molal heat of mixing, b a constant, N the mole fraction in the mixed crystal.

From the above relations and the conventional between partial molal quantities it is found that

$$b = H/N_1N_2 \qquad (5)$$

in which H is the heat of mixing per mole.

From equation (2) in the present paper it is found that

$$\log K = \log K' + \log (f_{Cl}/f_{Br})_{crystal} \qquad (6)$$

From Hildebrand's expressions it follows that

$$RT \ln f_{Cl} = bN_{Br}^2$$
$$RT \ln f_{Br} = bN_{Cl}^2$$

and

$$\log_{10}\left(\frac{f_{Cl}}{f_{Br}}\right) = \frac{0.4343b}{RT}(2N_{Br} - 1) \qquad (7)$$

Combination of equations (6) and (7) leads to

$$\log K = \log K' + \frac{0.434b}{RT}(2N_{Br} - 1) \qquad (8)$$

Hence, if $\log K$ is plotted as a function of $(2N_{AgBr} - 1)$, the slope of the line should be

$$\frac{0.4343b}{RT} = \frac{0.4343}{RT}\frac{H}{N_1N_2}$$

Eastman and Milner[6] give the change in heat content in the formation of one mole of a mixed crystal, in which $N_{AgBr} = 0.728$ and $N_{AgCl} = 0.272$ as 81 ± 10 calories.

Taking this as the heat of mixing the calculated slope is

$$\frac{0.4343}{1.99 \times 298} \times \frac{81}{0.728 \times .272} = 0.30 \pm 0.04$$

The calculated value deviates from the experimentally found slope (0.19 Küster, 18°; 0.17 Yutzy and Kolthoff, 27°) by more than the estimated error. Thus the consideration of the solid phase as a "regular solution" seems questionable.

Summary

1. The distribution coefficient K of bromide between solution and mixed crystals of silver chloride and bromide has been determined at 27 and 98° in aqueous medium and at one mole fraction of silver bromide in ethanol at 27°.

2. At 27° K changes as a linear function of the mole fraction of silver bromide in the solid. Evidence has been given that the mixed crystals cannot be considered as "regular solutions." At 98° the value of K becomes practically independent of N_{AgBr}, and the solid approaches the behavior of an ideal solution.

3. The value of K is approximately equal to the ratio of the solubility products as pointed out by Flood and Bruun[7] and not to the ratio of the solubilities of the components.

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

The Heat Capacity of Silver Nitrite from 15 to 300°K. The Heat of Solution at 298°K. of Silver Nitrite, Barium Nitrate and Thallous Nitrate. The Entropy of Silver Nitrite, Thallous Ion, Nitrate Ion and Nitrite Ion

BY OLIVER L. I. BROWN, WENDELL V. SMITH AND WENDELL M. LATIMER

The determination of the entropy of silver nitrite enables a calculation to be made of the entropies of both nitrate and nitrite ions. The entropy of nitrate ion can also be obtained by three other independent methods, making use of existing data on sodium nitrate, potassium nitrate and barium nitrate, combined with a value of the heat of solution obtained in this investigation. In the present paper we shall also present two methods of calculating the entropy of thallous ion.

Material.—The silver nitrite was a C. P. sample prepared in this Laboratory. It was recrystallized from distilled water and the product dried in a vacuum desiccator for several days. The final product was analyzed for nitrite by titration with permanganate solution, and for silver by thermal decomposition. Calcd. Ag, 70.10; nitrite, 29.90. Found: Ag, 69.89, 69.95, 69.90, 69.96; nitrite, 29.79, 29.74. The barium nitrate was a Mallinckrodt reagent grade sample, which was dried and used without further purification. The thallous nitrate was the same as that used by Latimer and Ahlberg.[1]

Heat Capacity Measurements.—The experimental method followed the general procedure described by Latimer and Greensfelder.[2] Specific

(1) Latimer and Ahlberg, THIS JOURNAL, **54**, 1900 (1932).
(2) Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928).

