HEATS OF SOLUTION OF
CERTAIN ALKALI HALIDES

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THE HEATS OF SOLUTION OF CERTAIN ALKALI HALIDES AND THE SPECIFIC HEATS OF THEIR SOLUTIONS.

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A Thesis
Presented to the Faculty of Graduate Studies and Research of
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by

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Introduction.

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Almost the earliest calorimetric work was that performed by Black in 1762 in his work upon the latent heat of fusion. Improvements in apparatus and refinements in technique were applied to thermochemistry from time to time, the first of importance being introduced by Favre and Silvermann about 1852. The greater part of the experimental work in the early days of thermochemistry was carried out by Thomsen and Berthelot, who, with their collaborators, produced much data relating to heats of reaction. While some of their experimental methods, limited by the accuracy of the scientific instruments then employed, were necessarily somewhat crude, they nevertheless led to ideas which, when investigated with more refined apparatus have produced deductions of the greatest importance.

Beginning with the epoch-making view of Hess on the "Constancy of Heat Summation", thermodynamics became a most important factor in scientific consideration. This was based on the complete overthrow of the "Caloric" theory which was brought about by the work of Sadi Carnot, Count Rumford and Joule. The work of Nernst and more modern investigators has given thermodynamics a place of the highest importance in our understanding of physical chemistry.

Among the earliest researches undertaken by Thomsen was the determination of the heat of solution, that is, the extent of the heat change occurring when a solid dissolves. It had been known for a long time that there was a considerable heat change during the process of solution. This heat change was either an absorption or an evolution of heat, depending on the nature of the solid and solvent employed. With sodium or potassium hydroxides and water the heat evolved is almost sufficient to cause the solution to boil. Ammonium nitrate and water produce a heat change in the other direction and the solution sools down almost to the freezing point of water. The introduction of the adiabatic calorimeter by T.W.Richards marked an important era in thermochemistry, and enabled far more accurate measurements to be made.

The heats of solution of a large number of salts have been determined and the results published. Recent work upon crystal structure and hydration of ions has given a position of greater importance to work of this character, and it was therefore felt than an investigation of the relation between heats of solution and concentration would be of interest, particularly as very little attention has so far been devoted to this side of the question.

The object of this work was therefore to determine the relation between the heats of solution of some of the alkali halides and their concentration, which might be of interest in connection with recent ideas on the energy of space lattices. It was also thought that some information might be obtained concerning the heat of ionization, the heat of hydration, and solubility.

In these fields there is a lack of experimental data on the heats of solution over an extended concentration range, and in some cases the published values do not agree with others at the same concentration. It was therefore decided to determine these heats of solution, using apparatus of new design, capable of handling small quantities of salt with great accuracy.

Much of the earlier experimental work in the realm of thermochemistry was carried out before the introduction of the adiabatic calorimeter. On this account, it was then impossible to prevent serious heat losses or to correct them accurately. The determination of the heats of solution entails dissolving a weighed amount of purified salt in a weighed amount of pure water and carefully measuring the change in temperature. While, at first sight, this would seem to be a most simple procedure, a critical study of the various methods employed shows that it is attended by great experimental errors which are difficult to overcome.

The salts employed in this investigation were sodium chloride, sodium bromide, potassium chloride, and potassium bromide. Considerable data on the heats of solution of these salts have been published.[1]

One of the first considerations in any experimental investigation of a thermochemical reaction is to make certain that all the reactants have come to a temperature equilibrium with each other and with their surroundings. It is also necessary that the reactants be so separated from each other that the reaction will not take place until desired. Several devices have been employed for this purpose but many of them introduce serious errors, such as the uncertainty of the initial temperature of the reactants.

Complete mixing of the reactants is another essential feature. A lack of complete understanding of which has introduced many errors in past work. Separate vessels for the reactants, the breaking or tipping of containers, and similiar devices have been tried, but unavoidable heat losses have taken place which have diminished the accuracy of the results.

The stirring of the mixture of the reactants has an important bearing on the accuracy of the results. Not only must the substances be well mixed to allow the reaction to proceed smoothly, but means for the measurement of the temperature must be considered. It is essential that a perfect temperature equilibrium exist in the resulting mixture to ensure a correct temperature reading. The design of the stirring mechanism must receive considerable attention and the chance of heat losses through stirrer shafts and wires must be taken into account.

The method by which the temperature change is to be measured is also of the greatest importance. An ordinary thermometer is not sensitive enough to measure the small heat changes. A Beckmann thermometer introduces errors in reading, and has a very large heat capacity which produces a serious error when small quantities of the reactants are employed. The platinum resistance thermometer has a smaller heat capacity than a Beckmann thermometer, but it offers chances for serious errors due to conduction. On the other hand it provides an excellent method of determining the temperature on account of its accuracy. A thermocouple used as an absolute instrument is not convenient on account of difficulties in its calibration.

The use of a thermocouple as a null-point instrument with a platinum resistance thermometer measuring the temperature of one junction, while the other is in contact with the reactants, is an excellent combination. The diameter of the thermocouple casing and the size of the wire employed can be cut down so as to minimize losses by heat conduction, at the same time providing a means of determining the temperature at all stages of the reaction with a great degree of accuracy. This method has been employed in conjunction with an adiabatic calorimeter.

If the thermal reaction which is being investigated involves the solution of a solid in a liquid, the difficulties mentioned with regard to the proper equalizing of the temperature, and the correct mixing of the reactants, are greatly increased. All methods so far employed for this purpose necessitate the use of relatively large quantities of material. This is not to be desired when working with salts of which only a small quantity is available, or when a low concentration is to be investigated.

With the older calorimetric apparatus it was impossible to avoid considerable heat losses to or from the surroundings. Methods of correction involve much detail and calculation, and are not exact enough to be employed with certainty when the apparatus is of small dimensions. The introduction of the adiabatic calorimeter into the experimental work of thermochemistry by T.W.Richards has solved many of the problems formerly existing. By this method perfect temperature control of the outer bath reduces heat transfers to or from the surroundings to a negligible amount, and, at the same time, the use of a platinum resistance thermometer with a multiple thermocouple used as a null-point instrument, as before mentioned, makes possible the most exact temperature measurements.

This method has therefore been employed in these determinations of the heats of solution, and in addition an apparatus has been designed to enable the reactants to be kept at the same temperature and to allow the reaction to take place when desired. Exceedingly small quantities of salt may be used and as little as 30 cc. of liquid. This apparatus will be described in detail and the results given.

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The Materials Employed.

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The substances investigated were sodium chloride, sodium bromide, potassium chloride, and potassium bromide of either Baker's or Mallinckdrodt's "C.P." quality. The salts were purified by dissolving in distilled water, filtering by suction, and crystallizing three times. The crystals were then dried over a small flame and pulverised in an agate mortar. The vessels were all of Pyrex glass.

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The General Method of Procedure.

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In the method employed, a weighed amount of salt was dissolved in a weighed amount of water, and the resulting temperature change measured. From the weights of the reactants and the calorimetric vessels, and their specific heats, the number of calories absorbed or given out during the solution of the salt could be calculated. It was therefore necessary to know the specific heat of the resulting salt solutions over the range of concentrations employed in the work.

An examination of the literature showed that there were many decided variations among the published values for the specific heats of the solutions. These were very marked in the case of sodium and potassium chlorides. The values given for sodium and potassium bromide were however consistent. The published values were given at various temperatures, some of them being averages over a consdierable temperature range. These latter values would not fall on a smooth curve with the others.

To bring out the apparent discrepancies existing in the published results, the accompanying figures have been drawn. The smooth curves are the results of the experiments about to be described, and the points plotted are the results of other experimenters.

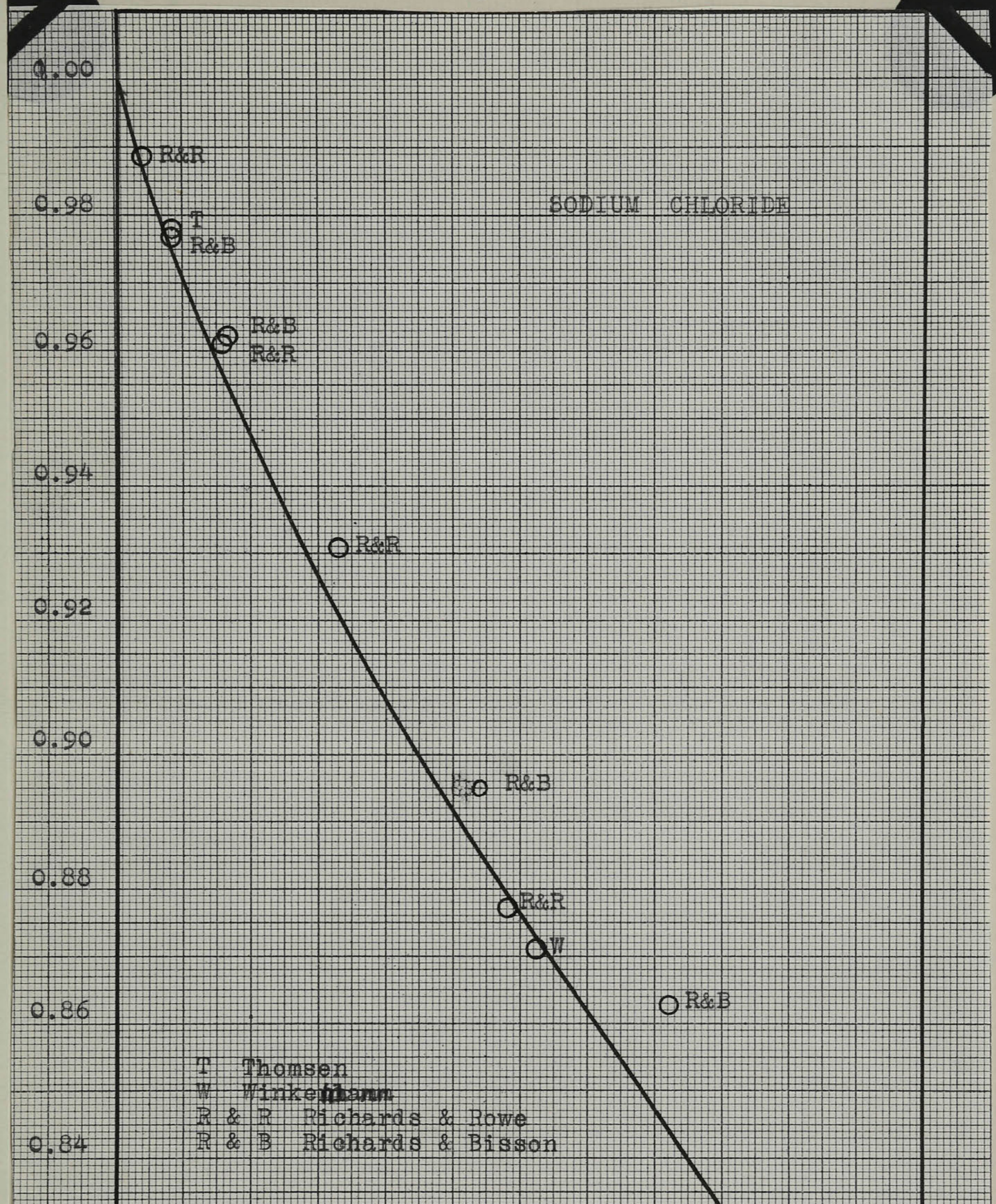
SODIUM CHLORIDE
1.00
0.98
0.96
0.94
0.92
0.90
0.88
0.86
0.84
0.82
0.80
Cp
2
4
6
8
10
12
14
16
18
20
22
Percentage Concentration.
R&R
T
R&B
R&B
R&R
R&R
R&B
R&R
W
R&B
R&B
T Thomsen
W Winkelmann
R & R Richards & Rowe
R & B Richards & Bisson

Figure 1

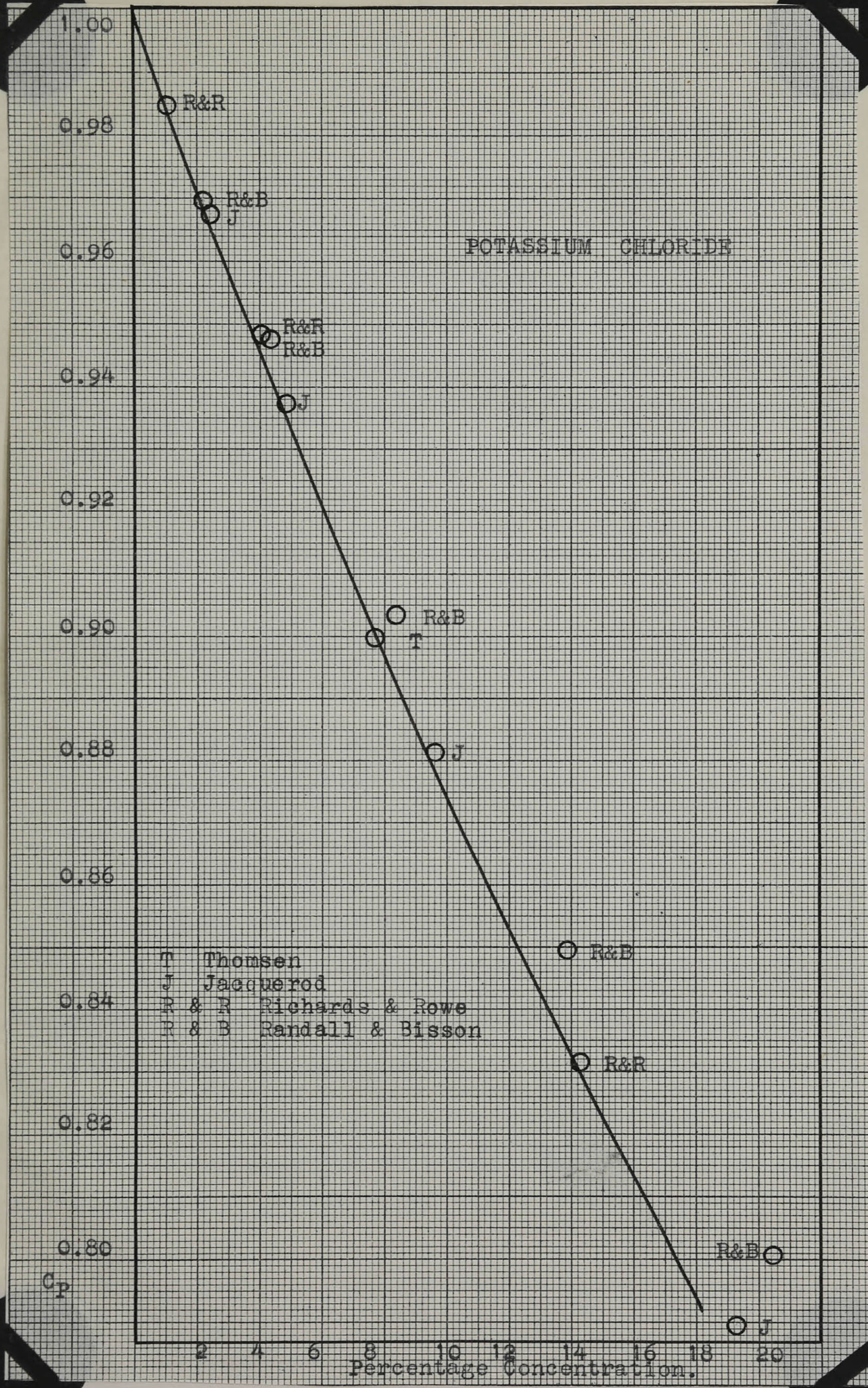
POTASSIUM CHLORIDE
1.00
0.98
0.96
0.94
0.92
0.90
0.88
0.86
0.84
0.82
0.80
C_P
2
4
6
8
10
12
14
16
18
20
Percentage Concentration.
R&R
R&B
J
R&R
R&B
J
R&B
T
J
R&B
R&R
R&B
J
T Thomsen
J Jacquerod
R & R Richards & Rowe
R & B Randall & Bisson

Figure 2.

