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ON THE LATENT HEAT OF FUSION AND THE SPECIFIC HEAT OF SALTS IN THE SOLID AND LIQUID STATE.

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THE latent heat of fusion of only a very few inorganic salts has been determined, and of the data known a number were obtained at an early date when the measurements were necessarily comparatively crude. Of the salts melting above 300° Landolt & Börnstein's Tabellen contain only the following:

Salt.	Molecular Heat of Fusion.	Reference.
KNO_3	4,900	Persons, Pogg. Ann., 70, 300, 1846.
$NaNO_3$	5,500	" " " 74, 525, 1847.
$PbBr_2$	4,500	Ehrhardt, Wiedemann Ann., 24, 257, 1885.
$PbCl_2$	5,800	" " " 24, 257, 1885.
PbI_2	5,300	" " " 24, 257, 1885.

It seemed to us, in the interest of obtaining additional information on the constitution of salts in the fused state, that further measurements of this important constant together with measurements of the specific heats of salts just above and below their melting point were desirable. The existing data on these specific heats are likewise scant and not in good agreement. In the present paper a convenient method for making these measurements with a fair degree

of precision is described, and the results obtained with twelve different salts presented and discussed.

METHOD AND APPARATUS.

General Method. — Briefly, the method adopted was to heat in an electric furnace, a known weight of the salt contained in a sealed platinum vessel, to a high temperature which was accurately measured. The vessel was then dropped into a calorimeter and the quantity of heat liberated determined. This experiment was repeated for a series of different initial temperatures extending over a range of 50 to 60 degrees, both below and above the melting point of the salt. By correcting for the heat capacity of the containing vessel, the quantity of heat Q required to raise one gram of the salt from room temperature to its initial temperature could be calculated. Plotting values of Q as ordinates and corresponding temperatures t as abscissæ, curves were obtained, the slope of which at any point gave the specific heat of the salt at the corresponding temperature, while the discontinuity in the value of Q at the melting point gave the latent heat of fusion for one gram of the salt.

The Containing Vessel. — The salt was contained in a hollow cylindrical vessel of platinum about 5 cm. high and 18 mm. in diameter. This was made from a sheet of platinum of proper dimensions which was shaped around a cylindrical brass model, and the joint soldered with gold in the oxy-hydrogen flame. One end of the hollow cylinder thus formed was closed by gold-soldering a thin sheet-platinum disc over it. The cylinder was then weighed, filled to about three fourths of its capacity with the purified dry salt, weighed again, and a similar platinum disc gold-soldered over the open end. The vessel and contents were again weighed in order to determine the total mass of platinum and gold. The salt was thus enclosed within a fluid-tight platinum vessel with which measurements could be repeated as many times as desired.

The Electric Furnace. — The platinum cylinder just described was heated in an electric furnace constructed as shown in vertical section, Fig. 1.

A is the platinum cylinder which fits nicely within a hollow

copper cylinder *B*.   *A* is of such a diameter that when introduced
at the top of the apparatus it slides down to its indicated position in
contact with the copper cylinder surrounding it.   The cylinder *A*
has a small groove pressed into it to allow the insertion of the tip
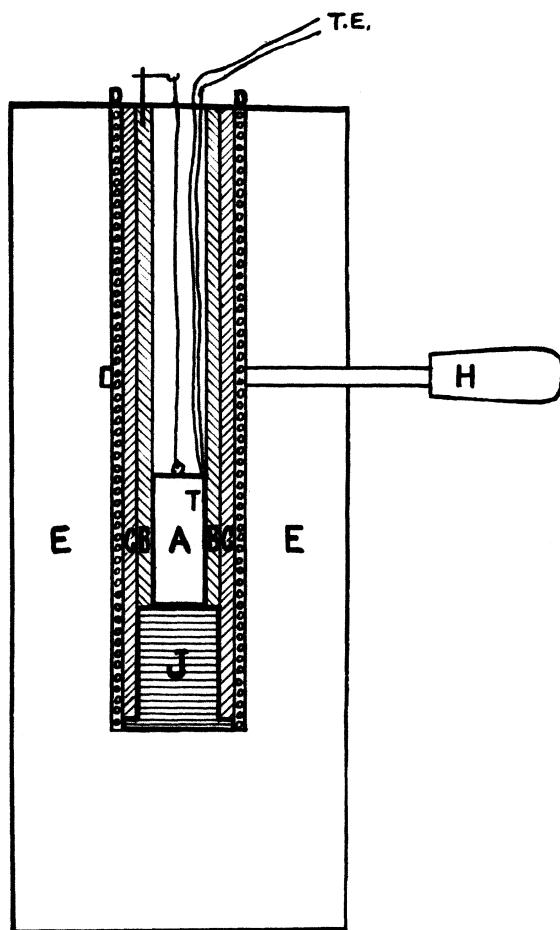of a thermoelement *T*, between it and the copper cylinder.   This

Fig. 1.

intimate contact assures uniformity of temperature between the
platinum cylinder, the surrounding copper and the thermal junction.
Surrounding the hollow copper cylinder is another similar one of
iron, *C*, upon which a heating coil of asbestos-insulated nickel-

steel wire *D* is wound. The iron cylinder extends about 10 cm. below the copper cylinder and is closed at the bottom during the heating by an iron piece *J*, which prevents the circulation of air currents within the heater.

The entire portion of the furnace thus far described was portable, and could be removed by means of the handle *H* from the heavy asbestos insulation *E*, into which it was set. The lead wires from the heating coil *D* were made long enough so that the heater could be removed from the asbestos shield and transported several feet to a position directly above the calorimeter, without interrupting the heating current. Upon lifting the heater, the iron piece *J* dropped out by its own weight and remained in *E*. A fine platinum wire was attached to the top of the cylinder *A*, so that it remained in position during the transportation to the calorimeter. This wire was cut at the desired instant, and the cylinder allowed to drop into the calorimeter.

