

	At. wt.	$\bar{V}$	$\alpha \times 10^6$	$\beta \times 10^6$	$C_p - C_v$	$C_p$	$\Delta_1$	$C_v$	$\Delta_2$
Na.....	23.0	23.7	15.4	72.	0.5	6.9	0.7	6.4	0.5
Mg.....	24.4	13.3	2.7	25.	0.2	6.0	0.2	5.8	0.1
Al.....	27.1	10.1	1.3	23.	0.2	5.8	0.4	5.7	0.3
K.....	39.1	45.5	31.5	83.	0.6	7.1	0.9	6.5	0.6
Fe.....	55.9	7.1	0.40	10.	0.1	6.0	0.2	5.9	0.0
Ni.....	58.7	6.7	0.27	13.	0.2	6.1	0.1	5.9	0.0
Cu.....	63.6	7.1	0.34	16.	0.2	5.8	0.4	5.6	0.3
Zn.....	65.4	9.5	1.5	29.	0.3	6.0	0.2	5.6	0.2
Pd.....	107.	9.3	0.38	11.	0.2	6.1	0.1	5.9	0.0
Ag.....	107.9	10.3	0.84	19.	0.3	6.1	0.1	5.8	0.1
Cd.....	112.5	13.0	1.9	28.	0.3	6.2	0.0	5.9	0.5
Sn.....	119.	16.2	1.7	22.	0.3	6.4	0.2	6.1	0.2
Sb.....	120.	17.9	2.2	11.	0.1	6.0	0.2	5.9	0.0
I.....	127.	25.7	13.	84.	0.9	6.9	0.7	6.0	0.1
Pt.....	195.	9.1	0.21	9.	0.2	6.1	0.1	5.9	0.0
Au.....	197.	10.2	0.47	14.	0.3	6.2	0.0	5.9	0.0
Tl.....	204.	17.2	2.6	28.	0.3	6.4	0.2	6.1	0.2
Pb.....	207.	18.2	2.2	29.	0.4	6.3	0.1	5.9	0.0
Bi.....	208.	21.2	2.8	13.	0.1	6.3	0.1	6.2	0.3
Average.....						6.2	0.26	5.9	0.15
Average excluding the first four						6.2	0.18	5.9	0.09

of  $\Delta_2$  are in no case greater than the possible error in  $C_p$  due to experimental errors. If the first four elements are excluded the mean value of  $C_p$  for the remaining fifteen is 6.2, and the average deviation from this mean is 0.18. The mean value of  $C_v$  is 5.9, and the average deviation is 0.09, only one-half the average deviation from  $C_p$ . This result is certainly not accidental. The law of Dulong and Petit may therefore be modified and stated as follows: *Within the limits of experimental error the atomic heat of constant volume, at 20°, is the same for all the solid elements whose atomic weights are greater than that of potassium.*

Whether this law will also be true for other temperatures cannot be ascertained until the change of compressibility with the temperature has been investigated.  $C_p$  in many cases increases rapidly with the temperature, but the term  $C_p - C_v$  probably increases also. It is not unlikely therefore that  $C_v$  may be nearly independent of the temperature.

RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,  
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## MOLTEN HYDRATED SALTS AS SOLVENTS FOR THE FREEZING POINT METHOD<sup>1</sup>.

BY J. LIVINGSTONE R. MORGAN AND H. K. BENSON.

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The depression of the freezing point of a solvent by the addition to it of a soluble substance has been employed now for a number of years as a

<sup>1</sup> Abstract from the Dissertation (Columbia 1907) of H. K. Benson.

means of determining the molecular weight, in solution, of the dissolved substance. Liquids of almost all types have been systematically studied as solvents for this purpose, but, with one exception, no results have been obtained for solutions in the liquids formed by the melting of salts containing water of crystallization. Löwenherz<sup>1</sup> using molten  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  for this purpose, has found that it may be used just as any other liquid, except that it prevents or drives back the ionization when the substance added has an ion in common with it. The object of this investigation is the similar study of other molten hydrated salts, to ascertain whether or not this behavior is general.

