DISCUSSION.

Professor W. A. Tilden, F.R.S., said he had been always deeply interested in the question of solution, and thirty years ago had put forward a view of the constitution of solutions such as was at that time possible, namely, an hydration theory based on the analogy of gaseous dissociation. Since then the gas theory and the ionic hypothesis had arisen, and no doubt the two theories were not incompatible with ideas of hydration. Some of the difficulties that had been stated were, he believed, merely due to the complicated phenomena involved.

If, as Messrs. Bousfield and Lowry maintained, both the ions of a dissociated molecule were hydrated, it was curious to note that in crystallisation it was the *metal* which appeared to determine the amount of water of crystallisation.

It was impossible to adopt the hydration theory without qualification in all instances; for example, in a solution of ammonia no doubt some hydroxide was present, but ammonia itself was certainly present as such. There were other similar cases. The fact was no *single* theory at present in the field was able to explain all the phenomena observed in every case, but it was a hopeful sign that whereas twenty-five years ago people actually would not listen to a discussion on solution, not even at a B.A. meeting, the Faraday Society had that night been able to arrange the fruitful and interesting discussion he had had the pleasure to take part in.

Mr. R. J. Caldwell said that the idea of attributing the diminution in the solvent power of liquids for gases, &c., on addition of salts to the formation of hydrates was a very old one, having been very definitely stated by Setchenow in 1875 and Tilden in 1880. The dissolution of a gas, although in accordance with Henry's law, is evidently a case of chemical combination with the solvent, since small molecules such as helium and hydrogen are very much less soluble than large molecules with residual affinity such as nitrous oxide and acetylene. Hence "internal pressure" or "electrostriction" cannot be the cause of the influence of neutral salts. In applying Dr. Philip's method of calculation, however, it must not be forgotten that the hydrated salt in some cases may possess a certain affinity or solvent power for the gas. The result is that hydration values calculated by this method are too low by an unknown amount. In some cases the error is very great, as, for example, in the case of the ammonium salts and the mineral acids.

The statement made by Dr. Senter that "the accelerating effect of neutral salts (on catalytic actions) is practically independent of the nature of the salt, so that neutral salt action is not connected with hydration," is at variance with the facts. Experiment shows that the accelerating action of each salt on the hydrolysis of sugar and on that of methyl acetate by mineral acids is a specific property of the salt. Careful measurements show that lithium nitrate, for instance, has almost three times the effect of silver nitrate. The conditions employed by Dr. Senter in his experiments on chloracetic acid (dilute solutions at 102°) were such that the hydration of added salts would hardly produce a measurable effect, and the alternative to hydration offered by Dr. Senter, that "neutral salt action is due to the action of the ions of the salt on H° or OH' ions," is not in the nature of an explanation. The only method of estimating hydration in solution which has given uniformly rational results is the sugar inversion method (*vide* "Discrimination of Hydrates in Solution,"

Armstrong and Caldwell, *Proc. Roy. Soc.*, 1907). Recent measurements by Whympers have shown that the nitrates are only slightly less hydrated than the chlorides. The values obtained by this method are in general somewhat higher than the values given by Dr. Philip in Table VI. of his communication. It should be pointed out that no weight can be attached to the values of Jones given in this Table, since in the cases in which he is not quoted his values are not comparable with those of Philip. Jones states that such salts as sodium and potassium chlorides are not hydrated in solution, and in the case of all the sulphates his method gives a zero value for the hydration also—results which are clearly irrational. Biltz, indeed, working on practically the same assumptions as Jones, arrives at the values $\text{KCl} \cdot 15\text{H}_2\text{O}$ and $\text{NaCl} \cdot 19\text{H}_2\text{O}$ for $\text{N}/2$ solutions.

The Chairman: The formation of a salt, such as potassium chloride, in the solid condition, when the atoms constituting it are undoubtedly united, evolves practically the same amount of heat, 105,600 cal., as does its formation in the dissolved condition, the difference, 4,400 cal., being fully accounted for by the mere physical change from the solid to the liquid, or, rather, quasi-gaseous, condition. If during dissolution the constituent atoms become disunited, 101,200 cal. must be absorbed, but since, as a matter of fact, no such absorption has taken place, it is only possible to accept the view that the atoms in solution are uncombined, by imagining that the heat-absorption has been exactly counterbalanced by some action evolving an equivalent amount of heat. This has been attributed variously to heat evolved by the combination of electric charges with the atoms to produce ions, or to the combination of the atoms with the water. Apart from the difficulty involved by the introduction of electric charges without the previous expenditure of energy, and the difficulty of showing that an electric charge will produce heat on uniting with matter, both views are beset with the further difficulty of affording no explanation of why such a change should take place at all, since it involves no change in the total energy of the system. Indeed, the mere postulation of an action evolving just the right amount of heat to counterbalance an absorption which would be fatal to the theory propounded does not appear to be a very sound scientific proceeding. Yet the view has been pushed still further, and not only do we find the heats of ionisation or hydration of the constituents of a salt given, but attempts are made to calculate the heat of ionisation of each separate atom. This has been brought forward in the paper of Mr. Bousfield and Dr. Lowry. Having calculated the heats of formation of the ions they add any pair of them together, e.g., $\overset{+}{\text{K}} + \bar{\text{Cl}}$, and show, in Table V., how closely the sum agrees with the observed heat of formation of potassium chloride in solution K, Cl, aq.

