

deed, it is possible to duplicate exactly the photoelectric characteristics of these metals by curves taken *in vacuo* in which the surface of the metal is partially covered with adsorbed ions. Taking curves of known ion density as a standard, the degree of dissociation of the different gases into ions is estimated.

Threshold measurements on surfaces of known ion density show the field of influence about an ion to extend out to many times its normal radius; at ten times the ion radius the field is of appreciable magnitude. This is true for both positive and negative ions, although the effect is opposite in sign.

It is suggested that the large field of force about the adsorbed ions might account for the phenomena generally attributed to "active centers," and, further, that the large effect of adsorbed ions on the work function of the surface might be responsible for poisoning and promoter action.

The observed ionization of nitrogen, hydrogen and ammonia on iron and platinum surfaces is shown to be in accord with an ionic mechanism for surface catalysis and with the activation results obtained in the glow discharge.

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

THE HEAT CAPACITY AND ENTROPY OF THALLOUS NITRATE FROM 17 TO 300° ABSOLUTE. THE ENTROPY AND FREE ENERGY OF NITRATE ION

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In a previous investigation² the entropy of nitrate ion was calculated from data on barium nitrate. A similar evaluation of the entropy of nitrate ion has now been made from data on thallos nitrate. A discrepancy of 1.6 entropy units has been found between the two results. As in the previous work in this field the entropy of the solid salt at 25° has been determined from specific heat measurements carried down to the temperatures of liquid hydrogen. The accuracy of these measurements is considerably greater than the discrepancy found in the two calculated values for the entropy of nitrate ion and attention must therefore be directed to a re-examination of the existing data which have been used in the barium nitrate evaluation.

¹ Du Pont Fellow in Chemistry, 1929-1930.

² (a) W. M. Latimer and J. E. Ahlberg, *Z. physik. Chem.*, **148**, 464 (1930). For references to details of theoretical and experimental method, see (b) Latimer and Buffington, *THIS JOURNAL*, **48**, 2297 (1926); (c) Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928); (d) Latimer and Kasper, *ibid.*, **51**, 2293 (1929).

Material.—The thallos nitrate was a mixture of two "c. p." samples from Eimer and Amend and C. A. F. Kahlbaum. This material was filtered and recrystallized four times. It was then dried at 65° for three weeks. The average of six precipitations with potassium iodide gave 100.0% of the theoretical amount of thallos iodide.

Thallos nitrate undergoes a transition at about 75° and the long heating at 65° was carried out to ensure complete transformation into the form stable at low temperatures. The authors are greatly indebted to Professor Linus Pauling and Dr. J. H. Sturdivant of the California Institute of Technology, who have made x-ray examinations of our sample and report that it gives a powder photograph which is identical with that of the low temperature modification.

Heat Capacity Measurements.—The measurements were made with a calorimeter and cryostat similar to that previously described.^{2c} Due apparently to repeated cooling, the bakelite, which cements the gold wire of the resistance thermometer to the walls of the calorimeter, loosened slightly during the course of the measurements and this gave rise to somewhat higher temperature heads during the energy input than had been previously obtained with this calorimeter. The maximum error which might have arisen from this source is less than 1% up to 140°K. and less than 3% from 140 to 300°K.; however, we believe it to be considerably less.

TABLE I

HEAT CAPACITY OF THALLOUS NITRATE (MOLECULAR WEIGHT 266.40)					
Mean <i>T</i> , °K.	ΔT	<i>C_p</i> /mole in cal./deg.	Mean <i>T</i> , °K.	ΔT	<i>C_p</i> /mole in cal./deg.
16.45	4.307	2.964	101.71	5.376	15.67
20.52	3.109	4.166	108.68	5.831	16.07
24.44	2.725	4.965	116.98	5.943	16.42
27.95	3.218	5.892	130.25	6.550	17.03
31.35	2.897	6.647	137.92	6.123	17.31
35.22	2.537	7.607	149.85	6.395	17.77
39.94	6.100	8.623	162.78	6.302	18.19
45.29	4.668	9.649	174.79	6.966	18.82
49.55	3.456	10.43	182.43	7.585	19.09
52.91	3.020	11.06	197.32	6.130	19.59
59.49	3.677	12.00	211.64	6.905	20.09
60.33	4.156	12.12	226.53	6.915	20.62
64.51	4.202	12.64	242.59	7.016	21.28
69.19	4.718	13.21	250.52	6.709	21.63
74.22	4.582	13.74	258.40	7.739	21.91
79.34	4.997	14.20	265.25	5.638	22.21
84.54	5.229	14.68	272.38	8.312	22.60
90.02	5.406	14.97	281.69	7.736	22.91
95.90	5.833	15.36	290.60	7.295	23.43

Entropy of Thallos Nitrate.—Figure 1 is the plot of *C_p* against log *T* from which the entropy has been obtained by the graphical integration

$S = \int_0^T C_p d \ln T$. A summary of the entropy calculation is given in Table II.