The Calorimeter. — A platinum calorimeter of about 750 c.c. capacity was used. This was placed within a highly polished copper vessel, with an insulating air space of about one and one half inches between each. Surrounding the copper vessel on all sides but the top, was a water jacket separated from the former vessel by a two-inch air space ; the whole was heavily insulated by a felt covering. The platinum and corresponding copper and felt covers had three openings in them to admit the stirrer, the thermometer, and the heated cylinder of salt, respectively. This last opening was provided with a thin mica cylinder extending about six inches vertically upward, which served to direct the falling hot cylinder into the calorimeter.

Stirring was accomplished by means of a flat strip of platinum which was bent into the arc of a circle to fit the calorimeter, the flat surface lying in a horizontal plane. A small motor operating a suitable mechanism gave this stirrer a vertical reciprocating motion, which produced a very effective agitation of the calorimetric liquid. With salts melting below 400°, water was used in the calorimeter while with salts of higher melting point aniline was used. This has the advantage of a low heat of vaporization and its specific heat is accurately known.[1]

[1] Griffiths, Proc. Phys. Soc., 13, 234, 1894. Bartoli, Rend. Lomb. (2), 28, 1032, 1895.

A standard calorimeter thermometer, calibrated against a standard bearing a certificate from the Bureau of Standards at Washington, and which could easily be read to $0°.01$ was used for measuring the rise of temperature in the calorimeter.

Temperature Measuring Apparatus. — The initial temperature to which the salt was heated was measured by a platinum-rhodium thermoelement, which was calibrated in the usual way with naphthalene, benzophenone and sulphur. The electromotive force of this couple was balanced against a Weston element through a very sensitive D'Arsonval galvanometer. The Weston element was compared with the laboratory standard element from time to time, and always found the same. Extraneous thermoelectromotive forces were compensated by an adjustable electromotive force introduced in the galvanometer circuit. Twenty millimeters deflection of the galvanometer corresponded to $1°$ change of temperature, the couple giving 8 microvolts per degree centigrade. The apparatus was identical with that used by Goodwin and Mailey in their work on the Density, Electrical Conductivity and Viscosity of Fused Salts, and described by them in detail in PHYS. REV., 25, 469, 1907.

Procedure, Sources of Error, Etc. — After the containing cylinder had been made and filled with salt, as already described, it was placed within the heater as shown in Fig. 1. The current (usually between 5 and 10 amperes), was turned on and at the expiration of about one half hour the desired temperature was attained. The current was then gradually diminished until no further rise in temperature was observed. An equilibrium temperature was thus finally reached, which with practice could be regulated to within $2°$ of any desired temperature; the temperature remained practically constant for hours. The salt was always kept at a constant temperature for at least one half hour before observations were begun. This was found to be sufficient to insure uniformity of temperature throughout the platinum cylinder. If the temperature chosen was slightly above the melting point of the salt, the equilibrium was approached from a somewhat higher temperature, to insure that all the salt was in the liquid state. During the ten minutes preceding the experiment proper, temperature (galvanometer) readings were made at one minute intervals, from which the exact temperature at

the instant of introducing the salt into the calorimeter could be determined. During this same time the calorimeter was mechanically stirred and readings of the calorimeter thermometer were also made at half minute intervals, in order that the exact temperature of the liquid at the instant the cylinder was introduced could be known, and also, to enable the cooling correction to be calculated. At the end of the ten minutes, the heater was removed to a position directly over the opening in the calorimeter, and the suspension holding the cylinder cut. At the outset it was feared that this operation might introduce considerable error. It was found, however, that the entire operation could be performed in less than one quarter of a minute, during which time the galvanometer deflections showed that no appreciable change in the temperature of the substance had occurred. The mass of metal immediately surrounding the platinum cylinder was so great that no noticeable change in temperature could take place during so short an interval. The second possible source of error arising at this stage of the experiment was the loss of heat by radiation and convection during the time the cylinder was falling from the heater into the calorimeter. This transfer was made within a mica shield, and since the total distance from the heater to the surface of the liquid was only about ten inches the time required was only about one quarter of a second. The possible magnitude of the error arising from this source and from the evaporation of the calorimeter liquid (to be discussed below) was studied by measuring the specific heat of a cylinder of pure platinum by the above procedure. The mean specific heat of platinum between $0°$ and $327°$ obtained in this way was 0.0344 which is in good agreement with the mean value of previous observations for the same interval. Hence only a very slight error could have been introduced by the heat loss during the transfer, probably not more than a small fraction of a per cent.

An obvious advantage of the arrangement employed is that the heater is removed from the neighborhood of calorimeter during the heating. During the transfer of the cylinder there is not enough heat absorbed by direct radiation from the heater through the multiple insulation of the calorimeter or through the cover to be observed by the calorimeter thermometer. This was tested by direct experiment.

Another possible source of error is that due to evaporation of the calorimeter liquid during the time the hot cylinder is passing through its surface. This was also tested by direct experiment, as follows : The platinum calorimeter, covered and filled with liquid as in the experiment proper, was placed on one scale of a sensitive balance. To this were added the cylinder, with its contained salt and suspending wire, these however, being placed without the calorimeter. The whole was carefully tared by weights placed on the other pan. Then the cylinder, supported by the fine suspending wire, was heated in a flame to approximately the highest temperature attained in the actual measurements, dropped into the calorimeter liquid, and any change of weight due to evaporation was noted. With aniline as a calorimeter liquid no change in weight was observed; with water when the cylinder was not heated above 450° the loss was less than 0.01 gram. This corresponds to a loss of less than five small calories which is negligible in comparison to the total heat effect of over 1,000 calories. Of course an appreciable quantity of water may have vaporized and recondensed upon the calorimeter cover, in which case there would be no attendant loss of weight or of heat.

