THEORY OF THE SPECIFIC HEAT OF ELECTROLYTES*

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No molecular theory of the specific heat of liquids has been deduced till now. The considerations given in this paper may be regarded as a first attempt to solve that problem. Most molecular theories of solutions regard the solvent as a continuum, treating only the solute as composed of molecules. In this theory this simplification is made wherever possible. For the treatment of certain phenomena, however, it is too great an idealization, and it is necessary to consider the molecular character of the solvent also. As in the theories of other properties of solutions, only differences between the specific heat of the solution and the pure solvent are calculated. The application of the principles to be deduced, to any dilute solution or liquid mixture does not seem to offer any serious difficulties. It seems possible, that by proceeding logically in this direction we may find the key to the explanation of the specific heat of liquids on the basis of molecular models.

We first examine a few cases of un-ionized solutions, drawing certain conclusions therefrom, and then proceed to a general consideration of the so-called strong electrolytes. (The solvent is always supposed to be water.) As shown farther on, the results thus obtained are found to be in very good agreement with the experimental data.

Electrolytes are in general distinguished from non-electrolytes by the following characteristics. If n mols of a substance are dissolved in n_o mols water, so that $n + n_o = 1$, then we have this relation for non-electrolytes

$$C > n_o C_o \tag{1}$$

whereas for electrolytes we find in general

$$C < n_o C_o \tag{2}$$

where C is the heat capacity of one mol solution and C_o that of one mol water. In case (1) for many substances with big molecules an approximate empirical relation can be found,

$$C \sim n_o C_o + n C_S \tag{3}$$

C_S being the molar heat of the solute in the solid state. The meaning of (3) is that the degrees of freedom of a molecule are nearly the same in both the solid state and in solution. Evidently the relation (3) will be expected to hold better for big molecules than for small ones. Table 1 gives some examples of non-ionized aqueous solutions.

TABLE 1

	GLUCOSE $C_6H_{12}O_6$	LACTOSE $C_{12}H_{22}O_{11}$	GLYCERINE $C_3H_8O_3$	TARTARIC ACID $C_4H_6O_6$	UREA CON_2H_4
$\overline{C} = \dfrac{C - C_o \, n_o}{n}$	55.2	104.5	56.0	67	24.8
C_s	51.7	98.5	53.0	62	19.3

(for liquid state)

These figures indicate that non-electrolytes behave normally; in other words that the interaction between the molecules of solute and solvent does not affect the specific heat appreciably. The specific heat of these solutions seems to be nearly additively composed of the specific heats of the solvent and solute in the pure states.

As indicated by (2) electrolytes behave quite differently. The interaction between the ions and the solvent (water) cannot be neglected. On the contrary, this effect is predominant. The factors which must therefore be considered in calculating the specific heat of electrolytes are the following:

1. Degrees of freedom of the molecules of the solute.

2. Change of the specific heat of water due to electric polarization in the field of the ions.

3. It is known that the H_2O-molecules act as rigid electric dipoles.[1] Now such a dipole in the inhomogeneous field of an ion will be attracted towards it. The result of this attraction is a high pressure around the ion. As the specific heat of water is very appreciably changed by pressure (see Fig. 2) this effect will play a great rôle.

4. Hydration of the ions.

5. Ion atmosphere. It has been shown by Milner[2] and Debye[3] that according to the Boltzmann principle the ions arrange themselves in such a way that around every positive ion is built up a negative space charge and vice versa. As the temperature is raised, these ion atmospheres are destroyed and the energy required by this process furnishes a positive member in the expression for the specific heat of the solution. But it may be shown that this effect can be neglected for the first approximation because it is proportional to $n^{3/2}$ whereas the other effects are proportional to n.

To have a definite basis for the discussion we consider a solution of n mols KCl in n_o mols water. If instead of the K^+ and Cl^- ions we dealt with neutral particles of the same shape we could write

$$C = n_o C_o + \lambda n \, R/2 \qquad (4)$$

where R is the gas constant and λ the number of degrees of freedom for one molecule in solution. In the case of KCl λ would be 12, if we ascribe $^1/_2 kT$ potential energy to each degree of freedom. If F_o is the free energy of such an ideal solution we find the same function F for the real solution

by substracting from F_0 certain amounts of energy A_i. These are determined by considering the following isothermal processes. First we destroy the ion atmospheres by going over to a random distribution of the ions. The energy necessary for this process we call A_1. This is negligible, as mentioned before, and will not be considered further. Then we discharge the ions, keeping their state of hydration, as well as the internal pressure of the water, constant. The energy required for this is A_2. Then we must reduce the internal pressure to one atmosphere, put-

