SPECIFIC HEAT OF SOLUTIONS. V.

BY WILLIAM FRANCIS MAGIE.

1. This paper is a continuation of others, published under the same title in previous volumes of this REVIEW. It deals with the heat capacities of electrolytic solutions and the possibility of representing them by a simple formula involving the dissociation factor. Most of the measurements of heat capacity employed are those of Julius Thomsen.[1] The measurements of solutions of potassium chloride were made by myself, and those of sodium and potassium nitrate, barium and strontium chloride, and barium and strontium nitrate by Mr. R. E. Trone, Instructor in physics at Princeton University. The calorimeter used by us was the modified form of the Pfaundler calorimeter described in No. III. of this series. It gives me pleasure to have an opportunity to express my obligations to Mr. Trone for his faithful and accurate work.

The volumes of electrolytic solutions exhibit in general the same peculiarities as their heat capacities, and admit of representation by a similar formula. I have accordingly introduced a discussion of these volumes *pari passu* with that of the heat capacities. Most of the measurements of volume employed were made by Thomsen.[2] Those for strontium chloride were worked over from data given by Kohlrausch and Holborn.[3] Mr. Trone, using a standardized Mohr's balance, contributed those for barium chloride and for barium and strontium nitrate.

2. *Peculiarity of the Heat Capacities of Electrolytes.* — The solutions which Thomsen studied were made up by dissolving one gram-molecule of the solute in some known number, N, of gram-molecules of water. The heat capacity of such a solution was determined and the heat capacity of the N gram-molecules of water subtracted

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[1] Thermodynamische Untersuchungen, Vol. I., Pogg. Ann., 142, p. 335.

[2] L. c.

[3] Leitvermögen der Elektrolyte, p. 145.

from it. The difference gave the apparent heat capacity of one gram-molecule of the solute — or its apparent molecular heat — in a solution of that concentration. It was found that the apparent molecular heat of the solute generally diminishes with increasing dilution, so that in practically all cases it becomes negative long before the solution becomes very dilute.

Similarly, the apparent molecular volumes of the same solutes diminish with increasing dilution, though it is only in a very few cases that they become negative within the range of Thomsen's observations.

3. *General Conclusion.* — These results demonstrate that in solutions, at least in electrolytic solutions, the water is affected by the presence of the solute in such a way that its heat capacity and specific volume are diminished.[1] They are therefore conclusive in favor of some form of what we may call the association theory of solutions, in distinction from that theory of solutions in which the solute is considered as having the properties of a gas, and the solvent as being merely an inert medium in which the molecules or ions of the solute are suspended. As will be seen later, they indicate that the association between the molecules or ions of the solute and the water, within the range of concentration covered by the observations, is fairly definite in its effects, so that we may conceive of each molecule or ion of solute as surrounded by a group of a definite number of water molecules, which are within its sphere of influence and affected by it. There is little or no evidence that the numbers of water molecules in these groups change with the concentration. In this respect the hypothesis which will explain the results under consideration differs from that adopted by Jones and his fellow-workers [2] to explain the abnormalities of the freezing and boiling points observed by them in concentrated solutions.

The conclusion that the negative values of the apparent molecular heats prove that the heat capacity of the water is affected by the presence of the solute has already been drawn by Tammann. [3]

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[1] Magie, Bull. Am. Phys. Soc., Vol. 2, no. 2; this Review, XIII., p. 91; XVIII., p. 449.

[2] Am. Chem. Jour., 23, p. 89; Zeitschrift für Phys. Chem., XLVI. p. 244; XLIX., p. 385; this Review, XVIII., p. 146.

[3] Zeitschrift für Phys. Chem., XVIII., p. 625.

4. *Formulas to Represent Heat Capacities and Volumes of Solutions.*—An examination of the tables which follow will show that the heat capacities of the solutions of any one solute, made up by dissolving one gram molecule of the solute in N gram-molecules of water, may be represented by the formula

$$H = WN + A + Bp.$$

In this formula W is the molecular heat of water, or 18, A and B are constants, and p is the dissociation factor, obtained in the usual way as the ratio of the molecular conductivity of the solute in a solution of the given concentration to the molecular conductivity of the same solute in an infinitely dilute solution. The values of p are calculated from the molecular conductivities given in the tables of Kohlrausch and Holborn, with the help of their tables of specific gravities.

