Mr. C. Beeson for samples used in this investigation, and to Professor Linus Pauling for his constant interest and his criticism. One of us (J. A. A. K.) is indebted to the Netherland-America Foundation for a gift enabling him to stay at the California Institute of Technology while carrying out this investigation.

Summary

The arrangements of atoms in the molecules of nitrosyl chloride and nitrosyl bromide have been determined by electron diffraction, the interpretation being made both by the radial distribution method and by the usual visual method. The following results were obtained—nitrosyl chloride: Cl–O = 2.65 ± 0.01 Å., Cl–N = 1.95 ± 0.01 Å., N–O = 1.14 ± 0.02 Å., angle Cl–N–O = 116 ± 2°; nitrosyl bromide: Br–O = 2.85 ± 0.02 Å., Br–N = 2.14 ± 0.02 Å., N–O = 1.15 ± 0.04 Å., angle Br–N–O = 117 ± 3°.

The surprisingly large halogen–nitrogen distances found are explained as caused by resonance between the normal covalent structure and the ionic structure.

LEYDEN, THE NETHERLANDS
PASADENA, CALIF.
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Silver Oxide: Heat Capacity from 13 to 300°K., Entropy, Heat of Solution, and Heat and Free Energy of Formation. The Heat of Formation and Entropy of Silver Ion

BY KENNETH S. PITZER AND WENDELL V. SMITH

A knowledge of the heat capacity of silver oxide makes possible a number of valuable thermodynamic calculations. In the light of our measurements of this heat capacity we have reconsidered the data on the dissociation pressure of silver oxide,[1] obtaining thereby values for both the heat and free energy of formation in which the uncertainties have been largely removed. Also we have calculated the heat of formation and entropy of silver ion, basing them principally on our determinations of the entropy and heat of solution of silver oxide. The results are particularly important because the thermodynamic constants of many silver compounds are dependent either on the constants for silver ion or on those for the oxide.

Material.—The first series of heat capacity measurements was made on a sample of a "reagent" grade of silver oxide which was dried at 110°C. for several days. Analyses for both silver content and acid neutralizing power gave between 99.8 and 100.0% of the theoretical value, while the absence of a hump in the heat capacity curve near the ice-point indicates the absence of a significant amount of water. The subsequent heat capacity measurements and the heat of solution measurements were made on samples prepared by precipitation from a dilute solution of "C. P." silver nitrate with a solution of carbonate-free sodium hydroxide. The sample used for the heat capacity work was washed, then dried and analyzed as above, the results being within 0.5% of the theoretical. In order to increase the rate of solution, the samples for heat of solution measurements were, after repeated washing, left under water until used. The amount of silver oxide was determined by analysis of the resulting solutions.

The Heat Capacity.—The heat capacity measurements were made with a calorimeter and cryostat similar to that described by Latimer and Greensfelder.[2] In the calculation of both heat capacities and heats of solution one calorie was taken equal to 4.1833 int. joules. The absolute temperature of the ice-point was assumed to be 273.10°K.

The first series of measurements, which were made on 179.60 g. of Sample I, showed a region of high heat capacity between 20 and 45°K. In order to confirm and investigate this region further, additional measurements were made on 158.30 g. of a different sample of silver oxide, using a new calorimeter. These results leave no possible doubt concerning the existence of high heat capacities in this region, but also indicate that equilibrium is not obtained readily with respect to the additional heat capacity. The

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[1] (a) Lewis, THIS JOURNAL, **28**, 139 (1906); (b) Keyes and Hara, *ibid.*, **44**, 479 (1922); (c) Benton and Drake, *ibid.*, **54**, 2186 (1932).

[2] Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928).

results are given in Table I and are shown graphically in Figs. 1 and 2. To avoid confusion only the results of the first two series and those on the smooth, supercooled curve are given in Fig. 1. The values of ΔC_p given in the table are the deviations of the heat capacity from the smooth curve in the abnormal region. These deviations are plotted in Fig. 2. The lines in Fig. 2 are intended merely as an aid in following the points of a given series and not as an accurate indication of the heat capacities.