It is clear, however, that no conclusions can be drawn from the agreement of these found and calculated values, for, as a matter of fact, they are both deduced from the same three experimental quantities.

Using Thomsen's notation, and omitting for brevity the water which is present in all cases, the found value is given by the equation—

$$(\text{K, Cl}) = (\text{K, aq}) + (\text{H, Cl}) + \text{N (heat of neutralisation)}.$$

For the calculated value, they first assume that—

$$\overset{+}{\text{H}} + \bar{\text{OH}} = (\text{H}_2, \text{O}) - \text{N},$$

and that $\overset{+}{\text{H}}$ is -600 cal., according to a determination of Ostwald's, which gives—

$$\bar{\text{OH}} = (\text{H}_2, \text{O}) - \text{N} + 600.$$

Secondly, the difference between the heats of formation of the ions $\bar{\text{O}}\text{H}$ and $\bar{\text{Cl}}$ is a constant, given by $(\text{K}, \text{OH}) - (\text{K}, \text{Cl})$, or, on expansion—

$$\bar{\text{O}}\text{H} - \bar{\text{Cl}} = (\text{K}, \text{aq}) + (\text{H}_2\text{O}) - [(\text{K}, \text{aq}) + (\text{H}, \text{Cl}) + \text{N}];$$

whence—

$$\bar{\text{Cl}} = (\text{H}, \text{Cl}) + 600.$$

Thirdly, $\overset{+}{\text{K}} - \overset{+}{\text{H}}$ is derived from—

$$\begin{aligned} [(\text{K}, \text{aq}) + (\text{H}_2\text{O})] - [(\text{H}_2\text{O}) - \text{N}] &= [\overset{+}{\text{K}} + \bar{\text{O}}\text{H}] - [\overset{+}{\text{H}} + \bar{\text{O}}\text{H}] \\ &= \overset{+}{\text{K}} - \overset{+}{\text{H}}; \end{aligned}$$

whence—

$$\overset{+}{\text{K}} = (\text{K}, \text{aq}) + \text{N} - 600,$$

and, therefore—

$$\begin{aligned} \overset{+}{\text{K}} + \bar{\text{Cl}} &= [(\text{K}, \text{aq}) + \text{N} - 600] + [(\text{H}, \text{Cl}) + 600] \\ &= (\text{K}, \text{aq}) + (\text{H}, \text{Cl}) + \text{N}. \end{aligned}$$

In other words, the found and, so-called, calculated values must be identical, and are quite independent of any value assumed for the heat of formation of the hydrogen ion.

Bousfield and Lowry's Table V. shows small differences between the found and calculated values—which, it may be remarked, are much smaller than the experimental errors of the heats of formation of the salts; these are simply due to the fact that in the found values they have taken the actual heat of neutralisation in the case in question, whereas in the calculated values they have taken a mean value. The differences are merely the deviation of the actual heat of neutralisation from the mean; and where that deviation is large, as in the case of barium, where the value is uncertain, or in that of hydrogen sulphide, where there is only partial neutralisation, there the differences between the observed and calculated values attain large dimensions. This would also have been the case with many of the ions given in Table VI., had they been subjected to a similar comparison.

The whole thing merely resolves itself into a statement that the heat of neutralisation is, in all ordinary cases, a constant,* a fact which may be used to support the ordinary hydrate theory of solution, just as much as to support the dissociation theory (Pickering, *Chem. Soc. Trans.*, 1887, 594, and *Phil. Mag.*, July, 1888, 53).

Dr. H. Borns: I hope Dr. Lowry is going to reply, and I should like to ask him a question. Which is his *modus operandi* of dissociation? He put down first the equation $\text{KCl} = \overset{+}{\text{K}} + \bar{\text{Cl}}$, and then he added the *aq.* to the two ions. This need not be his sequence, of course; but hydration seems to be the chief source of his energy, and the question concerns the arguing in a circle which the Chairman suggests. As regards Dr. Senter, might I ask why he passed over his third method for determining hydrates? I thought the experiments of Buchböck suggestive. Although all the authors have given references, they have not mentioned Walden. In his very thorough researches Walden also deals with hydration, and he finds that the arrangement as to ascending or descending atomic weights, to which the authors have alluded, often fails in apparently correlated properties, I think.