Fig. 1.
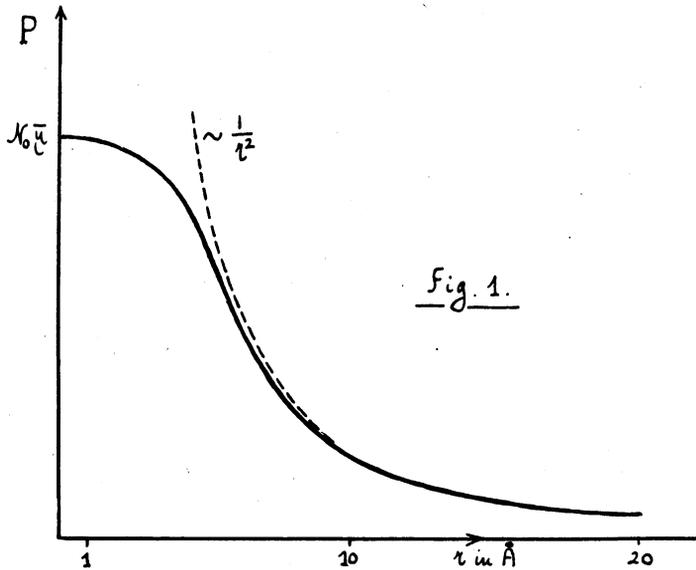
ting in the energy A_3. Finally we melt the hydrated complexes with an energy A_4. Then the following relation holds.

$$F = F_0 - (A_2 + A_3 + A_4)$$

and the specific heat at constant volume

$$C_v = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_v = -T\left(\frac{\partial^2 F_0}{\partial T^2}\right)_v + T\frac{\partial^2}{\partial T^2}\sum_{i=2}^{4} A_i =$$

$$n_0 C_0 + n\left[\lambda\frac{R}{2} + C_2 + C_3 + C_4\right]$$

(5)

where the C_i are defined by the equation

$$nC_i = +T\left(\frac{\partial^2 A_i}{\partial T^2}\right)_v.$$

In determining the different functions A_i we proceed in the following

way.   The assumption of a linear relation between P, the electric polariza-
tion of the water, and the electric field would give

$$A_2 = -2nN \frac{\epsilon^2}{2aD} \tag{6}$$

where D is the dielectric constant, a the ion radius, $\epsilon = 4.77 \cdot 10^{-10}$ e.s.u.,
and $N = 6.06 \cdot 10^{23}$ the Avogadro number.   But (6) cannot be quite exact
because the very high field in the vicinity of the ion will produce a satura-
tion effect so that P will approach a limiting value $N_0\bar{\mu}$, where N_0 is the
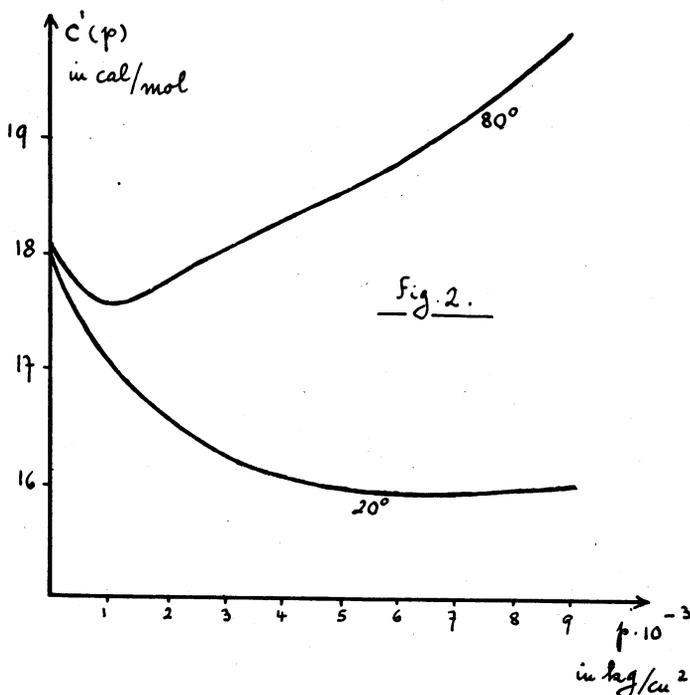