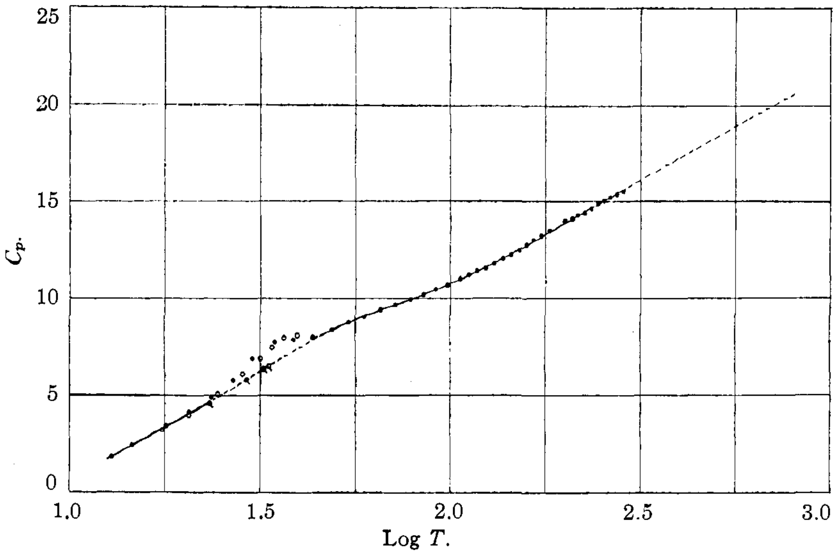

Fig. 1.—Molal heat capacity of solid silver oxide in calories per degree: ●, series I; ○, series II; ♀, supercooled (first two points of series V and special runs).

Since equilibrium is slow in the region from 25 to 45°K., the treatment preceding the various series of measurements is of interest. Series I started after cooling to 10.8°K. and remaining near that temperature for about one hour. Before series II the treatment was similar except that the lowest temperature attained was 11.8°K. Before Series III the silver oxide was held at 20° for seven hours, while preceding series IV it had been cooled slowly to 24°K. Series V was started after holding the sample near 32° for seven hours. Series VI began immediately after rapid cooling to 32°K. In Series VII the sample was held below 27° for ten hours, then cooled to 14° for one and one-half hours before starting measurements. Before Series VIII the sample, after being cooled, warmed from 12.5 to 14.5°K. during four hours, whereupon measurements were begun. The calorimeter and sample were held for three hours at 13.5°K. before Series IX. In each case the silver oxide had been warmed above 45°K. before cooling. The special runs were commenced immediately after rapid cooling to the initial temperature of the run.

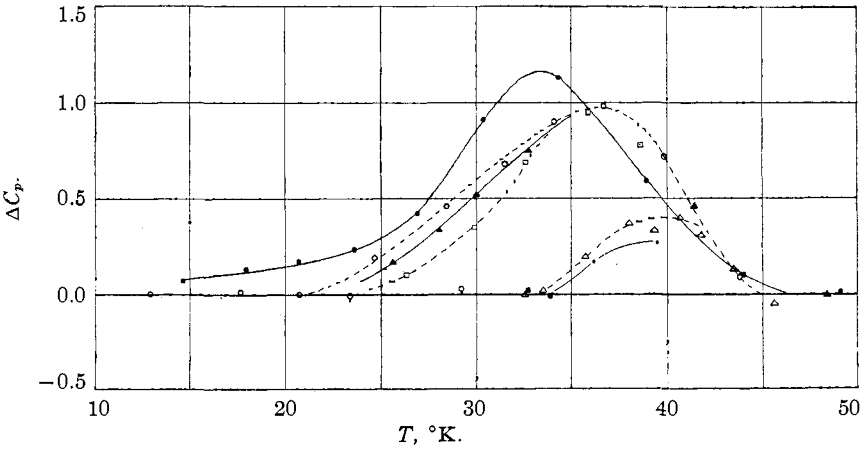

Fig. 2.—Deviations of the heat capacity of silver oxide from the smooth curve of Fig. 1: ●, series I; ○, series II; ▲, series III; □, series IV; △, series V; ■, series VI; ♀, special runs.