* From their placing SO_4 in Table VI., and not in Table V., it would appear that Bousfield and Lowry are unaware that the present writer has shown that the heat of neutralisation of sulphuric acid is really normal (*Chem. Soc. Trans.*, 1889, 323).

DISCUSSION

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Dr. H. J. H. Fenton, F.R.S., said that there appeared to be some want of uniformity in the conception of the meaning attached to the term "hydrate," and in discussing the general question of the existence of hydrates in solution, it would perhaps be advisable to have a more precise definition of the term.

He wished also to refer to the circumstance that the methods which have hitherto been employed in attacking this problem were almost exclusively physical ones, and that the results obtained were often capable of more than one interpretation. For this reason it had appeared to him desirable to select for the purpose of investigation such processes of hydration as would give rise to compounds having specific chemical properties recognisable by chemical means. A convenient example of a process of this kind was afforded by the hydration of ammonium carbamate, a change which, in aqueous solution, was found to be limited and reversible. The degree of hydration can in this case be readily followed by chemical analysis owing to the difference in properties between ammonium carbamate and ammonium carbonate. A detailed investigation of this change was carried out by the speaker very many years ago,* and the results obtained might possibly have a renewed interest when re-calculated in terms of the law of mass-action and the hypothesis of ionisation.

Mr. W. R. Bousfield: The criticism of the Chairman missed the point of the paper, which was not to prove the ionisation theory, but, accepting the ionisation theory, to show how one of its difficulties was removed. According to the ionisation theory as supplemented by the theory of hydration of the ions—

The object of the paper was to show that this great liberation of heat could be satisfactorily accounted for by water combination with the ions, and indeed in no other way.

At the same time, the proof of the extreme accuracy of the additive property of heats of ionisation furnishes important support to the theory of ionisation, though this was not the object of the paper, which took the theory for granted. Could the Chairman, or any other opponent of the ionisation theory, account for the fact that the heat of formation of any ion was absolutely independent of the other ion which might coexist with it in the same solution? The Chairman's view was that the 100,000 cal. was due to the existence of K and Cl *in combination in solution*, it being the original heat of combination of K and Cl, modified only by the change from the solid to the liquid state. But the paper showed that the figure 100,000 in the case of KCl, or the corresponding figure in the case of any other compound in solution, was entirely independent of the mutual affinities of the two elements of the compound, being the simple sum of two independent figures, each independently belonging to one of the components. There could be no stronger evidence to show that the ions in dilute solution were independent entities, and that their mutual affinities were entirely eliminated, being completely subjugated by their separate affinities for water.

Mr. Philip's paper was a valuable contribution to the solution of the difficult problem of determining quantitatively the amount of water attached to an ion. The speaker had shown ("Ionic Size in Relation to the Conductivity of Electrolytes," *Zeit. für Phys. Chem.*, **53**, 257, 1905) that the reciprocal of the cube of the mobility of an ion might be taken as an approximate guide to its size, and therefore to the water combined with it, but the problem required to

* *Proc. Roy. Soc.*, 1885 (**241**), 386.

be attacked from various points before quantitative results could be accurately established.

Mr. W. A. Davis pointed out that from Table I in Dr. Philip's paper it would appear that, although very soluble, chloral hydrate (unlike cane sugar) did not associate with the water in which it was dissolved. This was remarkable if solution were to be considered as due to residual affinity. A strong force has always appeared necessary to break up the cohesion of a crystal and cause it to dissolve. The two rival theories of solution at present advocated were intrinsically chemical—the association theory assuming combination to occur, whilst the dissociation theory involved disruption. It appeared possible that solution might in many cases be purely mechanical, the molecules of the solute, which in such cases must be regarded as a plastic body, simply sliding off the surface and mingling with those of the liquid. Did something of this kind occur when a solid hydrocarbon (e.g., paraffin) dissolved in a liquid one? Liquid hydrocarbons usually mixed freely among themselves. As regards the energy necessary to cause disintegration of the solid during dissolution, could it not perhaps be supplied by *surface-action*? It was well known that heat is generated when finely divided inert solids or their fibres are immersed in liquids in which they do not dissolve (Couillet, Massen). Solution was essentially, like osmotic pressure, a surface action, and at the present we know but little of the laws regulating this. Light would be thrown on solution by the study of dyeing phenomena; it had long been thought that chemical affinity was the cause of the attraction of the dye to the fibre, but most of the recent work indicated that dyeing was in reality mechanical, and not chemical, in its nature.

