TRANSACTIONS

THE HEATS OF SOLUTION OF CERTAIN ALKALI HALIDES AND THE
SPECIFIC HEAT OF THEIR SOLUTIONS.—By H. RITCHIE CHIP-
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ABSTRACT.

A new form of apparatus for the determination of the heat of
solution is described. This determination requires the specific
heats of the salt solutions and values have been obtained by a new
method. The salts investigated were sodium chloride, sodium
bromide, potassium chloride, and potassium bromide.

The heat of solution of the above mentioned salts have been de-
termined over a concentration range. With sodium bromide it was
found that the sign of the value changed at a certain concentration.
With the potassium salts a temperature coefficient was found and
this coefficient was found to vary with concentration.

The values obtained for the heats of solution of the salts and
also for the specific heats of their solutions are shown in suitable
figures, and a short discussion is given.

The heats of solution of a large number of salts have been
determined, but most of the experimental data were obtained
before the introduction of the adiabatic calorimeter and did
not extend over a large concentration range. It was therefore
decided to determine the relation between the heats of sol-
ution of some of the alkali halides and their concentration.
This work was carried out in 1925, at McGill University,
Montreal.

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In many of the earlier forms of apparatus it was impossible to prevent heat losses. In measuring the heat of solution a weighed quantity of salt is dissolved in a weighed quantity of water and the change in temperature measured. The salt and the water must be at the same temperature before mixing, and, when mixing occurs, it must be complete and the solution well stirred. The measurement of the temperature change is of great importance. Mercury or resistance thermometers possess too large a heat capacity, and a thermocouple used as a an absolute instrument is inconvenient. The method chosen for this work was to use a thermocouple as a null-point instrument, one junction being in contact with the reactants while the temperature of the other is measured by a resistance thermometer.

In previous forms of apparatus the design adopted to insure correct temperature equilibrium of the reactants and their complete mixing required a relatively large amount of material, which was a drawback when working with salts of which only a small quantity is available or when using low concentrations. In these determinations an apparatus has been designed to enable the reactants to be kept at the same temperature and allow the reaction to take place when desired. Very small quantities of salt may be used and as little as thirty cubic centimeters of liquid.

The substances investigated were sodium chloride, sodium bromide, potassium chloride and potassium bromide. All salts were of c. p. quality, recrystallized from distilled water, and the crystals pulverised in an agate mortar. All glass vessels used were Pyrex.

In determining the heats of solution it is necessary to know the specific heat of the salt solution over the concentration range employed. Several values for the specific heat of solutions are available in the literature but they were somewhat uncertain on account of the concentration at which they were determined. It was therfore decided to determine the specific heats of the solutions by a new method and at more suitable temperatures.

The usual method of determining specific heats is to add a definite amount of heat and observe the resulting change in temperature. An accurate knowledge of the heat capacities of the parts of the apparatus is required and many errors from heat losses are encountered. The new method is a relative one, water is taken as the standard and the errors due to heat losses are compensated. A definite amount of heat is taken from the solution and the temperature change measured. A quantity of distiled water is placed in a small container, frozen, and kept in a bath at a constant low temperature. This container is then placed in water in an adiabatic calorimeter and the drop in the temperature of the calorimeter measured. Heat will be absorbed by the melting of the ice in the container and by raising it and its contents to the temperature of the water in the calorimeter. The largest portion of heat will be absorbed by the melting of the ice, and as the same amount of water is sealed up in the container, this is always a constant quantity. The use of this container thus permits the abstraction of a constant amount of heat from the water in the calorimeter.

Having measured the drop in temperature produced when the container is placed in the water, and knowing the weights of the water and the calorimetric vessels, together with their specific heats, an equation may be obtained relating the drop in temperature to the number of calories taken up by the water in the container. This process is then repeated, using a salt solution in place of water in the calorimeter, whereupon a similar equation is obtained containing the specific heat of the solution as an unkown.

As the container always takes the same amount of heat from the solution, being at the same initial temperature in all cases, the number of calories absorbed by the water will be the same as the number absorbed by the salt solution, the different drop in temperature being caused by the difference between the specific heat of the water and that of the salt solution. From these relations the specific heat of the salt solution may be obtained. By the use of this method any heat losses existing as constant errors are compensated, as the value for the number

of calories absorbed are obtained by the same experimental procedure.