TABLE I

MOLAL HEAT CAPACITY OF SILVER NITRITE

T, °K.	C_p, cal./mole/deg.	T, °K.	C_p, cal./mole/deg.	T, °K.	C_p, cal./mole/deg.
14.36	1.56	72.32	10.58	189.00	16.77
15.77	1.83	77.10	11.04	195.94	17.04
17.09	2.07	82.86	11.59	202.25	17.29
19.21	2.46	89.26	12.10	215.27	17.53
21.65	2.85	94.07	12.56	223.49	17.67
23.84	3.22	107.35	13.40	232.36	17.91
26.32	3.72	113.53	13.72	240.05	18.15
28.82	4.17	124.51	14.22	248.24	18.34
31.24	4.60	129.71	14.54	255.45	18.54
37.72	5.83	135.02	14.84	260.44	18.57
41.04	6.40	140.48	15.13	265.92	18.87
44.15	6.88	145.93	15.31	273.93	18.83
47.40	7.35	151.31	15.51	274.16	18.86
51.67	8.02	156.59	15.68	284.13	18.96
56.73	8.76	156.60	15.68	284.30	18.84
62.21	9.41	163.45	15.92	294.94	18.67
67.37	10.00	174.86	16.24		

heat measurements were made on a sample weighing 103.893 g. *in vacuo* (0.67511 mole). One calorie was taken equal to 4.1833 int. joules. The heat capacities near the melting point of water showed the presence of 0.12% of water in the sample, in spite of the precautions taken to exclude it. The final heat capacities were corrected for this amount of water, even though the correction was small.[3] The results are summarized in Table I, and shown graphically in Fig. 1.

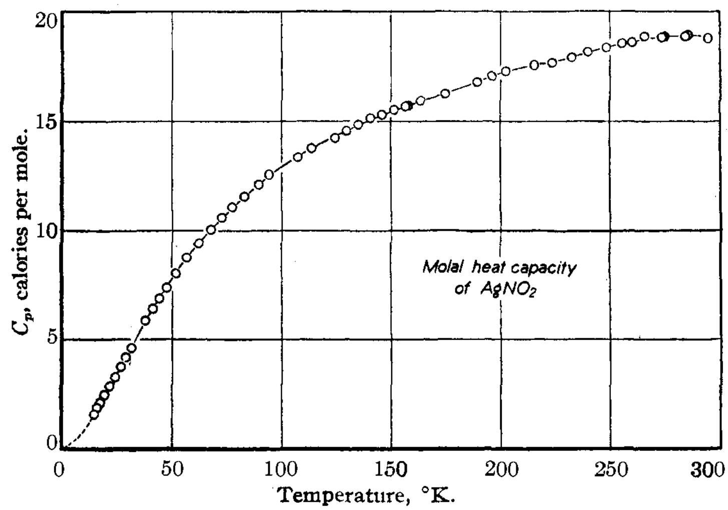

Fig. 1.—Molal heat capacity of silver nitrite.

Entropy of Silver Nitrite.—The entropy of silver nitrite at 298.1°K. was evaluated by graphical integration of the heat capacity data, combined with an analytical integration between 0° and 14.36° using the Debye specific heat equation. The result is summarized in Table II.

TABLE II

MOLAL ENTROPY OF SILVER NITRITE

0–14.36°K.	Debye extrapolation	0.55
14.36–298.1°K.	Graphical from data	30.07 ± 0.1
	Entropy at 298.1°K.	30.62 e. u.

Heat of Solution of Silver Nitrite.—We wish to acknowledge our indebtedness to Mr. Kenneth S. Pitzer whose work has enabled us to obtain an accurate value for this heat of solution. The work of Abegg and Pick[4] indicates that silver nitrite is not completely dissociated even in dilute solution so that a direct determination of the heat of solution does not give the quantity desired because of the very large uncertainty in the heat of dissociation and dilution. However, the heat of solution at infinite dilution can be obtained from the following three heats: (1) the heat of solution of silver nitrite in a dilute ammonia solution, (2) the heat of solution of silver nitrate in the dilute ammonia solution, and (3) the heat of solution of silver nitrate in an infinite amount of water. Adding (1) and (3) and subtracting (2) gives the heat of solution of silver nitrite in an infinite amount of water if one assumes that the heat effect going from nitrite ion in dilute ammonia solution to nitrite ion in an infinite amount of water is the same as that for nitrate ion. The heat of solution of silver nitrite in 0.14 M ammonia to form a 0.01 M solution was found to be -8020 ± 60 cal. Combining this with the heats for the other reactions[5] the heat of solution of silver nitrite at infinite dilution is found to be 10,070 ± 100 cal.