A similar formula,

$$V = UN + D + Ep,$$

will represent the volumes of the various solutions. In this formula U is the molecular volume of water, D and E are constants, and p again the dissociation factor.

$NaCl$. $A = 39$, $B = -70$; $D = 25.86$, $E = -12$

N	p	H Obs. *Th.*	H Calc.	V Obs. *Th.*	V Calc.
10	0.42			200.9	200.8
20	.544	361	361.0	379.3	379.3
30	.613	536	536.1	558.4	558.5
50	.668	892	892.2	917.8	917.8
100	.729	1,788	1,788.0	1,816.1†	1,817.1
200	.780	3,578†	3,584.4	3,616.0	3,616.4

KCl. $A = 96$, $B = -149$; $D = 47$, $E = -25$.

N	p	H Obs. *M.*	H Calc.	V Obs. *Th.*	V Calc.
15	0.672			300.4	300.2
30	.728			569.0	568.8
50	.753	880.7	882.0	928.2	928.2
100	.787	1,777.6	1,777.2	1,827.3	1,827.3
200	.818	3,571.8	3,572.2	3,625.0	3,626.0
300	.835	5,370.2	5,370.2		
400	.848	7,167.1	7,168.1		

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[1] The letters *Th.*, *M.*, *Tr.*, *K*, prefixed to the tabulated observations, indicate the various observers, Thomsen, Magie, Trone, Kohlrausch.

NH_4Cl. $A = 39$, $B = -62.1$; $D = 43.5$, $E = -7.5$.

N	p	H Obs. *Th.*	H Calc.	V Obs. *Th.*	V Calc.
10	0.593	181.6	182	219.0	219.1
25	.703	443.6	445	488.2	488.2
50	.742	893	893	937.8	937.9
100	.777	1,791	1,791	1,837.7	1,837.7
200	.806	3,588	3,589	3,637.6	3,637.5

HCl. $A = 4$, $B = -41$; $D = 27$, $E = -10.56$.

N	p	H Obs. *Th.*	H Calc.	V Obs. *Th*	V Calc.
20	0.596	339	339.6	379.2	380.7
50	.773	873	872.4	918.8	918.8
100	.84	1,770	1,769.6	1,818.5	1,818.1
200	.877	3,561†	3,568	3,617.7	3,617.7

$NaOH$. $A = 32$, $B = -65.6$; $D = 7$, $E = -15$.

N	p	H Obs. *Th.*	H Calc.	V Obs. *Th*	V Calc.
30	0.602	533	533	537.9	538
50	.696	885	886	896.4	897
100	.775	1,781	1,781	1,795.9	1,795.4
200	.824	3,578	3,578	3,594.8	3,594.7

KOH. $A = 59$, $B = -110$; $D = 22$, $E = -21$.

N	p	H Obs. *Th.*	H Calc.	V Obs. *Th.*	V Calc.
30	0.69	522	523	547.5	547.6
50	.76	876	875	906.3	906.1
100	.82	1,770	1,769	1,804.9	1,804.8
200	.855	3,565	3,565	3,604.1	3,604.1

$\frac{1}{2}H_2SO_4$. $A = 27.5$, $B = -40$; $D = 22$, $E = -10$.

N	p	H Obs. *Th.*	H Calc.	V Obs. *Th.*	V Calc.
9.5	0.337	180.6	185	189.8	189.6
24.5	.463	450	450	458.3	458.4
49.5	.510	898.5	898.1	907.7	907.9
99.5	.532	1,797.5	1.797.5	1,807.7	1,807.7

$NaNO_3$. $A = 55$, $B = -75$; $D = 37.5$, $E = -13.5$.