It is apparent from a consideration of these results that for any given amount of energy connected with these extra degrees of freedom (anomalous heat capacity), there is a region of indifference of a few degrees within which this energy neither increases nor decreases at an appreciable rate. In Series V, for example, the temperature was raised at least two degrees before any extra heat was absorbed; however, the later points of this series show definitely high heat capacities. Series VI gave similar results. This effect is further evidenced by the low points, designated by asterisks in Table I, in which the sample was allowed to cool appreciably between heat capacity runs. In other words, it is possible to cool to any portion of this region and the first measurement will not show the high heat capacity characteristic of the region, even if the initial temperature is maintained for many hours as in Series V.

TABLE I

MOLAL HEAT CAPACITY OF SILVER OXIDE

Measurements above 50°K., All Series I

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
54.01	8.77	151.53	12.51
59.50	9.05	158.75	12.76
65.35	9.40	166.26	13.01
71.73	9.67	174.32	13.25
78.40	9.95	182.29	13.50
84.74	10.19	200.67	14.01
91.33	10.47	208.78	14.14
98.26	10.68	216.90	14.34
106.11	10.99	225.12	14.41
111.86	11.23	234.97	14.65
117.91	11.43	244.30	14.98
124.11	11.59	253.43	15.08
130.56	11.82	263.80	15.24
137.32	12.06	274.77	15.39
144.66	12.27	285.30	15.50

Measurements below 50°K.

T, °K.	C_p, cal./deg. mole	ΔC_p	ΔT	Power, cal./min.
		Series I		
14.65	2.40	0.07	3.91	1.56
17.90	3.37	.13	2.70	1.52
20.71	4.12	.17	2.90	1.49
23.64	4.86	.23	2.95	1.43
26.90	5.73	.42	3.30	3.15
30.35	6.87	.91	3.52	3.02
34.31	7.73	1.13	4.41	2.84
38.91	7.83	0.59	4.80	4.70
44.03	7.95	.10	5.40	4.29
49.11	8.37	.01	4.71	3.94
		Series II		
12.90	1.81	0.00	2.06	0.47
17.63	3.18	.01	2.79	1.48
20.69	3.94	.00	3.56	1.40
24.61	5.02	.19	4.38	2.75
28.45	6.08	.46	3.29	2.50
31.52	6.84	.68	2.70	2.31
34.08	7.46	.90	2.29	2.14
36.72	7.92	.98	2.85	3.76
39.85	8.06	.72	3.35	3.37
43.78	7.91	.09	4.50	2.97
		Series III		
25.59	5.22	0.17	2.85	1.23
28.04	5.88	.34	2.00	1.18
29.98	6.41	.52	1.74	1.11
31.34	6.48	.36*	1.99	1.07
32.76	7.11	.75	0.85	0.30
35.16	7.47	.75*	.73	.27
41.39	8.00	.46	1.40	.80
		Series IV		
26.34	5.30	0.10	3.93	2.60
29.89	6.22	.35	3.06	2.38
32.63	7.03	.69	2.45	2.15
33.66	7.05	.55*	2.44	2.15
35.89	7.77	.95	2.07	2.01
38.62	7.99	.78	3.43	3.43
		Series V		
32.48	6.31	0.00	0.82	0.26
33.50	6.49	.02	1.08	.23
35.68	7.00	.20	3.15	2.20
37.96	7.48	.37	1.47	0.92
39.36	7.62	.33	1.33	.84
40.68	7.86	.40	0.95	.93
41.81	7.91	.31	1.21	3.20
43.50	7.92	.13	1.53	3.03
45.63	7.97	−.05	2.79	2.78
48.41	8.30	.00	3.14	2.61
		Series VI		
32.71	6.37	0.02	1.27	1.01
33.94	6.53	−.01	1.23	1.00
36.22	7.04	.17	3.17	3.72
39.49	7.58	.27	3.43	3.25
		Series VII		
17.73	3.09	−.10	4.10	1.58
56.17	8.93	.00	4.44	4.96
		Series VIII		
15.35	2.39	−0.11	1.24	0.37
16.78	2.80	− .09	1.48	.35
53.89	8.81	.05	4.74	5.22
		Series IX		
31.09	6.75	0.67	1.37	1.16
32.56	7.09	.77	1.23	1.09
		Special Runs		
29.17	5.78	0.03	1.29	1.24
23.36	4.54	−.01	0.87	0.33

