

rienced eye and hand are often said to serve the purposes of those concerned at the time; but will anyone doubt that scientific accuracy and system would be more reliable? I am aware that "practical men" doubt this, but repeated contact with "practical men" assures one that they pay a heavy penalty in loss of time for their triumphs.

It is repeatedly observable that the "practical man"—the man of experience, in other words—has to spend long periods of time in the acquirement of his unsystematized powers, and the conviction forces itself upon the observer that he could do much more if he were systematically and logically observant, instead of being merely spasmodically so. In other words, he is scientific in so far as his successes go, for in the end it all resolves itself into keenness of observation and comparison; and he would save himself many failures if he were properly trained. How often is it pointed out that such and such a man is unscientific but practical! Well, this resolves itself into a fallacy, for he is really practical in so far as he is scientific in his methods—clumsily so, it may be, and the science in him has been unconsciously acquired and pursued; but it is there, and it is just where his science breaks down that he becomes a mere bungler. This truth need not blind us to the further one that even a bungler occasionally stumbles upon success, but my argument is that his conclusions would be more constantly trustworthy if he pursued a consistent and recorded course of methodical observation and comparison, instead of trusting to the unsystematized impressions from which his keen mind draws the conclusions of of which he is so vain.

It is, to my thinking, one of the most curious problems of the human mind that "practical men" can persist in upholding empiricism, on the grounds that such knowledge as the above is most real and useful. Of course, it is real and useful in so far as it has been acquired during long years of experience in contact with facts; but look at the opportunities lost in this expensive and wasteful training—at the mistakes made and the wrong lines pursued, until correction comes, sharp and merciless because it involves failure. Surely, a better method is to prepare the man to gain his experience at least cost, and to profit to the utmost by his mistakes; and, when all is done, see the equivocal position the "practical man" is put into—his only real knowledge is scientific, and the wild hypotheses and ignorant fallacies to which he is a slave might have become fruitful thoughts, leading him to far higher attainments had he learnt to observe and record, and compare and judge when he was young. Personally, I know no more contradictory being than the one who prides himself on being a "practical man," and is continually throwing at one's head the adage, "An ounce of practice is worth a ton of theory," for at every turn one finds him involved in endless tangles of error, and his ignorance of this is only equalled by the obstinacy with which he contends the contrary.

The second speaker was Prof. F. W. Oliver, who considered the question of botanical teaching only so far as it bears upon the training of medical students. He argued that, since all scientific medicine is based upon elementary biology, it is necessary to bear in mind that, in a course of say fifty lectures, designed for the requirements chiefly of medical students, some things must be sacrificed in order that certain fundamental truths may be driven home. The only questions are, What must go? and what must be retained? And the reply is that much of the study of types, and of such transcendental subjects as the alternations of generations, and so forth, as found in the schedule of the London University, for instance, should be sacrificed in order that the teacher may concentrate his attention on such parts of the subject as are of real importance and interest to the medical student, and others composing large classes. He would go so far as to say that about thirty out of the fifty lectures should be devoted to the organography and elementary physiology of the higher plants; for in that case the teacher is dealing with beings of which everybody knows something, and there is more human interest to the student when the *facies* of the organism is so familiar as is that of common flowering plants. In conclusion, Prof. Oliver pointed out that the responsibility of these matters rests with the examiners and those who draw up such schedules as that of the London University, and laid some stress on the importance of this responsibility.

Prof. F. O. Bower followed, and directed his remarks chiefly to the subject of teaching mixed and elementary classes in a University. He wished especially to deplore the threatened divorce between morphology and physiology, and advocated that

such a divorce should be prevented at all hazards. In regard to this, and to some other points, he must differ from Prof. Marshall Ward's conclusions, though he heartily concurred with most of what he had said. He thought that, taking into account the value of the mental exercise, so useful a study as that of morphology should be introduced early, and that the teaching of the main homologies should be insisted upon. With regard to the cut-and-dried schedules now so universal, Prof. Bower was

of opinion that, while they protect the weaker teachers, they hamper the strong ones, and he wished very much that more individual freedom should be allowed to lecturers.

Mr. Forsyth was especially interested in Prof. Marshall Ward's remarks on the teaching of botany to children in schools, and described an experiment now being tried in the Leeds Higher Grade School. The children are being taught to bring plants themselves, and to observe them in the field, and the speaker was of opinion that the new departure is a signal success.

Prof. Green spoke very strongly against the "type-system" as now pursued in the teaching of botany. Not only does it occupy too much time, but it is quite a mistake to begin with an unknown and minute object like the yeast plant: not only is the *Saccharomyces* plant a strange object, but the student obtains no adequate notions of its size or properties. He advocated less section-cutting and less work with the compound microscope, and more observation with the simple lens, at any rate until the student is familiar with common objects.

Prof. Hartog differed from previous speakers in thinking it a mistake to be afraid to teach children technical terms, and pointed out that children take very readily to hard names, and are very proud of having acquired them. He also differed entirely from those who advocate that the fern is a good type to begin with: the fern is a difficult type, abnormal in its pith, its stomata, and other respects, and should be avoided for some time. He thought it much better to select the various tissues and elements from the first, and then pass on to the study of types.

Prof. Hillhouse agreed with Prof. Marshall Ward that technical terms should be introduced carefully and not too early, and considered that botany has suffered in the past from being regarded as associated with hard words. He also advocated that botany affords the best means for introducing students to the use of the microscope.