Reference to the work of the investigators whose results have been plotted in Fig.1 and Fig.2 are given in the list of references[2].

On account of the uncertainty of these values, it was decided to determine the specific heats of these solutions by a new method which would make it possible to determine these constants at the same temperature at which the heats of solution were to be measured.

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The Specific Heats of the Salt Solutions.

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In most determinations of specific heats, the usual method is to add a definite amount of heat to a solution and observe the change in temperature. The various experimental procedures involve an accurate knowledge of the heat capacities of the several parts of the apparatus, and many errors from heat losses are encountered. On this account an accurate determination of the specific heat of a solution by the methods usually employed ~~is~~ was extremely difficult, particularly before the introduction of the adiabatic calorimeter.

The method about to be described is a relative one. Water is taken as the standard, and the errors due to heat losses are compensated for.

The apparatus employed is not extremely complicated,and, though very sensitive, is not too delicately constructed. It was found possible to repeat determinations to .2% without taking elaborate precautions, and the average was even better.

In this method a definite amount of heat is taken from the solution and the change in temperature measured. A quantity of distilled water is placed in a small container, frozen, and kept in a bath at a constant low temperature. This container, whose function gives it the name "frigidor", is then placed in water in an adiabatic calorimeter, and the drop in temperature of the water is noted. The frigidor holds about 20 gms.of water, and as each gram of ice absorbs 80 calories on melting, this small container subtracts a relatively large amount of heat from the water in the calorimeter. When the frigidor is placed in the water, the water which it contains is in the form of ice. When the ice warms up from the temperature of the cold bath to zero, the number of calories absorbed is Xst, where X is the number of grams of ice, s the specific heat of ice, and t the change in temperature. On the melting of the ice the number of calories absorbed is 80 X. The heating of the resulant water in the frigidor absorbs XST calories, where S is the specific heat of water, and T the change in temperature from zero to the final temperature. The copper frigidor will also absorb heat, the number of calories being $YS'(t + T)$, where Y is its weight, S' its specific heat, and t + T the total change of temperature which the frigidor experiences. The total number of calories absorbed by the frigidor will therefore be given by the following equation:-

$$Xst + 80X + XST + YS'(t + T)$$

It will be noticed that the largest portion of heat will be absorbed by the melting of the ice, and this value is always a constant quantity as the amount of water in the frigidor never varies. If the temperature of the cold bath were to vary by 0.1° or the frigidor were to warm up by 0.1° during the transfer, it will be seen that this would not make a large change compared with the value of the expression 80 X. This may be better pointed out by considering an actual case, taking approximate figures for the weights of water and frigidor concerned.

Let us then consider the following data:-

Weight of water in frigidor = X = 20 gms.

Specific heat of ice = s = 0.5

Temperature of cold bath = -5.0°, so t = 5.0

and the term $XSt = 20 \times .5 \times 5 = 50$ calories.

Now let the final temperature be 20° so T = 20° and the term $XST = 20 \times 1 \times 20 = 400$ calories, the specific heat of water being taken as unity.

Let the weight of the frigidor be 30 gms., so Y = 30. If the specific heat of the frigidor be 0.8 then $S' = 0.8$ and $YS'(t + T) = 30 \times 0.8 \times (5 + 20) = 600$ calories. The term 80 X is $80 \times 20 = 1600$ calories.

For the whole amount of heat absorbed, we have

$$50 + 400 + 600 + 1600 = 2650 \text{ calories.}$$

From the above equation, it will be seen that were the temperature of the cold bath to vary by 0.1°, which would be a variation in the first term of 2%, it would only affect the final result by a little over one calorie. Thus a considerable variation in the temperature of the cold bath will make a relatively small difference in the total number of calories absorbed by the solution, as it does not affect the value of the term 80 X. The simplicity and accuracy of this method depends on the fact that the value of this term in the above equation cannot be altered by any experimental error.

Having measured the drop in temperature produced when the frigidor is inserted in the water in the calorimeter, 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. The process is repeated, using a salt solution in the calorimeter in place of the water, whereupon a similiar equation is obtained containing the specific heat of the solution as an unknown. As the frigidor always takes the same amount of heat from the solution, being at the same initial temperature in every case, 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 water and that of the salt solution. From these relations the specific heat of the salt solution may be calculated. This can be seen from the following:-

For the water.

Let dT be the drop in temperature,

w be weight of calorimeter and stirrer,

s be their specific heat,

W be the weight of water, its specific heat being taken as unity.

X be the number of calories absorbed by the water.

We have then the equation:-

$$dT(w \times s) + dT(W \times 1) = X \quad \ldots\ldots\ldots\ldots\ldots(1)$$

For the solution,

Let dT' be the drop in temperature,

w be weight of calorimeter and stirrer,

s be their specific heat, as before,

S' be the specific heat of the solution,

W' be the weight of the solution,

X' the number of calories absorbed by the solution We have then the equation:-

$$dT'(w \times s) + dT'(W' \times S') = X' \quad ....(2)$$

But as $X' = X$, we can write

$$dT'(w \times s) + dT'(W' \times S') = X \quad ....(3)$$

From equation (3) we can then obtain S' the specific heat of the salt solution.

In order to equate X and X' we have to consider them at the same temperature. The same end temperature, as registered on the thermometer in the adiabatic calorimeter, was arbitrarily chosen, and the value of X' was, in every case, corrected to this temperature. The method of correction will be discussed later.

A study of this method shows that any heat losses existing as constant errors are compensated, as the values for dT and dT' are obtained by exactly the same experimental procedure.

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The Apparatus for the Determination of the Specific Heats of the Salt Solutions.

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The apparatus was composed of the frigidor and the adiabatic calorimeter.

The frigidor consisted of a small copper cylinder about 7 cms. in length and ending in a copper tube with a cap.

The cylinder was filled with distilled water and the cap placed on the tube and soldered on. To test the soldering for leaks, the frigidor was weighed, placed in a vacuum dessicator which was evacuated, allowed to stand for some time, then removed and weighed again. No loss of weight occurred after remaining in the vacuum for several hours, thus showing that there were no leaks in the soldered joint. To test this joint further, the frigidor was weighed from time to time during the course of the experimental work. No appreciable change in weight was found during this time.

After the water in the frigidor had been frozen by placing it out of doors in winter weather, the cylinder was placed in its freezing bath. This bath is shown in detail in Fig.3.Page 18.

Pieces of fine thread were tied around the cap of the frigidor, and also to a piece of string. This string passed through a cork J,Fig.4, which exactly fitted the large hole in the calorimeter cover through which the frigidor was passed. A knot was placed in this string, and so adjusted that when it was pulled up against the cork J the frigidor was suspended at such a distance from that cork as to clear the bottom of the calorimeter.

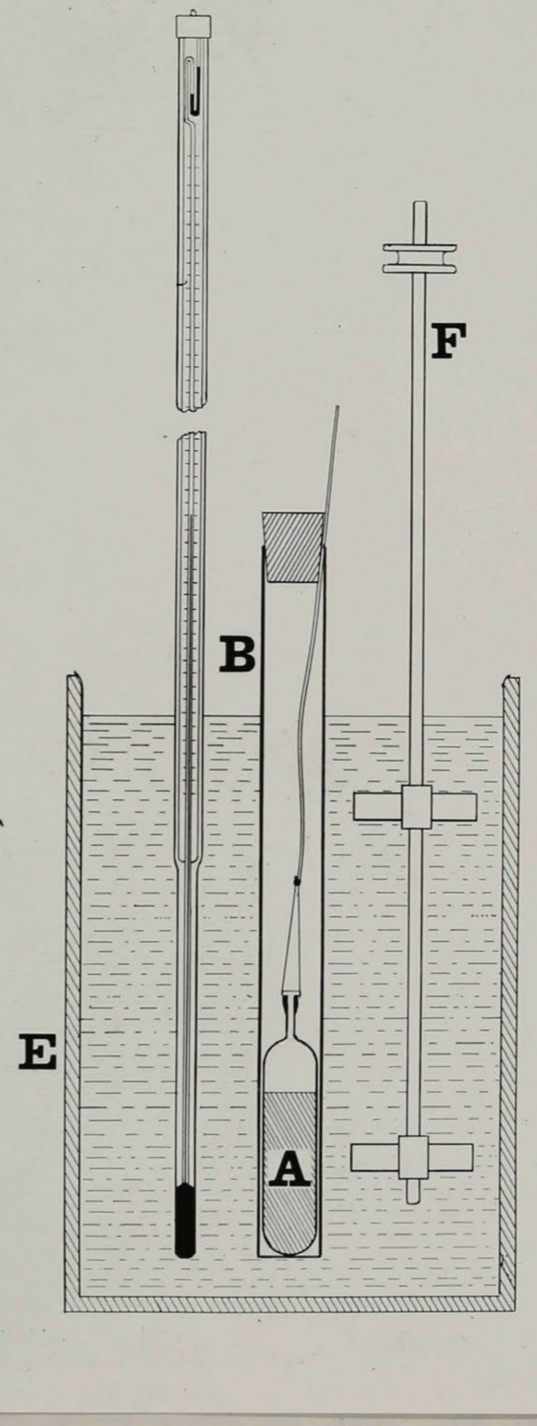

Figure 3.

During its preliminary freezing and while it was in the cold bath, the frigidor was kept inside of a brass tube which dipped into the bath. This tube was lined with copper foil so as to provide a good contact between the walls of the tube and the frigidor. The string which was fastened to the frigidor passed between the walls of the tube and a cork which closely fitted it. The cork J through which the string passed was allowed to hang on the outside. The general arrangement is shown in Fig.3, where the frigidor is represented by A, and the brass tube by B. A small piece of wool was pushed into the tube to form a guard ring above the frigidor and minimize heat losses. This piece of wool, which was inserted in the tube after the frigidor, is not shown in the diagrams.

The bath itself consisted of a porcelain beaker placed inside of a tin can E, the space between being filled with suitable insulating material. The bath was filled with concentrated sodium chloride solution. Ice was added to the bath to maintain a low temperature. A siphon was provided so that the level of the liquid could be kept constant. The addition of the ice lowered the concentration of the salt solution and solid salt was added from time to time to keep the bath concentrated.

The bath was stirred by a stirrer carrying two sets of blades as shown by F. These blades were so arranged that the water was driven in opposite directions, and very efficient stirring was obtained. The stirrer was driven by a small electric motor.

The temperature of the bath was measured by a Beckmann thermometer, as shown in the diagram. The point at which the thermometer registered 1.00° was arbitrarly chosen as the temperature of the bath, and was adhered to throughout the course of the experiments. When not in use the thermometer was withdrawn from the bath and placed in a secure place, so that there would be no danger of breaking the mercury thread when it was at room temperature, thus altering the reading of the thermometer.

In operating the bath, ice was added to the liquid which was rapidly stirred until the temperature was in the vicinity of -1.0° C. when the Beckmann was inserted. More ice was added until the proper point was reached on the Beckmann. This temperature was approximately -4.6° C. When this point was reached, the brass tube containing the frigidor was inserted. As mentioned before, the frigidor had first been frozen by allowing it to stand, in the tube, out of doors in winter weather. The temperature of the bath was kept constant by the addition of small pieces of crushed ice, and could be easily kept to within 0.1° of the proper point. The frigidor was allowed to remain in bath for one and one half hours.

The bath was then moved to the side of the adiabatic calorimeter which had previously been placed in operation and was correctly balanced. The cork was removed from the brass tube and the perforated cork pushed down the string until it came up against the knot which regulated the correct distance for the suspension of the frigidor in the calorimeter. The frigidor was then lifted out, the piece of wool being removed as it came out of the tube, and quickly placed in the calorimeter which was immediately balanced by the addition of cold water to keep pace with the cooling effect. The transfer of the frigidor to the calorimeter took place within a few seconds and the gain of heat was negligible. In any case, the same procedure was followed in obtaining the value with pure water, and any gain of heat would be compensated for.

The adiabatic calorimeter was essentially the same apparatus as that used by Maass and Waldbauer in their determination of specific heats and latent heats[3], and is shown in detail in Fig.4.

The calorimeter vessel was of polished copper having a capacity of about 1300cc. It rested on small ivory balls,which were fastened to small ebony feet, inside a metal vessel D which was fastened to the bottom of the outer

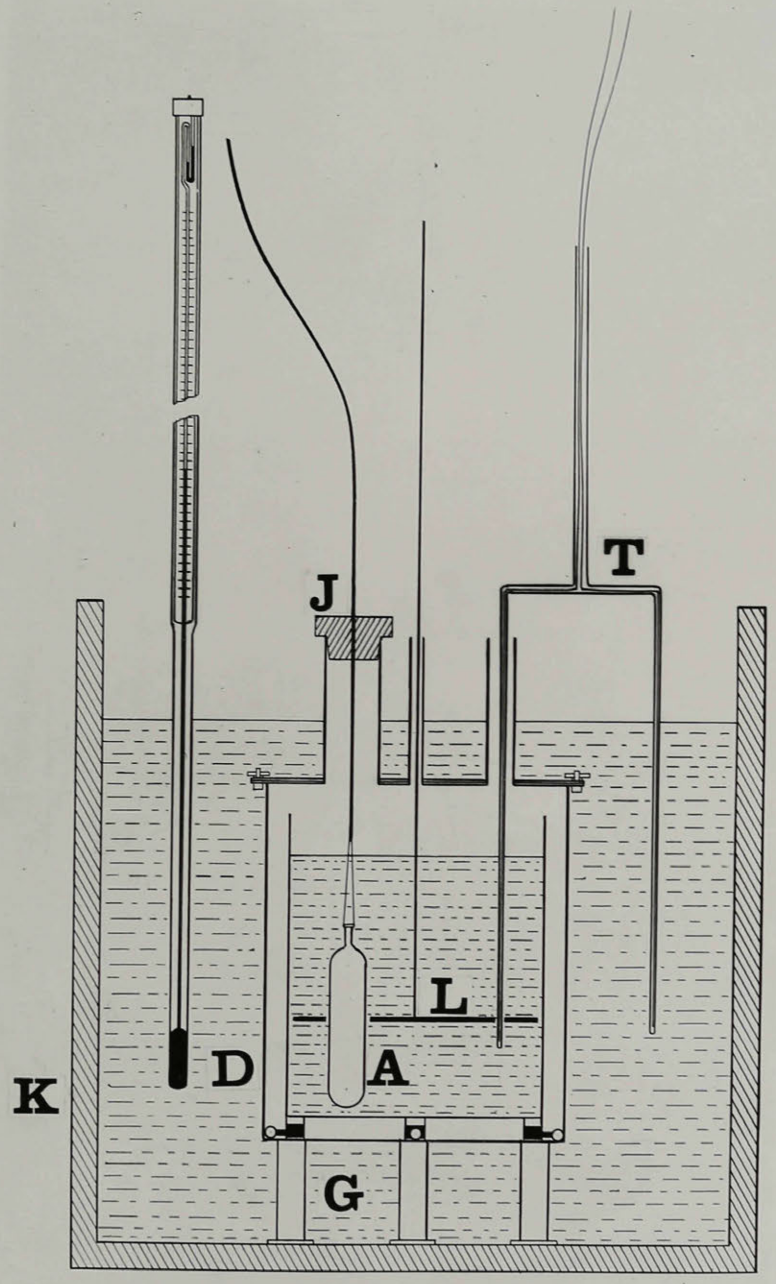

Figure 4.

bath by means of three legs G. These legs were fastened down by means of de Khotinsky cement. The small ivory balls projected from the periphery of the calorimeter vessel and besides supporting it on the bottom of the outer vessel kept it from touching the sides. The outer vessel was covered by a cover fitted with suitably placed tubes for the thermocouple, the stirrer and the entrance of the frigidor. This cover was bolted down on to a plate on the top of the vessel by means of small thumbscrews. The cover and the plate were well greased with vaseline to prevent leakage.