The stirring was so efficient that the maximum temperature of the calorimeter and contents was reached in from three to seven minutes after the introduction of the hot substance. The total rise in temperature was from 2° to 4° and the cooling correction never more than a few hundredths of a degree. This correction was determined by the usual Rumford method. By adjusting the temperature of the water jacket of the calorimeter to a temperature approximately midway between the initial temperature of the calorimeter liquid and its final equilibrium temperature after the introduction of the salt, the correction was rendered very small. After each measurement the platinum cylinder was weighed to insure that no liquid had leaked into it. If the weight were found constant the cylinder and contents could be used again and again for as many determinations as desired. At least two different cylinders were used for the series of measurements on each salt and the results always found to be in good agreement. On the completion of a series of measurements with a given salt one end of the cylinder

was removed and the cylinder emptied and refilled with a new salt.

The heat capacity of the metal cylinder itself was determined by direct experiment by the method described above. The value obtained agreed with that calculated from previously obtained data on the specific heats of platinum and gold to within 1 per cent., its magnitude being less than one tenth the heat capacity of the salt. Hence if it were uncertain by one or two per cent. it would affect the final result by only that many tenths of a per cent.

Preparation of the Salts. — The salts used were those of the greatest chemical purity purchasable from Eimer and Amend. The soluble salts were further purified by repeated crystallization. The insoluble salts, such as the silver halides, were prepared by precipitation from silver nitrate which had been several times purified by recrystallization.

The sharpness of the transition point of the curves (see below) indicates that the salts were very free from impurities.

Scope of the Measurements. — The salts investigated were principally those whose electrical conductivity, viscosity and density had been previously determined,[1] together with such additional nitrates and halides as it seemed might serve to bring to light any stoichiometrical relations existing between them. $NaClO_3$ was also studied in view of the recent interesting paper of Foot & Levy.[2] The entire list of salts investigated is the following: KNO_3, $NaNO_3$, $LiNO_3$, $AgNO_3$, $AgCl$, $TlCl$, $PbCl_2$, $AgBr$, $TlBr$, $PbBr_2$, $K_2Cr_2O_7$ and $NaClO_3$.

RESULTS.

Experimental Data. — In Table I. are given all the experimental data. Q represents the total quantity of heat expressed in small calories required to raise one gram of salt from $25°$ C. to $t°$ centigrade.

The above data are shown graphically in the following 12 plots, one for each of the salts studied. Plot 13 is an assemblage of all these curves drawn to the same scale on a single sheet. The ordinates represent the quantity of heat Q and the abscissæ the corresponding temperature t. The results of all determinations are given,

[1] Lorenz & Kalmus, Zeit. Phys. Chem., 59, 17 and 244, 1907. Goodwin & Mailey, PHYS. REV., 25, 469 and 26, 1908. Goodwin & Kalmus, PHYS. REV., 27, 322, 1908.
[2] Am. Chem. Jour., 37, 494.

TABLE I.

| Salt.	Temp.	Q	Salt.	Temp.	Q	Salt.	Temp.	Q
KNO_3	240°	70.2	TlBr	398°	17.5	AgCl	493°	68.9
"	268	80.3	"	427.5	18.8	"	511	70.0
"	295	86.5	"	453	19.7	"	533	72.7
"	310	90.5	"	487	35.4	K_2Cr_2O	329°	64.2
"	323	94.8	"	503.5	36.5	"	338	65.3
"	338	123.8	"	504	36.5	"	375	74.2
"	369	135.8	"	521	38.0	"	376	74.5
"	394	142.0	$AgNO_3$	168°	23.0	"	393	78.5
"	411	148.0	"	168	23.0	"	415.5	115.0
$NaNO_3$	235°	68.4	"	179	26.0	"	475	134.5
"	244	71.0	"	187.5	27.0	"	484	137.5
"	249	74.7	"	195	29.0	$NaClO_3$	184°	39.8
"	259	84.0	"	201	30.8	"	192	43.0
"	279	91.6	"	219.5	49.0	"	234.5	55.8
"	303	98.5	"	226	49.9	"	240	56.7
"	323.5	151.2	"	230	50.9	"	249	60.8
"	347	161.0	"	246	53.3	"	249.5	61.6
"	353.5	164.0	"	250	54.3	"	259	114.1
"	367	170.0	"	250	54.1	"	272	116.8
$LiNO_3$	169°	48.2	"	268	57.6	"	272	117.3
"	193.5	55.9	"	268	57.2	"	278	118.8
"	208	61.6	$PbCl_2$	265°	16.9	"	299	125.0
"	224	67.7	"	307.5	19.4	"	299	125.2
"	248	79.6	"	387	25.4	$PbBr_2$	299°	14.4
"	256	168.6	"	498	35.0	"	321	14.7
"	283	179.8	"	508	54.8	"	379	19.2
"	302.5	185.0	"	514	54.9	"	438	22.0
TlCl	350°	17.7	"	519	54.3	"	475	23.7
"	365	18.6	"	551	58.8	"	503	35.8
"	382	19.0	"	559	59.4	"	560	40.0
"	415	20.9	"	559.5	59.9	"	563	40.3
"	416.5	21.4	"	578	63.2	"	587	43.6
"	456	40.1	AgCl	371°	34.0	AgBr	316°	24.7
"	477	41.3	"	403.5	36.8	"	341	25.2
"	479	41.1	"	408	37.6	"	395.5	30.3
"	527	44.3	"	435	40.0	"	408	31.6
"	530	44.1	"	443	41.3	"	435	45.8
TlBr	321°	13.3	"	469	64.5	"	447	46.8
"	345	13.5	"	485	67.7	"	481	49.1
"	376	15.5	"	491	67.7	"	563	55.9