Prof. Geddes has often found that schools are detrimental to the observing powers of children, and that the real way to interest the pupils is to let them make discoveries for themselves. He advocated the establishment of a botanical garden for every school, and pointed out that very useful notions of geometry can be taught from flowers. Prof. Geddes objected to the type-system for children, and urged that the life of the plant, and not its destruction, should be the aim of teaching. He would interest students in such subjects as insectivorous plants, and so infuse general interest into their studies.

Prof. Johnson remarked that at South Kensington, the home of the type-system, they have for some years past tried varying the order of teaching the several types, and have found that it is best to work down from the higher to the lower plants.

Prof. Marshall Ward having briefly replied, the discussion was then closed by the President.

THE PRESENT POSITION OF THE HYDRATE THEORY OF SOLUTION.¹

IT is but four years since this Section devoted a day to the discussion of the nature of solution;² since then, however, the general aspect of the question and the position of the advocates of the two rival theories have undergone such a complete change, that in renewing the discussion we shall run but little risk of going over the same ground which we then trod. At Birmingham, Dr. Tilden opened the discussion by passing in review all the well-known and long-known facts which might by any possibility throw some light on the nature of solution, and those who followed him in the discussion each gave the interpretation of these facts which harmonized best with his own views, and, as the facts themselves were susceptible of several different interpretations, the not surprising result followed that

¹ Paper read before Section B, at the Leeds meeting of the British Association, as an introduction to a discussion on the nature of solutions and the theory of osmotic pressure.

² B. A. Report, 1886, p. 444.

each disputant departed holding precisely the same opinions which he had brought with him. Since then, however, each party has obtained, or thinks that he has obtained, positive evidence in favour of his own views; evidence which, if upheld, must be accepted as conclusive, or which must be overthrown before his opponents can claim the victory. The supporters of the hydrate theory claim that the curved figures representing the properties of solutions of various strengths show sudden changes of curvature at certain points, which are the same whatever be the property examined, which correspond to the composition of definite hydrates, and which, therefore, can only be explained by the presence of these hydrates in the solutions; while the supporters of the physical theory, now identified with the supporters of the osmotic pressure theory, claim to have shown that, with weak solutions at any rate, the dissolved substance obeys all the laws which are applicable to gases, and that, therefore, its molecules must be uninfluenced by, and uncombined with, those of the solvent.

In another respect also I may notice that our position to-day differs considerably from what it was four years ago; for instead of having to argue the matter out amongst ourselves, as we did then, we are now favoured with the presence of some of those whose work in this very subject has made their names familiar household words with every physicist and chemist throughout the scientific world.

I propose in the first place to give a brief summary of the evidence which has lately been adduced in favour of the hydrate theory, and in the second place to inquire whether the conclusions drawn from this evidence are invalidated by the important facts elucidated by Raoult, van't Hoff, Arrhenius, and Ostwald.

In one respect the supporters of the hydrate theory start now under a distinct advantage—namely, that their most active opponents do not altogether deny the existence of hydrates in solution, although it is only in the case of strong solutions that they will admit their presence; in such solutions, indeed, it is difficult to see how their presence could possibly be denied. The only means which we have of proving that a liquid is a definite compound is by ascertaining whether its composition remains unaltered by its passage through the gaseous or solid condition—by fractionating it by means of distillation or crystallization. With liquids of comparatively small stability, such as hydrates, crystallization is the only method available; the results of crystallization have led us to conclude that the liquid represented by H_2SO_4 is a definite compound, and precisely similar results must force us to accept the definiteness of the liquids $\text{H}_2\text{SO}_4\cdot\text{SO}_3$, $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$, and $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$: in the case of each of them the liquid freezes as a whole, and without change of composition; the temperature remains constant throughout the solidification, and any excess of either water or sulphuric anhydride which may have been added may be separated from the pure compound, which alone crystallizes from the mixture. Thus, in the instance taken, between the anhydride on the one hand and water on the other, we have four definite compounds, all existing in the liquid condition.

It does not follow, however, that every hydrate which exists in solution can necessarily be obtained in the solid condition; probably no solution, even when it possesses the exact composition of some existing hydrate, consists of that hydrate only, but of a mixture of it with the products of its dissociation (though the amount of these may be very small); and whether the hydrate or one of these dissociation products crystallizes out on cooling must depend on the relative ease with which the bodies in question assume the solid condition; when the hydrate does not crystallize easily we can hope to obtain evidence of its presence by indirect means only.

Mendeleeff's conclusions respecting the densities of solutions of sulphuric acid and alcohol,¹ mistaken though I believe they were, led to the discovery of the means whereby such evidence might be obtained.

He stated that on plotting out the rate of change of the densities with the percentage composition of the solution (the first differential coefficient) he got a series of straight lines, forming figures with well-marked breaks at points corresponding to definite molecular proportions; but on plotting out the experimental points which he said formed these figures, it is impossible to see any justification for this statement; in the case of sulphuric acid the points and Mendeleeff's drawing of them have been given side by side in the *Trans. Chem. Soc.*, 1890, p. 81, and in the case of

alcohol they will be found in the *Zeit. f. Phys. Chem.* VI. i. 10. Crompton then showed¹ from an examination of Kohlrausch's values for the electric conductivity of sulphuric acid solutions that a second differentiation might in some cases be necessary before rectilinear figures with breaks in them were obtained. In my own work on various properties of solutions of the acid I have made free use of this process of differentiation, but I have combined it with, and now nearly entirely rely on, an examination of the original curves with the help of a bent ruler.

