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The Entropy of Deuterium Oxide and the Third Law of Thermodynamics. Heat Capacity of Deuterium Oxide from 15 to 298°K. The Melting Point and Heat of Fusion

BY EARL A. LONG[1] AND J. D. KEMP

Aside from its usual thermodynamic utility, the entropy of deuterium oxide is of considerable interest in connection with the entropy discrepancy in ordinary water, first pointed out by Giauque and Ashley,[2] in which the calorimetric entropy does not agree with entropies calculated from the band spectrum and from reaction data. Explanations of this discrepancy have been discussed by Giauque and Ashley, and more recently by Pauling.[3]

In order to test these explanations, Giauque and Stout[4] have carried out a calorimetric investigation on ordinary water.

Since the substitution of deuterium for hydrogen in the water molecule does not appreciably change the internuclear distances, and probably has little effect on the nature of the bond forces, it seemed that an experimental investigation of the entropy of deuterium oxide would be valuable in any discussion of the entropy discrepancy in water. A calorimetric entropy value for heavy water should provide an additional test to distinguish between the theory of molecular rotation and the Pauling theory of random bond orientation, as has been pointed out by Giauque and Stout.[4]

Apparatus.—The measurements were made with the same copper calorimeter and auxiliary apparatus used by Giauque and Stout in their investigation of ordinary water. Although we did not have a sufficient quantity of pure heavy water to fill the calorimeter as completely as desired, the precision of the measurements was not seriously affected, and we feel that the use of the same calorimeter and temperature standard for hydrogen and deuterium oxide should lead to more accurate comparisons between the two isotopic forms.

The details of the apparatus and the method of making the measurements and calculations have been described previously.[5]

Purification of Deuterium Oxide.—The sample was taken from a preparation kindly supplied to us by Prof. H. L. Johnston. It had a density of 1.10781, corresponding to a deuterium content of 99.92 atomic per cent.,[6] if we compare our density with the maximum density of 1.1079 given by Taylor and Selwood.[7] The remaining 0.08 atomic per cent. of hydrogen does not affect our measurements, since the isotopes should of course form a perfect solution, and the thermal quantities are of nearly the same magnitude.

The heavy water container was broken in an

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[1] National Research Fellow.

[2] Giauque and Ashley, *Phys. Rev.*, **43**, 81 (1933).

[3] Pauling, THIS JOURNAL, **57**, 2680 (1935).

[4] Giauque and Stout, *ibid.*, **58**, 1144 (1936).

(5) (a) Giauque and Wiebe, *ibid.*, **50**, 101 (1928); (b) Giauque and Johnston, *ibid.*, **51**, 2300 (1929); (c) Giauque and Stout, *ibid.*, **58**, 1144 (1936).

(6) We are informed by Prof. Johnston that the sample contains not more than 0.01% above the normal concentration of the heavier oxygen isotopes, on the basis of the electrolytic separation coefficient 1.008 for the concentration of O^{18} by electrolysis with iron electrodes, determined by Johnston [*ibid.*, **57**, 484 (1935)].

(7) Taylor and Selwood, *ibid.*, **56**, 998 (1934).

atmosphere of pure helium, and the water was distilled at low pressures through a series of three bulbs, in order to eliminate a small amount of alkali in the original sample. After each distillation the solid was cooled with liquid air and the system was evacuated to a pressure of 10^{-5} mm. in order to get rid of traces of dissolved gas. The water was then transferred through a small german silver tube into the copper calorimeter. The calorimeter was filled with helium gas at one atmosphere pressure, the german silver tube was pulled out, and the very small opening was sealed with Wood's metal.

In order to determine the amount of liquid-soluble, solid-insoluble impurity, a series of short heat capacity runs was made in the temperature region just below the melting point. From the observed premelting effect in these runs, we estimate the soluble impurity to be less than 0.003 of one mole per cent. This is of course exclusive of the 0.08 atomic per cent. hydrogen content of the sample, as the presence of another isotopic form would not cause premelting.

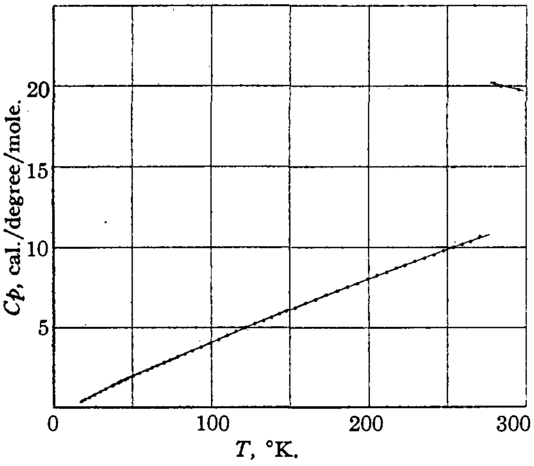

Fig. 1.—Heat capacity of deuterium oxide.