N	p	H Obs. *Tr.*	H Calc.	V Obs. *Th*	V Calc.
10	0.34			212.5	213
25	.514			480.4	480.7
50	.618	908.2	908.6	929.2	929.2
100	.698	1,802.7	1,802.7	1,828.2	1,828.2
200	.757	3,598	3,598.2	3,627.0	3,627.5
300	.785	5,396	5,396.1		

KNO_3. $A = 78,\ B = -120;\ D = 47.5,\ E = -12.$

N	*p*	*H* Obs. *Tr.*	*H* Calc.	*V* Obs. *Th.*	*V* Calc.
25	0.55	458.6	462	490.7	490.9
50	.633	902.2	902.1	939.8	939.8
100	.705	1,793.6	1,793.4	1,839.2	1,839.1
200	.76	3,586.6	3,586.8	3,638.3	3,638.4
300	.79	5,383.8	5,383.2		
400	.81	7,182.0	7,180.8		

$\frac{1}{2}BaCl_2$. $A = 10,\ B = -65;\ D = 29.2,\ E = -25.$

N	*p*	*H* Obs. *Tr.*	*H* Calc.	*V* Obs. *Tr.*	*V* Calc.
50	0.548	875.5	874.4	915.2	915.5
100	.606	1,770.5	1,770.6	1,814.2	1,814.1
200	.662	3,567	3,566.9	3,612.8	3,612.7
300	.69	5,365.6	5,365.2	5,411.8	5,412.0

$\frac{1}{2}SrCl_2$. $A = 16.6,\ B = -76;\ D = 18.8,\ E = -10.$

N	*p*	*H* Obs. *Tr.*	*H* Calc.	*V* Obs. *K*	*V* Calc.
50	0.56	873.5	874	912.6	913.2
100	.62	1,770.3	1,769.6	1,812.6	1,812.6
150	.66	2,666.3	2,666.6	2,712.3	2,712.2
200	.681	3,565.4	3,564.9	3,612.0	3,612.0
300	.717	5,361.5	5,362.1	5,411.6	5,411.6

$\frac{1}{2}Ba(NO_3)_2$. $A = 31,\ B = -76;\ D = 25.3,\ E = 0.$

N	*p*	*H* Obs. *Tr.*	*H* Calc.	*V* Obs. *Tr.*	*V* Calc.
100	0.469	1,795.7	1,795.4	1,825.5	1,825.3
150	.526			2,725.3	2,725.3
200	.563	3,588.4	3,588.2	3,625.3	3,625.3
250	.593			4,525.3	4,525.3
300	.618	5,382.3	5,384.0	5,426.3	5,425.3

$\frac{1}{2}Sr(NO_3)_2$. $A = 9,\ B = -40;\ D = 24.8,\ E = -3.$

N	*p*	*H* Obs. *Tr.*	*H* Calc.	*V* Obs. *Tr.*	*V* Calc.
50	0.442	895	892	923.5	923.5
100	.533	1,787.8	1,788	1,823.2	1,823.2
200	.607	3,584.8	3,584.7	3,623.0	3,623.0
300	.648	5,383.5	5,383.1		

The dissociations used here were determined by Professor William Foster (this REVIEW, VIII., p. 257). The curve of dissociations, plotted from Kohlrausch's data, is suspiciously irregular.

A few of the observations in these tables are marked with a (†). They differ by more than the probable error from the calculated numbers. In every one of these cases, if the curve of specific heats or of specific gravities is plotted, it will be found that the discordant result corresponds to an aberrant part of the curve; and when the curve is smoothed, the heat capacity or the volume calculated from the smoothed curve is in good accord with the quantity calculated from the formula. I think there can be no doubt that these discrepancies are due to experimental errors, and that it is legitimate to remove them by smoothing the curves. An error of two tenths of one per cent. in the determination of the specific heat would account for the largest discrepancy found.