The liquid in the calorimeter vessel was stirred by an up and down stirrer L, operated through an eccentric on a wheel driven by a small electric motor. The stirrer itself consisted of a metal plate suspended by two fine wires which passed through the cover of the outer vessel. Suitable openings were placed in this plate to allow for the passage of the thermocouple and the frigidor.

The outer bath consisted of an earthenware vessel K holding about ten liters of water, fitted with an overflow so that the level would remain constant. This bath was well stirred by means of four stirrers, not shown in the diagram. These stirrers each carried two sets of blades and were so arranged that two neighbouring stirrers rotated in one direction and two in the other. These stirrers were driven by an electric motor and very efficient stirring was obtained.

The temperature of the outer bath was measured by means of a Beckmann thermometer which had been calibrated by the Bureau of Standards.

The thermocouple used was made of copper and constantan wires sealed into glass tubes, and was fastened directly to a Leeds & Northrup galvanometer of great sensitivity. A "clothespin" switch was used to break the circuit. By this means the circuit was at all times completed by the original wires thus avoiding another thermal junction. Another switch was so arranged that it short-circuited the thermocouple. When this switch was opened the thermocouple delivered its electromotive force, when it was closed the true zero point of the galvanometer could be read. The galvanometer was read by means of a beam of light reflected from the mirror of the galvanometer on to a transparent scale placed at a suitable point. The beam of light was reflected between the galvanometer mirror and the scale so that the spot of light could be placed at any part of the scale by an adjustment of the mirror. One junction of the thermocouple dipped into the inner bath and the other into the outer bath. When the spot of light was at the zero point the temperature of the inner and outer baths was the same. The thermocouple was thus used as a null-point instrument. By the addition of hot or cold water the outer bath was kept at the same temperature as the inner to within 0.001°. When large temperature changes were taking place in the calorimeter it was possible to keep the temperature difference to within 0.1°.

The solution was made up to the desired concentration by weighing the salt and water. Needless to say, the water was distilled and all handling of the solution was done in Pyrex. After the salt had completely dissolved, the solution was brought to a temperature which was found by experiment to be the one most suitable to cause the Beckmann thermometer in the outer bath to read between 5.9° and 4.5° when the adiabatic calorimeter was initially balanced. The solution was then weighed into the inner calorimeter vessel. The calorimeter was then assembled and the baths balanced. After readings consistent to 0.002° had been recorded every five minutes for fifteen minutes, the frigidor was introduced as before described. The cooling down of the solution was then followed by the addition of cold water to the outer bath, and when the temperature became steady, readings were recorded. When readings consistent to 0.002° had been recorded, as before, the experiment was stopped. Thus the temperature interval was obtained.

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The Calculation of the Correction for the Final Temperature on the Beckmann.

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The correction for the final temperature on the Beckmann was made as follows. It was decided to take the final temperature as 2.000° on the Beckmann, and all calculations are based on that choice.

The correction is obtained by multiplying the water value of the frigidor by the difference between the observed reading of the Beckmann and the final temperature of 2.00° which had been chosen. In the determination of X, if the final observed reading was above 2.00° the correction was subtracted from the calculated value of X, and in the determination of X', if the final observed reading was above 2.00° the correction was added to the value of X'.

The water value of the frigidor is the weight of the vessel multiplied by its specific heat plus the weight of the water contained multiplied by its specific heat. The values obtained were as follows.

Weight of frigidor, filled = 58.66 gms.
" " " , empty = 37.62 gms.
so " " water = 21.04 gms.

The specific heat of water was taken as unity.

The specific heat of the copper frigidor is 0.08

Wt.of frigidor x specific heat = 2.98

Wt of water x specific heat = 21.04

so Water Value of frigidor = 24.9 calories

In all the calculations, the specific heat of water was taken as unity, the error being well within the accuracy of the method.

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The Determination of X in the Case of Water.

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In the following some actual readings are given. The frigidor was placed in the cold bath which was then maintained at the constant temperature. In the meantime the adiabatic calorimeter was set up as described. The inner vessel held distilled water instead of solution. Readings were taken on the Beckmann every five minutes.

Time	Beckmann readings
0 min.	4.502°
5 "	4.505°
10 "	4.512°
15 "	4.515°
20 "	4.515°

Average reading 4.515°

Beckmann correction + 0.001

Corrected initial temperature 4.516°

In the meantime, the frigidor had been standing in the bath at constant temperature. It was now transferred to the calorimeter which was immediately adjusted. When a steady temperature had almost been reached readings were commenced. They continued as follows,

Time	Beckmann readings
0 min.	1.682°
5 "	1.678°
10 "	1.680°
15 "	1.680°

Average Beckmann reading 1.680°

Beckmann correction -0.003°

Corrected final temperature 1.677°

Temperature difference 2.839°

Weight of water = 830.5 gms.

Calories absorbed by water = 830.5 x 2.839 = 2357.8

Weight of calorimeter and stirrers = 298.2

Specific heat of calorimeter and stirrer = 0.0827

Calories absorbed by calorimeter etc. = 298.2 x .0827 x 2.839
= 70.1

Total calories absorbed = 2357.8 + 70.1 = 2427.9

End temperature on Beckmann = 1.68°

Difference for correction = 2.00 - 1.68 = 0.32

Correction = 24.0 x 0.32 = 7.7

Corrected value of X = 2427.9 + 7.7 = 2435.8

The values obtained for X and their corrections to constant temperature were as follows,

Value	End Temp.	Correction	Corrected value
2434.2	2.37°	-8.8	2425.4
2427.4	1.78°	+5.3	2432.7
2427.9	1.68°	+7.7	2435.6

Accepted value 2431.2

This was the value used in the calculations as being equal to X', being corrected back to the end temperature in each case, as before described.

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The Determination of the Specific Heat of One of the Salt Solutions.

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The method of obtaining the specific heat of a solution will now be shown, taking as examples the data obtained with a solution of potassium chloride of a concentration of 0.331 gm.mols./liter.

Readings for balancing of calorimeter

Time	Beckmann readings
0 min.	5.312°
5 "	5.310°
10 "	5.312°
15 "	5.312°

Average	5.312°
Correction	- 0.003°
Corrected initial temp.	5.309°

The frigidor was now placed in the calorimeter.

Time	Beckmann reading
0 min	2.360°
5 "	2.360
10 "	2.360°

Average	2.360°
Correction	- 0.003°
Corrected final temp.	2.357°

Temperature difference 5.309 - 2.357 = 2.952°

End temperature of Beckmann = 2.36°

Temperature correction = 2.36 - 2.00 = 0.36

Correction applied = 24.0 x 0.36 = 8.6

Therefore X corrected = 2431.2 + 8.6 = 2439.8

Weight of solution = 830.5 gms.

Calories absorbed by solution = S' x 830.5 x 2.952

= S' x 2451.0

Weight of calorimeter and stirrer = 298.2 gms.

Specific heat of calorimeter and stirrer = 0.0827

Calories absorbed by calorimeter etc. = 298.2 x .0827 x 2.952

= 72.8

Total calories absorbed = (S' x 2451.0) + 72.8

As the total number of calories absorbed must be equal to the corrected value of X, we have,

$$(S' \times 2451.0) + 72.8 = 2439.8$$

$$S' \times 2451.0 = 2367.0$$

$$S' = 0.9651$$

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The Values Obtained for the Specific Heats.

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The specific heats of solutions of the same salts which were used for determinations of the heats of solution, namely, sodium chloride, sodium bromide, potassium chloride, and potassium bromide, were measured over a concentration range varying from 0.2 to 4.0 Molal, and the following values obtained.

Sodium Chloride.

Molal Concentration.	Temperature Difference.	Final Temperature. (Beckmann)	Specific Heat
0.423	2.935°	1.728°	0.9648
0.839	3.031°	1.847°	0.9353
1.650	3.135°	1.206°	0.8967
2.435	3.244°	1.723°	0.8697
2.435	3.256°	1.679°	0.8664
3.921	2.983° ⁂	1.707°	0.8157

⁂ The cause of the variation between this temperature difference and the preceeding values is that a different weight of solution was used.

Sodium Bromide.

Molal Concentration.	Temperature Difference.	Final Temperature. (Beckmann)	Specific Heat
0.241	2.924°	1.747°	0.9695
0.479	3.001°	1.228°	0.9381
0.946	3.163°	1.559°	0.8922
1.312	3.255°	1.358°	0.8643
1.833	3.397°	1.277°	0.8261

Potassium Chloride

Molal Concentration.	Temperature Difference.	Final Temperature. (Beckmann)	Specific Heat.
0.331	2.952°	2.357°	0.9651
0.653	3.019°	1.849°	0.9390
0.653	3.017°	1.519°	0.9334
1.290	3.176°	1.006°	0.8829
1.898	3.343°	1.438°	0.8408
2.476	3.487°	1.582°	0.8057

Potassium Bromide.

Molal Concentration.	Temperature Difference.	Final Temperature. (Beckmann)	Specific Heat
0.208	2.920°	1.281°	0.9659
0.208	2.944°	1.699°	0.9617
0.412	3.019°	1.642	0.9361

Potassium Bromide (continued)

Molal Concentration.	Temperature Difference.	Final Temperature. (Beckmann)	Specific Heat
0.632	3.107°	1.529°	0.9079
0.803	3.168°	1.642°	0.8907
0.803	3.181°	2.150°	0.8924
0.969	3.235°	1.529°	0.8708
1.199	3.330°	1.261°	0.8433
1.568	3.442°	0.881°	0.8116
1.568	3.453°	0.978°	0.8097

The specific heats are shown in Fig.5.

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Specific Heat Determinations at a Lower Temperature.

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The average temperature at which the preceeding determinations were carried out was 25.4° C. It was decided to carry out a few determinations with solutions of the same salts at a lower temperature to see if a change in the temperature made an appreciable difference. The method of precedure was exactly the same except that another standardized Beckmann thermometer was employed.

The average temperature at which these determinations were made was 18.8° C.

The value of X with water alone was first determined. The values obtained for X in this case were 2285.6 and

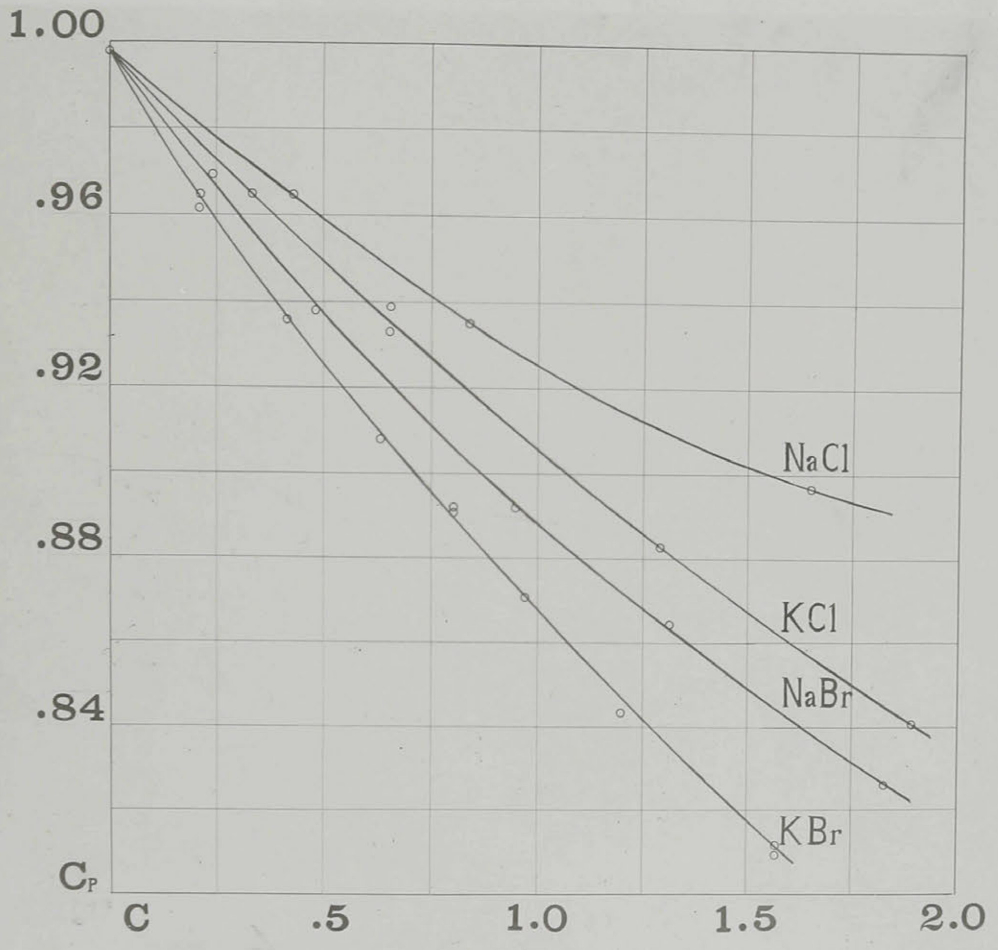

Figure 5.

2293.5 giving an average value of 2289.5 which was employed in calculation.

The results are here given, with the values found at the higher temperature and the same concentration for comparison.

Salt.	Molal Concentration.	Specific Heat at 18.8°	Specific Heat at 25.4°
Sodium chloride	1.79	0.8964	0.8930
	2.44	0.8664	0.8680
Sodium bromide	1.13	0.8862	0.8775
	1.40	0.8700	0.8575
Potassium chloride	1,57	0.8751	0.8563
	1.57	0.8732	0.8563
Potassium bromide	1.20	0.8511	0.8433
	1.20	0.8507	0.8433

It will be seen from these results that a change in the specific heat is, in general, shown with a change in temperature. This variation seems to be more marked with the potassium salts, and with sodium chloride is almost negligible.

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

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The Apparatus Used in the Determination of the Heats of Solution.

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The apparatus used in the determination of the heats of solution consisted essentially of three parts.

1. A system of calorimetric vessels containing weighed amounts of salt and water which were not in contact with each other although kept at constant temperature.
2. A device by means of which the salt might be dissolved in the water at will.
3. A means of accurately maintaining an adiabatic condition and measuring the temperature of the water before, during, and after, the solution of the salt.