The Heat Capacity of Deuterium Oxide

The results of the heat capacity measurements are given in Table I, and are shown graphically in Fig. 1.

TABLE I

HEAT CAPACITY OF DEUTERIUM OXIDE

Molecular weight, 20.0284. 0°C. = 273.10°K.

T., °K.	ΔT	C_p, cal./deg./mole	Series
14.81	3.652	0.243	I
17.56	2.189	.403	I
19.89	2.874	.532	I
22.60	3.160	.660	I
25.97	3.645	.831	I
29.56	3.115	1.027	I
32.96	3.114	1.194	I
37.06	4.685	1.376	I
38.07	5.145	1.434	III
41.44	3.795	1.577	I
42.87	4.253	1.664	III
45.14	3.347	1.764	I
46.98	3.730	1.844	III
50.70	3.668	2.016	III
54.64	3.831	2.174	III
59.23	5.226	2.354	III
59.32	2.448	2.374	II
62.37	3.307	2.504	II
65.96	3.737	2.643	II
69.77	3.773	2.813	II
73.99	4.535	2.988	II
78.61	4.612	3.179	II
83.16	4.345	3.359	II
87.92	4.860	3.541	II
93.51	6.211	3.776	II
99.32	5.340	4.005	II
104.57	5.051	4.254	II
110.10	5.749	4.519	II
115.67	5.092	4.781	II
121.44	6.276	4.996	II
127.51	5.736	5.236	II
133.17	5.313	5.428	II
138.40	4.932	5.634	II
143.23	4.509	5.861	II
147.79	4.182	6.011	II
153.38	6.911	6.217	II
159.98	6.156	6.534	II
166.27	6.175	6.741	II
173.10	7.065	7.027	II
180.00	6.588	7.275	II
186.59	6.136	7.539	II
192.88	5.769	7.747	II
199.19	5.875	8.029	II
205.36	5.754	8.270	II
211.45	5.934	8.456	II
217.19	5.641	8.711	II
223.11	5.401	8.894	II
229.34	5.538	9.138	II
235.39	5.681	9.324	II
241.57	5.594	9.519	II
247.69	5.671	9.785	II
253.87	6.034	9.999	II
259.50	5.020	10.18	II
264.81	5.159	10.36	II
270.52	5.756	10.69	II
276.92	Melting point		
279.46	3.561	20.17	IV
283.91	4.558	19.99	IV
289.45	5.700	19.98	IV
295.16	5.497	19.78	IV

In the calculations, one 15° calorie was taken as equal to 4.1832 international joules. The calorimeter contained 32.708 g. of deuterium oxide. For the calculation of the molecular weight we used the value 2.01471 given by Aston[8] for the atomic weight of deuterium, and the factor 1.00025 for conversion from the physical to the chemical scale.

We took no special precautions in cooling the sample, as the first series of measurements showed no evidence of bad thermal equilibrium. For ordinary water, Giauque and Stout[4] observed slow attainment of thermal equilibrium in the region from 85 to 100°K. However, their experiments on different rates of cooling showed no appreciable effect on the heat capacities. If, as Giauque and Stout suggest, this lag in equilibrium is caused by the initial stages of excitation of new degrees of freedom connected with the motion of the hydrogen atoms, it is not surprising that the phenomenon does not appear in deuterium oxide, when one considers the great difference between the masses of hydrogen and deuterium.

TABLE II

HEAT CAPACITY OF DEUTERIUM OXIDE

Molecular weight, 20.0284. 0°C. = 273.10°K. Values taken from smooth curve through data.

$T.$, °K.	C_p, cal./deg./mole	Ratio $C_{p_{D_2O}}/C_{p_{H_2O}}$	Deviations Brown, Barnes and Maass − This research %
15	0.272		
20	.532	1.086	
30	1.043	1.060	
40	1.524	1.040	
50	1.977	1.043	
60	2.403	1.043	
70	2.821	1.044	
80	3.234	1.052	
90	3.629	1.052	
100	4.047	1.066	
110	4.508	1.092	
120	4.931	1.112	
130	5.325	1.126	
140	5.709	1.143	
150	6.100	1.159	
160	6.500	1.171	
170	6.895	1.174	
180	7.282	1.186	
190	7.666	1.187	
200	8.050	1.194	−4.1
210	8.422	1.187	−3.9
220	8.802	1.191	−3.2
230	9.158	1.185	−1.9
240	9.500	1.186	+0.2
250	9.842	1.178	+2.6
260	10.19	1.179	+5.2
270	10.54	1.173	+8.0
276.92	Melting point		
280	20.15	1.115	
290	19.91	1.106	+2.4
295	19.78	1.100	

In Table II are listed values of the heat capacity at even temperatures, as read from a smooth curve through the data. These values are compared with those of Brown, Barnes and Maass,[9] who measured the total change in heat content from various initial temperatures to 25°, and have derived from these data values for the specific heats. In making this comparison we have used 20.0284 as the molecular weight.