The salts employed melt to form a clear liquid at comparatively low temperatures, and fulfil the condition necessary for the method, *i. e.*, on cooling, even in the presence of a second substance, they separate a solid phase of the same composition as the liquid.

The apparatus employed was the form designed by Smeaton, in which the stirring of both the cooling bath and the solution, after infection, is continuous, the stirrers being driven by a small motor. The temperatures were read either on a normal thermometer (G.S. No. 5853, 1903) reading to  $0.02^\circ$  or on a Beckmann reading to  $0.01^\circ$ . The cooling bath was retained at a temperature from  $4-8^\circ$  below the freezing point of the pure solvent; and the over-cooling was kept within  $1^\circ$  when possible; and when not, the concentrating effect was accounted for by the aid of the formula giving the fraction ( $f$ ) of solvent separated; *i. e.*,  $f = \Delta t \frac{c}{w}$ , where  $c$  is the specific heat as liquid,  $w$  is the latent heat of fusion, (both at the freezing point of the pure solvent) and  $\Delta t$  is the over-cooling in degrees.

In every case the separation of solid was induced by infection with a crystal and it was ascertained by analysis that the solid phase which separated had the same composition as the pure liquid solvent.

#### Preparation of the Solvents.

$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . The pure hexahydrate of calcium chloride melts in its own water of crystallization at  $29^\circ.48$ . Kahlbaum's pure salt was melted, over-cooled, infected with a crystal, and the solid separated drained from adherent liquid. This process was continued until the freezing point of the molten solid was constant at  $29^\circ.48$ .

To obtain the molecular depression of the freezing point in this solvent use was made of the relation  $K = \frac{0.02 T^2}{w}$  where  $w$  is the heat of fusion of 1 gram of solvent, *i. e.*,  $40.7^2$  calories, and  $T$  is its absolute freezing point,  $29^\circ.48 + 273^\circ$ . Substituting these data, we find  $K = 45.0$ .

<sup>1</sup> Z. physik. Chem., 18, 70, (1895).

<sup>2</sup> Tammann, Kristallisieren und Schmelzen, p. 45.

$\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ . This salt was prepared in the same way as the  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . The freezing point of the molten solid, after purification, was  $29^\circ.88$ . Since no value for its latent heat could be found in the literature,  $K$  for  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  was determined directly by experiment, using glycol, with the following result: 2.101 grams of glycol ( $M = 62$ ) in 100 grams of molten  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  depresses the freezing point from  $29^\circ.88$  to  $29^\circ.00$ , *i.e.*,  $0.880^\circ$ , from which  $K = 26.0$ . This value of  $K$  gave very satisfactory results for all the substances employed.

Using the value  $K = 26.0$  in the formula  $K = \frac{0.02 T^2}{w}$  and solving for  $w$ , we find the latent heat of fusion of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  at its freezing point  $29.88^\circ$ , to be 70.6 gram calories per gram.

$\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$ . The preparation of this salt gave much more trouble than the others, as the anhydrous salt separates if the solution is heated above  $30^\circ$ . It was possible, however, by infecting an over-cooled saturated solution of  $\text{Na}_2\text{CrO}_4$  with a crystal of  $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$  to obtain a salt which had a freezing point of  $19.92^\circ$ . This is the salt we have used as solvent, though owing to the apparent existence of other less stable forms, freezing in the same neighborhood, it is not easy to obtain.

#### MOLECULAR WEIGHTS IN SOLUTION.

In  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  as solvent.  $K = 45.0$ .

	Grams per 100 of solvent.	Depression of freezing point.	Molecular weight.
I.— <i>Glycerol</i> <sup>1</sup> (92)			
	3.160	1.55	90.
	5.484	2.74	91.
	6.962	3.46	91.
	7.864	3.73	87.
	9.590	4.91	83.
	13.425	7.26	83.
II.— <i>Urea</i> <sup>2</sup> (60)			
	0.891	0.595	67.
	1.185	1.185	66.
	3.860	2.560	65.
III.— <i>Glycol</i> <sup>3</sup> (62)			
	2.633	1.640	70.
	3.300	2.153	68.
	5.341	3.345	72.
IV.— <i>Potassium Chloride</i> <sup>4</sup> (74)			
	0.292	0.181	73.
	0.702	0.423	75.
V.— <i>Calcium Bromide</i> <sup>5</sup> (200)			
	0.371	0.087	192.