TABLE II

CALCULATION OF THE MOLAL ENTROPY OF THALLOUS NITRATE	
0-16.45°K. extrapolation	1.16
16.45-298.1°K. graphical from data	36.96
Entropy of thallos nitrate	<u>38.1 E. U.</u>

The maximum error arising from the cooling corrections is less than 0.6 entropy unit. The average deviations of the points on the C_p curve give, however, a calculated error of about 0.1 unit.

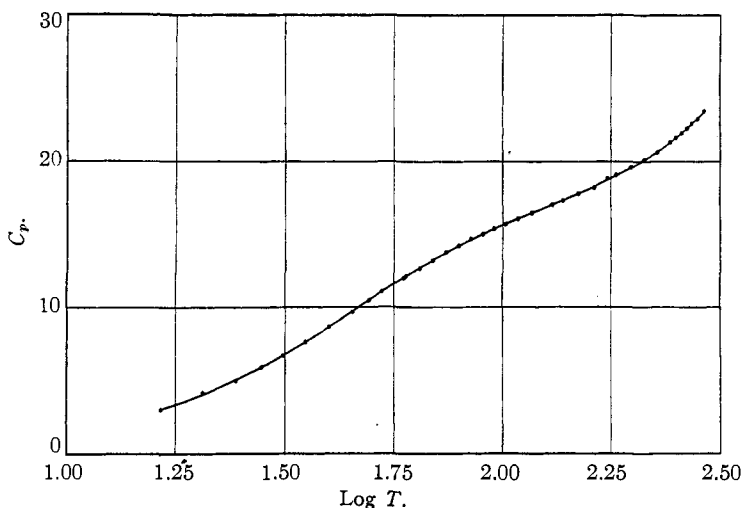


Fig. 1.—Molal heat capacity of thallos nitrate.

Entropy of Nitrate Ion.—The solubility of thallos nitrate at 25° is 0.434 M .³ The relative conductivities of solutions of thallos and silver nitrates and also activity data by Lewis and Randall indicate that the activity coefficient of thallos nitrate is slightly lower than that of silver nitrate, for which Lewis and Randall⁴ give 0.55 at 0.434 M . Hence we have chosen the value $\gamma = 0.50$ and calculate for the free energy of solution

$$\Delta F^\circ = -RT \ln (\Delta m)^2 = 1790 \text{ cal.}$$

Combining this with Thomsen's value for the heat of solution of thallos nitrate, $\Delta H = 9970$, we obtain for the entropy change, solid to form hypothetical one molal solution

³ Data from Berkeley, *Phil. Trans. Roy. Soc., London*, 203, 89 (1904); and Étard, *Ann. chim. phys.*, 2, 503 (1893).

⁴ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T} = \frac{9970 - 1790}{298.1} = 27.4 \text{ E. U.}$$

This gives for the sum of the entropies of nitrate and thallos ions, using the value obtained for the entropy of the solid, $27.4 + 38.1 = 65.5 \text{ E. U.}$

We now wish to express the entropy of nitrate ion in respect to $H^+ = 0$ and the most reliable method of carrying out this calculation employs the data for hydrochloric acid and thallos chloride. These have been summarized in Table III.