Entropy of Nitrite Ion.—Abegg and Pick[4] determined the solubility of silver nitrite at 298.1°K. and found a value of 2.0×10^{-4} for the equilibrium constant, from which $\Delta F^\circ_{298.1}$ of solution is 5050 cal. The entropy of solution is, therefore, $\Delta S^\circ = (10{,}070 - 5050)/298.1 = 16.8$ e. u. The entropy of silver ion[6] is 18.4, so that the entropy of nitrite ion is $S^\circ = 30.6 + 16.8 - 18.4 = 29.0$ e. u.

Heat of Solution of Barium Nitrate and Thallous Nitrate.—The integral heat of solution of

(3) A discussion of this correction is given by Brown, Smith and Latimer, *ibid.*, **58**, 2144 (1936).

(4) Abegg and Pick, *Z. anorg. Chem.*, **51**, 1 (1906).

(5) Smith, Brown and Pitzer, to be published.

(6) Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 89 (1934).

barium nitrate in 614 moles of water at 298.1°K. was determined using the calorimeter previously described.[7] Two determinations gave 9256 and 9236 cal. per mole. Combining the average value with the known heat of dilution,[8] the heat of solution at infinite dilution was found to be 9496 cal. per mole. We are greatly indebted to Mr. Kenneth S. Pitzer who has measured the heat of solution of thallous nitrate in 5000 moles of water at 298.1°K. and found a value of 10,050 ± 50 cal. per mole. Combining this value with an estimated heat of dilution we find the heat of solution at infinite dilution to be 10,020 cal. per mole.

Entropy of Nitrate Ion.—The reaction

$$2AgNO_2(s) = Ag^+ + NO_3^- + Ag(s) + NO(g) \quad (1)$$

has been studied by Abegg and Pick[4] and by Lewis and Adams.[9] The free energy change in this reaction at 298.1°K. has been fairly well established by these workers, but the $\Delta H°$ of the reaction which is necessary in computing the entropy change was not known with sufficient accuracy. Consequently, Randall, Manov and Brown[10] have studied the equilibrium reaction (2) and from the

$$2AgNO_2(s) = Ag(s) + AgNO_3(s) + NO(g) \quad (2)$$

change of equilibrium pressure with temperature have determined the $\Delta H°_{298.1}$ of reaction (2) to be 14,040 cal. Combining this with the heat of solution of silver nitrate in an infinite amount of water[5] 5360 ± 50 cal./mole we find $\Delta H°_{298.1}$ for reaction (1) to be 19,400 cal./mole. An extrapolation of the equilibrium measurements of Lewis and Adams and Abegg and Pick yields an average $\Delta F°_{298.1} = 3600$. The entropies of nitric oxide,[11] silver,[12] and silver ion[6] are 50.4, 10.2 and 18.4 e. u., respectively, so that the entropy change of the reaction, and the entropy of nitrate ion are given by the expressions

$$\Delta S° = (\Delta H° - \Delta F°)/T = (19{,}400 - 3600)/298.1 = 53.0 \text{ e. u.}$$

$$S°_{NO_3^-} = \Delta S° + 2S°_{AgNO_2} - S°_{Ag} - S°_{Ag^+} - S°_{NO(g)} = 35.2$$

Latimer and Ahlberg[13] determined the entropy of barium nitrate and calculated the entropy of nitrate ion. The principal uncertainties in their calculation were the entropy of barium ion, and the heat of solution of barium nitrate. The entropy of barium ion has recently been more accurately evaluated,[7] and with the heat of solution determined as described above, permits an accurate calculation of the entropy of nitrate ion. The entropy of solution and the entropy of nitrate ion are given by the expressions

$$\Delta S° = (\Delta H° - \Delta F°)/T = (9496 - 3200)/298.1 = 21.1 \text{ e. u.}$$

$$S°_{NO_3^-} = {}^1/_2(\Delta S° + S°_{Ba(NO_3)_2} - S°_{Ba^{++}}) = {}^1/_2(21.1 + 51.1 - 2.2) = 35.0 \text{ e. u.}$$