<sup>1</sup> Kahlbaum's "Special K."

<sup>2</sup> Kahlbaum's C.P., unpurified.

<sup>3</sup> Museum specimen.

<sup>4</sup> Kahlbaum's C. P., recrystallized three times.

<sup>5</sup> Prepared from Iceland spar and pure hydrobromic acid.

The value of  $K$  here, also, was found by experiment, using sodium nitrate as the dissolved salt, for work on the other two solvents had shown that the ionization of a dissolved salt, when it has an ion in common with the solvent, is prevented. 0.9016 grams of  $\text{NaNO}_3$  ( $M=85$ ) in 100 grams of molten  $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$  depresses the freezing point  $0^\circ.408$ , from which  $K=38.5$ . This value of  $K$  in  $w = \frac{0.02 T^2}{K}$  would lead to 44.5 calories as the heat of fusion of 1 gram of  $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$  at its freezing point,  $19^\circ.92$ . Although this value of  $K$  gives fairly satisfactory results for other substances, we cannot express the confidence in it that we have in the others.

In more concentrated solutions the freezing point is higher than that of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , due possibly to the separation of  $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$ .

VI.—*Hydrochloric Acid*<sup>1</sup> (36.5)

Grams per 100 of solvent.	Depression of freezing point.	Molecular weight.
0.347	0.421	37.
0.438	0.605	33.
0.861	1.181	33.

VII.—*Potassium Nitrate*<sup>2</sup> (101)

0.596	0.520	51.
1.513	1.198	56.
1.564	1.180	58.

VIII.—*Ethyl Alcohol*<sup>3</sup> (46)

0.2652	0.21	57.
1.0958	0.89	56.
1.8550	1.32	63.
3.5057	2.21	71.
4.2900	2.47	78.
5.2140	2.85	82.
7.2292	3.40	96.
9.2517	3.83	109.
11.4259	4.26	121.
13.5912	4.68	131.
19.6313	5.57	158.
25.2080	6.47	175.

IX.—*Acetic Acid*<sup>4</sup> (60)

1.041	0.63	74.
1.388	0.84	74.
1.975	1.20	75.
2.878	1.46	92.
13.034	4.99	121.
16.440	5.74	131.
22.180	6.68	150.
33.680	8.67	174.

X.—*Formic Acid*<sup>5</sup> (46)

1.146	1.00	52.
5.288	4.11	58.
8.647	6.12	64.
8.844	6.18	64.
14.775	9.58	69.

<sup>1</sup> Pure dry  $\text{HCl}$  was passed into the solution in the freezing tube, and titrated after the freezing point had been observed.

<sup>2</sup> Kahlbaum's c. p., not further purified.

<sup>3</sup> Kahlbaum's absolute.

<sup>4</sup> Kahlbaum's "Special K."

<sup>5</sup> " " " "

In  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  as solvent  $K = 26.0$ 

	Grams per 100 of solvent.	Depression of freezing point.	Molecular weight.
XI.— <i>Glycol</i> <sup>1</sup> (62)			
	2.101	0.880	62.
	3.553	1.500	61.
	4.153	1.811	59.
	6.107	2.620	60.
	22.120	9.880	58.
XII.— <i>Erythrite</i> <sup>2</sup> (122)			
	1.102	0.261	110.
	2.350	0.640	95.
	3.610	0.963	98.
	3.983	1.020	101.
	7.007	1.821	100.
XIII.— <i>Acetone</i> <sup>3</sup> (58)			
	0.898	0.400	58.
	3.644	1.511	63.
	4.075	1.642	65.
	8.020	2.870	73.
XIV.— <i>Mannitol</i> <sup>4</sup> (182)			
	0.412	0.062	174.
	1.529	0.220	180.
	1.842	0.281	171.
	3.011	0.450	174.
XV.— <i>Methyl Alcohol</i> <sup>5</sup> (32)			
	0.939	0.781	31.
	3.277	2.550	33.
	5.819	4.230	35.
	7.023	4.810	37.
	13.825	8.730	43.
XVI.— <i>Ethyl Alcohol</i> (46)			
	1.953	1.040	48.
	5.356	2.461	56.
	8.704	3.320	68.
	9.040	3.500	07.
	17.136	5.042	88.
XVII.— <i>Acetic Acid</i> (60)			
	2.700	1.160	60.
	4.310	1.791	62.
	5.631	2.262	62.
	8.486	3.118	70.
	8.974	3.180	73.