* Results thus designated are too low, as explained in the text, and are omitted from Fig. 2.

It is to be noted in comparing Series I to VI that the points are progressively higher as the initial temperature of the series is decreased. This at once raises the question whether there is more heat associated with these extra degrees of freedom than was obtained in either Series I or II. This is difficult to answer without making a series of measurements in which the initial temperature is considerably lower than that in any of these series. However, it seems quite improbable that there can be an appreciable amount of such heat in excess of that already found when one notes that in Series III, before which the sample was cooled only to 20°K., the heat capacities are only slightly smaller than in Series II, while even in Series IV where the initial temperature was 24° the difference is not very large. On the other hand, a very large difference is noted between Series IV and V.

In order further to confirm the total amount of heat associated with this "hump," two measurements of the total energy required to raise the temperature from about 20 to 50°K. were made in Series VII and VIII. In these measurements the current through and the potential across the calorimeter heater were measured simultaneously on two White potentiometers. The power was then computed for each minute of the thirteen-minute heating period, and an average taken which gave the total energy input with great accuracy. The resistance and thereby the temperature of the heater, which comprises the greater portion of the external surface of the calorimeter, was also obtained for each minute of the run, thus enabling accurate corrections to be made for energy exchange with the surroundings. The results are given in Table II, together with values of the total extra heat absorbed in Series I and II. These latter values were computed by summing the products of the extra heat capacity times the difference between the final temperature of the given run and the final temperature of the preceding run. Values of the extra entropy of Series I and II, computed in an analogous manner, are also included.

TABLE II

TOTAL EXTRA HEAT AND ENTROPY ABOVE THE NORMAL CURVE IN THE REGION 20 TO 50°K.

Series	Total heat, 20–50°, cal.	Extra heat, cal.	Extra entropy, cal./deg.
I	209.2	14.2	0.48
II	206.9	11.9	.35
VII	205.8	10.8	
VIII	206.6	11.6	

With Series II and VIII, where the previous treatment of the sample was similar and the same sample and calorimeter were used, the agreement is very satisfactory. The somewhat higher initial temperature can account for the difference between Series VII and VIII. The higher value obtained in Series I is less easily understood. Consideration of the other results indicates that the slightly lower initial temperature can account for only a fraction of the difference between I and II. The fact that a different sample was used might also contribute to a small extent, because of the presence of small but appreciable amounts of impurities. Although their amount in per cent. was small, it is conceivable that they might have an exaggerated effect on an anomaly such as this. The difference in the shape of the heat capacity curves between Series I and II is more easily attributable to the effect of impurities, especially in view of the fact that the various series made with the second sample show similar shapes of curves.