6. *Deduction of Formulas.* — The formulas given in § 4, from which the results of the tables have been calculated, admit of a simple interpretation. Let us suppose that n gram-molecules of the solute are dissolved in N gram-molecules of water, and that p gram-molecules of solute are dissociated into ions. Let us suppose further that each actual molecule and each ion of the solute collects around itself a group of water molecules and in general affects and modifies the heat capacity of the group. The heat capacity of the solution is additive of the heat capacities of the several homogeneous parts of the solution, and on our suppositions is the sum of the heat capacities (1) of the water outside the groups of water molecules affected by the solute; (2) of the undissociated molecules and the water affected by them; (3) of the ions and the water affected by them. This sum may be written out by the help of the following symbols:

M, S, N, molecular weight, specific heat, number of gram-molecules of water.
m, n, molecular weight, number of gram-molecules of solute.
p, number of gram-molecules dissociated into ions.
a, α, number of water molecules affected by one undissociated gram-molecule of solute, and by one dissociated gram-molecule of solute, respectively.
s, σ, specific heats of the groups containing an undissociated molecule of solute and a dissociated molecule of solute, respectively.

The heat capacity of the solution may be written,

$$\begin{aligned} H &= S\,(MN - a(n-p)M - apM) + s(m + aM)(n-p) + \sigma(m + aM)p \\ &= SMN + (sm + saM - SaM)(n-p) + (\sigma m + \sigma aM - SaM)p \\ &= WN + A(n-p) + Cp, \end{aligned}$$

in which WN is the heat capacity of the water used in making up the solution; A is a constant depending upon the undissociated molecules and the way they affect the water; C is a constant depending in a similar way upon the dissociated molecules, or the ions formed from them, and the way they affect the water.

In case n equals 1, p is the dissociation factor, and the formula then becomes

$$H = UN + A + Bp,$$

in which $B = C - A$.

On the same suppositions as to the constitution of a solution, its volume may be considered as the sum of the volumes of those parts of the solution whose heat capacities have been added to express the heat capacity of the solution. Writing out in a similar way the sum of these volumes, we find that the volume of the solution is expressed by a formula of the same form as that obtained to express the heat capacity. In this formula, which may be written in the form

$$V = UN + D + Ep,$$

UN is the volume of the water used in making up the solution; D is a constant analogous to A; E is a constant, equal to $F - A$, and the constant F is analogous to C.

It thus appears that the simple suppositions which we have made as to the constitution of electrolytic solutions lead to the formulas for the heat capacity and the volume of solutions which have been shown to represent the results of observation.

7. *Formulas of Mathias and of Tammann.* — Of the formulas which have heretofore been proposed to represent the heat capacities or the specific heats of solutions, it is worth while to notice those of Mathias and of Tammann.

Mathias[1] proposed a formula for the specific heats, with two

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[1] Journal de Physique, Vol. 8, p. 204.

constants, a and b, of the form

$$\gamma_n = \frac{a+n}{b+n} c;$$

in which γ_n is the specific heat of the solution containing n gram equivalents of the solvent, and c is the specific heat of the solvent. This formula sometimes represents the specific heats given by Thomsen and by Marignac exceeding well. In other cases it is not so successful. In his notice in the Comptes Rendus, 107, p. 524, Mathias presents his results for sodium chloride and hydrochloric acid solutions as examples of the applicability of his formula. In the following table his results are compared with Thomsen's observations and with the values given by the formula presented in this paper.

N	NaCl			HCl		
	H Obs. *Th.*	H Calc. *Mat*	H Calc. *M*	H Obs. *Th.*	H Calc. *Mat.*	H Calc. *M*
20	361	359	361	339	338.2	339.6
30	536	534.5	536.1			
50	892	890.6	892.2	873	873.8	872.4
100	1,788	1,786.2	1,788	1,770	1,772	1,769.6
200	3,585[1]	3,584	3,584.4	3,567	3,571	3,568

These tables show that the formula of Mathias, in which the concentration, as represents by n, is taken as the variable upon which the change of specific heat depends, does not represent the observations so exactly as the formula in which the dissociation is the variable.

Tammann[2] considers the peculiarities of the heat capacities of solutions to result from the change in the heat capacity of the solvent, due to an internal pressure caused by the presence of the solute. His main principle is like that upon which the formula presented in this paper is based, except that he considers the internal pressure as affecting the whole mass of solution. As might be expected from the difficulty of obtaining the data which he needs for his computations, Tammann's calculated heat capacities do not represent the observations with any accuracy.

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[1] Corrected by smoothing the curves of specific heat.

[2] Zeitschrift für Phys. Chem., Vol. 18, p. 625.