The small container consisted of a copper cylinder about 7 cms in length closed by a copper tube with a cap. The cylinder was filled with distilled water and the cap soldered on. The tightness of the cylinder was tested by allowing it to remain in a vacuum for some time. No loss in weight was found.

The initial bath for the container was a porcelain beaker containing salt solution and ice. The solution was well stirred with a paddle. The container was kept in the bath in a copper tube which it fitted tightly. The temperature of the bath was measured by a Beckmann thermometer and a temperature which was about –4.6°C was chosen and was held to within 0.1°C. The container was allowed to remain in this bath for one and one half hours.

The adiabatic calorimeter was essentially the same apparatus as used by Maass and Waldbauer[1] in their determination of specific and latent heats. The calorimeter vessel was of copper and held about 1300 cc. It was well insulated from its containing vessel. The liquid in the calorimeter was stirred by an up-and-down stirrer. The outer bath was stirred by paddles.

The temperature of the outer bath was measured by a Beckmann thermometer calibrated by the Bureau of Standards. The balancing of the calorimeter was done by a copper-constantin thermocouple which was directly connected to a sensitive galvanometer. One junction of the couple dipped into the calorimeter and the other into the outer bath. When a thermal balance was obtained the temperature of the calorimeter could be read by the Beckmann thermometer. The two baths could easily be kept to within 0.001° of each other.

The solution was made up to the desired strength by weighing the salt and the water. It was then brought to a temperature which was found by experiment to be the one most suitable for a convenient initial temperature when the calorimeter was balanced, and was weighed into the calorimeter.

1. **Maass & Waldbauer.** J. A. C. S., **42**, 1, (1925).

The apparatus was then assembled and the bath balanced when readings constant to 0.002° were recorded every five minutes for fifteen minutes. After a balance was obtained the container was introduced into the calorimeter. The resulting temperature change was followed by the addition of cold water and the baths finally balanced once more. The temperature interval could then be obtained.

Knowing the weights of the vessels and their specific heats, the number of calories given up by the water could be calculated. The same procedure was repeated using a salt solution in the calorimeter. The specific heat of the solution was an unknown in the resulting equation obtained by equating the number of calories given up by the solution to the number given up by the water.

The specific heats of solutions of the salts investigated were measured over a concentration range from 0.2 to 4.0 molar, and the following results obtained:

TABLE I.

SPECIFIC HEATS OF SALT SOLUTIONS.

Sodium Chloride

Concentration	Specific Heat
0.423	0.9648
0.839	0.9353
1.650	0.8967
2.435	0.8680

Sodium Bromide

Concentration	Specific Heat
0.241	0.9695
0.479	0.9381
0.946	0.8922
1.312	0.8643
1.833	0.8261

Potassium Chloride

Concentration	Specific Heat
0.331	0.9651
0.653	0.9362
1.290	0.8829
1.898	0.8408
2.476	0.8057

Potassium Bromide

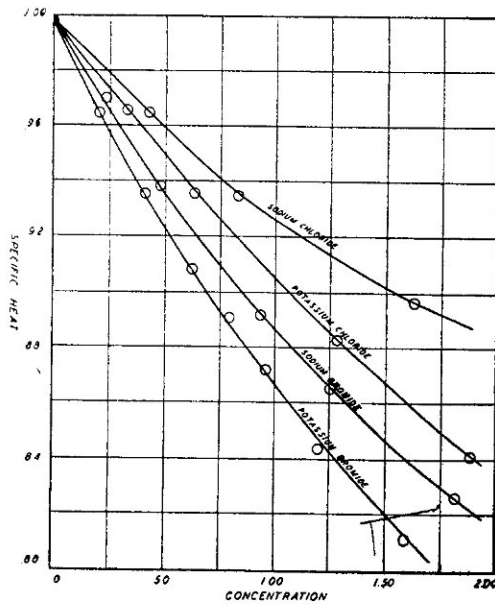| Concentration	Specific Heat
0.208	0.9638
0.412	0.9361
0.632	0.9079
0.803	0.8916
0.969	0.8708
1.199	0.8433
1.568	0.8107

These results are shown in Fig. I.

FIG I

The average temperature at which the preceeding determinations were carried out was 25.4°C. It was decided to carry out a few experiments with the same solutions at a lower temperature to see if there was an appreciable difference. The lower temperature was 18.8°C. The values found at the higher temperature are given for comparison.

TABLE II.

EFFECT OF TEMPERATURE OF SPECIFIC HEATS.