Another source of uncertainty in the entropy (but not the heat content) is the possibility that the true equilibrium temperature might be appreciably lower than the temperature at which the heat was actually absorbed, *i. e.*, the upper limit of the region of indifference. In the case of ordinary transitions between phases, appreciable superheating is not commonly possible even though supercooling may occur. However, the present case is clearly not an ordinary transition, so that the value of this analogy is very questionable. The fact that the heat capacities of Series V approach those of Series II a few degrees after the beginning of the series indicates that there can be no extensive superheating. In any event the various sources of error could hardly contribute more than 0.2 cal./deg. in the total entropy at higher temperatures. It should be emphasized also that this anomalous heat capacity is far from completely understood and that further investigations are desirable. Somewhat similar effects have been reported for acetone[3] and manganese dioxide.[4]

Thermodynamic Functions for Silver Oxide.—The heat content and entropy were calculated by graphical integration, using the smooth curve in the region 20–50°K. The extrapolation to the absolute zero was made with the aid of the Debye specific heat equation. The contribution of the "hump" was separately added. These calculations are summarized in Table III. The highest value attainable from our measurements is given as the entropy under the hump since the uncertainties mentioned above tend to make it too small.

The dissociation pressure of silver oxide has been measured at temperatures ranging from 440 to 770°K. so that in discussing this equilibrium it is necessary to calculate the free energy function for this temperature range. In the absence of high temperature heat capacity data for silver oxide we have assumed the curve shown dotted

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(3) Kelley, THIS JOURNAL, **51**, 1145 (1929).

(4) Millar, *ibid.*, **50**, 1875 (1928).

TABLE III

THERMODYNAMICS FUNCTIONS FOR SILVER OXIDE

		S^0	$H^0-H_0^0$
0–15°K.	Debye extrapolation	0.97	10.7
15–298.1°K.	Graphical (smooth curve)	27.64	3402.1
15–50°K.	Extra-under hump	0.48	14.2
Value of function at 298.1°K.		29.09 ± 0.2	3427.0 ± 5

$(H_0^0 - F^0)/T = S^\circ - (H^0 - H_0^0)/T = 17.60\pm0.2$ at 298.1°K.

in Fig. 1. The reasonableness of this curve was verified by comparison with the data for similar compounds, and it is further justified by the constancy of the resulting ΔH_0^0's. The free energy function obtained by combining this heat capacity curve with the value of the function at 298.1° is

$$(H_0^0 - F^0)/T = 33.623 - 146.3/T + (12.782 \log T - 37.907)\log T$$

The free energy function for silver at 298.1°K. was calculated from the heat capacity[5] by graphical methods, and was extended to higher temperatures, using the equation given by Kelley[6]

$$C_p = 5.60 + 1.50 \times 10^{-3}T$$

The resulting equation for the free energy is

$$(H_0^0 - F^0)/T = -27.765 + 360/T + 12.90 \log T + 0.75 \times 10^{-3}T$$

The free energy function for oxygen has been calculated by Johnston and Walker.[7]

The dissociation pressures[1] are given in column 2 of Table IV. Since some of the pressures are large it is necessary to correct to the fugacities, which in turn requires an equation of state for oxygen. While such an equation has been given by Keyes and Hara,[1b] we believe that the following equation, which is based on the data of Amagat,[8] is fully as satisfactory for the present purpose and is considerably more convenient:

$$\left(P + \frac{4.0 \times 10^7}{V^2T^{2/3}}\right)(V - 25.1) = RT$$

where P is in atm. and V in cc. per mole. Since this equation is at any given temperature of the van der Waals form we may use the following equation[9] to calculate the fugacities

$$\ln f = \ln \frac{RT}{V-b} + \frac{b}{V-b} - \frac{2a}{RTV}$$

The resulting fugacities are given in column 3 of Table IV.

Due to the high pressures involved in these experiments, the activities of the solids differ considerably from unity. The corrections arising from this source, which are given in column 4, were calculated from the equation[9]

$$R \ln \frac{\alpha_{Ag_2O}}{\alpha^2_{Ag}} = \frac{1}{T}\int_1^P (V_{Ag_2O} - 2V_{Ag})dP$$

where α_{Ag_2O} and α_{Ag} are the activities of silver oxide and silver, respectively, and the V's refer to the molal volumes. In using this equation $(V_{Ag_2O} - 2V_{Ag})$ was taken as constant and equal to 11.3 cc. Column 5 of the table gives the standard free energy change for the decomposition reaction. The values of ΔH_0^0 given in the last column are, of course, calculated from the values of $\Delta(H_0^0 - F^0)/T$ and $\Delta F^0/T$ given in the preceding columns.