<sup>1</sup> Same sample as used in  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ .<sup>2</sup> 5 grams of this sample in 100 grams of *water* depressed the freezing point  $0^\circ.765$ , which leads to  $M = 121$ .<sup>3</sup> Kahlbaum's not further purified.<sup>4</sup> 1.832 grams of this sample in 100 grams of *water* depressed the freezing point  $0^\circ.160$ , which leads to  $M = 178$ .<sup>5</sup> Kahlbaum's absolute.

	Grams per 100 of solvent	Depression of freezing point.	Molecular weight.
XVIII.— <i>Lithium Bromide</i> <sup>1</sup> (87)			
	1.492	0.441	88.
	1.585	0.480	86.
	2.570	0.782	86.
XIX.— <i>Potassium Nitrate</i> (101)			
	1.262	0.318	102.
	1.717	0.440	101.
	2.037	0.521	101.
XX.— <i>Potassium Chloride</i> (74)			
	0.304	0.200	39.
	3.545	2.760	33.
XXI.— <i>Hydrochloric Acid</i> (36.5)			
	0.321	0.48	18.5
	0.642	1.00	17.7
XXII.— <i>Lithium Chloride</i> <sup>2</sup> (42)			
	0.7864	0.50	41.
	1.3487	0.88	40.
XXIII.— <i>Cadmium Chloride</i> <sup>3</sup> (183)			
	0.430	0.071	158.
	In $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$ as solvent. $K = 38.5^4$ .		
XXIV.— <i>Urea</i> (60)			
	0.670	0.434	59.
	1.340	0.841	61.
	2.017	1.192	65.
XXV.— <i>Glycol</i> (62)			
	0.7360	0.434	65.
	1.9577	1.078	70.
	6.7100	3.640	71.
XXVI.— <i>Glycerol</i> (92)			
	1.672	0.720	90.
	4.541	1.891	93.
	10.736	4.370	95.
XXVII.— <i>Sodium Chloride</i> (58)			
	1.006	0.622	62.

### The Molecular Weight of Water.

Water in all three solvents gave peculiar results by the ordinary method, although in each case analysis showed no abnormality in the solid phase separated.

By the Richards method<sup>5</sup>, in  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , the following results were obtained.

<sup>1</sup> Prepared from pure  $\text{Li CO}_3$  and  $\text{HBr}$ .

<sup>2</sup> Prepared from pure  $\text{Li CO}_3$  and  $\text{HCl}$ .

<sup>3</sup> Kahlbaum's, not further purified. No stronger solutions could be made.

<sup>4</sup> In getting these results we were assisted by Mr. J. S. Mills.

<sup>5</sup> This Journal, 25, 291 (1903). Using a mixture of solid  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , in presence of its pure liquid phase, and finding the depression of the equilibrium point after the addition of varying amounts of water, analyzing a sample after each reading.

## XXVIII.—Water (18)

Grams per 100 of solvent.	Depression of freezing point.	Molecular weight.
3.80	0.82	24.
4.40	0.82	17.
8.00	2.32	21.

Higher concentrations than these caused the freezing point to rise, even though the water added had a temperature of  $10^{\circ}$  below that of the system.