Salt	Concentration	S. H. 18.8°	S. H. 25.4°
Sodium chloride	1.79	0.8964	0.8930
	2.44	0.8664	0.8680
Sodium bromide	1.13	0.9962	0.8775
	1.40	0.8700	0.8575
Potassium chloride	1.57	0.8751	0.8563
Potassium bromide	1.20	0.8509	0.8433

It will be seen from Table II. that a change in the specific heat is shown with change in temperature. This variation seems to be more marked with potassium salts than with sodium.

Having obtained values for the specific heats of the salt solution, the determination of the heats of solution were carried out.

The apparatus consisted of an adiabatic calorimeter where the calorimeter proper consisted of a small silver vessel so designed that salt could be held in it and water admitted at will. The small vessel is shown in detail in Fig.2.

The only openings in the vessel were the tube at the top and the openings at the bottom which were shielded by a system of vanes. Owing to the arrangement of the bottom

openings no water could enter the vessel unless the air could escape from the tube at the top. The entrance of the water could then be controlled by air pressure which was regulated by the pump as shown in Fig. 2.
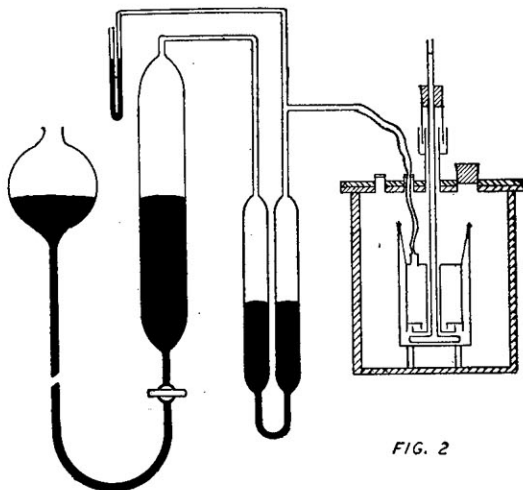

FIG. 2

The vessel containing the salt was fastened concentrically within another silver vessel, sufficient space being left at the bottom for a stirrer, and at the sides for the thermocouple. This vessel was in turn placed in a brass vessel which was immersed in the outer bath of the calorimeter. The silver vessel was insulated from the brass vessel by small glass legs. The brass vessel was closed by a brass plate having suitable holes for the tubes and stirrer. This plate was well greased before fitting and was held in place by means of three clamps The liquid in the inner vessel was stirred by a small glass stirrer which passed through the tube in the center. This stirrer was driven by a small motor and the hole by which it passed through the brass cover of the outer vessel was closed by a rotating mercury seal, in order to prevent leakage of air at this point. When air was pumped in or out of the inner vessel it could only come in or go out of the brass vessel by means of a tube which was connected with a series of bulbs

which were kept below the surface of the water in the outer bath. By this means the air was always at the same temperature as the rest of the apparatus.

It will be seen from Fig. 2. that the pump is so arranged that the air which is pumped in and out of the inner vessel comes from a cylinder which is below the surface of the outer bath and hence always at the same temperature as the inner vessel.

The connection between the inner vessel and the pumping system was made by a small rubber tube. This tube was made from a small surgical catheter. It was fastened at one end to a small silver plug which tightly fitted into the tube at the top of the inner vessel, and the other end was fastened to a tapering glass tube which passed through the cover of the brass vessel. An ordinary rubber tube connected this glass tube to the pump tubing. In assembling the apparatus the tapering glass tube was passed through the cover of the brass vessel and was cemented in place by deKhotinsky cement. After the cement had hardened the rubber connection could be made to the pump system.

A manometer placed in the pump system was so calibrated as to show the level of the water in the inner vessel. It will thus be seen that the salt and the water may be kept at the same temperature for any length of time. By manipulation of the pump the water may be admitted to the salt, and solution will occur. By pumping the solution in and out of the inner vessel thorough mixing takes place, and all the salt is dissolved. All the reactants and the air with which they come into contact are at the same temperature before mixing.

The thermocouple was a single junction of copper and constantin and led to a sensitive galvanometer. One junction of the couple dipped into the water in the inner vessel and the other dipped into the water in the outer bath. The calorimetric was balanced in the same way as was the one used for the specific heat work, except that the temperature of the outer bath was read by means of a resistance thermometer.