number of watermolecules per cm.³ and $\bar{\mu}$ the average of the dipole mo-
ment taken over all the molecules, simple and polymerized.   It can be
shown by considerations analogous to those used in the theory of ferro-
magnetism (concerning the "molecular field") that there is an upper limit
for $\bar{\mu}$ namely $\bar{\mu} = 9 \cdot 10^{-19}$ e.s.u.   But $\bar{\mu}$ can be restricted even more as
will be shown in another paper which deals with the theory of compressi-
bility, of the coefficient of thermal expansion, and of the change of volume
on solution.   There it will be found that $\bar{\mu} = 5 \cdot 10^{-19}$ e.s.u.   Now P must
be equal to $N_0\bar{\mu}$ near the ion and equal $\frac{\epsilon}{r^2} \frac{D-1}{4\pi D}$ far away.   The approxi-
mation for intermediate values of r will be given by a Langevin function.
The resulting curve for $P(r)$ is shown in figure 1.

Calculation of A_2 on the basis of this curve furnishes $C_2 = -10$ cal. per mol. dissolved substance.

In determining the pressure effect (3), it is convenient to calculate C_3 directly. It is easy to show that

$$nC_3 = \int_v [C'_{(p)} - C_o] \frac{\rho}{M} dv$$

where $C'_{(p)}$ = molar heat of water under pressure p, and ρ is the density of water. The integration is to be extended over all the water contained in the solution. $(C' - C_o)$ is known from Bridgman's measurements[4] (see Fig. 2).

Fig. 3.

+ Li Cl
o H Cl
r Cs Cl
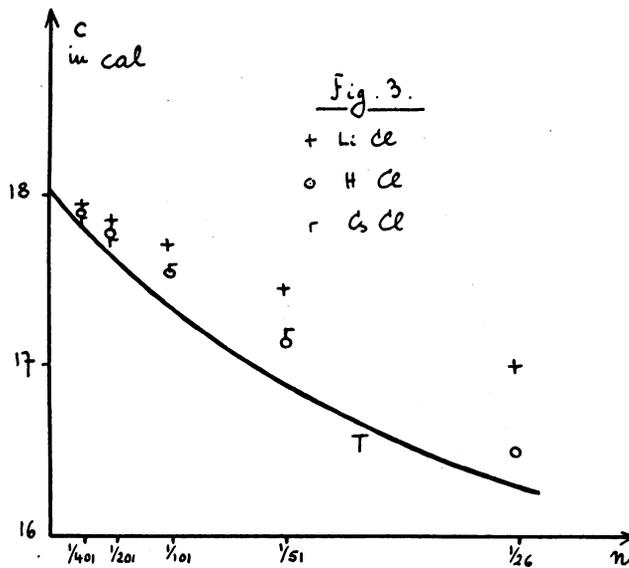
For very dilute solutions we find $C_3 = -119$ cal. At higher concentrations, however, the overlapping of the fields of force of neighboring ions

TABLE 2

r in Å	1	2	3	4	4.7	5	5.65
p in kg./cm.^{2}	76500	16640	4890	1554	383	124	0
$[C' - C_o]\frac{\rho}{M}$	...	0.100	0.112	0.0692	0.0250	0.00917	0
$r^2[C' - C_o]\frac{\rho}{M}$	...	0.400	1.01	1.11	0.546	0.229	0

must be taken into account, so that the decrease in the specific heat of the solvent produced by pressure will be less than stated above. It will be approximately

$$C_3 = 2N\int_a^{\bar{R}} [C' - C_o] \frac{\rho}{M} 4\pi r^2 dr \qquad (7)$$

where $\overline{R}$ is the effective radius of action for an ion. Table 2 gives the figures necessary for graphical computation of the integral (7) in the case $n = 0.02$ and $\overline{R} = 5.65$ Å.

