temperature of 20°. The methoxylated product, purified by precipitation from anhydrous 1,4-dioxane with anhydrous ether, was obtained as a light buff colored powder. Analysis by the Zeisel method of five different samples gave an average of 27.3% methoxyl as shown in Table I.

Summary

1. A method for extracting the lignin in bagasse by means of dilute nitric acid is described.

2. The lignin extracted by this method has an apparent molecular weight by the freezing-point method in 1,4-dioxane of 1650 ± 125 and has the following approximate formula: $C_{87}H_{54}O_{21}(NO_2)_2(OCH_3)_8(OH)_4$.

3. Methoxylation and acetylation data confirm the unreliability of these methods in determining the percentage of hydroxyl in the lignin molecule.

4. The absence of carboxyl groups is indicated from electrometric titration curves.

HONOLULU, HAWAII RECEIVED APRIL 6, 1937

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

The Heat Capacity and Entropy of Silver Nitrate from 15 to 300°K. The Heat and Free Energy of Solution in Water and Dilute Aqueous Ammonia. The Entropy of Silver Ammonia Complex Ion

BY WENDELL V. SMITH, OLIVER L. I. BROWN AND KENNETH S. PITZER

The data necessary to compute an accurate value for the free energy of solution and free energy of formation of crystalline silver nitrate are complete except for a calorimetric determination of the heat of solution and entropy of the salt. In view of this we have determined the heat capacity of the solid over the temperature interval from 15 to 300°K. and from this have calculated its entropy. We have determined its heat of solution in water and, by combining these and previously available data, have calculated its free energy of solution and the free energy of formation of solid silver nitrate from its elements. We have also determined the heat of solution of silver nitrate in dilute aqueous ammonia and, by combining this with other data already available, have obtained a value for the entropy of aqueous silver ammonia complex ion.

Material.—A "chemically pure" grade of silver nitrate was recrystallized from distilled water and dried in an oven at 130°C. for thirty-six hours. The heat capacity measurements through the ice-point showed that it contained not more than 0.02% water.

Heat Capacity Measurements.—The heat capacity measurements were made with a calorimeter and cryostat similar to that described by Latimer and Greensfelder.[1] In calculating the heat capacities and in the subsequent heat of solution calculations one calorie was taken equal to 4.1833 int. joules, and the molecular weight of silver nitrate was taken as 169.89. Measurements were made on a sample of 193.57 g. (weight *in vacuo*) of the silver nitrate. The results are given in Table I and shown as a function of temperature in Fig. 1.

TABLE I

MOLAL HEAT CAPACITY OF SILVER NITRATE

T, °K.	C_p Cal./deg./mole	T, °K.	C_p Cal./deg./mole
13.25	1.14	140.02	16.56
15.16	1.60	145.32	16.81
18.01	2.20	150.93	17.03
21.38	2.86	156.78	17.24
24.27	3.40	164.02	17.54
27.32	4.10	169.40	17.70
30.61	4.84	175.05	17.90
34.62	5.56	180.71	18.18
38.78	6.43	186.66	18.41
52.87	9.00	192.59	18.62
58.18	9.76	198.74	18.87
63.29	10.61	205.03	19.12
68.51	11.31	211.54	19.38
74.01	11.95	218.31	19.61
80.09	12.62	225.37	19.83
86.23	13.19	232.31	20.11
92.01	13.68	239.15	20.30
97.76	14.15	246.22	20.55
108.12	14.91	253.77	20.79
113.35	15.27	261.50	21.06
118.78	15.57	268.76	21.35
124.16	15.81	275.78	21.65
129.18	16.03	283.46	21.82
134.34	16.32	291.36	22.05
		296.62	22.19

Entropy of Silver Nitrate.—The entropy was calculated by the graphical integration of a plot of C_p *vs.* log T, combined with an extra-

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[1] Latimer and Greensfelder, THIS JOURNAL, 50, 2202 (1928).

polation to 0°K., using the Debye specific heat equation. The calculation is summarized in Table II.

TABLE II

MOLAL ENTROPY OF SILVER NITRATE

0–14.13°K.	Debye extrapolation	0.54
14.13–298.1°K.	Graphical from data	33.14 ± 0.1
	Entropy at 298.1°K.	33.68 e. u.