In the *Phil. Mag.*, 1890, vol. i. p. 430, will be found rough sketches of the figures representing the densities, contraction on formation, electric conductivity, expansion by heat, heat of dissolution, and heat capacity of the solutions, and in the *Trans. Chem. Soc.*, 1890, p. 338, that representing the freezing-points. In some cases, such as the freezing-points of solutions near 58 and 100 per cent. strength, a mere inspection of the figure enables us to locate the position of abrupt changes of curvature; in general, however, the recognition of such changes is more difficult. On attempting to draw any of these figures with the help of a bent ruler it was found that the whole figure could only be drawn in several sections, and it was also found that each section thus drawn consisted of a single curve of a parabolic nature, although a ruler, when bent by the pressure exerted by the two hands, by no means necessarily forms a parabola; and moreover—and this is the most important part of the evidence—it was found that these figures, though differing so greatly in their general appearance, all split up into the same number of sections, indicating the existence of changes of curvature at the same points; and, further still, these points corresponded to solutions of definite molecular composition in all cases where the ratio of the acid to the water was sufficiently large to render any such comparison possible; the average difference between the composition indicated by the changes of curvature and that of definite hydrates was only $0\cdot057\text{H}_2\text{O}$. With weak solutions it is, of course, impossible to assert that the changes occur at definite molecular proportions, owing to the smallness of the change in percentage composition which would be caused by an additional molecule of water to each H_2SO_4 ; but the changes with these weak solutions are of precisely the same character as those with strong solutions, and, unless some strong evidence to the contrary be forthcoming, we must attribute them to the same cause.

To discuss fully the value of the evidence thus obtained would take me more hours than I can now afford minutes; but I think that I may say that these results stand at present unquestioned and uncontroverted, and that unless they can be controverted we must accept the presence of hydrates in solution as having been proved. I may also add that my results with sulphuric acid solutions have been strengthened by obtaining analogous results with solutions of several other substances: that one of the hydrates indicated by them has been proved to exist by isolating it in the crystalline condition: and lastly, that a law governing the freezing-points of solutions has been formulated, according to which we can calculate within experimental error the freezing-point of any solution, whatever its strength may be, provided we acknowledge the existence of every hydrate which my work has indicated; whereas, if we deny the existence of these, the freezing-points calculated according to this or any other law show such divergences from the found values that all semblance of agreement disappears. I am indeed labouring under no small disadvantage in attempting to support the hydrate theory when the greater part of the evidence existing in favour of it is as yet unpublished.

Before proceeding to the second part of my subject I wish to draw attention to the great complexity of some of the hydrates which my work has indicated, as well as to the fact that the indications of sudden changes are nowhere more marked than they are with these very weak solutions. The changes, which are observed in the heat of dissolution curve from 5 per cent. downwards,² afford a good illustration of this latter fact; or, again, the freezing-points of weak solutions may be instanced,³ where the rate of fall from 0 to $0\cdot07$ per cent. is a quarter as great again as it is from $0\cdot07$ to $1\cdot0$ per cent. The complexity of the hydrates indicated is so great that in the extreme cases they must be represented as containing several thousand H_2O molecules, and the suggestion of such complexity will no doubt prejudice many against my conclusions in general; though on what grounds I know not, for we are entirely in ignorance at

¹ *Zeit. f. Phys. Chem.*, i. p. 275; *Chem. Soc. Trans.*, 1887, p. 778.

² *Ibid.*, 1890, p. 107.

³ *Ibid.*, p. 343.

present as to the possible complexity of liquid molecules. It is interesting to note that a similar complexity of molecular grouping must be admitted if we accept Raoult's original statement that one molecule of any substance dissolved in 100 molecules of a solvent lowers the freezing-point of this latter by about $0^{\circ}\cdot63$; for, if this be so, we must assign to the molecules of the various substances entered in the second column of Table I. the magnitude there indicated when they are dissolved in the solvent named in the first column, for it requires that proportion of these bodies to lower the freezing-point of 100 molecules of the solvent by $0^{\circ}\cdot63$; and, amongst these few instances which I have collected from my own determinations, we find molecular aggregates containing as many as 200 of the fundamental molecules, and even this number, I may mention, probably understates the complexity to a very considerable extent; for the depression in this and some of the other cases had to be estimated from that observed with solutions containing as much as 10 gram molecular proportions to 100 of the solvent, and the molecular depression increased rapidly with the strength of the solution: $1000\text{H}_2\text{O}$ would probably be a low estimate of the complexity of the molecules of water when dissolved in a large excess of the hexhydrate of calcium chloride, a complexity comparable with that of the hydrates, which my other work has indicated, and that too in the case of that very substance which these hydrates contain—water.

