

2. The rate of decomposition of silver trinitride was found to increase with an increase of temperature, and this decomposition took place more rapidly when quickly heated, but the tendency to explode was much greater.

3. When silver trinitride was decomposed in a Torricellian vacuum, the evolution of nitrogen was much more rapid than at atmospheric pressure. The melting point was considerably lowered, but the exploding temperature remained practically the same as when carried out under atmospheric pressure.

4. So far as can be ascertained, no definite intermediate compounds were formed during the decomposition of the silver trinitride.

5. It has been shown that mercurous, mercuric, barium and thallos trinitrides can also be satisfactorily and quantitatively decomposed into their elements, but lead, cupric, and ammonium trinitrides have not given very satisfactory results in this respect.

6. An ideal method has been satisfactorily devised whereby the atomic weight of nitrogen can very accurately be determined, and from this knowledge one can thereby easily determine the atomic weights of a number of the metallic elements which form trinitrides, by decomposing these trinitrides into their elements and weighing each directly.

In conclusion, the author wishes to express his gratitude to Professor A. W. Browne, who has suggested the present investigation and under whose direct supervision it has been carried out.

ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE FREEZING POINTS OF CONCENTRATED SOLUTIONS AND THE FREE ENERGY OF SOLUTION OF SALTS.

By WORTH H. RODEBUSH.

Received May 22, 1918.

A great deal of work has been done upon the freezing-point depression of dilute salt solutions, but owing to the defects of the experimental methods used many of the results are in error. In the case of concentrated solutions and eutectic mixtures of ice and salt the data are even more meager and unreliable. Since the freezing-point-concentration curve of a salt solution affords a direct means of calculating the free energy of solution for the salt, it seemed desirable to determine this curve for a number of salts of various types. This has been done in this investigation for the commoner salts, which are readily soluble below 0° .

Experimental.

The most accurate method of measuring freezing-point depression has been worked out by L. H. Adams¹ and used by him in measuring the

¹ L. H. Adams, THIS JOURNAL, 37, 481 (1915).

freezing points of dilute solutions. This method, with some modifications, has been used in this investigation upon concentrated solutions. Since the concentrations and freezing-point depressions measured were relatively great, the same percentage accuracy as in the work on dilute solutions could be obtained without the extreme refinements and precautions necessary in that work.

For the temperature measurements two thermoelements of 4 junctions each were made up from copper and constantan wire. No. 35 copper wire was used and the constantan wire was the No. 30 Ideal wire used by Adams. The constantan wire was tested for inhomogeneities by the method of White,¹ any portions which gave noticeable e. m. f.'s when passing through the temperature gradient being rejected. The wire for one element was tested in the gradient between liquid air and room temperature, while the other was tested in the gradient between kerosene at 100° and room temperature. The two elements checked as closely as the e. m. f.'s could be read when placed with one terminal in liquid air and the other in ice-water. One of these elements gives an e. m. f. of about 160 microvolts per degree difference in temperature of its terminals at zero centigrade. The potentiometer used was the Leeds and Northrup double combination potentiometer installed according to the method of White,² with some modifications and improvements,³ in this laboratory.

One of the thermoelements was sent to the Bureau of Standards for calibration. The Bureau was able to calibrate it with an accuracy of only 0.01 to 0.02° between the freezing points of mercury and water on the Kelvin scale, and the accuracy of the temperature measurements is limited to this calibration. As it was possible to read e. m. f.'s on the potentiometer with an accuracy approaching 0.1 microvolt, it will be seen that the electrical installations were much more sensitive than were actually required. As a precaution against change both thermoelements were calibrated in this laboratory by placing one terminal in melting mercury and the other in ice-water, and this calibration was repeated at frequent intervals. No change took place in either element in a year's time.

In the measurement of the freezing points two silvered Dewar tubes of about 2.5 inches inside diameter by 10 inches deep were used. One served as a container for the mixture of ice and salt solution, and the other contained ice and water and was used as a standard temperature bath. The thermoelement was placed with a terminal extending about half-way to the bottom of each vessel. No stirring was required in the ice-water mixture as the temperature remained constant within 0.001°

¹ White, *THIS JOURNAL*, 36, 2292 (1914).