TABLE IV

FREE ENERGY OF DISSOCIATION OF SILVER OXIDE

T, °K.	P_{O_2}, atm.	f_{O_2} atm.	$R \ln \frac{\alpha_{Ag_2O}}{\alpha^2_{Ag}}$	$-\frac{\Delta F^0}{T}$	$\frac{\Delta(H_0^0 - F^0)}{T}$	ΔH_0^0, cal.
Data of Lewis[1a]						
575.1	20.5	20.6	0.010	2.996	15.03	6919
598.1	32.0	32.2	.015	3.435	15.02	6929
718.1	207.0	219.9	.080	5.278	14.95	6944
Data of Keyes and Hara[1b]						
647.1	74.3	75.9	0.032	4.269	15.00	6944
676.1	114.5	118.3	.047	4.696	14.99	6957
725.1	213.5	226.9	.081	5.309	14.95	6987
740.8	257.8	276.8	.096	5.491	14.93	6993
757.1	323.5	355.5	.118	5.718	14.92	6965
773.1	388.3	434.6	.138	5.897	14.91	6965
Data of Benton and Drake[10]						
446.1	0.555	0.555	0.000	−0.590	14.96	6936
451.1	.670	.670		− .398	14.97	6934
456.2	.796	.796		− .227	14.98	6934
461.3	.943	.943		− .060	14.98	6938
464.3	1.039	1.039		+ .039	14.99	6939
					Accepted value	6940

In selecting the final value of ΔH_0^0 for the dissociation of silver oxide most weight was given to the data for pressures below 100 atm. In this region the magnitude of the special corrections for high pressure is small, and the uncertainty in the free energy function of silver oxide due to the extrapolation of the heat capacity to higher temperatures is also small. The values of ΔH_0^0 in this region show no drift with temperature, nor are there significant differences between the results of the various observers. The satisfactory

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[5] Kelley, *Bur. of Mines* Bull. 350 and 394, gives various references.

[6] Kelley, *ibid.*, Bull. 371. We wish to thank Dr. George Manov for the value of $(H_0^0 - F^0)/T$ at 298.1°K.

[7] Johnston and Walker, THIS JOURNAL, **55**, 172 (1933).

[8] Amagat, *Ann. chim. phys.*, **29**, 68 (1893).

[9] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 196.

agreement of the ΔH_0^0's obtained from the measurements at higher pressures and temperatures may be considered as a confirmation of the extrapolated heat capacity curve for silver oxide. We thus obtain the following thermodynamic constants for the formation of silver oxide at 298.1°K.

$$\tfrac{1}{2}\,O_2 + 2Ag = Ag_2O$$
$$\Delta F^0_{298.1} = -2585 \text{ cal.}$$
$$\Delta H^0_{298.1} = -7301 \text{ cal.}$$
$$\Delta S^0_{298.1} = -15.82 \text{ cal./deg.}$$

This value of ΔF^0 may be compared with the result obtained from the following data, all at 298.1°K.

$2Ag + 2H^+ + 2Cl^- = 2AgCl + H_2$	$\Delta F^0 = 10{,}259$[10] cal.
$2AgCl + 2OH^- = Ag_2O + H_2O + 2Cl^-$	$\Delta F^0 = 5{,}596$[11]
$2H_2O = 2H^+ + 2OH^-$	$\Delta F^0 = 38{,}186$[12]
$H_2 + \tfrac{1}{2}O_2 = H_2O$	$\Delta F^0 = -56{,}690$[13]
$2Ag + \tfrac{1}{2}O_2 = Ag_2O$	$\Delta F^0 = -2{,}649$

The difference of 64 cal. between the free energies obtained in the two ways is not large, but it is perhaps more than might be expected since all the data upon which these calculations are based are of considerable accuracy.