TABLE I.—Molecular Weights of Substances in Various Solvents.¹

Solvent.	Dissolved substance producing $0^{\circ}\cdot63$ depression. ²
$100\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$	$32\text{H}_2\text{O}$
... ..	$63\text{H}_2\text{SO}_4$
$100\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$	$8\text{H}_2\text{O}$
... ..	$15\text{H}_2\text{SO}_4$
$100(\text{CaNO}_3)_2\cdot 4\text{H}_2\text{O}$	$90\text{H}_2\text{O}$
... ..	$42\text{Ca}(\text{NO}_3)_2$
$100\text{CaCl}_2\cdot 6\text{H}_2\text{O}$	$210\text{H}_2\text{O}$
... ..	63CaCl_2

Now as to the question of how far the theory of osmotic pressure, and the results on which it is based, are antagonistic to the hydrate theory: and let me first define clearly the position which I take in this matter. I do not for one moment call in question any of Raoult's classical work, which is now so familiar to us, nor do I question that these results reveal the existence of a depression of the freezing-point which is approximately and generally constant; and I consequently admit that we can generally obtain an approximately correct value for the molecular weight of the substance by observing the depression which it causes; nor, again, do I wish to question the correctness of the mathematical relationship which van't Hoff and Arrhenius have shown to exist between osmotic pressure, the lowering of the freezing-point, and other properties, provided we accept the fundamental assumptions on which their calculations are based—the truly gaseous nature of dissolved matter, and the dissociation of salts into their ions. But what I do question is that the facts of the case warrant such assumptions, and that the constancy and regularity of the results are so rigorous as to justify the conclusion that the solvent has no action on the dissolved substance, and that there are no irregularities such as would be caused by the presence of hydrates.

According to the osmotic pressure theory, the dissolved matter, so long, at any rate, as it is not present in greater quantity than it would be in the same volume of its gas, if it were gasified under normal conditions, is really in the gaseous condition, and obeys all those laws which apply to gases. According to the hydrate theory this will be but partially true. That the dissolved substance is in a condition comparable with that of a gas, in so far as the separation of its own particles from each other is concerned, must be admitted—indeed, I arrived independently at this same conclusion from a study of thermochemical data; but inasmuch as there is present the solvent, which we believe is *not* an inactive medium, its molecules cannot have the same freedom as if they were truly gaseous, and will, therefore, obey the laws of gases imperfectly only.

It will be well to confine our attention to but one of those properties connected with osmotic pressure, and to select for

¹ Other instances of high molecular weights are mentioned by Brown and Morris (Chem. Soc. Trans., 1888), and Gladstone and Hibbert (*Phil. Mag.*, 1889, vol. ii, p. 38).

² Determined from the freezing-points of very weak solutions.

that purpose the one which has been most fully investigated—the lowering of the freezing-point of a solvent: and the tests which may be applied to ascertain whether in producing this lowering the dissolved substance behaves as a perfect gas or not, may be grouped under three principal headings:—

1. Is the molecular depression (*i.e.* that produced as calculated for one molecule dissolved in 100 molecules) constant, independent of the nature of the solvent?

2. Is it independent of the strength of the solution, so long as this strength does not exceed the limits ("gas" strength) above mentioned? (Boyle's law.)

3. Is it independent of the nature of the dissolved substance? (Avogadro's law.)

In the *Phil. Mag.*, 1890, vol. i. p. 495, will be found instances of the variation in the molecular depression which may be noticed by altering the solvent (see also Table I. above). With water in six different solvents it varied between $1^{\circ}\cdot072$ and $0^{\circ}\cdot003$; with sulphuric acid in four different solvents, between $2^{\circ}\cdot15$ and $0^{\circ}\cdot01$; with calcium chloride in two different solvents, from $2^{\circ}\cdot773$ to $0^{\circ}\cdot01$; and with calcium nitrate in two solvents, from $2^{\circ}\cdot5$ to $0^{\circ}\cdot015$; while many instances may be collected from Raoult's data showing that the same substance which acts normally in one solvent may act abnormally (give only half the usual depression) in another. Such variations are so great—from 100 to 35,600 per cent.—that there can be no doubt but that the solvent is *not* that inert medium which the supporters of the physical theory would have it to be, but that it has a very great influence on the results obtained. It must be noted, however, that this objection, though applying to Raoult's original views, does not, or, at any rate, may not, apply to van't Hoff's theory, for according to this theory the nature of the solvent has an influence in determining the lowering of the freezing-point, W, in van't Hoff's equation, $\delta t = \frac{0^{\circ}\cdot02 T^2}{W}$, representing the heat

of fusion of the solvent. But the lowering is according to this equation independent of the nature or the amount of the dissolved substance, so that the two following objections will apply to van't Hoff's theory as well as to Raoult's statement.

Secondly, as to the influence of the strength of the solution. It is remarkable that, although the osmotic pressure theory depends on the behaviour of solutions below a certain strength, no attempt whatever has been made by its supporters to obtain any data respecting such solutions. The data on which their views were founded referred to solutions considerably stronger than the requisite "gas" strength, and though, no doubt, it was convenient to work with data which afforded a ready excuse for any awkward irregularities which might be met with, such data must lack the conclusiveness which is so eminently desirable. The few data which I have accumulated as to solutions of an "ideal" strength can leave no doubt that, even in their case, the depression is not a constant independent of the strength.