The salt was contained in a silver vessel A,Fig 6, shaped as shown in the diagram. The only openings leading to the interior of this small vessel were the tube at the top and the openings at the bottom. The latter were shielded by a system of vanes V, as can be seen from the diagram. It will thus be seen that owing to the shape and position of these openings in the bottom no water could enter the vessel if the upper tube was closed so that the air could not get out. Also, on account of the presence of the vanes, no salt could drop out into the water. The entrance of the water could be controlled by the air pressure within the small vessel. The air

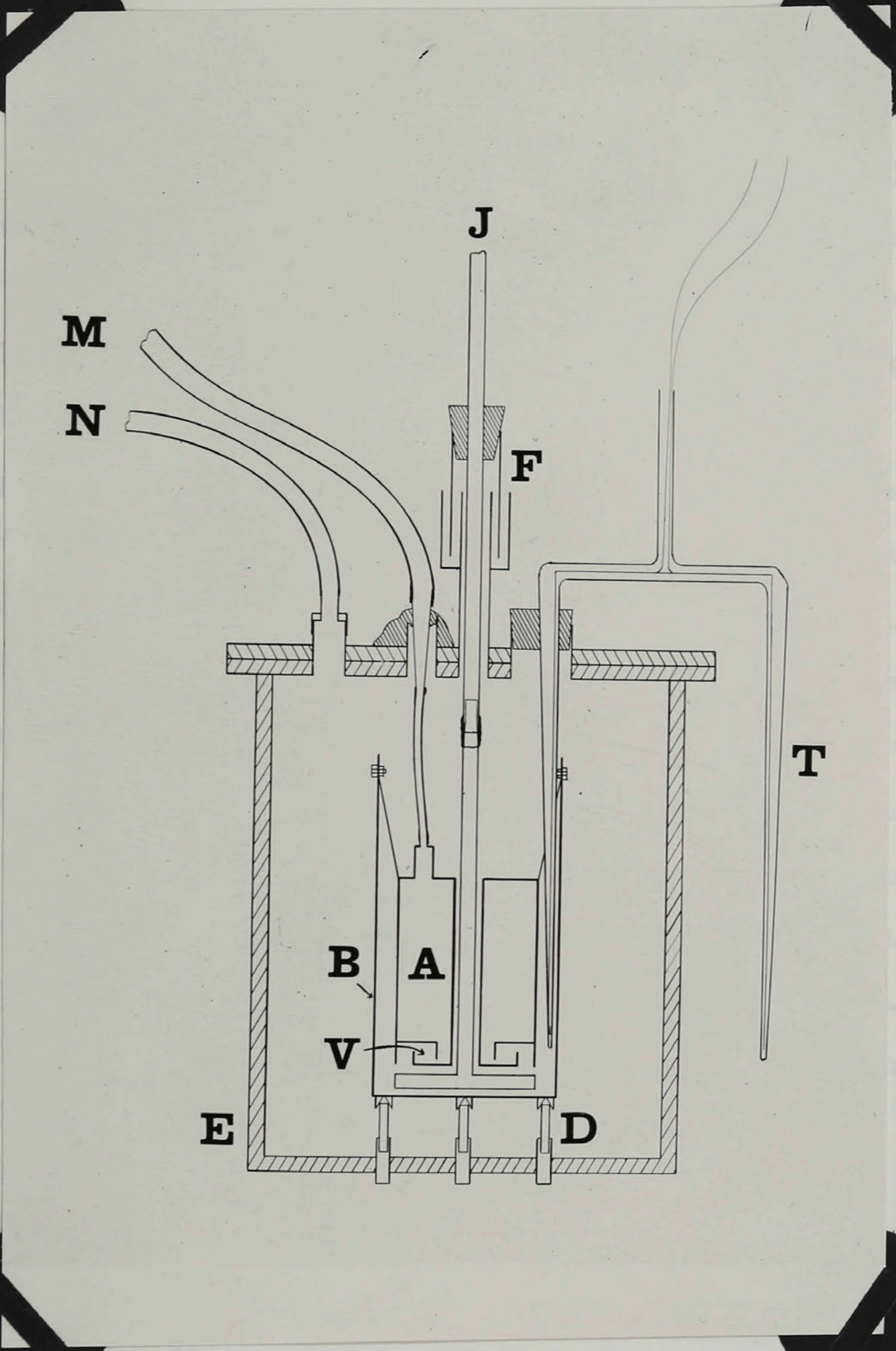

Figure 6.

pressure was regulated by means of a pump which is shown in Fig.7, and will be described later. A tube extended downwards through the inner vessel and permitted the use of a stirrer in the outer silver vessel.

This stirrer was made of glass rod of small diameter with glass blades fused on. The glass rod was cemented to a brass tube J which passed out of the apparatus, and, being connected to a removeable pulley, could be driven by means of a small motor. The length of the glass portion of the shaft of the stirrer was so adjusted that there was a fairly long section of glass rod between the upper level of the liquid and the brass rod, thus minimizing the conduction of heat along the stirrer. The pulley was supported by a long bearing so that no vibration or strain was placed upon the glass shaft. The shaft to which the pulley was attached was hollow and the lower end fitted with a set screw. When the apparatus was assembled in the outside calorimeter, this shaft was placed over the projecting end of the brass shaft of the stirrer. The pulley was then aligned so that the stirrer turned easily and was then fixed with suitable clamps. The set screw was then tightened. The small electric motor which was used to drive this stirrer was mounted on the frame of the calorimeter case and was geared down by suitable reduction gears. It was controlled by a switch separate from that belonging to the main stirrers of the outer bath so that the motion of the small stirrer could be controlled at will.

To prevent air or water from entering the hole in the large calorimeter vessel through which the shaft of the small stirrer passed a mercury seal F was employed. A brass cylinder was carried upon a rubber stopper which slid tightly over the brass shaft of the stirrer and turned with it. This cylinder, which was well coated with Valspar varnish, dipped well below the surface of some mercury placed in the annular trough. This device formed an effective seal, and prevented convection currents of air from affecting the inner vessel.

Some preliminary experiments showed that the motion of the stirrer caused a heating effect. This heating effect was very small, but it was decided to reduce it to a minumum by running the stirrer as little as possible. Hence this stirrer was only used during the time when the salt was actually being dissolved. As the water was being pumped back and forth from the inner vessel, it was sufficiently stirred by the vanes over the openings in the bottom of the vessel.

The silver vessel which contained the salt was fastened concentrically within another small silver vessel B. Three silver arms projected from the top of the vessel which contained the salt and these were fastened to the top of the outer vessel by means of silver bolts and nuts. The vessels were so designed that there was sufficient space at the bottom of the inner one to allow for the proper motion of the stirrer, and enough room on the sides to allow for proper placing of the thermocouple. The bottom of the outer silver vessel contained silver plugs fitted with tapering holes. Small glass legs D were cemented into brass plugs which were in turn screwed into the bottom of the brass calorimeter vessel projecting on the inside. The outer silver vessel stood on these glass legs and was thus completely insulated from the brass vessel.

Great difficulty was encountered with the connection between the inner vessel and the pump. This connection had to be air tight, possess a certain flexibility, and be easily adjusted. Attempts were made to use fine glass tubes but they were too fragile. In addition to having the above mentioned structural qualities, this connection had to provide the minimum amount of material for the transfer of heat from the inner vessel to the brass vessel. The problem was finally solved in the following manner. A piece of rubber tubing of extremely fine bore was obtained by cutting off the ends of the smallest surgical catheter that could be obtained. This tubing had walls about 0.25mm. thick and had a bore of about 1 mm. One end of this tube was placed over a small silver plug which was well smeared with vaseline and inserted into the tube on the top of the inner vessel. As this plug was tapered a good fit was obtained. The other end of the rubber tubing, which was of sufficient length to enable it to just reach through a hole in the cover of the brass calorimeter, was slipped over the tapered end of a piece of glass tubing which passed through the cover of the brass calorimeter and was sealed to it by means of de Khotinsky cement. For this purpose a specially small blow torch was constructed from capillary glass tubing. The glass tube which projected from the brass calorimeter was connected to the tubes of the pump by small bore pressure rubber tubing as shown by M.

As has been stated, the admission of water to the inner silver vessel to cause solution of the salt was effected by the regulation of the air pressure within the vessel. This regulation was made by means of a hand operated mercury pump placed outside the bath. It was essential that any air that might be admitted to the inner vessel at any time during the reaction be at the same temperature as the water in the outer bath, otherwise the inner vessel would be subjected to thermal changed due to any change that might have taken place in the temperature of the air of the room during the experiment. To avoid such heat transfer the air which was pumped back and forth came from the barrel of a compensating device R Fig.7 which was placed in the outer bath and hence its temperature was always that of the inner vessel when the adiabatic calorimeter was correctly balanced. This compensating device consisted of a large U tube, suitably supported under the water of the outer bath, and having its arms half filled with mercury. One arm was connected to the inner vessel as described. This connecting tube, which was of small bore,had a branch leading to a open-air manometer filled with coloured water. All portions of any tubing which extended above the water level were of small diameter and any temperature changes which occurred in the air contained in them was considered negligible. The other arm of the U tube led out of the bath to the pump proper, which consisted of a long cylinder S containing mercury which could be moved up and down by means of a levelling bulb K. The flow of mercury in the levelling bulb tubing was controlled by a large tap at the bottom of the pump barrel. A side tube with a tap was placed on the connecting tube between the pump barrel and the U tube in order to adjust the pressure to that of the atmosphere. The levelling bulb was supported from a stand by means of a cord which passed over a system of pulleys

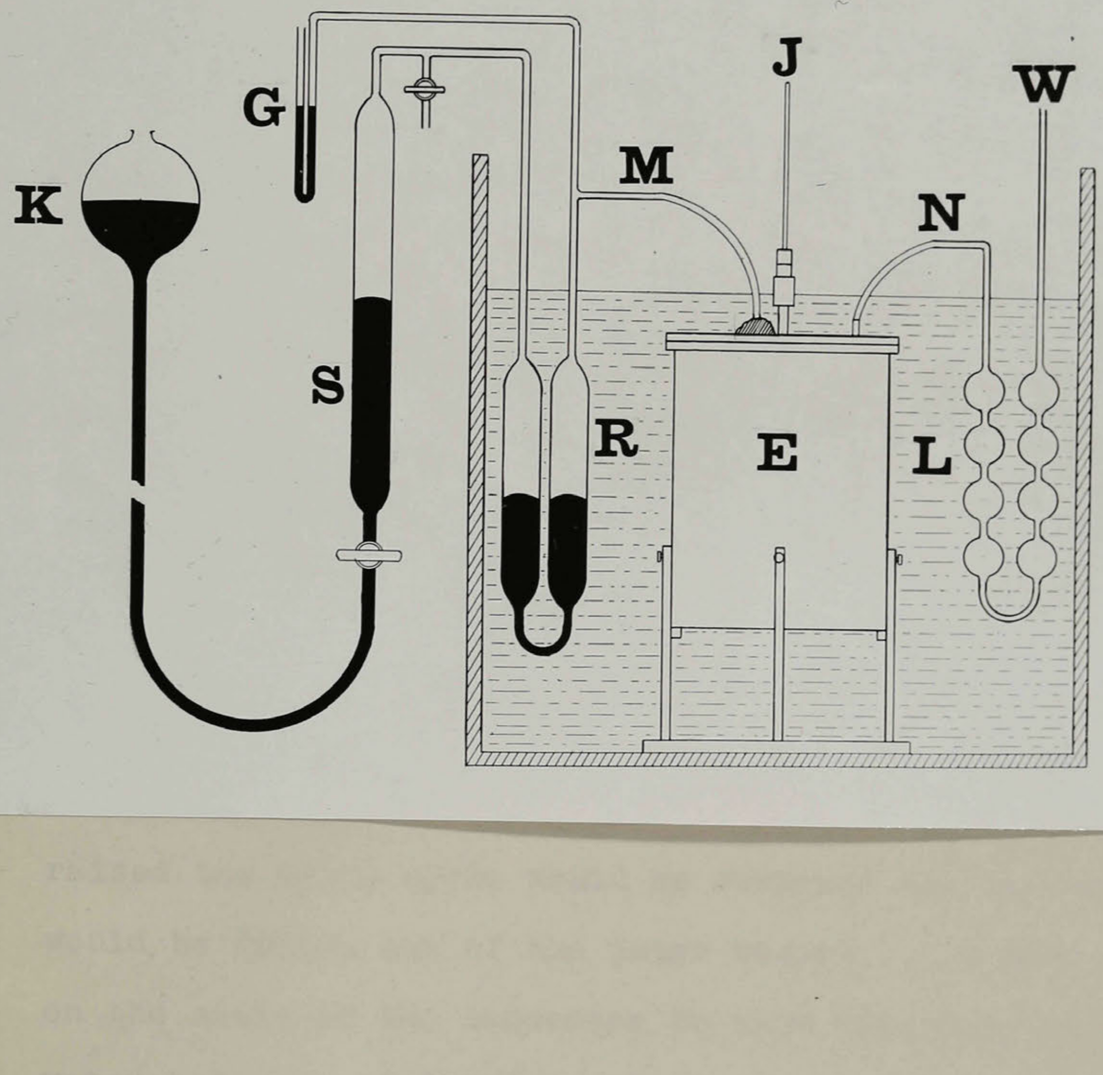

Figure 7.

to a lever placed in a convenient position. The motion of this lever was controlled by two adjustable stops so that it might be moved backwards and forwards between them, the mercury in S always coming to the same level at the end of the path of the lever.

A scale was placed on the manometer G and the point marked where the water level would be when all of the water was out of the inner vessel. It will be seen that when the apparatus was assembled and water was placed in the outer silver vessel it would increase the pressure of the enclosed air by an amount which would be shown by the water level in the manometer. If now the levelling bulb was lowered it would lower the mercury in the pump causing the mercury to rise in the arm of the U tube connected to the pump. The mercury in the other arm of the U tube was therefore lowered and the pressure in the inner vessel thus reduced. The water would then enter the inner vessel and dissolve the salt. If the levelling bulb was raised the above cycle would be reversed and the water would be driven out of the inner vessel. A mark was made on the scale of the manometer to show when sufficient water had been admitted to the inner vessel to completely cover all of the salt. The motion of the lever controlling the levelling bulb was then adjusted by means of the moveable stops so that these two points could be automatically reached by moving the lever back and forth without watching the manometer. The point at which the inner vessel was filled with water was so chosen that the water did not enter the silver plug at the top. If this happened it meant that some of the solution was removed from the reacting chamber and the capillary action of the small rubber tube produced disturbing pressure changes which were registered on the manometer.

It will be seen that by manipulation of the lever and watching the manometer at the same time, the process of solution and dilution of the resulting solution could be followed and controlled at will.

As air was moved in and out of the small inner vessel, air had to move out and into the whole system. It was of great importance that this volume of air which was moved back and forth should be at the same temperature as that of the outer bath. To ensure this condition the air was drawn from a system of bulbs L Fig 7 which was kept beneath the surface of the water in the outer bath. These bulbs, as can be seen from the diagram, were in the form of a U tube, one arm of which was connected to the brass calorimeter vessel while the other led to the outside air. The tubes between the bulbs were somewhat constricted and the tube leading to the outside air was loosely packed with glass wool to prevent the entrance of dust. When air was drawn from the system of bulbs it was supplied from the first two or three and as diffusion would be slight this air was practically at the same temperature as that of the water in the outside bath.

It has been mentioned that the silver vessels were kept inside of a brass vessel being separated by suitable thermal insulators. This brass vessel E was supplied with a wide flange on the top and was covered by a brass plate fitted with suitable openings for connections to the inner vessel. This brass plate also carried the mercury seal for the stirrer which has been described. Before the brass plate was placed on the top of the vessel the wide flange was well coated with vaseline to ensure a water-tight joint. The brass plate was held down tightly by means of three clamps which are not shown in the diagrams. In addition to carrying the mercury seal surrounding the tube which carried the stirrer for the inner vessel, the tube leading to the compensating device of the pump, and the tube leading to the system of bulbs for the air, the brass cover had a large hole through which the water was delivered by means of a pipette to the inner vessel. This hole was so situated that it was directly over the annular space between the two silver vessels and after the water had been added the thermocouple was inserted. The thermocouple was carried by a small rubber stopper which was well greased with vaseline before being placed in the hole. The brass vessel was supported in the middle of the outer bath by means of an iron tripod carrying three uprights. These uprights carried set screws so that the brass vessel might be clamped but this found to be unnecessary. The iron tripod was fastened to a heavy iron plate which was firmly fastened to the bottom of the earthenware outer bath by means of pitch.