with the exception of a very few which deviated by eight or ten times the mean deviation of the others, and which it was fair to assume con-

tained some huge accidental error. The first (lower) portion of each curve represents the data for the salt in the solid state, the third (upper) part in the liquid state, and the intercept of these lines on
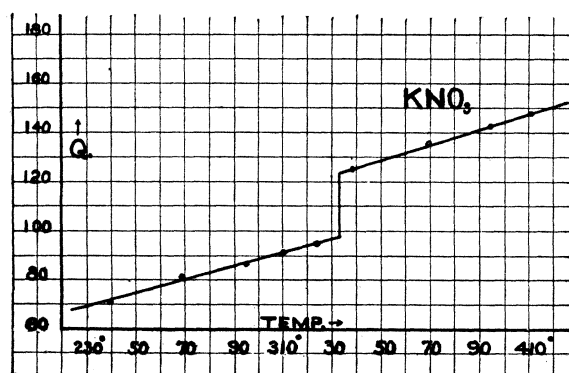

Plot 1.

the ordinate through the melting point, gives the latent heat of fusion for one gram of the salt. The tangent of the angle which the first and third portions of the curve make with the axis of temperature gives the specific heat of the salt in the solid and liquid state respectively, in the neighborhood of the melting point. In drawing these
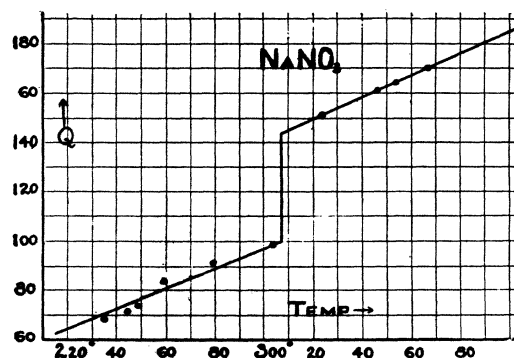
Plot 2.

lines the best representative straight line has been chosen, *i. e.*, no attempt has been made to take into account any variation in the specific heat with the temperature over a temperature interval of

about 50° above and below the melting point. Further data will be necessary before this variation can be accurately determined.
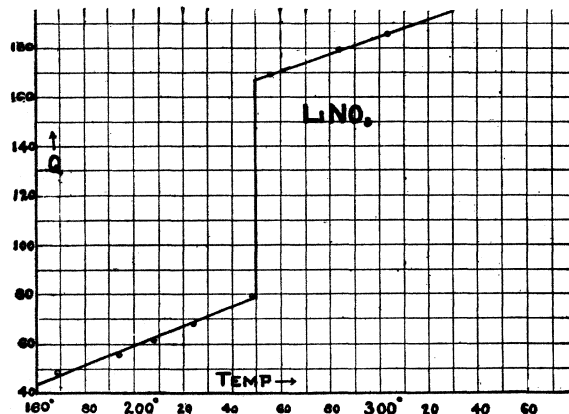
Plot 3.

It should be noticed that the data for the solid and liquid salt show no tendency to gradually merge into one another at the melting point as indicated by the dotted line on plot 7 for $PbCl_2$.
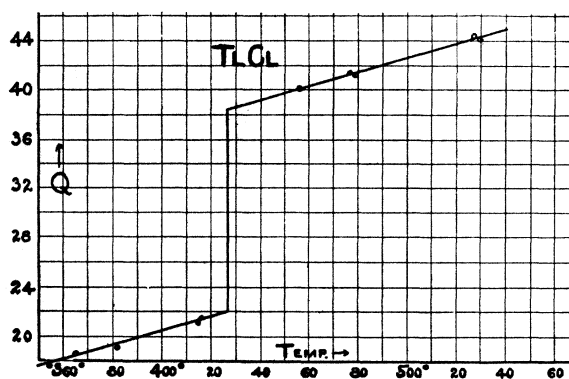

Plot 4.

This dotted line is the form of curve obtained by Ehrhardt,[1] for the lead halides, and is that which one would expect if the salt were impure.

From a discussion of our data we find that the combined effect

[1] Wied. Ann., 24, 257, 1885.

of experimental errors and errors of plotting lead to results for the latent heat which are probably reliable to better than two per cent. It should be noted that owing to the slight difference in the slope of the lines locating data for the liquid and solid salt, an error of several degrees in the melting point introduces only a very slight error in the value of the latent heat as determined from the plot. The slope of the lines determining the specific heats, however, is probably not defined to this degree of precision, and the values of
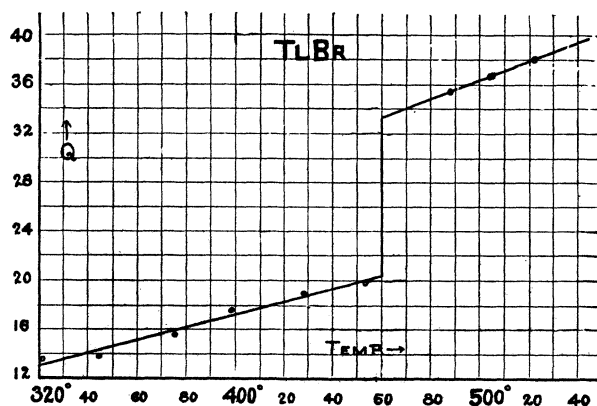
Plot 5.

the specific heats in the two states may therefore be in error by as much as two per cent. or in some cases even more.