The Heat of Solution of Silver Oxide.—The heat of solution of silver oxide in dilute nitric acid was measured in a calorimeter described elsewhere by one of the authors.[14] As is explained above, the samples of freshly prepared and thoroughly washed silver oxide were left under water until used. They were placed in small, breakable glass bulbs which contained only a fraction of a cubic centimeter of water around the oxide. The bulbs were then placed in the calorimeter, and were broken under the surface of the nitric acid at the proper moment. The time required for all the oxide to dissolve was of the order of ten minutes. Five determinations of the heat capacity of the calorimeter were made, the maximum deviation from the mean being 0.2%. The results of the four solution measurements are presented in Table V. The amount of oxide was determined in each case by analysis of the resulting solution for silver. At least two analyses were made of each solution, the results being concordant within 0.1%. In each case the total volume of nitric acid was 884 ml. The uncertainties given for the individual results in Table V were determined by the amount of reaction in each case.

TABLE V

THE HEAT OF SOLUTION OF SILVER OXIDE IN DILUTE NITRIC ACID

Concn. of acid, *M*	Amount of oxide, moles	Molal heat of solution, cal.
0.10	0.00243	10,750 ± 300
.10	.006704	10,470 ± 110
.10	.008349	10,400 ± 90
.05	.007954	10,420 ± 90
	Accepted value	10,430 ± 60

Since the highest concentration of silver ion obtained was less than 0.02 molal, and because each silver ion in the final solution replaced a hydrogen ion in the initial solution, the difference in heat of dilution between the initial and final solutions may be expected to be small. The satisfactory concordance of the results for different concentrations of silver and acid is in agreement with this view.

The Heat of Formation and Entropy of Silver Ion.—Latimer, Schutz and Hicks[15] calculated a value for the entropy of silver ion, using data which were accurate with the exception of the heat of solution of silver chloride determined by Lange and Fuoss.[16] This value was obtained by precipitation methods and was a preliminary value, only roughly corrected for heats of dilution. The reagents employed were silver nitrate and potassium chloride solutions, the latter being the more concentrated. The final solution was virtually pure potassium nitrate in each experiment. If we assume the heats of dilution of silver and potassium nitrates to be approximately the same at 0.15 molal concentration or less, and use the known heats of dilution of potassium chloride,[17] we obtain the results given in Table VI.

TABLE VI

HEAT OF SOLUTION OF SILVER CHLORIDE AT 22.5°
(Based on data of Lange and Fuoss[16])

No. of expt.	Concn. $AgNO_3$, *M*	Concn. KCl, *M*	Average heat pptn., cal.	Heat of diln. of KCl, cal.	Heat of soln. at ∞ diln., cal.
3	0.1482	1.607	15,722	−125	−15,847
3	.0988	1.072	15,769	− 50	−15,819
4	.0493	0.535	15,864	+ 40	−15,824
			Accepted value at 22.5°C.		−15,830
			Accepted value at 25.0°C.		−15,740

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[10] Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

[11] Randall and Halford, *ibid.*, **52**, 178 (1930).

[12] Harned and Mannweiler, *ibid.*, **57**, 1873 (1935).

[13] Obtained from the heat of formation (Bichowsky and Rossini, "Thermochemistry," Reinhold Pub. Co., New York, 1936) and entropy of formation (see refs. 5 and 7 and discussion in text below).

[14] Pitzer, THIS JOURNAL, **59**, 2365 (1937).

[15] Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1934).

[16] Lange and Fuoss, *Z. physik. Chem.*, **125**, 431 (1927).

[17] (a) Rossini, *Bur. Standards J. Research*, **6**, 791 (1931); (b) Landolt-Börnstein Tabellen.