² *Ibid.*, 36, 1868 (1914).

³ Randall, von Bichowsky and Rodebush, *THIS JOURNAL*, 38, 1266 (1916).

or less. The ice-solution mixture was stirred by means of a glass cage made from the upper half of a bottle, which enclosed the ice. This was drawn up by a silk thread and allowed to sink by its own weight. As it moved slowly up and down it carried the ice with it and forced the solution back and forth in intimate contact with the ice with a minimum of friction and heating. For most salts a metal gold-plated cage could be used and would be a more simple and efficient stirring device than the pump used by Adams. The silk thread passed through a very small hole in the stopper of the Dewar tube and was attached to a reciprocating device driven by a motor.

The chief heat leak in a Dewar tube is the radiation and convection from the top. For the ice-water vessel a metal cover served to keep out radiation and air currents sufficiently well, since the equilibrium temperature of melting ice is very easily maintained. In the case of the salt solution, however, equilibrium is constantly shifting since the melting of ice dilutes the solution and lessens the freezing-point depression. Furthermore, the stirring tends to produce air currents in the vessel. It was necessary to provide a stopper which fitted tightly, was a good heat insulator, and was not wet by the liquid. The most satisfactory material was found to be "balsa" wood, a light spongy wood which was so soft that it could be forced into the mouth of a Dewar tube like a cork. The wood had been kiln-dried and paraffined so that it was impervious to moisture and was a good insulator. With this stopper the temperature of the ice and salt solution inside the Dewar tube rose at the rate of about 0.01° in 5 minutes, when the freezing-point depression was not more than 20° . Since the stirring was effective it is probable that the temperature recorded was not far from the true equilibrium temperature of ice and the solution actually in the vessel.

The procedure was as follows: The one Dewar vessel was filled with ice and water. Into the other was put about 500 cc. of a concentrated solution of the salt, together with about one-third its volume of rather finely cracked ice. The thermoelement and stopper were inserted and the stirrer started. When the temperature ceased falling and began to rise slowly a pipet with a piece of muslin cloth tied over the end was plunged into the solution through a hole in the stopper and a sample quickly drawn off and transferred to a stoppered flask for analysis, care being taken to prevent dilution of the solution by condensation of moisture from the air. Since the pipet did not come into contact with the ice in the Dewar vessel there was no opportunity for melting ice to change the concentration of the solution. After a sample was taken the solution in the Dewar vessel was diluted and the procedure repeated, samples being obtained at intervals in the range between saturations and the molal solution.

For the salts which could be dried and weighed a conductivity method of analysis was used. A cell with a conductance suitable for solutions of about molal concentrations was calibrated in this range with solutions made up by weighing out the salt. The samples drawn from the freezing-point solutions were diluted to approximately molal, their conductivity measured and their composition read off from a curve. In the measurement of conductivities the apparatus installed in this laboratory for that purpose was used. It consisted of a Siemens and Halske high-frequency generator, with extended bridge, balanced reactance and tuned telephones, etc. The solutions of calcium, magnesium and lithium chlorides were analyzed by precipitating the chlorine as silver chloride.

For the determination of eutectic temperatures theoretically it should only be necessary to place solid salt in contact with ice and solution and stir until equilibrium is obtained between the three phases. Actually it was found that a salt dissolves very slowly in its nearly saturated solution while the heat leak into the container melts the ice and keeps it surrounded by a more dilute solution and thus limits the concentration obtainable in contact with the ice. The following method was found to give a reproducible temperature for the equilibrium between solid salt, ice and solution. Solid salt and ice were mixed in a mortar until a considerable quantity of solution was formed and the whole was then frozen to a solid mass by pouring liquid air over it. The frozen mass was then broken up into small pieces and placed in a small Dewar tube surrounding the thermocouple. This mixture in the case of most salts warmed up rapidly to a definite temperature and then remained constant within 0.01° for 20 to 30 minutes. For salts which form hydrates with a number of mols of water of crystallization at the eutectic point, as calcium and magnesium chlorides, it was not possible to determine this temperature with an accuracy of more than a degree. This is probably due to the fact that as the salt dissolves, the water of crystallization released is almost enough to dissolve it, thereby requiring the melting of a smaller amount of ice and causing the temperature to be affected much more by heat leak from the surroundings. In the case of the salts which are easily obtained pure and which do not form high hydrates the eutectic temperatures are so easily reproduced that they should be useful as fixed points in thermometry. No direct method of analysis was found available for eutectic solutions so that the data given for the compositions have been obtained by extrapolation of the freezing-point curves. In the case of salts which give eutectics of very low temperatures considerable extrapolation is necessary, and hence the compositions given are only approximate.