8. *Formulas for Non-electrolytic Solutions.* — In the case of solutions which are not electrolytes, in which, therefore, p is equal to zero or is negligibly small, the formula for the heat capacities reduces to the sum of two terms, of which the first represents the heat capacity of the water and the second is a constant characteristic of the solute. Such a formula has been shown[1] to represent the heat capacity of many non-electrolytic solutions. In cases in which it does not do so, as in the case of the solutions of the alcohols in water, other considerations, notably the heat developed on solution, lead us to conclude that an interaction takes place between the solvent and the solute of a nature similar in general to that supposed to occur in the cases of the electrolytes. The laws of this interaction are not known, and I have not been able to find a formula which will adequately represent the results of observation in these exceptional cases.

In the normal cases, in which the simple additive formula for the heat capacity applies, a similar formula holds for the volumes of the solutions. This has been shown by Wade and by Wanklyn[2] for solutions of cane sugar, and calculations from the data given by various observers for the volumes of solutions of dextrose, of levulose, of urea, and of glycerine, chosen as typical examples, show that the volumes of solutions of these substances obey the same law. In the tables given by Traube[3] several other examples of the same law appear.

9. *Apparent Heat Capacities and Volumes of Ions.* — The range of observation within which our formulas, especially the one for the heat capacity, can be tested, is not very great, and it is desirable to have further confirmation of our hypothesis than that afforded by the agreement between calculated and observed results shown in the tables. This may be obtained from the following considerations:

In the construction of the general formula to which both the heat capacities and the volumes conform, the ions formed by dissociation were considered together, the symbols σ and α being in a way composite quantities, expressing the action of all the ions. It is, how-

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[1] Magie, this REVIEW, IX., p. 65; XIII., p. 91.

[2] Phil. Mag., June–Dec., 1891, p. 475.

[3] Liebig's Ann., 290, p. 43.

ever, possible, by introducing separate symbols for the ion of each sort, to write out the term C as the sum of similarly formed terms referring to each ion. Indicating these terms by subscripts 0 and 1 in the case of a simple binary electrolyte, like sodium chloride, C becomes

$$\sigma_1 m_1 + \sigma_1 \alpha_1 M - S\alpha_1 M + \sigma_0 m_0 + \sigma_0 \alpha_0 M - S\alpha_0 M.$$

If now we have another binary electrolyte, like potassium chloride, containing the ion indicated by the subscript 0 and another indicated by a subscript 2, the C for that substance becomes

$$\sigma_2 m_2 + \sigma_2 \alpha_2 M - S\alpha_2 M + \sigma_0 m_0 + \sigma_0 \alpha_0 M - S\alpha_0 M.$$

The difference between these quantities is independent of the common ion, and we should therefore expect to find their difference the same, say for the sodium and potassium compounds, whatever the common ion may be.

A similar relation may be expected to hold among the values of F relating to the volumes of the solutions.

This expectation is fairly well met in the cases of the simpler solutions, in which we have no reason to suspect that there is more than one type of dissociation. For the sodium and potassium compounds we have the following values of C and F, and of their respective differences :

Solution.	C	Diff.	F	Diff.
NaCl	−31	22	13.9	−8.1
KCl	−53		22	
NaOH	−33.6	17.4	−8	−9
KOH	−51		1	
$NaNO_3$	−20	22	24	−11.5
KNO_3	−42		35.5	

Similarly the difference of the constants C referring to the chlorine and NO_3 ions is the same for either sodium or potassium chloride and nitrate and for barium chloride and nitrate.

Solution.	C	Diff.	Solution.	Diff.	C
NaCl	−31	−11	$\frac{1}{2}BaCl_2$	−55	−10
$NaNO_3$	−20		$\frac{1}{2}Ba(NO_3)_2$	−45	

A much larger collection of data than I have been able to obtain is needed to prove that these differences are generally constant, and the matter is so complicated by the probability that more than one type of dissociation occurs in most of the available solutions, that exceptions to the rule are rather to be expected than not. Such complicated dissociations occur with the barium and strontium compounds and may account for the failure of their solutions to follow the rule to which the simpler solutions of the sodium and potassium compounds conform.