In the following Table II. are given the numerical values of the

TABLE II.

| Salt.	M.P.	M	L	$\lambda = ML$	λ/T	C_s	MC_s	C_l
KNO_3	308	101	25.5	2,570	4.5	0.292	29.5	0.333
$NaNO_3$	333	85	45.3	3,690	6.1	0.388	33.0	0.430
$LiNO_3$	250	69	88.5	6,100	11.5	0.387	26.7	0.390
$AgNO_3$	218	170	15.2	2,580	5.3	0.195	33.2	0.195
$AgCl$	455	143	21.3	3,050	4.2	0.100	14.3	0.129
$TlCl$	427	240	16.6	3,980	5.7	0.0580	13.9	0.0590
$PbCl_2$	498	278	18.5	5,150	6.7	0.0778	21.6	0.121
$AgBr$	430	188	12.6	2,370	3.4	0.0755	14.2	0.0760
$TlBr$	460	284	12.7	3,610	5.0	0.0525	14.6	0.0800
$PbBr_2$	488	367	9.9	3,650	4.9	0.0566	20.8	0.0780
$NaClO_3$	255	106	49.6	5,250	10.0	0.320	32.4	0.325
$K_2Cr_2O_7$	397	295	29.8	8,800	13.2	0.231	68.3	0.335

constants for the various salts, taken from plots drawn on accurately ruled paper, to such a scale that values could be interpolated to 0.1 cal. and 0.1°. From left to right the columns are : (MP) melting point of the salt, (M) molecular weight, (L) latent heat of fusion for
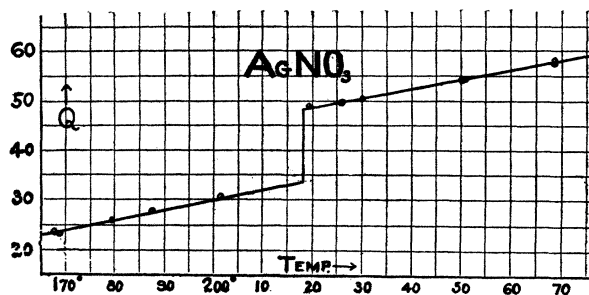
Plot 6.

1 gm., ($\lambda = ML$) molal heat fusion, (λ/T) ratio of molecular heat to the *absolute* melting point, (C_s) specific heat in the solid state, (MC_s) molecular heat of solid, (C_l) specific heat in the liquid state.

Heat of Fusion.—Stoichiometrical relations between the specific or the molecular heat of fusion and other properties of similar substances remain still to be discovered. The values of the molecular
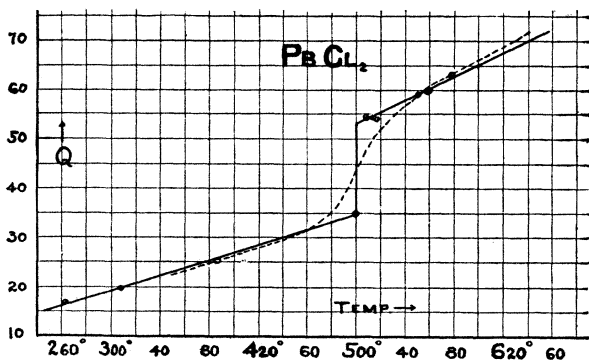
Plot 7.

heat of fusion show no apparent regularities, not even in the case of salts which crystallize in the same system and class. For instance, silver nitrate and potassium nitrate, both of which crystallize in rhombic prisms, have practically identical molal heats of fusion,

while sodium nitrate and lithium nitrate which crystallize in the hexagonal system, calcite type, show no such equality, nor is it apparent with chlorides and bromides of the same type. Neither the latent heats of fusion of the salts themselves, nor the differences in them, show any simple functional relationship to the atomic weights or atomic volumes of their elements. The property is clearly not additive, nor would one expect it to be so.
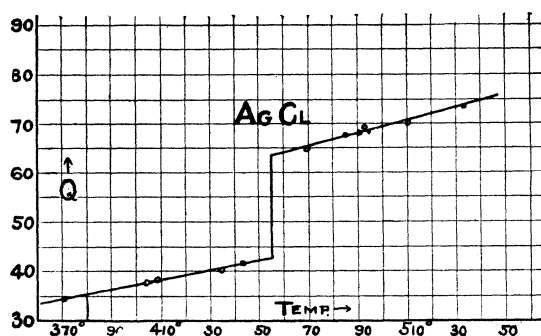
Plot 8.

On the other hand a number of well-known thermodynamic relations involving the latent heat of fusion, *e. g.*, Van't Hoff's freezing point formula, Thomson's pressure formula and the general relation[1]

$$C_s - C_l = \frac{dL}{dT} - \frac{L}{T} + \frac{L}{v_s - v_l}\left[\left(\frac{dv_s}{dt}\right)_p - \left(\frac{dv_l}{dt}\right)_p\right]$$
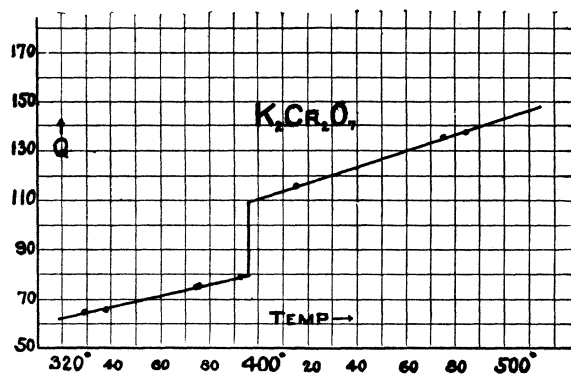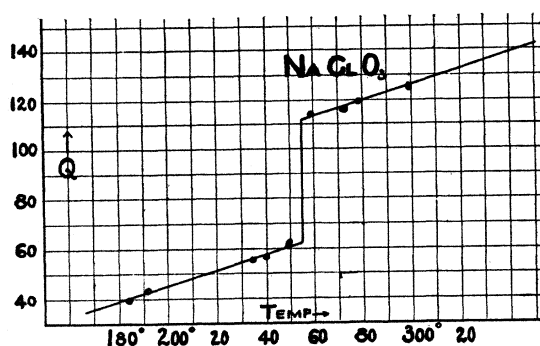

Plot 9.