The earthenware pot which served as the outer bath was of sufficient size to contain all of the apparatus. It was boxed in by a wooden frame and was lagged with excelsior. The wooden frame carried iron rods to which were clamped the stirrers and various other pieces of apparatus. An overflow was provided so that the water level might be kept constant, and suitable pipe lines were provided for filling and emptying.

The water in the outer bath was well stirred by four brass stirrers. Each stirrer carried two two-bladed paddles so fixed that each pair of stirrers at the front and back moved the water in opposite directions. These stirrers were driven by an electric motor and very violent agitation was produced. On this account a very rapid adjustment of the temperature of the outer bath was easily obtained. Rapid and thorough stirring is a most important factor in the satisfactory operation of calorimeters and thermostats.

The thermocouple employed in this work was made of copper and constantan wire. The junctions were encased in fine glass tubes which fitted into a large T tube, being cemented into place. The couple was so designed that the junctions were well below the surface in each bath and that the cross bar of the T tube was under the surface of the outer bath. As mentioned before, one junction of the thermocouple dipped into the annular space between the two silver vessels, being held in place by a small rubber stopper passing through the cover of the brass vessel. This can be seen from the diagram,Fig 6. The other end dipped into the water in the outer bath. The wires led directly to the galvanometer, care being taken that they were free from strain. The circuit was broken by a "clothespin" switch so that when the circuit was closed the original wires would be touching and the presence of another thermal junction would be avoided.

The galvanometer was of a very sensitive type made by Leeds and Northrup for use with their platinum resistance thermometer. Considerable trouble was encountered with stray currents which caused a drift of the mirror. For some weeks experiments were carried out to determine the

the cause of this, and the conclusion reached was that it was due to thermal effects. Necessity compelled placing the galvanometer in a rather exposed position near a window, and attempts were made to screen it and keep it at a constant temperature. To avoid the effect of stray electrostatic effects the galvanometer was grounded and was placed on a grounded metal plate. To avoid induction from any wires in the vicinity the leads to the galvanometer were twisted together. To provide thermal insulation the galvanometer was surrounded by two cases. The inner one was of metal and was grounded. The outer one was of wood and the space between them was loosely packed with wool. This arrangement seemed to relieve the situation and no further trouble was encountered.

The thermocouple was employed as a null-point instrument and the variation in temperature between its junctions was denoted by the deflection of a beam of light which was reflected from the galvanometer mirror on to a ground glass scale. A sliding paper marker denoted the zero point of the scale and this zero point was constantly checked. A suitable beam of light was obtained by focussing the image of a portion of the filament of a tungsten lamp on the galvanometer mirror. A sharp narrow beam of light was thus obtained.

The electrical connections may be seen from Fig 8.

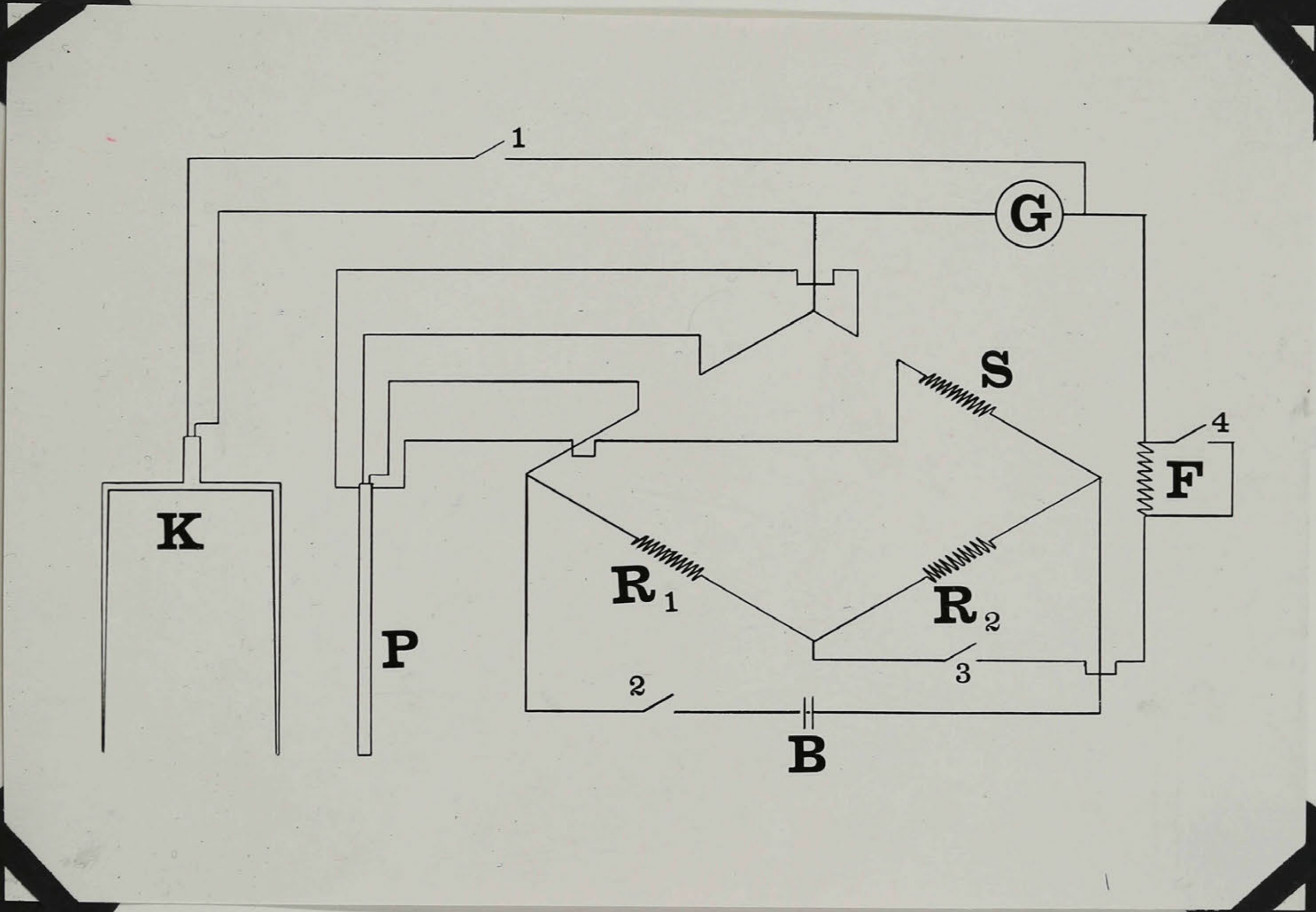

Figure 8.

The same galvanometer and scale were used for the reading of temperature by the platinum resistance thermometer. The galvanometer is shown at G Fig 8., the thermocouple at K and the platinum resistance thermometer at P. The thermometer was made by Leeds and Northrup and was suspended in the water in the outer bath. It was fitted with compensating leads connected as shown. The bridge, which is shown in detail in the diagram, was a decade bridge box made by Leeds and Northrup for use with their own thermometer and galvanometer and capable of reading accurately to 0.0001 ohm or approximately 0.001°. In the diagram the fixed resistances of the bridge are shown by R_1 and R_2, the adjustable one by S. The switch 4 allowed the high resistance F to be placed in series with the galvanometer so as to reduce its sensitivity if desired. The galvanometer circuit was broken by the switch 3 which was left open when switch 1 was closed and vice versa. The current for the operation of the bridge was supplied by a dry cell B with a switch 2 in its circuit. All switches shown were copper knife switches. Some troubles with thermal effects developed at one time and were traced to a knife switch which was in the circuit. An examination of this switch showed that it was of copper-plated iron and that it gave a decided thermal effect when handled. It was replaced by one made entirely of copper.

The Calibration of the Platinum Resistance Thermometer.

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The resistance thermometer was placed in a Dewar flask containing a mixture of finely crushed ice and distilled water. The bridge was balanced and readings were taken as follows,

Time	Readings
0 min.	25.3676 ohms
10 "	25.3680 "
20 "	25.3680 "
30 "	25.3680 "

To test the constantcy of the thermometer it was then removed from the crushed ice, placed in water at room temperature and then replaced in the ice.

Time	Readings
0 min.	25.3680 ohms
15 "	25.3680 "

A reliable thermometer was selected as a comparison instrument which, when placed in crushed ice, gave the following readings,

Time	Readings
0 min.	-0.20°
1 "	-0.20°
3 "	-0.20°
6 "	-0.20°

This correction was then applied to all readings with this thermometer. The comparison thermometer and the platinum resistance thermometer were placed in a well stirred bath and readings taken as follows,

Comparison thermometer	Bridge readings
20.40°	27.3998 ohms
20.40°	27.4002 "

Therefore the bridge reading for an interval of 20.40° was 27.4000 - 25.3680 = 2.0320 ohms, and a bridge reading of .1 ohm was equal to 1.003°

This method of calibration was chosen to avoid subjecting the resistance thermometer to any high temperature as would have been the case had the boiling point of water been chosen as an upper fixed point.

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The Detailed Method of Procedure.

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The experimental determination of the heats of solution was carried out in the following manner. The silver vessel was weighed empty. The required amount of the salt was weighed out roughly on to a sheet of glazed paper and introduced into the silver vessel through a small glass funnel. The silver vessel was then weighed again giving, by difference, the weight of the salt. The apparatus was then put together as follows. The small stirrer was pushed up through the hole in the silver vessel which was then placed in the outer silver vessel and bolted to it. The small silver plug to which the fine rubber tube was fastened was well coated with vaseline and inserted tightly into the tube at the top of the inner vessel. In all handling of the apparatus care was taken that the inner vessel was not shaken in order to prevent any salt being shaken through the openings at the bottom. The outer silver vessel was then placed upon the glass legs in the brass vessel, and the brass lid put on and clamped. The stirrer and the glass tube at the end of the fine rubber tube protruded through the brass cover. The rubber stopper carrying the varnished copper cylinder was then slid over the stirrer shaft and pushed down until the cylinder dipped into the mercury seal. Fragments of de Khotinsky cement were placed around the glass tube and were formed into a solid block of cement by means of a blow torch. This cement held the glass tube in place and furnished a water-tight seal. To enable the cement to stick to the brass, a layer of rubber cement was first applied and allowed to become dry.

The brass calorimeter containing the silver vessels was then carefully lowered into the iron frame in the outer bath. The rubber tubes connecting the inner vessel to the pump and the brass calorimeter to the series of bulbs were then adjusted. Before the rubber tube was connected to the pump the mercury was raised to its fullest extent in the pump cylinder and the pressure between the U tube and the pump brought to atmospheric pressure by means of the tap as described. The pulley was then slipped over the top of the stirrer shaft and clamped tightly after being well aligned so that the stirrer turned smoothly. The belt was then adjusted.

A weight pipette was filled with distilled water and weighed. A large beaker of water was brought to a temperature approximating that at hich the determination was to be made and the whole pipette lowered into the beaker. After it had remained there for a sufficient time it was removed and the tip carefully introduced through the hole in the brass cover of the calorimeter into the space between the inner and outer silver vessels. By blowing thraugh the other end of the pipette the contents were thansferred to the outer silver vessel. The water pressure developed was then shown on the manometer.

After the weight pipette was withdrawn and again weighed to ascertain the weight of water, the thermocouple was inserted. The level of the water in the outer bath was then raised so as to cover the cross arm of the thermocouple and the balance obtained as quickly as possible. If the temperature at which the determination was being made was far from the room temperature, the water in the outer bath was brought to approximately the right temperature before the calorimeter was inserted.

After the balance had been obtained readings were taken by the resistance thermometer every five minutes, the balance being maintained between readings. It was found that the readings were not constant but that a decrease in temperature was noticed at the start. In order to obtain the correct initial temperature these readings were plotted against the time in minutes and the curves extrapolated to the time at which the reaction took place. As a constant temperature was not always obtained at the end, the final curve was also extrapolated to get the final temperature. The temperature change was the difference between these extrapolated readings.

After sufficient readings had been obtained to provide a curve exact enough for extrapolation, the small stirrer was started, the tap on the outside cylinder of the pump opened, and by a slow motion of the lever the pump was operated so as to allow some of the water to enter the small silver vessel. As the water entered the pressure registered by the manometer decreased. The extent to which the water had entered could be seen at any time by glancing at the manometer. As soon as the salt commenced to dissolve the temperature dropped and the thermocouple showed a difference of potential.

Cold water was then added to the outer bath until the spot of light was again at the zero position. After the water had entered the motion of the pump was reversed and the water was driven out again. This was kept up, the water being pumped backwards and forwards until there was no noticeable change of temperature. The small stirrer was then stopped and readings were taken until, as initially, the curve was suitable for extrapolation. During this time the water was occasionally admitted to the inner vessel and pumped out again to provide additional stirring. When sufficient readings had been taken, the experiment was stopped and the apparatus taken apart and cleaned. The silver vessels were washed out with water several times, then with ethyl alcohol and ethyl ether to remove any vaseline that may have entered from the top of the small tube. The alcohol and ether were removed by repeated washings with distilled water. A suction tube was then inserted and the inner vessel placed in an electrically heat oven at 90° for half an hour.

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.

An example of the method of calculation will now be given.

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The Determination of the Heat of Solution.

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As an example of the method of calculation the data for a run on sodium chloride will be given below.

Weight of vessel and salt = 31.6186 gms.
Weight of vessel, empty, = 27.6768 "
Weight of salt used, = 3.9418 "

Weight of pipette and water,= 70.076 gms.
Weight of pipette, empty, = 39.839 "
Weight of water, = 30.2372 "

Concentration = 11.55% or 2.12 molal.

The specific heat of this solution, from values previously given was 0.877

The following readings were taken on the resistance thermometer,

Time in minutes	Readings in ohms
0	27.4994
5	27.4990
10	27.4982
15	27.4973
20	27.4967
25	27.4951
30	27.4945

Time in minutes	Readings in ohms
45	27.3712
50	27.3630
55	27.3566
60	27.3524
65	27.3503
70	27.3503
75	27.3495
80	27.3494

These readings were plotted as shown in Fig 9 and smooth curves drawn through the points. It will be noticed that the variation in temperature before and after the reaction is linear. Straight lines were then drawn through these points as shown. A straight line AB was drawn to represent the average time at which the reaction took place. The straight lines were then extrapolated to the line AB, the reading at A being taken as the initial temperature and that at B as the final temperature. It was found necessary to carry out this procedure in every case as steady conditions were never found.

The difference obtained from the extrapolated curves as described was 0.1433 ohms = 1.4373°.