Heat of Solution of Silver Nitrate.—The heat of solution was measured in a calorimeter consisting of a vacuum flask equipped with a resistance thermometer and electrical calibration heater.[2]

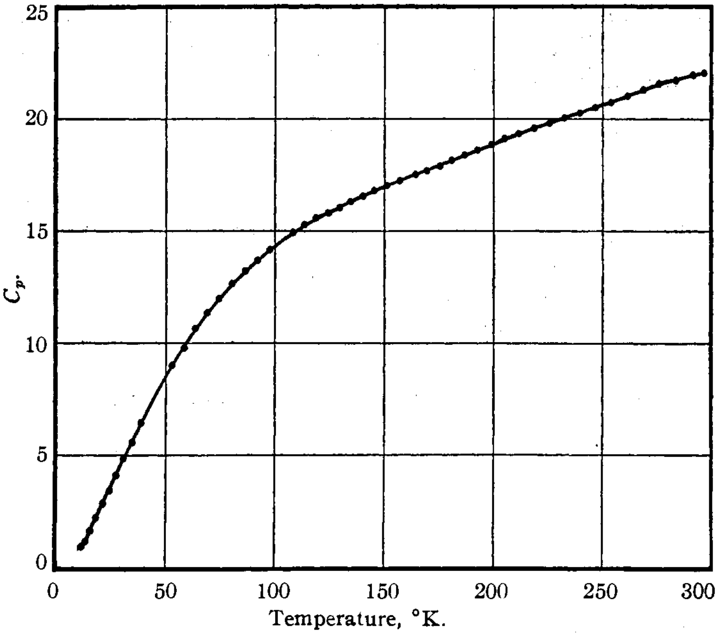

Fig. 1.—Molal heat capacity of solid silver nitrate in calories per degree.

The value found for the integral heat of solution at 298.1°K. of one mole of silver nitrate in 6500 moles of water (0.0085 *M*) was 5385 ± 50 cal. Combining this with an estimated heat of dilution gives $\Delta H^\circ = 5360 \pm 50$ cal. for the heat of solution of one mole of silver nitrate in an infinite amount of water.

Entropy and Free Energy of Solution of Silver Nitrate.—Using the known entropies of silver ion[3] and nitrate ion,[4] and the entropy of silver nitrate determined above, we find the entropy change when one mole of solid silver nitrate at 298.1°K. dissolves to form a hypothetical one molal solution to be

$$\Delta S^\circ = S^\circ_{Ag^+} + S^\circ_{NO_3^-} - S^\circ_{AgNO_3} = 18.4 + 35.0 - 33.7 = 19.7 \text{ e. u.}$$

By combining this with the heat of solution given above, we are able to calculate an accurate value for the free energy of solution. Thus, the change in free energy at 298.1°K., when one mole of solid silver nitrate dissolves to give a solution of unit activity, is found to be

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ = -510 \pm 100 \text{ cal.}$$

It is interesting to compare this value with another value which can be obtained from entirely independent data. The equilibrium reaction

$$2AgNO_2(s) = AgNO_3(s) + Ag(s) + NO(g) \quad (1)$$

has been studied recently by Randall, Manov and Brown,[5] and we are grateful to them for supplying us in advance of publication with their tentative value of $\Delta F^\circ_{298.1} = 4200$ cal. for this reaction. The change in free energy for the reaction

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

is 3600 cal.[6a] Subtracting the free energy change for reaction (1) from that for (2) gives −600 cal. for the free energy of solution of silver nitrate at 298.1°K.

The Free Energy of Formation of Solid Silver Nitrate.—From the free energy of formation of silver ion,[6b] of nitrate ion,[4] and the free energy of solution given above we obtain for the free energy of formation of solid silver nitrate from the elements

$$\Delta F^\circ_{298.1} = \Delta F^\circ_{Ag^+} + \Delta F^\circ_{NO_3^-} - \Delta F^\circ_{sol.} = 18{,}450 - 26{,}310 + 510 = 7350 \pm 150 \text{ cal.}$$

The Heat of Solution of Silver Nitrate in Aqueous Ammonia Solution and the Entropy of Silver Ammonia Complex Ion.—Using the calorimeter referred to above, the integral heat of solution of one mole of silver nitrate in a 0.14 *M* aqueous ammonia solution to form a solution 0.024 *M* with respect to silver nitrate was found to be −8020 ± 60 cal. By subtracting from this value the integral heat of solution in water to form a 0.0085 *M* solution, and neglecting the small heat of dilution, we obtain $\Delta H^\circ_{298.1} = -13{,}400 \pm 100$ cal. for the reaction

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(2) A complete description of this apparatus will appear in a future publication.

(3) Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1934).

(4) Brown, Smith and Latimer, to be published.

(5) Randall, Manov and Brown, unpublished data.