In making a determination a weighed amount of salt was introduced into the inner vessel and the apparatus put together. A known weight of water was introduced into the inner vessel by means of a weight pipette: the air pressure within the small vessel preventing the water from reaching the salt.   The baths were then balanced and temperature readings taken every five minutes.   It was found that a constant temperature was not obtained but there was a steady decrease.   To obtain a correct initial temperature the readings were plotted against time in minutes and the curve extrapolated to the time at which the reaction took place.   This procedure was also necessary at the end of the reaction.

After sufficient readings had been taken to allow exact extrapolation, the pump was started and the water allowed to enter the vessel containing the salt.   There was immediately a change of temperature and the baths were kept balanced during the solution.   The solution was pumped in and out of the inner vessel to ensure sufficient solution and mixing, until there was no further change in temperature.

Knowing the weights of the calorimeters, the salt, and the water, and having obtained the temperature change, the heat of solution could then be calculated.

The following results were obtained with sodium chloride. With this salt it was found inadvisable to use concentrations less than 0.2 molar as the heat change was so slight that the errors produced a larger effect.

TABLE III.

HEAT OF SOLUTION OF SODIUM CHLORIDE.

Concentration	Heat of solution per gram mol.	Average
0.202 molar	1199 calories	
0.202	1198	
0.202	1181	1193
0.404	1173	
0.404	1159	
0.404	1142	
0.404	1161	1159
0.604	1004	
0.604	1049	
0.644	997	
0.644	1043	1023
0.821	994	
0.821	1026	
0.821	1004	
0.821	1017	1010
1.23	917	
1.23	918	918
1.63	832	
1.63	841	836
2.12	753	
2.12	757	755
2.62	702	
2.62	679	
2.62	691	686
3.18	555	
3.18	566	560
4.03	478	
4.03	475	477

These results are shown in Fig. 3.
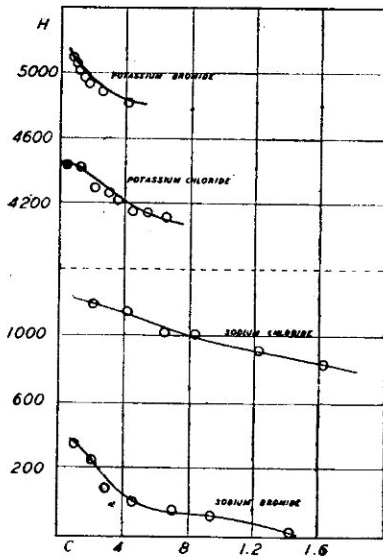
FIG 3

Sodium bromide forms a dihydrate and a pentahydrate. The transition point of the anhydrous salt and the dihydrate is about 50.7° while that of the pentahydrate and ice is about –27°. The sodium bromide was carefully dehydrated and it was found that the salt would remain long enough in the anhydrous condition to allow a determination of the heat of solution to be made.

The same procedure was used as with sodium chloride. At lower concentrations a similiar effect was obtained but the heat of solution was much smaller. At a concentration of about 0.5 molar no temperature change was observed. With higher concentrations a positive value was obtained due to the effect of the formation of the hydrate. Evidence points to the fact that the dihydrate is first formed and then this goes into solution. This was shown by the fact that when the salt was first dissolved heat was evolved and after a time heat was suddenly absorbed. Large concentrations could not be used on account of the large amount of heat evolved and then absorbed. The results are shown in Table IV.

TABLE IV.

HEAT OF SOLUTION OF SODIUN BROMIDE.

Concentration	Heat change per gm. mol.	Average
0.106 molar	— 324 cals	
0.106	— 355	
0.106	— 378	— 352
0.203	— 259	
0.203	— 260	— 260
0.297	— 86	
0.297	— 98	— 92
0.486	— 17	
0.486	+ 17	0
0.705	+ 38	
0.705	+ 35	+ 36
0.945	+ 75	
0.945	+ 72	+ 72
1.41	+ 187	
1.41	+ 192	+ 190

These values are shown in Fig. 3.

Attempts were made to prepare sodium bromide dihydrate, but a stable hydrate could not be obtained.