A solution of sulphuric acid containing $0\cdot08\text{H}_2\text{SO}_4$, $100\text{H}_2\text{O}$ would be of a strength comparable with the gas: from the acid if it could be gasified at normal pressure and temperature, and the molecular depression should be constant for all solutions below this strength: it should be represented by a horizontal line such as AB in Fig. 1, whereas the observed deviations from constancy are very great, being represented by the lines marked H_2SO_4 ; and, moreover, these deviations are by no means regular, and cannot therefore be attributed to imperfect gasification; they possess none of the characteristics of the deviations of gases from Boyle's law. The determinations on which these results are based are very numerous; there are about sixty experimental points on the portion here shown, and the mean error of each point as determined in two different ways was only $0^{\circ}\cdot0005$, a quantity represented by one-tenth of one of the divisions of the paper; the deviations from regularity amount to thirteen times this quantity, and to as much as 16 per cent. of the total depression measured.

The other lines in Fig. 1 represent the deviations from regularity in the case of calcium chloride, calcium nitrate, and alcohol respectively, and these, though they are smaller than in the case of sulphuric acid, are far too great to be attributed to experimental error; and the fact that they occur sometimes in one direction, sometimes in the other, precludes the possibility of attributing them to any constant source of error in the instruments used or in the method adopted.

Remembering that these are the only data which we have at present respecting very weak solutions, we must conclude that the hypothesis that such solutions exhibit perfect regularity is

wholly untenable; and it must be specially noticed that one of the substances showing these irregularities—alcohol—is a non-electrolyte, in which case the theory of dissociation into ions cannot be brought forward as an explanation of their existence.

It is important to observe that when we pass on to stronger solutions, where the actual magnitude of the deviations becomes so great that they would be revealed by the roughest experiments—deviations of even 70°—and where, I believe, even the

supporters of the osmotic pressure theory would not hesitate to attribute them to the disturbing influence of hydrates; these deviations occur in precisely the same irregular manner as they do in the case of weak solutions, and must evidently be attributed to the same cause. The results with alcohol given in Fig. 2 illustrate these irregularities in a very striking manner. It must also be pointed out that, apart from the irregularity of these deviations, their very direction shows that they cannot be attributed to the

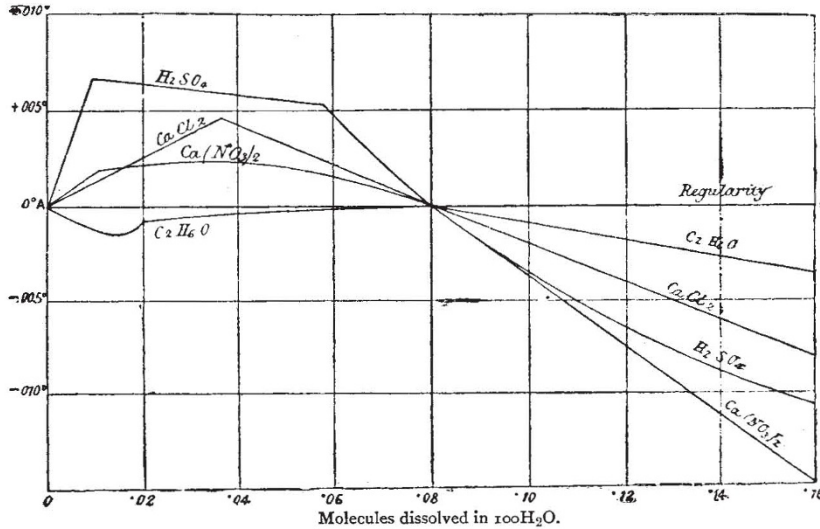


FIG. 1.—Deviation from regularity of the freezing-points of very weak solutions.

dissolved particles being brought within the sphere of each other's attraction, as in the case of the deviation of gases from Boyle's law, for the result of this would be that their attraction on the particles of the solvent would be diminished, and the freezing-point of this latter would consequently be lowered to an abnormally small extent, whereas precisely the reverse is the case in nearly every instance at present investigated: the freezing-points of strong solutions are abnormally low. Various

instances of this will be found in the *Phil. Mag.*, 1890, vol. i. p. 500, that of sulphuric acid, which is illustrated here in Fig. 2, being by no means the most prominent; while the case of alcohol, now for the first time displayed (Fig. 2), is the only exception which has, so far, been met with, and that is an exception only in the case of excessively strong solutions.

From the instances above mentioned some answer may be obtained to the third question—whether the molecular depression

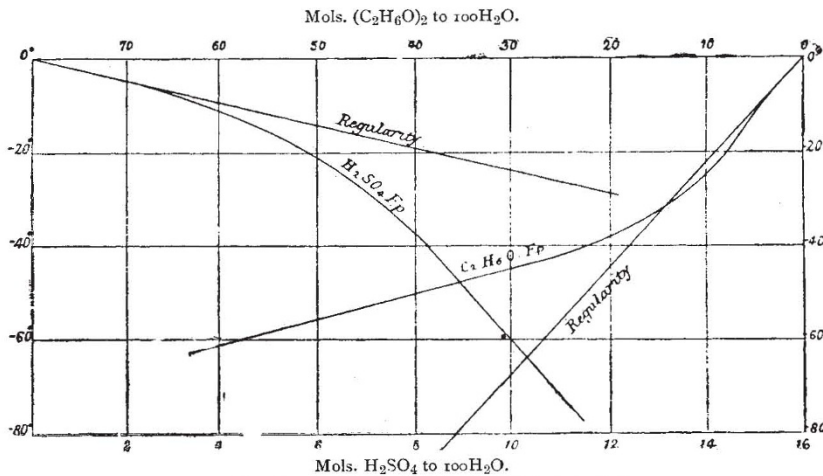


FIG. 2.—Freezing-points of sulphuric acid and alcohol solutions.