(6) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929. (a) Vol. VII, p. 269; (b) Vol. VII, p. 265; (c) Vol. V, p. 213 and Vol. VII, p. 240.

$$\mathrm{Ag^+ + 2NH_3(aq.) = Ag(NH_3)_2{}^+} \qquad (3)$$

The free energy change for this reaction may be obtained from the following

$\mathrm{AgCl(s) + 2NH_3(aq.) = Ag(NH_3)_2{}^+ + Cl^-}$; $\Delta F^\circ = 3472$ cal.[6a] (4)

$\mathrm{Ag^+ + Cl^- = AgCl(s)}$; $\Delta F^\circ = -13{,}329$ cal.[3] (5)

The sum of the free energy changes for reactions (4) and (5) gives $\Delta F^\circ_{298.1} = -9857$ cal. for reaction (3). Combining this with $\Delta H^\circ_{298.1}$ gives the change in entropy for reaction (3) to be

$$\Delta S^\circ = (-13{,}400 + 9857)/298.1 = -11.9 \pm 0.5 \text{ e. u.}$$

Reaction (3) may be considered as the replacement of two bound water molecules by ammonia molecules. Since the ammonia molecules are undoubtedly more tightly bound and the entropy of aqueous ammonia is greater than that of water, one would expect a considerable decrease in entropy for this reaction, as is found experimentally.

The heat and free energy of solution of gaseous ammonia in water at 298.1°K. as given in the "International Critical Tables"[6c] are −8290 and −2390 cal., respectively, from which the entropy of solution may be calculated to be $\Delta S^\circ = -19.8$ e. u. Combining this value with the entropy of gaseous ammonia at 298.1°K., 45.9 e. u.,[7] the entropy for $\mathrm{NH_3}$(aq.) is found to be $S^\circ_{298.1} = S^\circ_{\mathrm{NH_3(g)}} + \Delta S^\circ_{\mathrm{sol.}} = 26.1$ e. u. Using this value in combination with the entropy of silver ion[3] and the entropy change for reaction (3) we find the entropy of aqueous silver ammonia complex ion to be

$$S^\circ_{298.1} = 2S_{\mathrm{NH_3(aq.)}} + S_{\mathrm{Ag^+}} + \Delta S^\circ = 58.7 \pm 1.0 \text{ e. u.}$$

Summary

The heat capacity of silver nitrate has been determined from 15 to 300°K., and the entropy of the salt at 298.1°K. has been found to be 33.68 e. u. The heat of solution of silver nitrate in water and in dilute aqueous ammonia has been measured at 298.1°K. The free energy of solution of silver nitrate has been calculated to be −510 cal./mole, and the free energy of formation of the solid from its elements calculated to be −7350 cal./mole. The entropy of aqueous silver ammonia complex ion has been calculated to be 58.7 e. u. at 298.1°K.

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(7) Overstreet and Giauque, THIS JOURNAL, 59, 254 (1937).

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA

Studies on Aging of Fresh Precipitates. XIII. The Aging of Freshly Precipitated Silver Chloride as Indicated by the Adsorption of Wool Violet

BY I. M. KOLTHOFF AND HENRY C. YUTZY[1]

The term "aging" has been used in a collective sense involving any changes occurring in a precipitate after it has been formed. In previous studies with lead sulfate[2] and barium sulfate[3] we have been concerned mainly with the "self-perfection" of micro-crystalline particles, aged under various conditions. In these cases, under the conditions studied, changes in the external surface were found to be relatively small. In the present study, with silver chloride, it was found that upon aging of freshly precipitated silver chloride in the mother liquor, a very pronounced reduction of the total surface occurred.

Changes in the external surface of a precipitate can be followed by measuring the amount of a dye adsorbed upon precipitates of various ages. The dye used, wool violet 4BN, was found to be strongly adsorbed by silver chloride. It consists of a large molecule so that the amount adsorbed is probably a measure of the external surface only. Attempts to make use of smaller molecules in order to measure the internal surface, not accessible to the large dye molecule, were abortive.

The adsorptions of such substances as ammonia, aniline, *p*-nitrophenol, picric acid, urea and others[4] on silver chloride were found to be so small that the difficulty in determining the amounts adsorbed made their use impractical. Attempts to follow the changes in surface by means of photomicrographs were unsuccessful, mainly because the very small particles quickly agglomerated into undistinguishable clumps.

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(1) From a thesis presented to the Graduate School of the University of Minnesota by H. C. Yutzy in partial fulfilment of the requirements for the degree Doctor of Philosophy, June, 1936.

(2) I. M. Kolthoff and C. Rosenblum, THIS JOURNAL, 56, 1264 (1934).

(3) G. Noponen, Thesis, Univ. of Minnesota, 1936.

(4) For details see thesis of the junior author.