[1] Planck, Thermodynamik, 2d ed., p. 144.

are well established, and data like the above are necessary for the applications of these formulæ to specific cases. An example will be considered below.
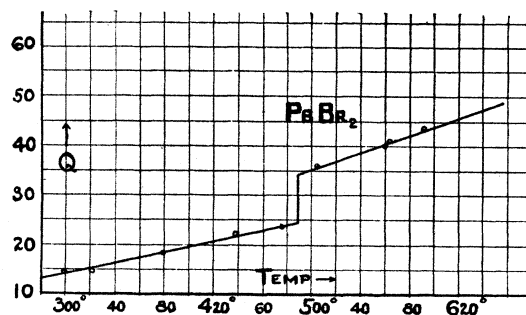
The values of the ratio

$$\frac{\lambda}{T} = \frac{\text{molecular heat of fusion}}{\text{absolute melting point}}$$

Plot 10.

given in column six are seen to be greater than four, with the exception of that for silver bromide for which the ratio is 3.4. Roozeboom[1] has shown that four is a unique value for this ratio,
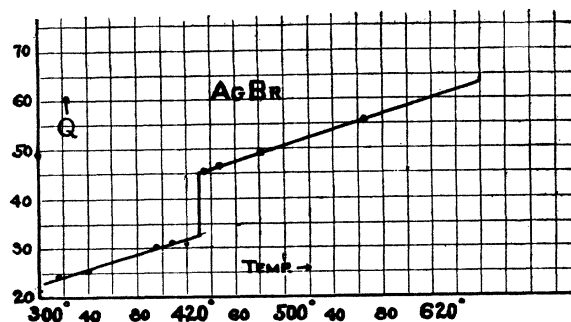

Plot 11.

in that all substances for which the ratio is greater than four, give ideal melting point curves for their dilute solutions, which are concave to the axis of concentrations.

Specific Heat in the Solid State. — For our knowledge of specific

[1] Heterogene Gleichgewichte, II., pp. 274 *et seq.*

heat relations of substances in the solid state we have to thank in the first instance Dulong and Petit, and later Regnault, and especially Kopp. Thanks to the two last named investigators we possess considerable reliable data on the mean specific heat of inorganic salts between about 50° and room temperature and 100° and the same temperature.

These data afford a sufficient verification of the general validity of Kopp's law, with however, certain pronounced exceptions. The atomic heat of most elements is shown to be about 6.4, for oxygen

Plot 12.

4.0, for carbon 1.8, etc., these values holding for temperatures below 100°. Since the specific heat of solids in general increases with rising temperature, we should expect if Kopp's law holds at the higher temperatures of our investigation that the atomic heats would possess corresponding higher values. This we find to be the case.

Thus if we except those compounds containing oxygen, which at lower temperatures are found to have an abnormally low atomic heat, the average atomic heat for the elements in the chlorides and bromides investigated is 7.1, this value holding for temperatures from about 430° to 500°, the melting point of the salts. Thus we have

$$AgCl = 14.3$$
$$TlCl = 13.9$$
$$AgBr = 14.2$$
$$TlBr = \underline{14.6}$$
$$\text{Average} \quad 14.2$$

Therefore atomic heat of Ag, Tl, Cl and Br is 14.2/2 = 7.1.
Again

$$PbCl_2 = 21.6$$
$$PbBr_2 = 20.8$$
$$Average \quad \overline{21.2}$$

Therefore atomic heat of Pb, Cl and Br $= 21.2/3 = 7.1$.

The atomic heat of these elements increases therefore by over 10 per cent. for a rise of temperature of about 400° C. It is hoped that a more detailed investigation of the variation of the specific heat with the temperature for substances of the above type may be undertaken in the near future.
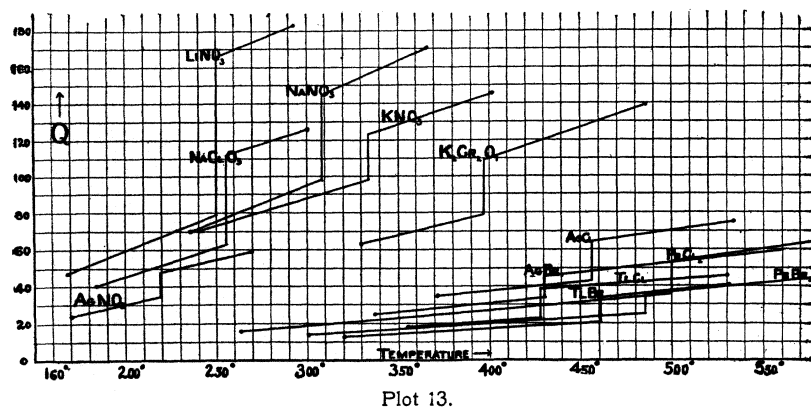
Plot 13.

The molecular heats of the four salts containing five atoms in the molecule agree less well than those just considered, but it should be noticed that they are not all referred to even approximately the same temperature as the melting points of the several salts vary between wide limits. Omitting lithium nitrate, which is so hygroscopic that the data on it are believed to be much less reliable than those on the other salts, and assuming the atomic heat of potassium, sodium and nitrogen to be that just computed, namely, 7.1 (probably somewhat too high for the lower temperatures in question), we have from the data

$$KNO_3 = 29.5$$
$$NaNO_3 = 33.0$$
$$AgNO_3 = 33.2$$
$$NaClO_3 = 32.4$$
$$Average \quad \overline{32.0}$$

$$2 \times 7.1 + 3O = 32.0$$

the equation, from which the mean value of the atomic heat of oxygen is calculated to be 5.9. With this value we may calculate the molecular heat of potassium bichromate $K_2Cr_2O_7$ as follows: $4 \times 7.1 + 7 \times 5.9 = 69.7$. The observed value is 68.3 which is in better agreement with the computed value than the precision of the data would warrant one in predicting.