The entropy of nitrate ion can be determined by a third independent method. The entropy of sodium nitrate[14] is 27.87 ± 0.08 e. u. The activity coefficient of sodium nitrate[15] at saturation (10.83 M) and a temperature of 298.1°K. is 0.355. The free energy of solution is then $\Delta F°_{298.1} = -1363.8 \log (10.83 \times 0.355)^2 = -1596$ cal./mole. The heat of solution of sodium nitrate in an infinite amount of water at 291.1°K. is given by Bichowsky and Rossini[16] as 5051 cal./mole. Correcting this value to 298.1, using Rossini's[17] value for the partial molal heat capacity of sodium nitrate, we obtain $\Delta H°_{298.1} = 4810$ cal./mole. The entropy of sodium ion[6] is 14.7 e. u., so that the entropy of solution and the entropy of nitrate ion are given by the expressions

$$\Delta S° = (\Delta H° - \Delta F°)/T = (4870 + 1596)/298.1 = 21.5$$

$$S°_{NO_3} = \Delta S° + S°_{NaNO_3} - S°_{Na^+} = 21.7 + 27.9 - 14.7 = 34.7 \text{ e. u.}$$

The entropy of nitrate ion can be determined by still another method, which is independent of the three already described. The entropy of potassium nitrate[14] is 31.77 ± 0.10 e. u. The solubility in water[18] at 298.1°K. is 3.74 M, while the activity coefficient[19] at saturation is 0.233. The free energy of solution is then $\Delta F°_{298.1} = 163$ cal./mole. The heat of solution in an infinite amount of water[16] at 291.1°K. is 8633 cal./mole. Correcting this value to 298.1°K., using Rossini's[17] value for the partial molal heat capacity of potassium nitrate, we obtain $\Delta H°_{298.1} = 8341$ cal./mole. The entropy of potassium ion[3] is 24.2 e. u., so that the entropy of solution and the entropy of nitrate ion are given by the expressions

$$\Delta S° = (\Delta H° - \Delta F°)/T = (8341 - 163)/298.1 = 27.4$$

(7) Brown, Smith and Latimer, THIS JOURNAL, **58**, 1758 (1936).
(8) Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931).
(9) Lewis and Adams, THIS JOURNAL, **37**, 2308 (1915).
(10) Randall, Manov and Brown, unpublished data.
(11) Johnston and Chapman, THIS JOURNAL, **55**, 153 (1933).
(12) Kelley, Bull. 350, Bur. of Mines, 1932.
(13) Latimer and Ahlberg, *Z. physik. Chem.*, Abt. A, **148** (6), 464 (1930).
(14) Southard and Nelson, THIS JOURNAL, **55**, 4865 (1933).
(15) William H. Hopson, Ph.D. Dissertation, State University of Iowa, 1935. Vapor pressures of aqueous solutions of sodium nitrate at 25°.
(16) Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Co., New York, 1936, p. 142.
(17) Rossini, *Bur. Standards J. Research*, **7**, 47 (1931).
(18) "International Critical Tables," McGraw-Hill Book Co., Inc New York, 1923.
(19) Robinson, THIS JOURNAL, **57**, 1165 (1935).

$$S_{NO_3^-} = \Delta S^\circ + S^\circ_{KNO_3} - S^\circ_{K^+} = 27.4 + 31.8 - 24.2 = 35.0 \text{ e. u.}$$

The average value of $S^\circ_{NO_3^-}$ is then 35.0 ± 0.1 e. u.

