a high cohesion, as is shown by its high surface tension and high latent heat of vaporization. The hydroxyl group which is characteristic of the water molecule certainly exhibits great tendency to cling to other hydroxyl groups. So, for instance, though hydrocarbons are not soluble in water, they become soluble when one of their hydrogen atoms is replaced by hydroxyl, provided that the number of carbon atoms in the compound is small. However, when more than one hydroxyl group is in an organic compound, the latter may have even a relatively high carbon content and yet be soluble in water. A study of organic hydroxyl derivatives shows that compounds consisting of carbon, hydrogen and oxygen, and containing one or more hydroxyl groups for every carbon atom present, are soluble in water, though, to be sure, even considerably less than one hydroxyl group per each atom of carbon in the molecule is frequently sufficient to cause solubility. On the other hand, the multiplication of hydroxyl groups in such compounds tends to diminish their solubility in hydrocarbons. From this and similar illustrations that might readily be given it is clear that a study of the solubility of a compound in different solvents may well serve as a means to investigate the nature of that compound.

It need not be feared that by accepting the chemical view of solutions we should lose the advantage of the molecular weight determinations by the boiling-point and freezing-point methods. These methods would serve us as well as ever. But we should not argue that common salt is dis-

sociated in water because a gram molecule of it added to a liter of water produces a solution that has a higher boiling point than the solution obtained by adding a gram molecule of sugar to a liter of water. We should rather hold that the higher boiling point of the former solution is due to the greater affinity between salt and water as compared with that between sugar and water.

The study of solutions then was begun with the chemical conception of solutions, and upon this conception many relationships have been worked out during the first eighty-seven years of the nineteenth century. The older chemists clearly recognized that whether solution will take place or not in a given case is first of all determined by the chemical nature of the substances brought into contact with each other. They saw that the temperature factor was next in importance, and that pressure was of vital consequence when a gas was under consideration, but of slight importance in the case of solids and liquids. When the conception that solutions are mere physical mixtures came to the foreground, through the introduction of gas analogies and the intense propagandism of the dilute school, the fact that the act of solution is really chemical in character was lost sight of by many able, enthusiastic young investigators. In the ardor of their quest they were misled, and unwittingly they naturally misled others. It is really pitiable to see how our physiologists, having thus taken up these misconceptions of the nature of solutions, are still wasting precious time in endeavoring to work out the complicated and very important processes that occur in living plants and animals. In these problems, which are in reality perhaps the very greatest that confront us at the present day, theories of solutions based on

gas analogies are of no avail. They are thoroughly misleading and worse than worthless here.

The clear recognition that solutions are really chemical in character and that there is no wide gulf that separates the act of solution from other chemical phenomena, will do much toward furthering the future study of the subject. I do not claim to have prophetic ability, but nevertheless I venture to express it as my conviction, based upon years of experimental study of the chemical, physical and physiological properties of a long list of both aqueous and non-aqueous solutions, that the act of solution is chemical, that solutions are chemical combinations, and that we can only make real progress toward a better understanding of the various solutions by recognizing this as the basis of all of our future work. The efforts to gain a better insight into the different solutions that confront us must be chiefly experimental, rather than mathematical; for in the study of solutions, just as in the study of chemical compounds in the narrower sense of the word, we are continually confronted with discontinuities. Now discontinuous functions can not be handled mathematically at present, not even by the greatest of our mathematicians, for though work of this kind has been begun, it is still in a very rudimentary stage. It is highly probable too that the renewed study of solutions from the chemical point of view will greatly aid us in getting a broader and more correct conception of the nature of chemical action itself. Certainly in living beings we have numerous, fundamental and deep-seated chemical changes going on continually with apparently the greatest ease at ordinary temperatures and pressures, and it is tantalizing that we are unable to comprehend how this is all brought about. In the unraveling of the

questions that here confront us a clear recognition that solutions are chemical in nature will be of greatest service.

<div align="right">Louis Kahlenberg</div>

ON THE NATURE OF RESPONSE TO CHEMICAL STIMULATION [1]

In its last analysis we may readily enough suppose that the response of organisms to any stimulus is indirectly, at least, a result of chemical stimulation. That is to say, we may suppose that any change of environmental or internal conditions, whether it be of a chemical nature or of what is ordinarily called a strictly physical nature, awakens response by reason of chemical changes which are induced by its action, and these chemical changes are themselves the starting point for the chain of reactions which eventually evince themselves as the response.

A factor like increase of temperature very likely depends for its effect considerably, if not very largely, upon the chemical readjustments which it causes within the protoplasm. We have of course in the first place what might be called the primary or unmodified effect of increased temperature—the general acceleration of chemical processes which under such conditions is axiomatic in both inorganic and organic reactions and which does not necessarily imply any change in the chemical constitution of the protoplasm. But we should not assume too readily that the case is as simple as this, for organisms do not respond in the manner in which they would were their protoplasm a stable compound. In short, we are justified in supposing that certain changes of a more or less profound nature, due to altered chemical constitution, are the net result of rise in temperature. For instance, a change of temperature will in-

crease the intracellular activity of the protoplasm and may readily disturb the balance of the metabolic processes so that the production of a larger amount of excreted waste products will further accentuate or perhaps even modify the response by reason of a purely chemical stimulation caused by these very waste substances. Again, it is well known that one of the critical points of protoplasm as regards temperature— the coagulation point—depends upon the amount of water held by the protoplasm, including without doubt chemical as well as physical constitution of water. The less water, the higher the coagulation point, or in other words, the less water the less readily the final chemical reaction of protoplasm to heat takes place. The longer the organism is subjected to new conditions of temperature the more permanent the changes become, as is shown by the phenomena of acclimatization; and the more gradual these changes are, the less likely are they to result in the destruction of the plant.

In the response of protoplasm to light we have another instance where an external physical factor affects the chemical structure within the organism and thereby sets up reactions which are traceable to chemical stimuli. Without referring to the action of the red-orange rays in photosynthesis, I may call your attention in this regard to the action of light as a whole as a formative stimulus in tissue differentiation. In the absence of light, as is now well known, the production of the more elaborate prosenchymatic tissues is, to a large extent, if not wholly, inhibited. Now we can not suppose that light rays alone are directly responsible for, let us say, the lignification of the mechanical tissue in a stem, but their action is to cause certain chemical changes which constitute the stimulus which enables the living tissue to