The free energy of solution of silver chloride can be obtained either from the directly measured solubility product or the difference between the silver–silver ion,[9] (p. 414) and the silver–silver chloride[10] electrode potentials. Using the latter method, we obtain for the reaction

$$\begin{aligned} \mathrm{AgCl} = \mathrm{Ag}^+ + \mathrm{Cl}^- \qquad \Delta F^0 &= 13{,}311 \text{ cal.} \\ \Delta H^0 &= 15{,}740 \\ \Delta S^0 &= 8.15 \text{ cal./deg.} \end{aligned}$$

and with the entropy of silver chloride[18] (22.97 ± 0.1) we obtain for silver ion: $S^0_{298.1} = 17.62 \pm 0.2$ cal./deg.

The data on silver oxide also permit the calculation of a value for the entropy of silver ion. The heat of solution was determined for the reaction

$$\mathrm{Ag_2O} + 2\mathrm{H}^+ = \mathrm{H_2O} + 2\mathrm{Ag}^+ \qquad \Delta H^0 = -10{,}430 \pm 60$$

The free energy change for the same reaction may be obtained as follows

$$\begin{array}{ll} \mathrm{Ag_2O} + \mathrm{H_2O} + 2\mathrm{Cl}^- = 2\mathrm{AgCl} & \\ \quad + 2\mathrm{OH}^- & \Delta F^0 = -5{,}596^{11} \text{ cal.} \\ 2\mathrm{AgCl} = 2\mathrm{Ag}^+ + 2\mathrm{Cl}^- & \Delta F^0 = 26{,}622 \\ 2\mathrm{H}^+ + 2\mathrm{OH}^- = 2\mathrm{H_2O} & \Delta F^0 = -38{,}186^{12} \\ \hline \mathrm{Ag_2O} + 2\mathrm{H}^+ = \mathrm{H_2O} + 2\mathrm{Ag}^+ & \Delta F^0 = -17{,}160 \text{ cal.} \\ & \Delta S^0 = 22.58 \text{ cal./deg.} \end{array}$$

The entropy of liquid water at 298.1°K. is 16.75 cal./deg. This can be obtained either from the low temperature calorimetric data of Giauque and Stout,[19] combined with the zero point entropy predicted by Pauling;[20] or from the spectroscopic entropy of steam[21] less the entropy of vaporization.[22] The two methods give results identical to 0.01 cal./deg. Combining this with the entropy of silver oxide given above we obtain for silver ion: $S^0 = 17.46 \pm 0.2$ cal./deg. The close agreement of this value with that obtained above is very satisfactory and as a final, best value we may take the average of the two: $S^0 = 17.54 \pm 0.15$ cal./deg. for Ag^+ at 298.1°K. Taking the free energy of formation of silver ion used above[9] (p. 414), together with the entropy of formation[5] we obtain

$$\begin{aligned} \mathrm{Ag} + \mathrm{H}^+ = \mathrm{Ag}^+ + {}^1\!/_2\mathrm{H_2} \qquad \Delta F^0 &= 18{,}441 \text{ cal.} \\ \Delta S^0 &= 22.96 \text{ cal./deg.} \\ \Delta H^0 &= 25{,}285 \pm 60 \text{ cal.} \end{aligned}$$

This value of the heat of formation of silver ion should be useful as a standard for obtaining the heat of formation of many silver compounds.

Summary

The heat capacity of silver oxide was measured from 13 to 300°K. and the entropy at 298.1 computed to be 29.09 cal./deg. mole. High heat capacities and slow equilibrium were found in the neighborhood of 30°K. Equations are given for the $(H^0_0 - F^0)/T$ function for silver oxide and silver. These were employed in correlating the data on the dissociation pressure of silver oxide, yielding values for its heat and free energy of formation. The heat of solution of silver oxide in dilute nitric acid was found to be 10,430 ± 60 cal. at 25°C. The heat of solution of silver chloride in water was recalculated from the data of Lange and Fuoss to be −15,740 cal. at 25°C. Values for the entropy of silver ion ($S^0 = 17.54 \pm 0.15$ cal./deg.) and the heat of formation of silver ion ($\Delta H^0 = 25{,}285 \pm 60$ cal.) were obtained.

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