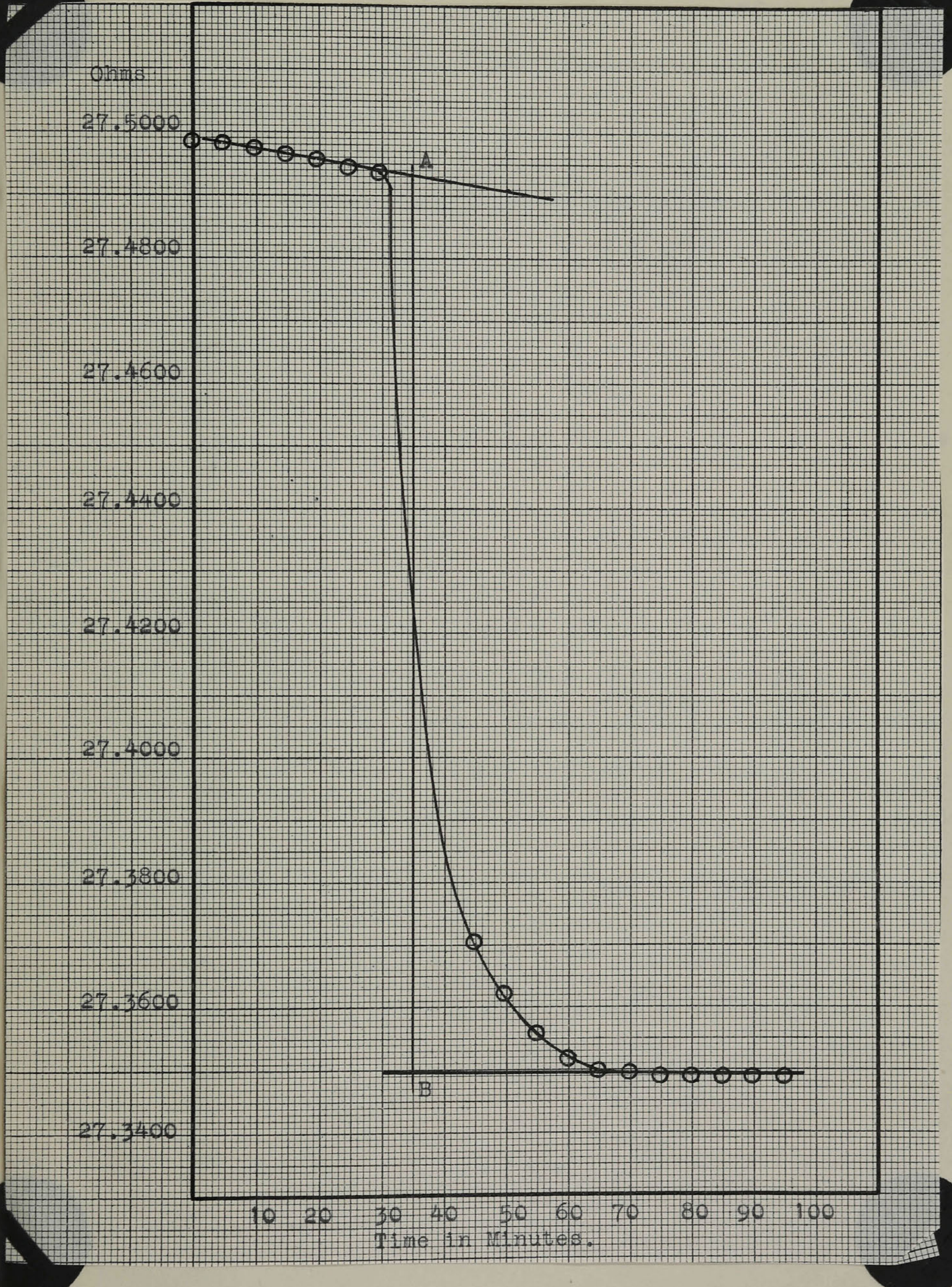
Ohms
27.5000
27.4800
27.4600
27.4400
27.4200
27.4000
27.3800
27.3600
27.3400
A
B
10
20
30
40
50
60
70
80
90
100
Time in Minutes.

Figure 9

Weight of silver vessels = 93.976

Specific heat of silver vessels = 0.0565

Weight allowance for glass, = 1.00

Specific heat of glass, = 0.1706

Calories absorbed by the system,

By the solution, $34.179 \times 0.877 \times 1.4373 = 43.083$

By the vessels, $93.976 \times 0.0565 \times 1.4373 = 7.649$

By glass parts, $1.000 \times 0.1706 \times 1.4373 = 0.245$

Total = 50.977

Heat absorbed per gram molecule of salt, = 756.5 cals.

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The Heat of Solution of Sodium Chloride.

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When using sodium chloride it was found inadvisable to work with smaller concentrations than 0.2 molal, as the heat change was so slight with such low concentrations that the experimental errors produced a larger effect.

The following values were obtained with sodium chloride.

Molal concentration	Heat absorbed per gm.mol.	Average
0.202	1199 cals.	
"	1198	
"	1181	1193
0.404	1173	
"	1159	

Molal Concentration.	Heat absorbed per gm.mol.	Average
0.404	1142 cals.	
"	1161	1159
0.644	1004	
"	1049	
"	997	
"	1043	1023
0.821	994	
"	1026	
"	1004	
"	1017	1010
1.23	917	
"	919	918
1.63	832	
"	841	836
2.12	753	
"	757	755
2.62	702	
"	679	
"	691	686
3.18	555	
"	566	560
4.03	478	
"	475	477

These values are plotted in Fig. 13.

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The Heat of Solution of Sodium Bromide.

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Sodium bromide forms a dihydrate and a pentahydrate. The transition point of the anhydrate and dihydrate is about 50.7°, while that of the pentahydrate and ice is about -27° Sodium bromide was crystallized from solution and the crystals carefully dehydrated by long heating over a small flame. It was believed that the salt would remain long enough in the anhydrous condition to allow a determination to be made. Experiments were carried out by allowing some of the anhydrous salt to remain in a dish and determining its increase in weight with time. The results of these experiments showed that the salt would not take up sufficient water in the course of two hours to introduce an appreciable error. This time interval was quite sufficient to carry out the experiment.

The same method of procedure was followed as with sodium chloride. At the lower concentrations a similiar effect was obtained but the heat of solution was very much smaller. At a concentration of about 0.5 molal no temperature change was observed. With higher concentrations a positive value was obtained due to the effect of the formation of the hydrate. It is interesting to note that the evidence points to the fact that the dihydrate is first formed and this then goes into solution. This was shown by the fact that when the salt was first dissolved heat was evolved. After a while heat was suddenly absorbed. Experiments could not be carried out with very high concentrations, although the salt is very soluble in water, on account of the large amount of heat evolved and then absorbed. It was found impossible to keep the calorimeter in an adiabatic condition owing to the speed of the heat changes taking place.

The following values were obtained with sodium bromide.

Molal concentration.	Heat change per gm.mol.	Average
0.106	- 324	
"	- 355	
"	- 378	- 352
0.203	- 259	
"	- 260	- 260
0.297	- 86	
"	- 98	- 92
0.486	- 17	
"	+ 17	0
0.705	+ 38	
"	+ 35	+ 36
0.945	+ 75	
"	+ 72	+ 73
1.41	+ 187	
"	+ 192	+ 190

These values are plotted in Fig 13.

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The Heat of Solution of Sodium Bromide Dihydrate.

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Attempts were made to prepare the dihydrate and determine its heat of solution. Several weeks were spent in trying to obtain a stable hydrate but without success. The salt would crystallize from solution as the dihydrate, but any attempt to remove excess water produced some of the anhydrous salt. Attempts were made to hydrate the anhydrous salt by leaving it in a vacuum over water or by adding water directly, but the resulting salt was not constant in composition.

Some determinations of the heat of solution were made, and, although the values showed great divergence, it was decided to take into account the effect produced by the amount of anhydrous salt present. Thus an approximation would be reached which would give some idea of where the curve would lie with reference to the others.

The heat effect which was measured on the solution of the dihydrate consisted of two factors. One was due to the anhydrous salt present as such and the other to the dihydrate. The composition of the salt varied rapidly but an approximation could be obtained, and the amount of anhydrous salt present determined. The heat changes due to the anhydrous salt could then be subtracted from the values obtained giving those due to the dihydrate alone.

In calculating the heat change produced by the amount of anhydrous salt present several things had to be considered. If the amount of anhydrous salt present was, say, 10%, one could not forget that the resulting solution in which the heat change occurred contained much more salt that this due to the presence of the dihydrate. The amount of anhydrous salt was found and the amount of anhydrous salt equivalent to the amount of dihydrate was added to this. This total would give the concentration of the anhydrous salt in the final solution. From the results previously obtained with the anhydrous salt, the heat change on the solution of one gram molecule of the anhydrous salt was obtained, at this concentration. From this value was calculated the heat effect due to the weight of anhydrous salt actually present in the original mixture. The difference between this amount and the heat change which was measured was then assumed to be due to the presence of the dihydrate, and this amount was then expressed in terms of the amount of heat per gram molecule of dihydrate. Averages were then taken of the different values for the same concentration and the result gave an approximate curve for the dihydrate.

The results are shown in the following tables. H_1 is the heat effect due to one gram molecule of anhydrous salt at the concentration existing in the final solution.

H_2 is the amount of heat due to the amount of anhydrous salt actually present in the original mixture. All weights are in grams and heat values in calories.

92% dihydrate in original mixture.

Molal conc.	Wt.salt in mixture.	Wt.NaBr.2H_2O present	Wt.NaBr present	Wt.NaBr total	H_1	H_2
.098	0.3282	0.3019	0.0266	0.2502	-400	-.103
"	0.3480	0.3202	0.0278	0.2650	-400	-.108
"	0.3416	0.3143	0.0273	0.2602	-400	-.108
"	0.3760	0.3459	0.0301	0.2863	-400	-.117
.306	0.9486	0.8727	0.0759	0.7224	-170	-.125
"	0.9822	0.9036	0.0786	0.7511	-170	-.130
.432	1.5310	1.4085	0.1225	1.1660	- 50	-.059
"	1.5660	1.4407	0.1253	1.1926	- 50	-.061
.865	3.0500	2.8060	0.2440	2.3228	+ 30	+.071
"	3.0432	2.7997	0.2435	2.3176	+ 30	+.071

(87% dihydrate in original mixture)

Molal conc.	Wt.salt in mixture.	Wt.NaBr.2H_2O present	Wt.NaBr present	Wt.NaBr total	H_1	H_2
.098	0.3800	0.3306	0.0494	0.2943	-400	-.118
"	0.3812	0.3316	0.0496	0.2953	-400	-.118
.210	0.7516	0.6539	0.0977	0.5821	-230	-.218
"	0.7576	0.6580	0.0996	0.5879	-230	-.223

In the following table the calculations forthe heat effect due to the dihydrate is shown. H_3 is the heat effect measured, H_2 the heat effect of the anhydrous salt, as before and H_4 is H_3 - H_2. H_5 is the heat change per gm.mol.of dihydrate. In the average for concentrations 0.098 molal the values obtained with the 87% mixture have been averaged with those of the 92% mixture for the same concentration.

(92% mixture)

Conc.	Wt.$NaBr.2H_2O$	H_2	H_3	H_4	H_5	Average
.098	0.3019	-0.103	10.942	10.839	4987	
"	0.3202	-0.108	10.797	10.689	4636	
"	0.3143	-0.108	10.339	10.231	4521	
"	0.3459	-0.117	11.214	10.097	4456	4588
.306	0.8727	-0.125	28.809	28.684	4565	
"	0.9036	-0.130	29.157	29.027	4477	4521
.432	1.4085	-0.059	45.313	45.254	4464	
"	1.4407	-0.061	45.314	45.253	4363	4418
.865	2.8060	+0.071	86.062	86.133	4263	
"	2.7997	+0.071	85.669	85.740	4253	4258
		(87% mixture)				
.098	0.3306	-0.118	10.746	10.628	4465	
"	0.3316	-0.118	10.782	10.664	4467	
.210	0.6539	-0.218	21.242	21.024	4466	
.210	0.6580	-0.223	21.691	21.468	4531	4498

Owing to the unreliability of these results it was decided not to plot them with the other values. On this account, they will not be found in Fig.13. Comparison with the curves shown in Fig.13 shows, however, that the curve for sodium bromide dihydrate lies between that for potassium bromide and potassium chloride. This position will be discussed later.

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The Heat of Solution of Potassium Chloride.

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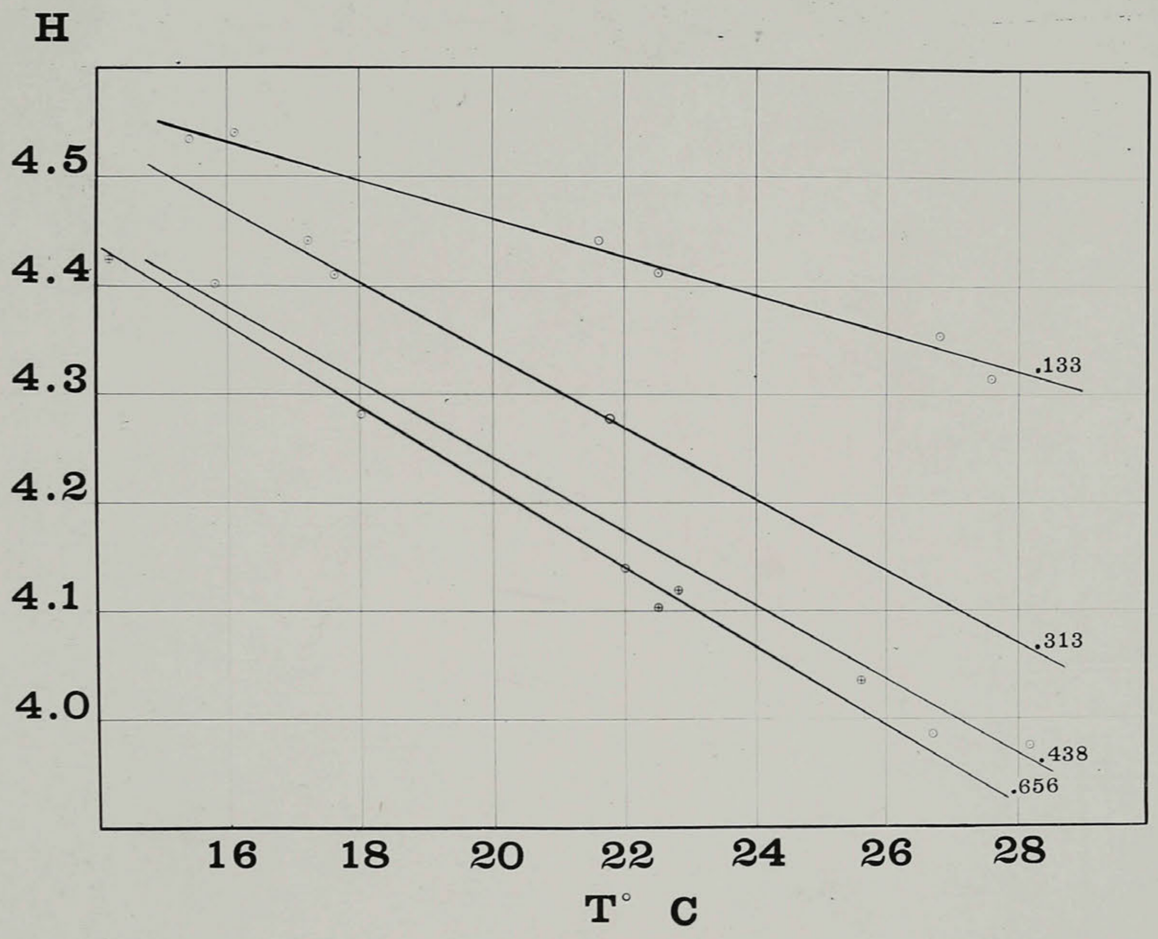
Very interesting results were obtained with potassium chloride. Determinations were made exactly as with sodium chloride but the results were not at all consistent. It was suspected that the heat of solution varied with the temperature, and the fact that the determinations were not all at the same temperature might be the cause of the discrepancies. Experiments were then carried out as nearly at the same temperature as possible, by leaving the weight pipette containing the water in a beaker of water at the required temperature. Even with these precautions the results were no better. Some of the published data mentioned a temperature coefficient and attempts were made to apply this to the results obtained. Some of the points were brought into line but others still remained some distance away. On this account it was believed that not only was there a temperature coefficient, but that the coefficient itself varied with the concentration. The procedure was then altered to investigate this fact.