**Effect of Infection of Molten  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  with a Crystal of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ .**

If the over-cooled molten  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  is infected with a crystal of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  in place of one of the hexahydrate, a solid phase is separated at a lower temperature, *i.e.*, at  $26^{\circ}.80$ . If to this system a crystal of the hexahydrate is added, the temperature at once rises to the value  $29^{\circ}.48$ . This would indicate, contrary to the conclusion of Roozeboom<sup>1</sup>, that  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  can exist as a solid, in presence of the liquid phase, below  $60^{\circ}$ , for analysis of the solid phase at  $26^{\circ}.80$  showed this composition.<sup>2</sup>

**Discussion of Results.**

It will be seen from the foregoing results that as found by Löwenherz for molten  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , molten salts, containing water of crystallization, when employed as solvents for the freezing point method, behave very much as does water, with the exception that they reduce or drive back completely the ionization of dissolved salts, when these have an ion in common.

Just as in water solutions we find in many cases an apparent increase in the molecular weight with the concentration, so here the alcohols and acetic acid in molten  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  lead to values which, by the ordinary method of calculation, are decidedly abnormal, and which increase in abnormality with increased concentration. Before attempting to draw conclusions from these results, it will be necessary to decide whether they really are abnormalities, or only apparent abnormalities, due to a common and mistaken use of the freezing point law when applied to higher concentrations.

In the usual derivation of the freezing point law the assumption is made that either the heat of dilution is zero, or that the solution is so dilute that the addition or removal of solvent is accompanied by no appreciable heating or cooling effect. Hence if one of these conditions is not fulfilled, it is certainly not correct to conclude that the results are abnormal; and it is absurd to attempt to explain their assumed abnormality by assuming changes within the system itself.

Bancroft<sup>3</sup> has shown by thermodynamical reasoning that the osmotic

<sup>1</sup> Z. physik. Chem., 4, 31 (1889.)

<sup>2</sup> This point will be further investigated.

<sup>3</sup> J. Physic. Chem., 10, 319, (1906).

pressure of a solution must vary with the magnitude and sign of the heat of dilution, *i.e.*, when heat is evolved on dilution, we may expect to find an abnormally high osmotic pressures; and vice versa. It can also be shown, thermodynamically, on this assumption, that the freezing point depressions of solutions which absorb heat on solution and dilution should be smaller throughout than those calculated by aid of the usual formula; in other words for the determination of the molecular weight, the depressions observed should be compared to a smaller value of  $K$  than the usual uncorrected one. This would cause the molecular weights, so calculated, to be lower than those found by the usual formula; and, as the heat of dilution would be the greater, the greater the concentration, the magnitude of the correction to be applied to the calculated molecular weight would also be the greater, the stronger the solution. As solutions of acetic acid or alcohol in molten  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  absorb considerable heat on dilution we suggest that this may be the explanation of the increasing molecular weights found for them above; for it is conceivable that such a correction would lead to molecular weights for these substances which are independent of the dilution, as they appear actually to be from the determinations of Morgan and Benson, based on the coefficient of distribution. As the necessary data are not as yet at hand for the testing of such a formula quantitatively, we offer this theory as a tentative explanation for the discrepancies of this sort found here and elsewhere, leaving the actual quantitative application of it to a later date.

### Summary.

I. Molten salts, containing water of crystallization, may be used as solvents for the freezing point method, and lead to molecular weights similar to those observed in water, except that the ionization of the substance dissolved, when it has an ion in common with the solvent, is decreased or prevented.

II. The freezing point constants for  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ , and  $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$  are respectively 45.0 ( $m.p. = 29^\circ.48$ ); 26.0 ( $m.p. = 29^\circ.88$ ); and 38.5 ( $m.p. = 19^\circ.92$ ).

III. The latent heat of fusion of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ , calculated from the experimentally determined freezing point constant and the formula  $K = \frac{0.02 T^2}{w}$ , is equal to 70.6 gram calories per gram, at the freezing point  $29.88^\circ$ .

IV. Acetic acid and the alcohols, in both  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ , by the freezing point method, show increasing molecular weights with increasing concentration. It is suggested that this is due to the heat absorbed when these solutions are diluted.