It was found that the potassium salts possessed a temperature coefficient which apparantly varied with the concentration. A different procedure was then followed for the potassium salts. Determinations were made at the same concentrations but at different temperatures, the temperature being taken as the mean between the initial and final temperatures. The results were then plotted against temperature. The relation between the heat of solution and temperature is linear and a series of straight lines were drawn through points of the same concentration. The temperature coefficient would be the slope of these lines, which would be parallel if the coefficient is independent of the concentration. It was found that such was not the

case.   As the heats of solution had been determined at a temperature of about 22° the values for the heats of solution of the potassium salts were taken from the ordinate of 22° and are shown in Fig. 3.   The results obtained for potassium chloride are given in Table V.

TABLE V.

HEAT OF SOLUTION OF POTASSIUM CHLORIDE.

Concentration	Heat absorbed per gm. mol	Average Temperature
0.067 molar	4495 calories	23.1°
0.067	4411	22.6°
0.067	4335	23.6°
0.133	4412	22.5°
0.133	4442	21.6°
0.133	4540	16.1°
0.133	4353	26.8°
0.133	4315	27.6°
0.224	4316	21.0°
0.224	4459	19.4°
0.271	4304	22.6°
0.271	4283	22.6°
0.271	4468	21.0°
0.313	4411	17.6°
0.313	4441	17.2°
0.313	4280	21.6°
0.351	4255	21.3°
0.390	4230	21.9°
0.390	4253	20.7°
0.390	4253	20.6°
0.438	3986	26.7°
0.438	3973	28.6°
0.438	4402	15.8°
0.438	4141	22.0°
0.438	4282	18.0°
0.528	4181	22.0°
0.528	4332	18.3°
0.656	4105	22.5°
0.656	4123	22.8°
0.656	4424	14.2°
0.656	4036	25.6°

It was difficult to work with greater concentrations of potassium chloride than 0.7 molar account of the large heat changes which took place.

With potassium bromide a temperature coefficient was also found and the same procedure was followed.   The results are in Table VI.

TABLE VI.

HEAT OF SOLUTION OF POTASSIUM BROMIDE.

Concentration	Heat absorbed per gm. mol.	Average temperature
0.090 molar	5148 calories	16.5°
0.090	5128	15.5°
0.090	4992	25.6°
0.090	5000	26.3°
0.090	4952	27.0°
0.090	4811	26.3°
0.106	4879	26.1°
0.110	4783	26.2°
0.110	4693	26.3°
0.110	4694	27.2°
0.110	4789	27.3°
0.130	4735	27.2°
0.130	4742	26.3°
0.170	5095	15.7°
0.170	5138	16.1°
0.170	4601	26.8°
0.170	4688	26.3°
0.170	5046	15.9°
0.170	4685	25.7°
0.170	5049	16.4°
0.250	5132	14.7°
0.250	5056	15.6°
0.250	4759	23.5°
0.250	4627	26.2°
0.250	5109	17.0°
0.420	4573	26.3°
0.420	4557	26.6°
0.420	4936	17.2°
0.420	5019	15.1°

The results obtained for potassium salts showed not only a temperature coefficient but a change in that coefficient with temperature. The temperature coefficient plotted against temperature is shown in Fig. 4. It will be noticed that here is a tendency for the coefficient to approach a constant value, but in the case of potassium bromide this is reached more quickly.

A qualitative explanation for the general shape of the heat of solutions curves may be obtained by the use of two thermochemical magnitudes introduced by Born[2] and Fajans[3]: "the lattice energy of crystals" and the "heat of hydration of gas ions".

Since the ions in the space lattice of a crystal maintain their relative positions as is shown by the stability of the crystal, there must be forces of attraction which result in the structure of the crystal. When the crystal goes into solution the ions leave their places in the space lattice and move about in the solvent. Energy must be supplied to overcome the forces of attraction, and, according to Born, the energy necessary for the formation of free gaseous ions from crystals is defined as the lattice energy. Born has calculated the magnitude of this energy for a number of crystals from a knowledge of their molecular volumes.

It would be expected that changes of energy would be found when the ions associate themselves with solvent molecules, and to express these energy changes due to hydration Fajans employes the term, "heat of hydration of gas ions." According to Fajans the heat of solution of a salt in water is dependent upon the amount of heat evolved by the dissociation of the salt into ions, and the amount of heat developed by the solution of these ions in water. Butler[4] relates the solubility of a salt to its heat of solution, heat of hydration of ions and lattice energy. The solubilities of the salts are not proportional to their lattice energy and no doubt there are other factors governed by the heat of hydration.