is independent of the nature of the dissolved substance. The values obtained with these four substances, taking solutions of a strength corresponding to that of their gases, are:—

Calcium chloride	2°·850
Calcium nitrate	2°·744
Sulphuric acid	2°·313
Alcohol	2°·180

a variation of 30 per cent., which must give an emphatic denial to the idea of absolute constancy; and if we take instances from

other substances, where the data available refer to solutions of somewhat greater strength, we find that the very substances on which the idea of constancy was originally founded show variations reaching 60 per cent. (*Phil. Mag.*, 1890, vol. i. p. 492), while in other cases, which I have quoted elsewhere (*loc. cit.*, p. 493),¹ the variation attains the still larger dimensions of 260 per cent.

¹ The depression produced by H₂O in 100H₂SO₄ is 1°·07 instead of 0°·07 as there given.

To every one, therefore, of the three test questions as to constancy and regularity, the experimental results give an unhesitating negative.

In the instances quoted above the depression actually found for alcohol has been doubled in order to simplify the comparison of it with the other substances. Alcohol belongs to that class of bodies which give just half the value in water that the majority do, and of which there are some instances in the case of every solvent yet examined. The explanations which the supporters of the chemical and physical theories give of these half values differ so radically from each other that it is hopeless to attempt to arrive at any agreement as to the nature of solution till this difference is settled. The chemists say that these half values are in all cases the abnormal ones, just as Raoult did originally, and explain them by representing the molecules of the dissolved substances which give them to consist of two fundamental molecules. The physicists give exactly the same explanation in the case of every solvent except water, but in this case they say that the smaller values are the normal ones and the larger the abnormal, the double magnitude of these being caused by the dissociation of the dissolved molecule into its two ions, whereby two molecules or acting units are formed from every one originally added.

If Raoult's views as to the constancy of the molecular depression can be maintained, the data themselves are conclusive against making this exception in the case of water; for, since the substances which give the lower values are supposed to act normally, it is evident that, if the values given are in any way abnormal, this abnormality must be due to the solvent. Now the values certainly *are* abnormal; they are about $1^{\circ}03$, whereas the normal value for one molecule dissolved in 100 molecules of other solvents is $0^{\circ}63$, and the excess can, therefore, only be explained by assuming that the molecules of water are more complex than those of other solvents in the proportion of $1^{\circ}03$ to $0^{\circ}63$, or $1\frac{1}{2}$ to 1; in other words, the water molecules must be $1\frac{1}{2}H_2O$. This view cannot be reconciled with the atomic theory.

Indeed the theory of dissociation into ions is altogether unintelligible to the majority of chemists. It seems to be quite irreconcilable with our ideas of the relative stability of various bodies, and with the principle of the conservation of energy. Of course we know that each ion when dissociated is not supposed to be permanently dissociated, but to be continually combining with its neighbours and separating again from them as in every other case of dissociation; but at any particular moment a very large proportion of them is supposed to be free; a proportion which, according to the very results under discussion, must be very nearly, if not quite, 100 per cent. of the whole; and we have to settle whether it is probable or possible that a decomposition such as this could have been effected by introducing the compound into water. And how can we regard it probable that compounds of such stability and compounds formed with such a development of heat as sulphuric or hydrochloric acid should be thus entirely dissociated by water; still less that these, and all the most stable compounds which we know, should be thus demolished, while all the less stable ones—such as hydrocyanic, sulphurous, boric acids, &c.—remain intact? How can we admit that the more stable a body is, the more prone it is to be dissociated?

And if such a dissociation has occurred it must have been without any absorption of heat, and, consequently, energy must actually have been created. Take one of the simplest instances, that of hydrochloric acid. If anything at all is certain about atoms, it is that the atoms in an elementary molecule are united very firmly together, and that therefore in separating them a very large absorption of heat would occur. To separate $2HCl$ into $2H$ and $2Cl$ would absorb far more than the 44,000 cal. which we know are absorbed in separating $2HCl$ into H_2 and Cl_2 . Yet the supporters of the dissociation theory would have us believe that this separation has actually taken place, not only without any absorption of heat, but actually with a development of 34,630 cal.; that is, that $44,000 + 34,630 + x$ cal. have been *created*, and that too through the intervention of the water, which has *ex hypothesi* no action whatever.

This difficulty is realized by the supporters of the physical theory, but the way in which they meet it does not appear to me in any way to overcome it. To explain the non-absorption of heat in the dissociation of the salt, they suppose that a charge of electricity combines with the liberated atoms, and, in doing so, evolves an amount of heat exactly equivalent to that ab-

sorbed in the separation of the atoms from each other; and a later development of the theory is, I believe, that the atoms, though separated, are still held together by means of these charges, so that the net result is the supplanting of the chemical bond by an electrical bond of a precisely similar value. It appears to me that nothing substantial is gained by such a substitution, and that its occurrence is not merely hypothetical but impossible. Whence come these electric charges, and by what agency are they brought into play? On what grounds can it be maintained that a charge can combine with matter so as to evolve heat, and that the heat so liberated is always exactly equal to that absorbed in the decomposition of the compound? If this equality exists, how can we account for the force which develops the one overcoming the *equal* force which develops the other? and how, again, can we account for the heat developed in the act of dissolving? If, on the other hand, the heat of the combination of these charges is supposed to be equivalent to the heat of combination of the atoms *plus* that of the heat of dissolution, we are met by the objection that the latter is often negative, and that, therefore, the heat of the combination of the charges must often be less than that of the combination of the atoms and molecules, so that the lesser force must be regarded as overcoming the greater.