The water used was kept for some time at approximately the desired temperature and the exact temperature of the experiment noted. This temperature was taken as being the mean between the initial and final temperatures. Experiments were made with the same concentration and at different temperatures, the range covered being over 10°.

The results were then plotted against temperature as shown in the curves in Fig 10. It was seen that the relation between heat of solution and temperature was linear, and a series of straight lines were drawn through points of the same concentration. The temperature coefficient will be the slope of these lines. If the temperature coefficient is independant of the concentration the resulting curves will be approximately parallel. It can be seen from Fig.10 that this is not the case, showing that there is a change in the temperature coefficient with concentration. The temperature at which the sodium salts were investigated was about 22° and it was decided to plot the values for potassium chloride at that temperature. The values of the various ordinates of the curves shown in Fig.10 were then plotted on the final curves shown in Fig.13. There were some values at odd concentrations which had been obtained before the temperature coefficient had been investigated. These values were corrected to 22° by applying the temperature coefficient for their particular concentration. This was obtained from the curve shown in Fig 12. where the temperature coefficient was plotted against concentration. The corrected values were then placed on the final curve shown in Fig.13.

It was found undesirable to investigate solutions stronger than 0.7 molal owing to the very large heat changes occurring, which made it difficult to control



H in large calories per gm. mol.

Figure 10

the calorimeter. The heat of solution of potassium chloride is about four time as great as that of sodium chloride.

The following results were obtained for potassium chloride.

Molal Concentration.	Heat absorbed per gm.mol.	Average temperature.
0.067	4495 cals.+	23.1°
"	4411 +	22.6
"	4335 +	23.6
0.133	4412	22.5
"	4442	21.6
"	4540	16.1
"	4353	26.8
"	4315	27.6
0.224	4316 +	21.0
"	4459 +	19.4
0.271	4304 +	22.6
"	4283 +	22.6
"	4468 +	21.0
0.313	4411	17.6
"	4441	17.2
"	4280	21.6
0.351	4255 +	21.3
0.390	4230 +	21.9
"	4253 +	20.7
"	4253 +	20.6

Potassium chloride (continued)

Molal concentration.	Heat absorbed per gm.mol.	Average temperature
0.438	3986	26.7
"	3973	28.2
"	4402	15.8
"	4141	22.0
"	4282	18.0
0.528	4181 +	22.0
"	4332 +	18.3
0.656	4105	22.5
"	4123	22.8
"	4424	14.2
"	4036	25.6

The values marked + are those which were corrected to 22° before plotting. The## values in this table are plotted in Fig.13.

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The Heat of Solution of Potassium Bromide.

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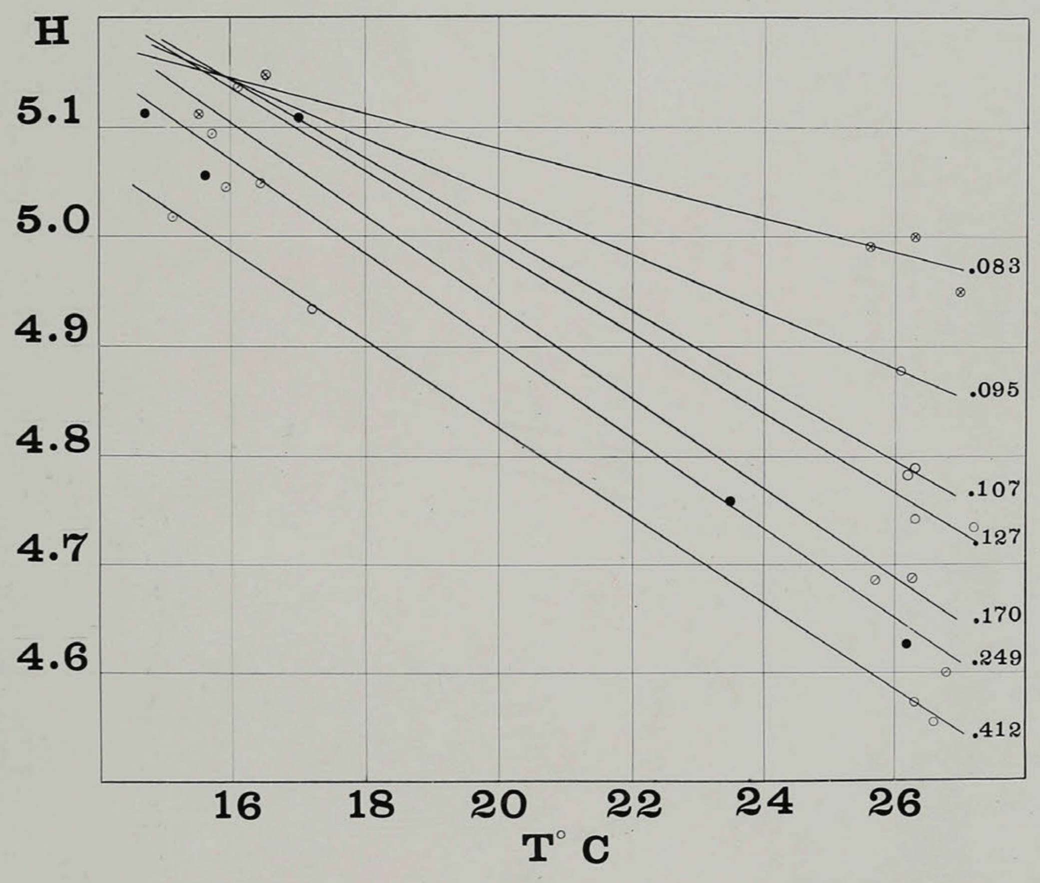
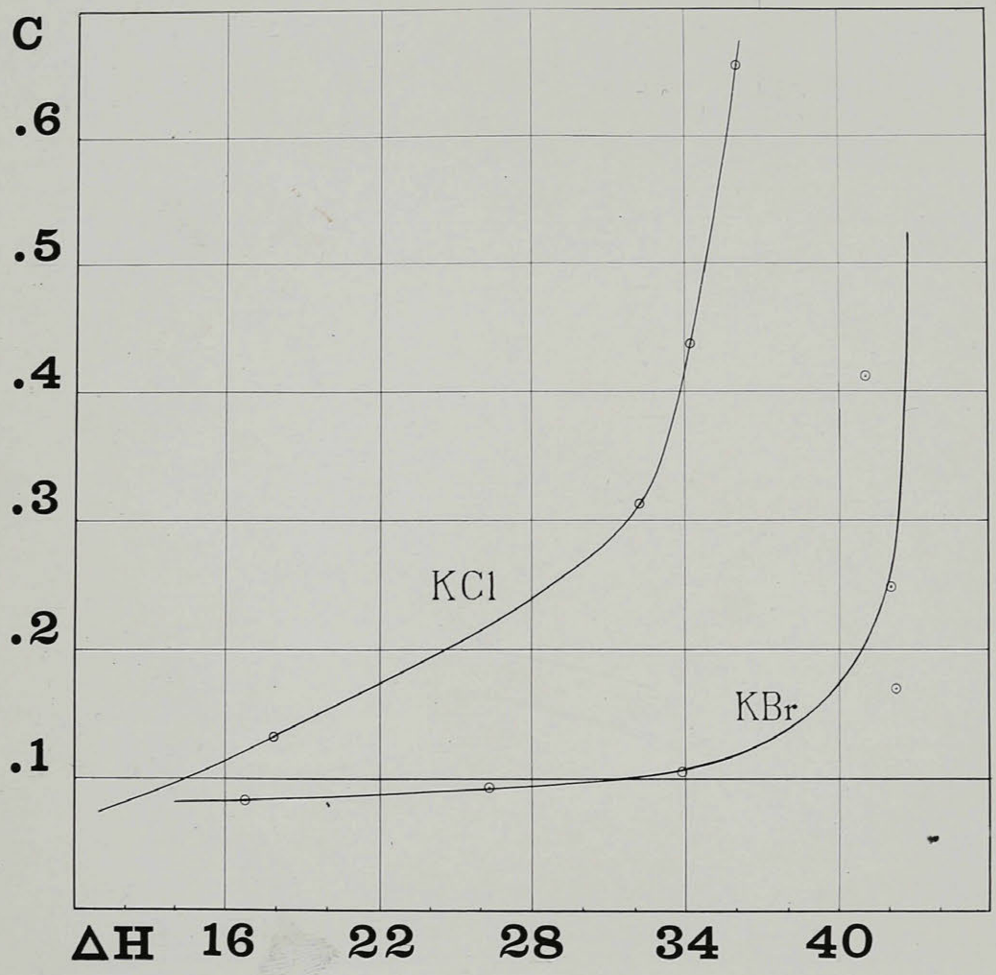
It was expected that a temperature coefficient would exist with potassium bromide and this was found. The investigation was approached in a similiar manner to that of the potassium chloride. Experiments were carried out at different temperatures and the results plotted against temperature. Straight lines were then drawn through these points and the ordinates of these



H in large calories per gm.mol.

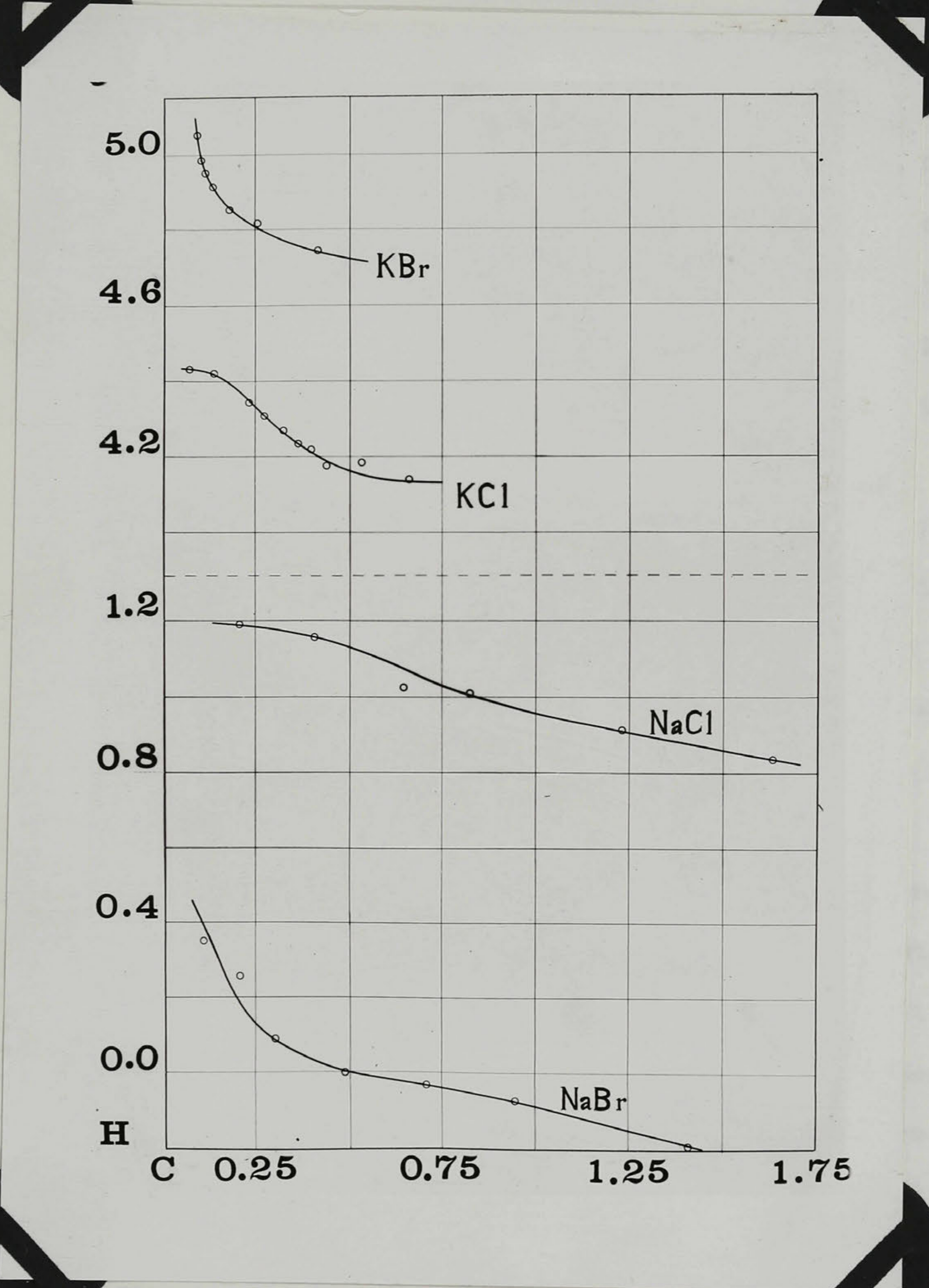
Figure 11



C in gm.mols. per liter.

dH in calories per degree.

Figure 12



C in gm.mols.per liter.
H in large calories per gm.mol.

Figure 13

lines at 22° were plotted in the curve shown for potassium bromide in Fig.13. The straight lines obtained for potassium bromide are shown in Fig 11. On account of the convergence of the lines, two of them have no values determined at low temperatures, the lines being drawn through the values at high temperatures and the converging point. In the diagram Fig.11 the points are marked by different styles of circles so that the points may be separated.

The value of the temperature coefficient is plotted against concentration in Fig 12. It will be noticed that in both cases there seems to be a tendancy to approach a constant value, but in the case of potassium bromide this is reached more quickly. The shape of these curves will be discussed later.

As with potassium chloride, the investigations could not be accurately carried out at high concentrations, the limit being a little over 0.4 molal, on account of the magnitude of the temperature changes. The heat of solution of potassium bromide is very large compared to that of the other salts investigated, and the resulting temperature changes are very large and very rapid.

The following results were obtained for potassium bromide.

Molal concentration.	Heat absorbed per gm.mol.	Average temperature.
0.090	5148 cals	16.5°
"	5128	15.5
"	4992	25.6
"	5000	26.3
"	4952	27.0
"	4811	26.3
0.106	4879	26.1
0.110	4783	26.2
"	4693	26.3
"	4694	27.2
"	4789	27.3
0.130	4735	27.2
"	4742	26.3
0.170	5095	15.7
"	5138	16.1
"	4601	26.8
"	4688	26.3
"	5046	15.9
"	4685	25.7
"	5049	16.4
0.250	5132	14.7
"	5056	15.6
"	4759	23.5
"	4627	26.2

Values for potassium bromide, (continued)

Molal Concentration	Heat absorbed per gm.mol.	Average temperature.
0.250	5109 cals	17.0°
0.420	4573	26.3
"	4557	26.6
"	4936	17.2
"	5019	15.1

These values are plotted in Fig 13.

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A Discussion of the General Shape and Position of the Heat of Solution Curves.

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A qualitative explanation for the general shape of the curves giving the value of the heats of solution at various concentrations may be obtained by the use of two new thermochemical magnitudes introduced by Born[4] and Fajans[5]: the "lattice energy" of crystals, and the "heat of hydration of gas ions".