The Entropy of Thallium Ion.—Latimer and Ahlberg[20] determined the entropy of thallous nitrate and calculated a value for nitrate ion. Since the entropy of nitrate ion is now known with greater exactness than the entropy of thallous ion, and particularly since any large uncertainty in the heat of solution of thallous nitrate has been removed by the measurements of Mr. K. S. Pitzer referred to above, we believe it preferable to calculate a value for the entropy of thallous ion. The entropy of solution of thallous nitrate and the entropy of thallous ion are given by the expressions

$$\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T = (10{,}020 - 1790)/298.1 = 27.6 \text{ e. u.}$$

$$S^\circ_{Tl^+} = \Delta S^\circ + S^\circ_{TlNO_3} - S^\circ_{NO_3^-} = 27.6 + 38.1 - 35.0 = 30.7$$

Another value for the entropy of thallous ion can be calculated from the electromotive force measurements of Cowperthwaite, La Mer and Barksdale.[21] These authors find for the reaction

$$Tl(s) + AgCl(s) = Ag(s) + Tl^+ + Cl^-, \ \Delta F^\circ_{298.1} = -12{,}877 \text{ cal.}, \ \Delta H^\circ_{298.1} = -8307 \text{ cal.}$$

The entropies of Tl(s),[12] AgCl(s),[12] Ag(s),[12] and Cl^-[6] are, respectively, 15.5 ± 0.1, 23.0 ± 0.1, 10.2 ± 0.1 and 13.5 ± 0.1 e. u. The entropy change of the reaction and the entropy of thallous ion are given by the expressions

$$\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T = (-8307 + 12{,}877)/298.1 = 15.3$$

$$S^\circ_{Tl^+} = \Delta S^\circ + S^\circ_{Tl(s)} + S^\circ_{AgCl(s)} - S^\circ_{Ag(s)} - S^\circ_{Cl^-} = 15.3 + 15.5 + 23.0 - 10.2 - 13.5 = 30.1 \text{ e. u.}$$

The values previously calculated for thallous ion[6] have involved considerably greater uncertainties in the entropy and heat of reaction data than the two values calculated here. We therefore recommend the average value $S^\circ_{Tl^+} = 30.4$ e. u.

(20) Latimer and Ahlberg, THIS JOURNAL, **54**, 1903 (1932).

(21) Cowperthwaite, La Mer and Barksdale, *ibid.*, **56**, 544 (1934).

The Free Energy of Nitrate Ion.—Since the heat of formation of nitrate ion has been determined with considerable accuracy,[22] it can be combined with the entropy of formation to obtain a reliable value for the free energy of formation. Becker and Roth obtain −49,020 ± 80 cal. for the heat of formation from the elements at 293°K. of one mole of nitric acid in 1079 moles of water. Correcting this to infinite dilution and 25° gives $\Delta H^\circ_{298.1} = -49{,}290$ cal. for the heat of formation of nitrate ion. The entropy of formation of nitric acid at 25° is

$$\Delta S^\circ = S_{H^+} + S_{NO_3^-} - \frac{1}{2} S_{N_2} - \frac{3}{2} S_{O_2} - \frac{1}{2} S_{H_2} = 0 + 35.0 - \frac{1}{2}45.79^{23} - \frac{3}{2}49.03^{24} - \frac{1}{2}31.23^{25} = -77.1$$

Thus, the free energy of formation of nitrate ion from its elements is $\Delta F^\circ_{298.1} = -26{,}310 \pm 90$ cal. The value given by Lewis and Randall[26] is −26,500 cal., which agrees with our value within the limits of accuracy of their calculation.

Summary

The heat capacity of silver nitrite has been determined from 15 to 300°K. The entropy of silver nitrite has been calculated at 298.1°K. The entropy of nitrite ion has been determined as 29.0 e. u. The entropy of nitrate ion has been calculated by four independent methods and the values 35.2, 35.0, 34.7 and 35.0 e. u. obtained. The entropy of thallous ion has been calculated by two independent methods and the values 30.7 and 30.1 e. u. obtained. The heats of solution of silver nitrite, barium nitrate and thallous nitrate at 298.1°K. have been determined. The free energy of formation of nitrate ion at 298.1°K. has been calculated to be −26,310 cal.

BERKELEY, CALIF. RECEIVED MARCH 1, 1937

(22) Becker and Roth, *Z. Elektrochem.*, **40**, 836 (1934).

(23) Giauque and Clayton, THIS JOURNAL, **55**, 4875 (1933).

(24) Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

(25) Giauque, *ibid.*, **52**, 4816 (1930).

(26) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.