Specific Heat in the Liquid State. — The specific heat in the liquid state of each salt investigated was found in every case to be greater than the specific heat of the salt in the solid state. This is in accord with the few previously obtained data on the specific heat of the same substance in the liquid and the solid state. Thus the specific heat of solid mercury is 0.0319, of liquid 0.0535 ; solid bromine 0.0843, liquid 0.1109 ; of ice 0.48, and of water 1.0. The most marked increase in the value among the salts which we investigated is in the case of lead chloride and bromide and the still more complex salt potassium bichromate. The nitrates show the least change. The great increase (over 100 per cent.), observed in the specific heat of water in passing from the solid to the liquid form as compared with the slight increase observed in mercury, is probably to be attributed to a far greater change in the molecular condition of the former substance in changing state than in the latter. It seems not unreasonable to assume that the change in the value of the specific or molecular heat of a substance will be less, the less the change in its molecular structure as it passes from the one state to the other. Hence the relatively small increase in the specific heat of the salts investigated as they pass through their melting point from the solid to the liquid condition points to a relatively slight change in their state of association or dissociation. The marked increase in the electrical conductance of these salts would therefore on this supposition be due not to an increase in dissociation but to an increase in migration velocity of the ions present resulting from the enormously increased fluidity of the molten salt.

The fact that the specific heat of aqueous solutions of inorganic salts cannot be computed from the specific heat of water and of the solid salt[1] indicates that when the salt passes into a highly ionized state as a result of solution, its heat capacity changes, in general

[1] Ostwald, Lehrbuch, Vol. I., p. 602.

decreases, since the observed molecular heat of a solution is less than the calculated value. How large a part the now established phenomenon of hydration of the ions may play in producing this effect is open to question. Reasoning by analogy however from the results on solutions, one would naturally conclude that ionization of a salt tended to diminish its heat capacity rather than to increase it.

RECENT INVESTIGATIONS ON RELATED SUBJECTS PARTICULARLY WITH REFERENCE TO THE DEGREE OF IONIZATION OF FUSED SALTS.

Recently there appeared an article by Plato [1] in which he describes measurements of the latent heat of fusion of several salts of high melting point such as sodium chloride and barium chloride, by a modification of Tamman's cooling curve method, together with measurements of the lowering of the freezing point of these salts due to the addition of small quantities of a second salt. Some very interesting results were obtained, which, however, permit of quite a different interpretation to that given by the author.

Plato calculates the normal lowering of the freezing point due to one mol of solute in 100 mols of solvent according to Van't Hoff's formula

$$\Delta t = \frac{RT^2}{M_0 L_0} \frac{N}{N_0}$$

and compares the observed with the calculated value. The results which he obtained are given below.

Solvent.	Solute.	Calculated Depression. t° C	Observed Depression. t° C.
KCl	KF	3.4	3.2
NaCl	NaF	3.2	3.4
KF	KCl	4.1	4.0
NaF	NaCl	4.1	3.4
$BaCl_2$	BaF_2	5.3	14.4
$SrCl_2$	SrF_2	6.4	11.6

For the first four salts, the observed depression is substantially equal to the normal calculated value from which he concludes that the degree of dissociation is very small. Since in the case of $BaCl_2$

[1] Zeit. Phys. Chem., 58, 350, 1907 ; 55, 721, 1906.

and BaF_2, the solute presumably splits into three ions, and since the observed depression is nearly three times that calculated, Plato further concludes that in this case the solute is nearly, complete dissociation.

Before discussing these conclusions further, we would call attention to a theorem first demonstrated by Stortenbeker,[1] namely, that the active mass of a liquid phase AB, dissociating into components A and B, is not changed by the addition of a small quantity of A or of B, and it will therefore remain in equilibrium with solid AB without change in freezing point, after the addition of small quantities of either A or B.

A shorter proof of this theorem, recently published by Lewis[2] is based upon the following equation, thermodynamically deduced by Duhem, for the change in active mass of various constituents of a mixture with change in active mass of any one of them :

$$\left\{ \frac{N_1 \partial ln\xi_1 + N_2 \partial ln\xi_2 + N_3 \partial ln\xi_3 + \cdots}{\partial N_1} \right\}_{p.t.} = 0, \tag{1}$$

in which ξ is the active mass of the component whose molal concentration is N. For a fused salt such as KCl for example this equation becomes

$$\left\{ \frac{N_K \partial ln\xi_K + N_{Cl} \partial ln\xi_{Cl} + N_{KCl} \partial ln\xi_{KCl}}{\partial N_{Cl}} \right\}_{p.t.} = 0. \tag{2}$$

From the mass law

$$\frac{\xi_K \times \xi_{Cl}}{\xi_{KCl}} = C \text{ (constant).} \tag{3}$$

Hence taking the logarithm of both sides of (3) and differentiating we have

$$\partial ln\xi_K + \partial ln\xi_{Cl} = \partial ln\xi_{KCl}. \tag{4}$$

Since K and Cl in this case are the products of dissociation of KCl, it follows that

$$N_K = N_{Cl}. \tag{5}$$

Combining (2), (4) and (5), we have

$$N_K \partial ln\xi_{KCl} + N_{KCl} \partial ln\xi_{KCl} = 0 \quad \text{or} \quad \partial ln\xi_{KCl} = 0, \tag{6}$$

[1] Zeit. Phys. Chem., 10, 183, 1892.
[2] Proc. American Academy, October, 1907.

that is, the activity of the active mass of the liquid KCl is not changed by the addition of a small amount of K (or Cl) and it will therefore remain in equilibrium with solid KCl without change of freezing point.