The ingenious ideas of Laue in 1912, followed by their experimental confirmation by Friedrich and Knipping in 1913, together with the work of the Braggs from 1923 on, have introduced new conce#ptions of the crystal structure of electrolytes. According to these ideas, a crystal is built up, not by the molecules as was previously supposed, but by the arrangement in a space lattice of the very ions into which the crystal will dissociate when in solution. The whole crystal may thus be considered as one large molecule, and the process of dissociation may be more easily understood. The ions in the space lattice occupy definite positions in space, although they may be thought of as possessing motion by virtue of their vibrational energy, which is proportional to the absolute temperature. Since the ions maintain their relative positions to one another, as is shown by the stability of the crystal, it is apparent that there must exist forces of attraction which result in that particular structure. If the crystal is placed in contact with a liquid in which it is soluble the ions leave their places in the space lattice and move about in the solvent like molecules of a gas. It is clear that energy must be supplied to overcome the forces of attraction and enable the ions to leave the space lattice and go into solution. According to Born, the amount of 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.

For many years, researches in the realm of electrochemistry have pointed towards the hydration of the ions.

Considerable work has been done along this line by Jones and Washburn, not to mention several other well known investigators. Their evidence shows that ions, during their existence in the solution have associated with them varying amounts of water depending on the nature of the ion. As many phenomena are explained by an ionic hypothesis, the existence of the hydration of ions and its magnitude plays an important role in physico-chemical considerations.

It would be expected that when the ions leave their positions in the space lattice and, entering the solution, associate themselves with water molecules, that changes of energy in the form of heat would be encountered. The lattice energy has already been mentioned, and to express the energy changes due to hydration Fajans has employed the expression"the heat of hydration of gas ions."

According to Fajans, the heat of solution of a salt in water is dependent on two factors, the amount of heat which is evolved by the dissociation of the salt into the gaseous ions, and the amount of heat developed by the solution of these ions in water. He gives the following diagram to represent this idea.

$$\begin{tikzcd}
 & M^+ \arrow[dd] & + & X^- \arrow[dd] \\
Mx \arrow[ur, "G"] \arrow[dr, "Q"'] & & H & \\
 & M^+Aq. & + & X^-Aq
\end{tikzcd}$$

In this diagram MX represents the solid and M^+ and X^- the positive and negative ions respectively. G is the lattice energy: H is the heat of hydration of the gaseous ions_ and Q stands for the heat of solution.

A discussion of this idea together with an equation relating the solubility of a salt to its heat of solution is given by Butler[6]. Butler gives several tables showing values for the lattice energy, the heat of hydration of gas ions, and the heat of solution, from which the following values relative to the four salts under discussion in this thesis have been taken.

	G	H	Q
Sodium chloride	204.6	203.6	-1.0
Sodium bromide	192.4	192.1	-0.3
Potassium chloride	188.7	184.3	-4.4
Potassium bromide	178.0	172.9	-5.1

It will be seen that Butler connects G,H and Q by the relationship, H - G = Q, and he says in his paper that the values given in the table were obtained directly from the thermochemical heat of solution,Q,by addition of the lattice energy,G. In his complete table, he points out that constant differences exist in the value of H in passing from one ion to another, so that, knowing the value obtained for one salt of a series, it is possible to calculate the heat of hydration of another. He then says that, knowing this constant difference, the heat of hydration of a salt may be obtained when the heat of solution cannot be determined experimentally. Having calculated the heat of hydration, the heat of solution can be obtained by subtracting the value of the lattice energy.

Butler defined the heat of solution as that heat obtained by the solution of the anhydrous salt in a large amount of water. He expresses all his figures in large calories per grm molecule. It will thus be seen that he only considers the heat of solution at complete ionization and does not consider its change with concentration. His values for the heat of solution agree well with those discussed in this thesis at very low concentrations.

In the paper above quoted, and also in another paper[7] Butler employs the equation relating the solubility of a salt and its heat of solution, which has the form,

$$\ln P = \frac{U}{RT} + K$$

to connect the solubility with the heat of solution, heat of hydration of gas ions, and the lattice energy. In this equation P is the solubility product of the salt, U is the heat of solution per gm.mol. in saturated solution, K is a constant, and R and T have their usual meaning.

It would be expected that the solubility of a salt would depend upon the ability of the ions to leave their space lattice, and upon their conduct towards the molecules of the solvent. As Fajans shows that a relation exists between lattice energy, heat of hydration of gas ions, and heat of solution, it would be expected that the last named quantity would be intimately connected with the solubility of the salt. As the solubilities of the salts are not proportional to the values of the lattice energy, according to Butler's tables, it would seem that there were several other factors which are no doubt governed by the heats of hydration of the several ions and would be complicated. As Butler's deductions in no way concern themselves with the change in the heats of solution with concentration they will not be discussed further.

As the lattice energy is a magnitude which relates solely to the ions of the salt as they exist in their positions in the space lattice, and not to their condition in solution, it is apparently not affected in any way with changes in concentration. If we consider the presence of a large amount of solvent, one would imagine that the ions leave the lattice and diffuse throughout the medium of the solvent until the crystal has completely disappeared. On the other hand if there is only a small amount of solvent present, one could think of the ions as leaving the lattice and entering the solvent until their osmotic pressure in the latter medium prevented further solution. No doubt en equilibrium condition is reached. We may then consider the lattice energy as a constant, although it is quite possible that it is influenced by temperature. If the lattice energy be a constant, variations in the heats of solution will depend solely upon the heats of hydration of the gas ions.

An examination of the curves for the heats of solution at various concentrations shows that in general they exhibit a decrease with increasing concentration, and the rate of decrease becomes less at the higher concentrations. At low concentrations the ionization approaches its maximum value and a large number of ions are present giving a proportionately large value for the heat of hydration of these ions. On this account the heats of solution would be relatively large as is shown by the curves. If the concentration be increased the ionization decreases and the number of ions present is lessened, the heat of hydration of the ions becomes less and the heats of solution are smaller.

An examination of ionization curves at low concentrations shows that the extent of ionization falls off rapidly with small increases in concentration. At higher concentratiions this falling off is less rapid. This then explains the general shape of the heat of solution curves.

The considerations discussed above refer merely to the general appearance of the curves. As a matter of fact the curves showing the degree of ioinization have the same relative positions with reference to one another as do those showing the heats of solution, with the exception of the ionization curve for sodium bromide which lies above that of sodium chloride. It must be remembered that the curve shown for sodium bromide among the other heat of solution curves is for the anhydrous salt. It will also be remembered that an attempt was made to utilize some unreliable data which had been obtained with the sodium bromide dihydrate. The curve thus calculated, which is not shown in the photographs, lies above the curve for potassium chloride. This curve is not very reliable and it may be that its proper position is between potassium chloride and sodium chloride as this would then agree with the curves for the degree of ionization.

An examination of the figures given from Butler's table shows that the values of the heat of solution have the same relative order as has been found in the work presented in this thesis. It may then be concluded that the position of the curves, relative to one another, depend upon both the lattice energy and the heat of hydration of the gas ions. Their slopes depend upon changes in the heat of hydration of gas ions alone.

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A Discussion of the Temperature Coefficients.

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It will be remembered that a temperature coefficient was encountered with the potassium salts which were investigated, while the temperature seemed to have no influence on the heats of solution of the sodium salts. It is of interest to consider this from the point of view of thermodynamics.

Consider two temperatures T_1 and T_2. Dealing with the same masses, we may perform a cycle as follows. We may allow the reaction to proceed at T_1 and heat up 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.

Now consider the formation of one gram of solution. Letting the reaction proceed at T_1 we have an absorption of heat H_1. 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. We may now allow the reaction to proceed in the reverse manner at T_2 with an evolution of heat H_2. Finally we may cool down the products to T_1 whereupon 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 the 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. As the temperature range is small, the variation of the specific heats of the salt and water has a negligible effect.

Equating the total heat changes in the above cycle to zero, we have the following,

$$H_1 - H_2 + S(T_2 - T_1) - m_1S'(T_2 - T_1) - m_2(T_2 - T_1) = 0$$

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

It will be seen from this expression that the relation is given between the changes of the heat of solution with temperature and the heat capacities of the products and the reactants.

Let this equation be applied to the case of the solution of potassium chloride whereby one gram of a solution of a concentration 0.438 molal is formed.

At this concentration the weight of salt in a gram of solution is 0.032 gms. The specific heat of solid potassium chloride is 0.0661 (Landolt-Börnstein). The values for H_1 and H_2 are 1.83 and 1.71 respectively. These values were calculated from the determinations of the heat of solution of potassium chloride made at the concentrations and temperatures chosen. The temperatures T_1 and T_2 are 18.8° and 25.4° respectively, and were so chosen as it was at these temperatures that values were obtained for the specific heat of the solution. The difference $T_2 - T_1$ is 6.6° The specific heat of potassium chloride solution of this concentration at 18.8° is 0.9570 and at 25.4° is 0.9550, the avergge specific heat between the two temperatures being therefore 0.9560.

Applying these values to the equation we get,

$$0.018 = (0.032 \times 0.1661) + 0.968 - 0.956$$
$$= 0.017$$

In this case a fairly good agreement is shown. It was not found however that the two sides of the equation always agreed. For two other concentrations of potassium chloride the following values were obtained.

0.313 molal	0.018 = 0.023
0.656 "	0.011 = 0.013

Potassium bromide gave the following values,

0.249 molal	0.011 = 0.016
0.412 "	0.014 = 0.019

A consideration of the equation,

$$dH/dT = m_1S' + m_2 - S$$

gives an explanation of the slopes of the curves showing the change in dH/dT with change in concentration which is shown graphically in Fig 12, where the slopes of the curves in Fig.10 and Fig.11 are plotted against concentration.

As infinite dilution is approached, the term m_1S becomes less, and at zero concentration it vanishes. There is then left the two terms m_2 and S. It will be seen that as m_1 is diminished m_2 increases and approaches the limit of unity. At this limit there is nothing but pure water and, the terms m_2 and S being equal, dH/dT is zero. It will be seen in Fig. 12 that the curves tend to approach zero with zero concentration. This is shown particularly in the case of potassium chloride.

As the concentration is increased the term m_1S' increases and the term m_2 decreases. At the limit m_1S' becomes unity and m_2 equals zero. Therefore a limiting value is reached which is clearly shown in Fig 12. This limiting value is not the same in the case of different salts on account of the differences in the specific heats of the salts and their solutions.

The discrepancies which have been shown to exist when actual values have been fitted to the equation are very pronounced in the case of a salt which does not show a change in the heat of solution with temperature. This is the case with the sodium salts which have been investigated.

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 should also be zero. On the right hand side there is simply a relation between the weights of the salt, water, and solution, and their specific heats, which is equated to zero. On filling in values for the case of sodium chloride, it was found that the right hand side was not equal to zero. The value for this side of this equation was calculated for different concentrations with the following results,

0.25 molal	0.011
0.50 "	0.016
0.75 "	0.024
1.00 "	0.029
2.00 "	0.027

In the case of sodium bromide,

0.25 molal	0.011
0.50 "	0.019
1.00 "	0.028
2.00 "	0.025

It will be seen that the figures are almost the same for both salts for the same concentration. The value seems to pass through a maximum or reach a limiting value.

The fact that the right hand side of the equation should be zero, rests upon thermodynamical concepts which cannot be disputed, and one must look elsewhere for an explanation. The natural question to ask is whether there is a variation in the heat of solution with change of temperature which has escaped attention. A study of the published values for the heats of solution of sodium chloride gave no indication of any such variation, except some data published by Berthelot and Ilosvay in 1883[8]. These investigators give some values for the heat of solution of sodium chloride together with an equation representing the variation with temperature, but give no indication of how they arrived at these values. These values were merely given with a list of heats of solution of different salts and with no discussion of their derivation. More recent and more reliable data do not mention any variation with temperature.

The values in this work were determined at different temperatures which happened to vary by as much as 5°, and any variations on the heat of solution were not only within the experimental error, but were not proportional to the change in temperature.

It was therefore decided to calculate the magnitude of the variation in the heat of solution which would correspond to the value obtained for the right hand side of the equation, if such a variation existed.

Consider a 0.25 molal concentration and assume that the temperature at which the heat of solution was determined was the higher of the two temperatures. At this concentration a gram of solution contains 0.0145 gm. of salt and from the values obtained, the heat of solution due to this amount of salt in a solution of that concentration is 0.294 calories. At this concentration the value for the right hand side of the equation is 0.0109. Let X represent the heat of solution due to the same amount of salt at a temperature 6.6° lower than the one considered. The equation then becomes,

$$\frac{X - 0.294}{6.6} = 0.0109$$

therefore $$X = 0.3659$$

If this value be calculated in terms of a gram molecule of salt we have the value 1476 calories. The value obtained for a gram molecule at this concentration and at a temperature which has been assumed to be the higher one was 1185 calories. The difference is therefore 291 calories which ~~shows~~ would give a variation of nearly 30% over a temperature range of the same magnitude as was encountered in the work. It is clear that if a variation of the heat of solution had occurred it could not have escaped notice. It might be pointed out that if, instead of assuming the temperature at which the experiment was performed to be the higher one, it is assumed to be the average temperature, there is still a variation corresponding to 15% which is much larger than the experimental error of 1%.

This discrepancy presents a problem, for which, at the present time, no solution can be offered. If attention be turned to the factors entering into the calculation of the right hand side of the equation, it is found that they involve data which ~~is~~ are supposed to be very reliable. Supposing that the value for the specific heat of the solution be wrong, and using other values which have been published, it is found that the right hand side of the equation is still far from being zero.

The relation between heat of hydration of gaseous ions and heat of solution has been pointed out, and it may be seen from this that a decrease in the extent of hydration of the ions results in a decrease in the heat of solution. It is known that an increase in tempperature decreases the extent of hydration and hence it should produce a decrease in the heat of solution. In the cases where there is a change in the heat of solution with change of temperature, it has been found that the heat of solution does decrease with rising temperature, as would be predicted. It is hard to see why one would not expect to find a change in the heat of solution of every salt with a change in temperature, provided that the ions were hydrated, but such is apperently not the case.

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 on the of solution, its effect on the lattice energy and heat of hydration of the ions must be considered. This consideration presents such a degree of complexity that, at the present time, a suitable discussion cannot be attempted. It may be that in the case of those salts which do not show a temperature coefficient, the effect of temperature upon the lattice energy and upon the heat of hydration of the ions produces a balancing action which results in no measurable change in the heat of solution. To apply this discussion to the right hand side of the equation which has been presented would require a knowledge of the relations existing between the specific heats and the lattice energy and heat of hydration of the ions. Very little work has been done in this direction, and sufficient data is not available.

To sum up: from theroetical considerations the right hand of the equation, which has been discussed, should be zero, but from calculation with reliable data it is not. As mentioned above, no explanation of this interesting discrepancy can be given.

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Conclusion.

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The work presented in this thesis consists of an investigation of the changes in the heats of solution of certain alkali halides with changes in concentration. In connection with this work, it was thought necessary to make new determinations of the specific heats of the solutions of these salts over a suitable concentration range. A new type of apparatus has been devised and this work has been performed.

An apparatus has been designed for the determination of the heats of solution with a view to obviating many of the errors existing in earlier work. With this apparatus the heats of solution of sodium chloride, sodium bromide, potassium chloride and potassium bromide have been determined.

Attempts have been made to explain the shape of the resulting curves based on considerations of lattice energy and heats of hydration of gas ions, and a thermodynamic consideration of the effect of temperature on the heats of solution has been given.

In concluding, the writer wishes to tender his most sincere thanks to Dr.F.M.G.Johnson and to Dr.O.Maass, whose inspiration and advice has rendered this work possible.

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