Dr. T. M. Lowry (*in reply*): The considerations which the Chairman had urged in reference to the thermochemical data were already familiar to the authors, who were by no means prepared to plead guilty to a charge of arguing in a circle. Tables III. to V. were inserted in order to demonstrate the additive character of the heats of formation of the salts in dilute solutions—a relationship the proof of which was of fundamental importance in any attempt to deduce separate values for the heats of formation of the ions. This point was fully developed in the paper as it would appear in the *Transactions*. (See also S. W. Richards, *Trans. Amer. Electrochem.*, vol. iv.)

Thomsen's experimental values for the heats of formation of the salts were not deduced from any assumed constant value for the heat of neutralisation. In comparison with the additive law in reference to the heats of formation of the salts, the law of constant heat of neutralisation was inaccurate and of very limited application. It broke down in the case of weak acids—

	HCl	HF	HCN	HNO ₃
NaOH	13,745	16,270	2,770	13,680
$\frac{1}{2}$ Ca(OH) ₂	13,950	18,155	3,200	13,900

and was inapplicable to the case of insoluble bases, whether oxides or hydroxides—

HCl	13,845	9,940	7,460	7,640	7,695
$\frac{1}{2}$ Mg(OH) ₂		$\frac{1}{2}$ Zn(OH) ₂	$\frac{1}{2}$ Cu(OH) ₂	$\frac{1}{2}$ CuO	$\frac{1}{2}$ PbO

Its application was thus practically limited to the formation of alkali salts of strong acids.

In reply to Dr. Borns, the process of ionisation was regarded as a final stage in the progressive hydration of the salt molecule. In an earlier paper it had been compared with the biological process of karyokinesis, whereby the growth of a cell resulted in the formation of two separated units, each

with its own nucleus. The force required to separate the radicals of the salt was supplied by the energy of water-combination, but it was difficult to say exactly at what stage the radicals acquired their charges.

Dr. J. C. Philip, in reply to Mr. Caldwell, said that the general idea of attributing the influence of salts on the solvent power of water to the formation of hydrates was certainly not new, but, so far as he was aware, he (the speaker) was the first to deal with the matter quantitatively. In a recent communication to the Chemical Society (*Fourn. Chem. Soc.*, 1907, **91**, 711) he had done this and pointed out the necessity of making a correction for the volume occupied by the solute before any attempt was made to calculate the extent of hydration.

Dr. G. Senter (*in reply*): With reference to a remark by Dr. Borns, the third method for determining hydration given in my paper was omitted in the summary simply to save time. I quite agree with Dr. Borns as to the importance of the method, which in principle is perhaps to be preferred to any of the others, but the experimental error is large, so that the few results so far obtained are of uncertain value.

Mr. Caldwell's remarks on my experiments with sodium chloroacetate do not appear quite logical. It is an experimental fact (compare Senter, *Trans. Chem. Soc.*, 1907, **91**, 460), that the rate of reaction between sodium hydroxide and chloroacetate in dilute aqueous solution at 102°, is increased at least 30 per cent. by the addition of sufficient sodium chloride (or other sodium salt) to make the solution molar with respect to the latter. If, as Mr. Caldwell maintains—and as is very probable—"the conditions (in this case) are such that the hydration of added salts would not produce a measurable effect," the accelerating action of neutral salts must, at least in some cases, be explained on some other basis than hydration—which is just my contention. Moreover, Mr. Caldwell's statement contains the implicit assumption—also probably quite justifiable—that hydration falls off fairly rapidly with rise of temperature, whereas the results of Arrhenius, Spohr, Euler, and some unpublished experiments of my own show conclusively that neutral salt action is practically independent of the temperature. This, as I have previously pointed out, appears to be one of the strongest arguments against the hydration view of neutral salt action.

My statement that (in the cases so far fully investigated) "the accelerating effect of neutral salts is practically independent of the nature of the salt" is based on experiments by Arrhenius, Spohr, Kay, and others which show that, for example, the chlorides of the alkali metals exert the same accelerating effect within the limits of experimental error. Hence, according to Mr. Caldwell's method, these chlorides are equally hydrated, whereas various considerations, more particularly migration experiments, show that lithium chloride is considerably more hydrated in solution than the chlorides of the other alkali metals. It can scarcely be said that the cane sugar method leads to "rational" results in this case, and other instances to the same effect could easily be adduced. It is not, of course, to be expected that the rule in question will hold for salts which are much less ionised than those of the alkali and alkaline earth metals, and other disturbing causes may also occur.

The statement that "neutral salt action is due to the action of the ions of the salt on H⁺ and OH⁻ ions" was not, of course, meant as an "explanation" of neutral salt action, but was a provisional attempt at a generalisation, which may, however, require modification in the light of further experimental data.