Applying this theorem to the experimental results of Plato, we find just what theory would lead us to expect in the case of the addition of a small amount of KF to KCl, and other salts of the same type. The *common ion* does not lower the freezing point of the solution, while the sum of the concentrations of the other ion and of the undissociated portion of the solute is constant and equal to the concentration of the salt added, independent of its degree of ionization. Hence the freezing point lowering should be proportional to the total concentration of added salt, as observed. This requires, however, *that the solvent itself, e. g., fused potassium chloride, be highly dissociated,* for the more it departs from the state of complete dissociation the less will be the concentration of the K ions due to it, and hence the greater the tendency of the K ions coming from the solute (*e. g.*, KF) to change the active mass of that component. Thus it appears from Plato's results, that the lowering of the freezing point due to an addition of as great an amount as 3.5 mols NaF to 100 mols of NaCl (and corresponding concentrations for the other salts) is still normal, indicating that the concentration of Na ions in the fused solvent NaCl must be very great. In other words, the results point to a *high degree of dissociation* of the pure fused salt.

In the case of the addition of barium fluoride to barium chloride and similar combinations, Plato's results are so discordant (owing doubtless to uncertainty in the values of the latent heats of fusion) that very definite conclusions cannot be drawn. Combinations of binary salts offer, however, further evidence as to the order of magnitude of the dissociation of the fused solvent. This point was first called to our attention by Dr. Bray of this laboratory. Consider, for example, the lowering of the freezing point of fused lead chloride due to the addition of a small amount of lead bromide. The common Pb ion of the $PbBr_2$ would here again be inactive in lowering the freezing point if the solvent were highly dissociated into Pb and Cl ions; but in this case there would be two Br ions for every

equivalent added and hence *twice* the normal lowering would be expected if the degree of dissociation of both solvent and solute were complete. To test this prediction we determined the approximate freezing point lowering with these two salts, using a sensitive thermoelement for a thermometer. Temperature differences of 0.05° could be readily measured.

TABLE III.

Gms. $PbCl_2$.	Gms. $PbBr_2$.	Calculated Depression.	Observed Depression.	Ratio.
17.8	0.199	1.95°	3.14°	1.63
32.9	0.403	2.15	3.67	1.71
39.9	0.322	1.42	2.44	1.70

These few approximate measurements serve to differentiate this type of combination from that of a common ion with univalent salts, and make it very probable that the solvent is highly dissociated.

The results published in a recent paper by Foote & Levy[1] also bear out the above conclusions. These investigators dissolved small quantities of a series of salts having one ion in common with the solvent in sodium chlorate and determined the resulting lowering of the freezing point. The value of the latent heat of fusion of sodium chlorate obtained by them was 48.4 calories, as against 49.6 obtained by us. With this value they calculated the normal lowering of the freezing point for this solvent, and the molecular weight of the various solutes studied, by the usual Van't Hoff formula. The molecular weights calculated in this way, agree very closely with the normal molecular weights for concentrations as great in some cases as 10 per cent. (by weight). The agreement we find is even better if our value of the latent heat of fusion of sodium chlorate is used. In this case the differences between the observed and calculated molecular weight do not exceed a few per cent. for the following solutes: NaCl, $NaNO_3$, NaBr, Na_2CO_3, Na_2CrO_4, NaF, $KClO_3$, $CsClO_3$ and $Ba(ClO_3)_2$, all of which possess a common ion with the solvent sodium chlorate.

From these results the authors conclude that there is no polymerization. They point out that the data give no clue to the degree of dissociation, but conclude that neither solvent nor solute

[1] Am. Chem. Jour., 37, 494, 1907.

can be approximately completely dissociated, for in that case, they say, there would result the same lowering of freezing point whether KNO_3 or $NaNO_3$ be added to $NaClO_3$. Measurements showed, however, that the lowering with KNO_3 was twice as great as with $NaNO_3$. According to the above deduction, however, this is what should occur if the solvent and solutes are highly dissociated. For from each molecular weight of $NaNO_3$ or KNO_3 added, there would be formed two mols of ions, and if the solvent $NaClO_3$ is highly dissociated into Na and ClO_3 ions, the common Na ion from the $NaNO_3$ will not tend to lower its freezing point appreciably, while the K ion from the KNO_3 will, and hence the lowering should be twice as great in the latter as in the former case. This is what Foote & Levy find to be the case, and hence their results also substantiate our conclusion that pure fused salts are probably highly dissociated.

SUMMARY.

1. A method and apparatus were devised for measuring the latent heat of fusion of substances melting up to about 600° C.; this constant was determined for the following salts : KNO_3, $NaNO_3$, $LiNO_3$, $AgNO_3$, AgCl, TlCl, $PbCl_2$, AgBr, TlBr, $PbBr_2$, $K_2Cr_2O_7$ and $NaClO_3$.

2. The specific heats of these salts at temperatures just above and just below their melting points were also determined.

3. Kopp's Law was found to hold for these substances, but with an atomic heat at the temperatures employed of 7.1 instead of 6.4, for all of the elements investigated with the exception of oxygen.

4. The atomic heat of oxygen was found to be abnormal as it is at lower temperatures, with a value of 5.9.

5. The specific heat of all salts investigated is slightly greater for the liquid than for the solid state.

6. No stoichiometrical relations were apparent between the values of the latent heat of fusion, and the molecular, atomic or crystallographic properties of the salts investigated.

7. The values of the latent heat of fusion of certain salts were used to calculate the theoretical lowering of the freezing point of the salts due to the solution of a small quantity of a second salt. These values were compared with values observed by other inves-

tigators. A discussion of the results indicates that the pure fused salt and the dissolved salt are probably both highly dissociated.

8. The lowering of the freezing point of lead chloride due to small additions of lead bromide was approximately determined and the results compared with the theoretical lowering calculated from the latent heat of fusion of lead chloride. The results again point to a high degree of ionization of both solvent and solute.

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