The ice used in this work was washed carefully and was apparently free from impurities. When the thermoelement was placed with one terminal in a mixture of ice and pure water and the other in a mixture of

ice and water formed from the melting ice no difference in temperature was observed.

The salts used in the freezing-point determinations were the purest commercially obtainable in this country. Their purity was determined by determining the eutectic temperature before and after recrystallization. Impurities lower the eutectic temperature in the same manner as they do the freezing point of a solvent, and a similar thermodynamic equation can be shown to hold for this lowering.¹ The effect of impurities would be greatest at the eutectic, and since a conductivity method of analysis was used the presence of salts of similar conductivity would not cause serious error, since the freezing-point lowering would be greater by an amount approximately proportional to the apparent increase in concentration caused by the conductivity of the impurities. No difference of the eutectic after recrystallization was obtained for most salts and the error in the data for these is probably not greater than 0.1%. In the case of ammonium sulfate a satisfactory recrystallization was not obtained, and in the case of the very soluble calcium, magnesium and lithium chlorides several recrystallizations did not remove all impurities. Furthermore, with these very soluble salts, when the freezing-point depression reaches 30 to 40° equilibrium is very difficult to obtain. It is necessary to pre-cool the ice with liquid air, the solutions are very viscous and hard to stir, and the heat leak becomes very considerable. However, the data obtained for these salts show the general form of the freezing-point curve, and the error is not great enough to vitiate the results for any practical calculations:

The freezing-point data follow:

G. anhydrous salt per 100 g. H ₂ O.	Freezing-point lowering. Degrees C.
Sodium Chloride.	
6.11	3.48
8.92	5.17
10.77	6.32
14.20	8.52
15.46	9.41
17.87	11.04
22.25	14.33
22.99	14.77
24.75	16.21
27.70	18.73
29.70	20.56
30.4	21.12 eutectic
Potassium Chloride.	
7.09	3.07
10.77	4.66
17.38	7.51

¹ Lewis, *Proc. Am. Acad.*, 43, 284 (1907).

G. anhydrous salt per 100 g. H ₂ O.	Freezing-point lowering. Degrees C.
12.69	9.84
13.80	10.34
14.60	10.66 eutectic
Ammonium Chloride.	
9.28	5.73
12.27	7.63
12.56	7.80
13.76	8.60
16.89	10.58
18.80	11.80
19.94	12.44
19.93	12.60
22.40	14.03
24.13	15.10
24.50	15.36 eutectic
Lithium Chloride.	
5.48	5.11
10.68	12.22
15.04	18.75
18.58	25.44
eutectic not determined.	
Magnesium Chloride.	
8.79	5.71
11.74	8.46
16.31	13.79
20.36	19.57
24.21	25.86
28.00	33.50 eutectic
Calcium Chloride.	
8.51	4.21
14.83	8.63
22.02	15.23
34.87	29.83
36.04	31.25
48.00	51.00 eutectic
Potassium Bromide.	
11.53	3.19
20.42	5.61
23.82	6.57
30.87	8.51
38.33	10.55
39.50	10.90
45.65	12.60 eutectic
Sodium Nitrate.	
20.83	6.67
28.77	8.78
34.15	10.17
44.56	12.85
53.14	15.08
62.50	17.46 eutectic

G. anhydrous salt per 100 g. H ₂ O.	Freezing-point lowering. Degrees C.
Ammonium Nitrate.	
8.82	3.19
20.60	6.52
31.43	9.06
49.95	12.70
62.08	14.72
71.10	16.17
74.80	16.67 eutectic
Ammonium Sulfate.	
28.86	7.10
32.03	7.94
40.78	10.15
41.13	10.43
46.77	12.00
52.60	13.99
59.24	15.99
63.57	17.49
66.40	18.34 eutectic

The Free Energy of Solution.