Combining our results, we find that $C - nC_4 = n_oC_o + n\left(\lambda\dfrac{R}{2} + C_2 + C_3\right)$ has the values plotted in figure 3. There are added also some measurements concerning solutions similar to KCl. The curves for NaCl, KCl and RbCl lie between those of HCl and LiCl.[5]
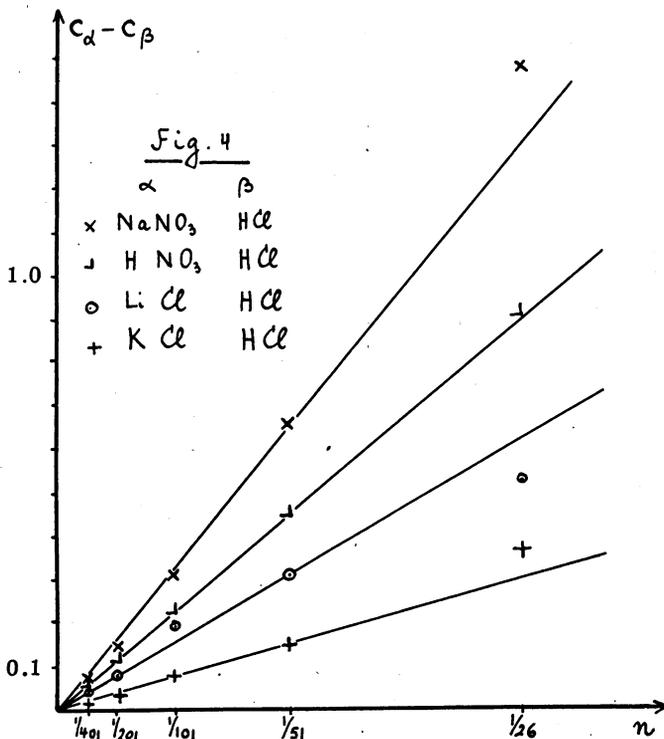
The order of magnitude and also the general shape of the curve is correct. The systematic differences must be ascribed to different hydrations of the ions. Their character is well shown in figure 4, where the difference, $C_\alpha - C_\beta = n(C_{4\alpha} - C_{4\beta})$ for two similar electrolytes α and β, is plotted. As the curves in figure 4 are linear, the effect contributed by the hydration of one ion is constant in this range of concentrations.

Figure 3 shows a somewhat greater curvature for the theoretical curve than for the experimental ones. This is probably because in computing C_3 we have not taken into account the fact that ions of opposite sign are on the average nearer together than charges of the same sign.

The variation of the specific heat of an electrolyte with the valence of

the ions is also in agreement with the theory. A very good check for the latter is found in calculating the variation of the specific heat with temperature. Again C_3 turns out to be the most important factor. Considering the curves in figure 2, it can be shown that C_3 increases very slowly with the temperature from 10° to about 60°C. A sudden change from negative to positive values occurs, however, in the region between 60° and 80°C. The result is, that the true specific heat shows small variation from 10° to 60° and increases very rapidly afterwards. A preliminary check of this strange behavior being predicted by the theory is possible in the case of KCl and NaCl where the average specific heat from 15° to 50° and from 15° to 80° is known. However, it would be desirable to have exact measurements of the true specific heat from 0° to 100° so as to be able to compare a whole curve with the theory.

It is possible to extend these considerations and to deduce the free energy of an electrolyte in terms of volume, temperature and concentration for a relatively dilute solution (up to some mols. per liter). It can be shown furthermore that the pressure effect (3) will probably play an important rôle in the theory of osmotic phenomena, necessitating a correction to the treatment of this problem by Milner and Debye.

* In the present paper we give a general outline of the considerations underlying our theory and some of the results. A detailed account of the intermediate mathematical steps will be published in another place.

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[1] P. Debye, *Phys. Zeitschr.*, **13**, 97 (1912).

[2] Milner, *Phil. Mag.*, **23**, 551 (1912).

[3] P. Debye and E. Hückel, *Phys. Zeitschr.*, **24**, 185 (1923).

[4] P. Bridgman, *Proc. Amer. Acad. Arts and Sciences*, **48**, 310 (1912–13).

[5] T. W. Richards and A. W. Rowe, *J. Amer. Chem. Soc.*, **43**, 770 (1921) and **44**, 684 (1922).

THE SPECTRUM OF NEON IN THE EXTREME ULTRA-VIOLET

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The study of the spectrum of helium in the extreme ultra-violet recently carried through by one of us[1] brought to light a persistent pair of lines apparently due to an impurity, and, as the most reasonable assumption was that this impurity was neon, the investigation of the spectrum of this gas was undertaken. A preliminary account of this work[2] was published