2. **Born.** Ber. Deut. Phys. Ges., **21**, 13, (1919).
3. **Fajans.** Ber. Deut. Phys. Ges., **21**, 549, (1919).
4. **Butler.** Zeit. Phys. Chem., **113**, 285, (1924).
    Butler. Jour. Phys. Chem., **28**, 438, (1924).

As the lattice energy is a magnitude which relates solely to the ions of the salt as they exist in their position in the space lattice, and not to their condition in solution, it is not affected by changes in concentration. It may be considered as a constant, although it may be influenced by temperature. If the lattice energy is a constant, variations in the heats of solution will depend upon the heats of hydration of the ions.

The curves for the heats of solution show a decrease with increasing concentration and the rate of decrease becomes less at the higher concentrations. At low concentrations the ionization approaches its maxium value and a large number of ions are present giving a larger value for the heat of hydration of these ions. If the concentrations be increased the ionization decreases and the number of ions decrease, the heat of hydration becomes less and the heats of solution are smaller.

Let us consider the temperature coefficient which was found with potassium salts and which is shown in Fig. IV. We may perform a cycle with the same masses as follows. We may allow the reaction to proceed at T_1 and heat the resulting solution to T_2, then we may allow the reaction to proceed in the reverse order at T_2 and cool down the products to T_1. In this cycle the sum of the heat changes will be zero. In the formation of one gram of solution at T_1 we have an absorption of heat H_1 and heating up the resulting solution to T_2 requires a further absorption of heat, $S(T_2-T_1)$ where S is the average specific heat of the solution between T_1 and T_2. Allowing the reaction to proceed in the reverse way at T_2 with an evolution of heat H_2 and then cooling down the products to T_1, we have a further evolution of heat, $(m_1S' + m_2)(T_2 -T_1)$ where m_1 is the weight of salt required to form one gram of solution at the concentration chosen, S' being its specific heat: m_2 is the weight of the water, its specific heat being taken as unity. Equating the heat changes to zero we obtain the well known equation,

$$\frac{H_1 - H_2}{T_2 - T_1} = m_1S' + m_2 - S$$

$$\text{or} \quad dH/dT = m_1S' + m_2 - S$$

If actual values are inserted into this equation good agreement is found with the potassium salts where a temperature coefficient was found to exist. A consideration of this equation gives an explanation of the slopes of the curves showing the change in dH/dT with change in concentration as shown in Fig. 4.

As infinite dilution is approached, the term m_1S becomes less and at zero concentration it vanishes, there being left the two terms m_2 and S. As m_1 is diminished m_2 increases and approaches the limit of unity. At this limit there is nothing but water present and the terms m_2 and S_2 being equal, dH/dT is zero. It will be seen from Fig. 4. that the curves approach zero with zero concentration.
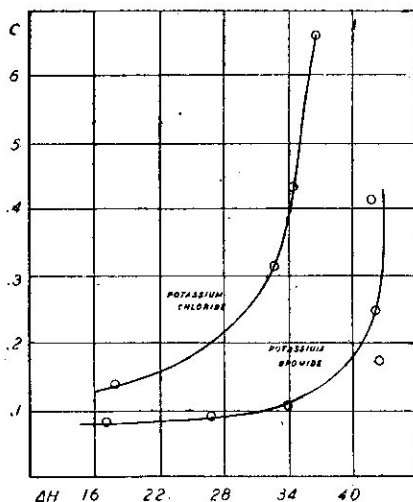

FIG 4

As the concentration is increased the term m_1S' increases and m_2 decreases. At the limit m_2 is zero. Therefore a limiting value is reached which is not the same in the case of different salts on account of the difference in the specific heats. Where there is no change in the heat of solution with temperature the left hand side of the equation will be zero and hence the right hand side will be zero.

The relation between the heat of hydration of the ions and the heat of solution has been pointed out, and it may be seen that a decrease in the extent of hydration results in a decrease in the heat of solution. It is known that an increase in temperature decreases the amount of hydration and hence it should produce a decrease in the heat of solution. Where a change in the heat of solution has been found the heat of solution does decrease with rising temperature as would be expected.

It has been mentioned that changes in the lattice energy would be expected with changes in temperature. The vibrational energy of the ions in the lattice would be increased with rising temperature and this would doubtless have an appreciable effect on the amount of energy required to remove them from their positions in the lattice. Therefore in discussing the effect of temperature upon heat of solution its effect upon lattice energy and heat of hydration must be considered. This is so complex that a suitable discussion cannot be attempted at the present time.

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