That free ions exist in solution is supposed to have been proved by a recent observation of Ostwald's, to the effect that the ions may be separated and brought into different parts of the liquid by the proximity of a charged body. The separation of the ions is, of course, recognized by the subsequent liberation of hydrogen, oxygen, acid, alkali, &c., and it is certain that on allowing these to mix and combine heat will be developed, and the salt solution re-formed; and thus, by replacing and removing the charged body, it would evidently be possible to produce an unlimited amount of heat. Now, if the charged body has lost none of its charge, and if no mechanical energy has been expended, this heat must have been produced out of nothing, and the whole ground-work of physical science must be false; whereas, if energy in some form has been expended on the solution, the experiment proves nothing, for there is nothing to show that this energy has not been utilized in bringing about the very dissociation the previous existence of which was in question.

I have already shown that the experimental data prove the absence of that constancy and regularity which ought to exist according to the physical theory, and to place the hydrate theory on unassailable grounds it is only necessary to show that deviations from constancy and regularity are of a magnitude such as might reasonably be assigned to deviations due to the presence of hydrates. That variations of 260 and 36,000 per cent. in the value of the depression—such as are observed by altering the dissolved substance or the solvent respectively—are amply sufficient to satisfy the most exalted views of the influence of chemical attraction, requires, I think, no demonstration, and we may therefore content our-elves with examining the deviations observed when the proportions of the solvent are altered—such deviations as are illustrated in Fig. 1.

It cannot be maintained that the energy of the chemical combination of, say, water with sulphuric acid, is the only reason why the temperature of the mixture of the two must be cooled below 0° before any of the latter will crystallize out; some lowering of the freezing-point will be caused by the mere interposition of the foreign molecules of sulphuric acid between those of the water, and on certain grounds, which I have explained elsewhere,² I estimate this mechanical lowering, as I term it, at $0^{\circ}56$ for each dissolved molecule to 100 of the solvent (a molecule of solvent water being $3H_2O$), a value which, it may be noted, is not far removed from Raoult's experimental value of $0^{\circ}63$. There is also another source of lowering depending mainly on the heat capacities of the substances concerned, which I term for convenience the physical lowering; but its value, in the case of weak solutions, is very small, and I need, therefore, say no more about it here. Both these lowering causes would exist whether there were hydrates present or not; but if these were present we should get a further depression due to their existence. Any given hydrate would have to be decomposed into the next lower one before it could give up any water for crystallization, and a certain amount of resistance would thus be offered to this crystallization, to overcome which the solution would have to be further cooled.

¹ On the view that hydrates exist in solution, there is a difficulty, as I have shown elsewhere, in explaining the absorption of heat during dissolution, without violating the principle of the conservation of energy.

² Proc. Chem. Soc., 1889, p. 149.

The necessary cooling may be estimated in the following way: Supposing the solution to be a mixture, and to be cooled below its normal freezing-point, then, on solidification, the temperature would rise to this point, but if this solidification involved a chemical decomposition which absorbed x cal., the rise of temperature would be thereby reduced, the reduction thus caused amounting to $x \div$ the heat capacity of the solution. As the heat absorbed in the decomposition of the various hydrates of sulphuric acid is known, we can calculate the lowering produced by their presence.

TABLE II.—Freezing-Points of Solutions of Sulphuric Acid.

I. Per cent. H ₂ SO ₄ .	Calculated.				IV. Found F. p.	Next hydrate.	
	II. Mech.	III. Phys.	IV. Chem.	V. Total.		VII. Calc.	VIII. Found.
0°068	0°0209	0°0	0°0110	0°0347 ¹	0°0354	0°37	0°36
0°362	0°1114	0°0004	0°0248	0°1508 ¹	0°1532	1°43	1°06
1°06	0°3275	0°0044	0°0589	0°4314 ¹	0°4272	3°54	4°02
4°02	1°285	0°071	0°077	1°582 ¹	1°59	8°40	8°59
8°59	2°879	0°388	0°189	3°815 ¹	3°80	18°17	18°49
18°49	6°96	3°23	1°59	11°78	11°83	29°7	29°5
29°53	12°85	13°82	3°50	34°17	34°00	37°5	37°7

In Cols. II., III., and IV., I have given the depression due to the three above-mentioned causes in the case of certain solutions, Col. V. containing their sum; and it will be seen what a small proportion of this total lowering can be attributed to purely chemical causes. With most solutions it does not exceed 10 per cent. of the total, and with weak solutions, such as are generally used in freezing-point determinations—say 5 per cent.—it amounts to considerably less than 0°1; this, too, in the case of sulphuric acid, where the heat of formation of the higher hydrates is greater than with any other known substance.