Similar differences, and interpreted in a similar manner as the differences of the effective volumes in solution of two different ions, have been discovered and fully discussed by Traube.[1]

10. *Apparent Change of the Heat Capacity of the Water Associated with the Ions.* — By proceeding upon our hypothesis a relation can be deduced from the constant C for the different solutes examined, which may serve as an additional confirmation of the hypothesis. This constant represents the heat capacity of a gram-molecule of the dissociated solute and of the water associated with it, diminished by the heat capacity of the water when not in association with the ions. If we suppose that the ions of the solute retain the heat capacities which they have as atoms, which is practically the same thing as giving to the dissociated molecule its heat capacity when in the solid state — or, if this is not known, making up a heat capacity for it by adding the atomic heats of its atoms as determined by Kopp — we then find the amount by which the heat capacity of the water associated with the dissociated molecule is diminished by subtracting its heat capacity from the value of C in each case. When this is done, the numbers obtained, with one or two exceptions, fall into two groups, which are presented in the following tables. The

	C	h	$C-h$		C	h	$C-h$
NaCl	−31	12.5	−43.5	KCl	−53	12.8	−65.8
NH_4Cl	−23.1	20.9	−44	KNO_3	−42	24.1	−66.1
$NaNO_3$	−20	23.6	−43.6	KOH	−51	13.3	−64.3
NaOH	−33.6	13.3	−46.9	$\frac{1}{2}BaCl_2$	−55	9.4	−64.4
HCl	−37	8.8	−45.8	$\frac{1}{2}SrCl_2$	−59.4	9.5	−68.9
		Mean	−44.8	$\frac{1}{2}Ba(NO_3)_2$	−45	19.9	−64.9
						Mean	−65.7

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[1] Zeitschrift für anorg. Chem., 3, p. 11.

symbol *h* represents the heat capacity of the molecule of solute. The values for $\frac{1}{2}H_2SO_4$ and for $\frac{1}{2}Sr(NO_3)_2$ do not fall into either of these groups. In the case of the sulphuric acid, this can be accounted for by the mode of dissociation.

Viewed in the light of our hypothesis, these results indicate that the influence of ions of various sorts upon the water molecules which surround them, though not always the same, is practically the same in many cases. It is noticeable that the sodium compounds are all in one group, the potassium compounds in the other.

If we assume that each water molecule is equally affected by the ion with which it is connected, we may use these numbers to obtain an inferior limit to the number of water molecules thus affected. The mean loss of heat capacity of the water connected with the ions of the first group is 45, that is 2.5 times the heat capacity of one water molecule. There must therefore be at least three molecules of water affected by the two ions, and that there may be so few, it must be admitted that they lose five sixths their heat capacity. So great a change in heat capacity seems to be out of the question, and one is naturally led to assume that the sphere of influence of each ion contains several water molecules. This assumption, furthermore, is supported by the occasional failure of the formulas to represent the observations for the higher concentrations. The differences between the calculated and observed heat capacities and volumes for the most dilute solutions can be ascribed to experimental errors in determining specific heats and specific gravities; but experimental errors have less influence in the case of the more concentrated solutions, and the differences between the calculated and observed results for those concentrations are no doubt real. They may easily be explained if we consider the spheres of influence of the ions, and of the undissociated molecule, as extending so far as to include groups of water molecules. When the concentration becomes such that these groups interpenetrate, or even come into frequent collision, it may reasonably be expected that their heat capacities and volumes should be altered.

11. *Nature of the Association.* — The association between the water and the solute must be of such a sort as to permit an explanation of the laws of osmotic pressure and of electrolytic conduc-

tion. It does not seem possible to account for these laws, especially for those of conduction, if the association is of such a sort as to form definite hydrates or permanent groups of water molecules around the molecules and ions of the solute. If, however, the groups are not permanent, but are loose and unstable, so that the molecules and ions of the solute can slip along through the water without dragging all the water molecules of the group with them, the way to a kinetic explanation of osmotic pressure is left open, and the different ions may still exhibit their different characteristic velocities, postulated for them in Kohlrausch's theory of electrolytic conduction.

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