Following the notation of Lewis,¹ Duhem's equation may be written

$$d\bar{F}_1 = -\frac{N_2}{N_1} d\bar{F}_2 \quad (1)$$

where N_1 and N_2 represent the mol fractions and \bar{F}_1 and \bar{F}_2 the partial molal-free energy, of salt and water, respectively. Lewis² has derived the following equation for the change in free energy of the reaction:



$$\Delta F = -5.26t - 0.0165t^2 + 0.00002t^3 \quad (2)$$

where t is the freezing-point depression. Since the water in a solution at its freezing point is in equilibrium with ice at that temperature the difference in free energy between the water of the solution and pure liquid water at this same temperature is also given by the above equation.

In order to calculate free energy at 25° it is necessary to make use of the equation

$$\frac{d(\Delta F)}{dT} = \frac{\Delta F - \Delta H}{T} \quad (3)$$

ΔH is the change in heat content when a mol of water is added to a large amount of solution of the given concentration. This quantity is directly related to the heat of dilution for the salt. Sufficient data upon heats of dilution are not available although an investigation upon this subject has been undertaken in this laboratory. For solutions of the salts with

¹ Lewis, *THIS JOURNAL*, **34**, 1635 (1912).

² Lewis, *Ibid.*, **36**, 1985 (1914).

which we are concerned, ΔH cannot be large and for the temperature interval between the freezing point of the solution and 25° no serious error can be made in assuming ΔH constant. If we do this we can then integrate the equation and we have

$$\begin{aligned}\Delta F &= \Delta H + IT \\ I &= \frac{\Delta F_0 - \Delta H}{T_0}\end{aligned}\quad (4)$$

where ΔF_0 has the value given by Equation 2 and T_0 is the absolute temperature of the freezing point.

Substituting the value of I we have

$$\Delta F_{298} = \frac{298 \Delta F_0}{T_0} - \left(\frac{298 - T_0}{T_0} \right) \Delta H. \quad (5)$$

It is seen that ΔH appears as a separate term with a fraction as a coefficient. We can, therefore, proceed to calculate the free energy of solution leaving the term of the above equation involving ΔH to be calculated as a relatively small additive correction when the values of ΔH are obtained.

Upon substituting values of T_0 and ΔF_0 from Equation 2, in the second term of Equation 5, we find that this term $\left(\frac{298 \Delta F_0}{T_0} \right)$ becomes numerically equivalent to so nearly a constant $(k) \times t$, the freezing-point lowering, that it may be so written without appreciable error, using the average value of k for the temperature interval under consideration. Then since $d(\Delta F_{298})$ is the $d\bar{F}_2$ of Duhem's equation we have

$$d\bar{F}_1 = - \frac{N_2}{N_1} k dt. \quad (6)$$

Here $\frac{N_2}{N_1}$ may be written as $\frac{55.5}{n}$ where n is the number of mols of salt per 1000 g. of water. Upon inspection of the freezing-point curves obtained in this work it is found that the curves can be fitted with sufficient accuracy over a considerable range of concentration by an empirical equation in which n is expressed as a function of t .

$$n = at + bt^2. \quad (7)$$

Substituting this value of n in Equation 6 we have

$$d\bar{F}_1 = - \frac{55.5 k dt}{at + bt^2}. \quad (8)$$

The partial molal free energy of the salt in a saturated solution is equal to the free energy of the solid phase of the salt, with which it is in equilibrium. Therefore, if we integrate Equation 8 between t_0 , the freezing-point lowering of a solution of a concentration equal to saturation at 25° , and t , the freezing-point lowering of a solution of any given concentra-

tion, we obtain the free energy of solution for the salt in that concentration at 25°; that is, the change in free energy in passing from solid salt to solution of the given concentration.

$$\Delta F_{298}^{\circ} = -55.5k \int_{t_0}^t \frac{dt}{at + bt^2} = -\frac{2.3026 \times 55.5k}{a} \log \frac{n_0 t^2}{nt_0^2} \quad (9)$$

It will be noted that it is necessary to evaluate only one of the empirical constants (a) of Equation 7 above.