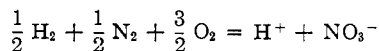
TABLE III

THE ENTROPY OF HYDROCHLORIC ACID AND THALLOUS CHLORIDE IN AQUEOUS SOLUTIONS

	Entropy of substance 298.1°K.	ΔH of soln., cal.	ΔF of soln., cal.	ΔS of soln., E. U.	Sum of ionic entropies, E. U.
HCl	44.7 ⁵	-17,750 ⁷	-8604 ⁸	-30.5	14.0
TlCl	25.8 ⁶	-10,100 ⁷	5086 ⁸	16.8	42.6

From these values the entropies, referred to $S_{H^+}^\circ = 0$ are: Cl^- , 14.0 and Tl^+ , 28.6. Using the sum of the entropies of thallos and nitrate ions as given above, we then calculate for the nitrate ion $S_{298.1}^\circ = 65.6 - 28.6 = 36.9 \text{ E. U.}$ In our previous determination² based upon analogous calculations for barium nitrate, we obtained 35.3 E. U. for nitrate ion. We believe that the value from thallos nitrate is accurate to 1 E. U., *i. e.*, to 300 cal. and that the discrepancy probably is due to errors in the data used to calculate the entropy of barium ion. Investigations are under way to check these quantities. It might also be mentioned that the theoretical evaluation of the entropy of aqueous ions by Latimer and Kasper^{2d} has indicated that the experimental value for barium ion is too high.

Free Energy of Nitrate Ion.—For the heat of the reaction



Berthelot gives $\Delta H = -48,800 \text{ cal.}$ and Thomsen $-49,100 \text{ cal.}$ These values are for 18° but may be corrected to 25° since the specific heats of all the substances are known. The average value for $\Delta H_{298.1}$ then becomes $-49,400$. Using the entropies: H_2 , 31.2;⁹ N_2 , 45.8;¹⁰ O_2 , 49.0;¹¹ H^+ , 0 and NO_3^- , 36.9, we calculate $\Delta S = 36.9 - 15.6 - 22.9 - 73.5 = -76.1$. With the value for the heat of the reaction, the free energy then becomes

⁵ Giauque and Overstreet, *THIS JOURNAL*, **54**, 1731 (1932).

⁶ Calculation by Rodebush and Rodebush, "International Critical Tables."

⁷ "International Critical Tables." The value for hydrochloric acid has been corrected to 25° using the heat capacity values given by Rossini, *Bur. Standards J. Research*, **7**, 47 (1931).

⁸ From data in Lewis and Randall, Ref. 4, modified by recent work of Randall and Young, *THIS JOURNAL*, **50**, 989 (1928), and Randall and Vietti, *ibid.*, **50**, 1526 (1928).

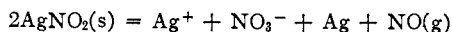
⁹ Giauque, *ibid.*, **52**, 4816 (1930).

¹⁰ Giauque and Clayton, to be published.

¹¹ Giauque and Johnston, *THIS JOURNAL*, **55**, 2300 (1929).

$\Delta F^\circ = -49,400 - (298.1 \times -76.1) = -26,700$ cal. This is an excellent agreement with the Lewis and Randall⁴ value $\Delta F^\circ = -26,500$ cal.

Entropy of Nitrite Ion.—We may make use of the values given by Lewis and Randall for ΔF° and ΔH° of the reaction



and the known entropies of the reaction products, to calculate the entropy of solid silver nitrite. This we find to be 27.7. From this value together with the free energy and heat of solution of silver nitrite and the entropy of silver ion we calculate for the entropy of nitrite ion, 24.0 E. U. The direct determination of the entropy of solid silver nitrite will afford an interesting check upon the entropies of both nitrate and nitrite ions.

Entropy of Hydration of Nitrate.—It is of interest to compare the entropy of nitrate, 36.9, with that of carbonate, -14. Since the entropies of the two substances as gases should be very nearly the same, the difference must arise from the effect upon the entropy of the water molecules of the double charge on the carbonate. Latimer and Kasper^{2d} have found for the simple ion that the entropy of hydration is $22 e^2/r$ E. U. where e is the charge on the ion and r the distance in Ångström units from the center of the ion to the center of the water dipoles surrounding the ion. Estimating r as approximately 3 Å. for carbonate and nitrate would lead to a difference of only 30 E. U. between the two ions instead of the 51 units found. It seems probable that part of the discrepancy is due to the dissymmetry of these ions, which permits one or more water molecules to be drawn very much closer to the center of the ion. The calculation also assumes that the effective charge is located at the center of the ion cavity whereas actually the field outside the ion probably corresponds to a more complex distribution.

The authors wish to express their appreciation to Professor Linus Pauling and Dr. J. H. Sturdivant for their x-ray examination of the sample of thallos nitrate.

Summary

The specific heat and entropy of thallos nitrate has been determined from 17 to 300° absolute. These values have been employed in a calculation of the entropy and free energy of nitrate ion.

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