The reason, therefore, why the deviations from constancy are so small as to have escaped detection hitherto, and the reason why solutions behave almost as if their chemical nature was non-existent, becomes apparent; but this near approach to constancy and regularity, instead of proving the correctness of the physical theory and giving a death-blow to the chemical theory, is really one of the strongest arguments which can be adduced in favour of the latter. If the hydrate theory is right, the influence of hydrates must often be nearly inappreciable.

But it is not only a general concordance between the found and calculated magnitude of the irregularities which the hydrate theory is capable of affording, but a concordance so exact that the precise value of the deviation at any point may be calculated. In Col. VI. of Table II. are given the observed freezing-points of the solutions, and these show an average difference of but 0°004 for the three weaker solutions, and 0°06 for the four stronger solutions, from those calculated (Col. V.). The last two columns exhibit this concordance in a different manner; from the observed freezing-point we can calculate the composition of the hydrates which must exist in the solution (Col. VII.), and these are found to agree so fully with those indicated by the examination of the curved figures representing various properties of the solution (Col. VIII.) that the maximum difference between the two is only 0°48 in the percentage of acid present.

When we can by simple calculations, based on one series of determinations, prove that the hydrates in solution must be the same as those which totally independent experiments have led us to suppose, we have, I think, arrived at proof as nearly absolute as it is possible to conceive; and, if I have succeeded in showing that this proof may be accepted without in any way rejecting the facts on which the advocates of the osmotic pressure theory rely—approximate constancy, approximate regularity, and approximate similarity between dissolved and gaseous matter—I shall feel that I have done far better work than the mere establishment of the hydrate theory, by pointing out a possible *modus vivendi* for both theories almost in their entirety, and by helping to break down that wall of separation between physicists and chemists which is fast crumbling into dust.

SPENCER UMFREVILLE PICKERING.

¹ The actual total has been increased by 10·4 per cent. of its value to give the figures quoted in these five cases, for reasons which will be given elsewhere. Some of the numbers in this table may be subject to slight corrections, as they have been quoted in the absence of the original calculations.

A TEACHING UNIVERSITY FOR LONDON.

THE following letter has been addressed to the Lord President of the Privy Council:—

MY LORD,—We, the undersigned, the President of University College, London, and the Principal of King's College, London, beg leave to address your Lordship in reference to the joint petition from the Councils of our two Colleges for the incorporation of a Teaching University in London, which has for some time been before the Privy Council. Your Lordship had the goodness to receive a deputation from the Councils of our two Colleges in July 1889; and your Lordship then intimated your judgment that the University of London should be allowed a reasonable time in which to propose a new charter in accordance with the recommendations of the Royal Commission on the question of a Teaching University in London. In obedience to this intimation from your Lordship, our Councils have, at the request of the Senate, entered into negotiation with them, and have consented, subject to the satisfactory settlement of some points affecting the Faculties of Law and Medicine, to a scheme for our union with the University, embodying a separate system of graduation for our students in the Faculties of Arts and Science. We desire that power should be reserved in certain events to make similar arrangements in regard to the Faculty of Law. With respect to medicine, the Senate have stipulated that they should be at liberty to make different arrangements, separately from our Colleges; and in the absence of opportunities for conference with the other institutions specially interested in this Faculty, we have not thought fit on this ground to break off the negotiations; but we reserve power to reconsider our position, if arrangements are contemplated by which it would be seriously affected. We claim, further, as essential to the efficiency of our teaching in science, that our medical students, for the purpose of their examination in pure science, known as the "Preliminary Scientific Examination," shall be considered as belonging to the Faculty of Science on the teaching side of the University, and not to a separate Faculty of Medicine.

Having been informed that urgent protests are raised by University Colleges in the country, particularly at Birmingham, against influence being given to London Colleges in the Senate while they are excluded, we beg to remind your Lordship that the amalgamation of the proposed Teaching University for London with the existing University was not our proposal, but has been, thus far, accepted by us in deference to the principal Report of the Royal Commissioners. We consider that, if this amalgamation is effected, we are entitled to a representation on the governing body of the reconstituted University proportionate to our concern in University teaching for London, considered as one of its two spheres of work; and that the nature of the case does not admit of a similar effective representation of institutions elsewhere. If this reconstitution of the existing University should be found, by reason of such opposition, or for any other reason, impracticable, we desire to be replaced in our original position, as petitioners for the establishment in London of a Teaching University upon the lines of our petition presented in 1887, and of the draft charter thereto appended, to which, in that case, we still respectfully adhere.

We have the honour to remain, your Lordship's obedient humble servants,

JOHN ERIC ERICHSEN,
President of University College, London.

HENRY WACE,
Principal of King's College, London.

UNIVERSITY AND EDUCATIONAL INTELLIGENCE.

CAMBRIDGE.—The election of a Professor of Mechanics and Applied Mechanics, in succession to Prof. James Stuart, will take place on November 12. The names and testimonials of candidates are to be sent to the Vice-Chancellor by Saturday, November 8. The electors are the Vice-Chancellor, Mr. W. Airy, Dr. Besant, Sir F. J. Bramwell, Dr. Cayley, Mr. H. Darwin, Mr. Martin, Dr. Phear, and Lord Rayleigh. The stipend is £700. The Senate has approved a new scheme for the management of the department, under which the Professor is directly responsible for the carrying on of the workshops.

Mr. Chaplin, the President of the Board of Trade, has proposed to the Chancellor that the University should undertake