The free energies of solution have been calculated for sodium and potassium chlorides. These salts have been chosen because accurate values for the freezing point at tenth molal are to be found in the literature. The values of t at molal and saturation are read off the curve made from the data obtained in this laboratory. Since the solubilities of these salts increase with the temperature considerable extrapolation beyond the eutectic is required to obtain the value of t corresponding to saturation at 25°. The solubilities at 25° were obtained from the Landolt-Börnstein-Roth tables. The integration of Equation 8 has been performed in two steps; from saturation to molal and from molal to tenth molal, to fit the equation better to the curve. Between saturation and molal the average value of k is -5.78 ; between molal and tenth molal -5.75 .

For sodium chloride we have the values of n and t .

n .	t .
6.16	27.45
1.0	3.33
0.1	0.344 ¹

This gives us for the free energies of solution:

$$\begin{aligned} \Delta F_{298} \text{ sat. to } 1.0 M &= -2477 \\ \Delta F_{298} \text{ } 1.0 M \text{ to } 0.1 M &= -2464 \\ \Delta F_{298} \text{ sat. to } 0.1 M &= -4941 \end{aligned}$$

Lewis² has defined a solution of hypothetical molal concentration as one in which the activity of the ions is n times as great as in a solution which is $1/n$ molal with respect to the ions where n is a large number. The activity of the ions even in dilute solution cannot be calculated directly from freezing-point data. From other considerations, however, Lewis, Brighton and Sebastian³ have calculated the activity of the ions of a salt like sodium chloride $0.1 M$ to be 0.078 . We can then calculate the free energy of dilutions from molal-ion concentration to $0.1 M$ by the equation

$$\Delta F_{298} = RT \ln \left(\frac{0.078}{1} \right)^2 = -3024. \quad (10)$$

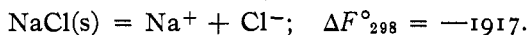
Subtracting this from the free energy of solution at $0.1 M$ we get as the

¹ Harkins and Roberts, *THIS JOURNAL*, **38**, 2679 (1916).

² Lewis, *Ibid.*, **35**, 25 (1913).

³ Lewis, Brighton and Sebastian, *Ibid.*, **39**, 2258 (1917).

free energy of solution at molal-ion concentration, that is, the change in free energy in passing from solid salt to ions of hypothetical molal concentration,



Substituting this value in Equation 9 and solving for n we get as the actual concentration at molal-ion concentration

$$n = 1.64.$$

For potassium chloride we have the values

n .	i .
4.80	15.57
1.0	3.23
0.1	0.345 ¹

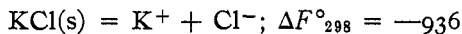
This gives us for the free energies of solution:

$$\Delta F_{298}^{\circ} \text{ sat. to } 1.0M = -1550$$

$$\Delta F_{298}^{\circ} \text{ } 1.0M \text{ to } 0.1M = -2410$$

$$\Delta F_{298}^{\circ} \text{ sat. to } 0.1M = -3960$$

Hence for the free energy of solution at molal-ion concentration



$$n \text{ (molal-ion concentration)} = 1.85.$$

This work was done under the direction of Major G. N. Lewis, to whom the writer wishes to acknowledge his indebtedness. It is because of Major Lewis' absence with the American Expeditionary Force in France that this paper has not been written in collaboration with him.

Summary.

1. Recent improvements in the method of determining freezing-point depression have been utilized in measuring the freezing points of concentrated solutions and the data for a number of salts have been obtained.
2. The thermodynamic equations necessary for the calculation of free energy of solution are given and their application illustrated by a calculation of the free energies of solution of sodium and potassium chlorides.

BERKELEY, CAL.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA.]

THE TITRATION OF OXALIC ACID BY THE CONDUCTANCE METHOD.

BY HERBERT S. HARNED AND CLINTON N. LAIRD.

Received June 14, 1918.

Introduction.

Kuster, Gruters and Geibel² have shown that acids can be accurately titrated with sodium or barium hydroxides by means of the conductance

¹ L. H. Adams, *Loc. cit.*

² *Z. anorg. Chem.*, **35**, 455 (1903); **42**, 225 (1904).