We have also included in Table II values for the ratio of the molal heat capacities D_2O/H_2O over the whole temperature region, calculated from our data and those of Giauque and Stout.[4] For the heat capacity of liquid H_2O, the values given in the "International Critical Tables"[10] were used.

The Melting Point and Heat of Fusion.—The melting point was determined with various percentages of the D_2O melted. In each measurement the temperature was observed for several hours after heat input, until readings on the sensitive resistance thermometer indicated that thermal equilibrium had been attained. From these measurements, the melting point was selected as 276.92 ± 0.05°K. (3.82°C.), after taking into account the slight freezing point depression due to the 0.003 mole per cent. of soluble impurity present.

Table III summarizes the measurements of the melting point by various observers.

TABLE III

MELTING POINT OF DEUTERIUM OXIDE

0°C. = 273.10°K.

	M. p., °K.
Lewis and Macdonald[11]	276.9
La Mer and Baker[12]	276.90
Taylor and Selwood[13]	276.92
This research	276.92 ± 0.05

The heat of fusion was determined by the usual procedure of starting heat input at a temperature slightly below the melting point and heating to a temperature a little above. In this case, due to the fact that the less dense ice floated on top of the melted material, it was necessary to heat to almost 11° above the melting point in order to obtain sufficiently rapid thermal equi-

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(8) Aston, *Nature*, **137**, 357 (1936).

(9) Brown, Barnes and Maass, *Can. J. Research*, (a) **12B**, 699 (1935); (b) **13B**, 167 (1935).

(10) "Int. Crit. Tables," McGraw-Hill Book Co., Inc., New York, 1926, Vol. V, p. 113.

(11) Lewis and Macdonald, THIS JOURNAL, **55**, 3057 (1933).

(12) La Mer and Baker, *ibid.*, **56**, 2641 (1934).

(13) Taylor and Selwood, *ibid.*, **56**, 998 (1934).

librium after energy input. This necessitated a larger $\int C_p dT$ correction, which, however, could be applied with high accuracy.

The measurements are summarized in Table IV. Column two gives the heat input per mole, corrected for all experimental factors, but not including the $\int C_p dT$ correction, given in column three. A small correction for premelting is also included in the $\int C_p dT$ correction to the total energy. The last column gives the molal heat of fusion. We have also included in Table IV values for the heat of fusion given by other workers. These include the value of Bartholomé and Clusius, a direct determination with an ice calorimeter; that of Jacobs, an extrapolated value from heat of fusion measurements on equilibrium mixtures of light and heavy water; and indirect determinations by La Mer and Baker, and by Brown, Barnes and Maass.

In this connection it is of interest to point out that the heat of fusion of H_2O measured by Giauque and Stout[4] in the same calorimeter agreed with the accepted value within 0.1%.

TABLE IV

HEAT OF FUSION OF DEUTERIUM OXIDE

Molecular weight, 20.0284

Temp. interval, °K.	Corr. total heat input, cal./mole	$\int C_p dT$ +premelting/mole	ΔH fusion cal./mole
274.07–288.43	1872.7	373.5	1499.2
273.84–285.43	1796.4	293.5	1502.9
274.97–287.06	1818.3	317.8	1500.5
		Mean value	1501 ± 3
Bartholomé and Clusius[14]			1522
Brown, Barnes and Maass[9a]			1484
La Mer and Baker[15]			1510
Jacobs[16]			1525

The Entropy of Deuterium Oxide.—The entropy between 18 and 273.10°K. was obtained by graphical integration of our measured heat capacities. The entropy between 0 and 18°K. was calculated from the Debye equation, using $\theta = 185$.

The only direct value for the heat of vaporization of D_2O is that of Bartholomé and Clusius,[14] who determined the heat of sublimation at 0° using an ice calorimeter. They give 630.9 calories per gram as the mean of three determinations, with an average deviation of 0.4 cal./gram. Converting this to a molal basis, using our molecular weight (20.0284), we obtain 12,636 cal./mole as the heat of sublimation at 0°. The vapor pressure of D_2O at 0° is given by Bartholomé and Clusius as 3.65 ± 0.05 mm. The entropy correction to the ideal gas state should be negligible at this low pressure.

A summary of the entropy calculation at 273.10°K. is given in Table V.

TABLE V

ENTROPY OF DEUTERIUM OXIDE AT 273.10°K.

0–18°K., Debye function, $\theta = 185$	0.135
18–273.10°K., graphical	10.099
Sublimation at 273.10°K., 12636/273.10	+46.269
Compression $R \ln (3.65/760)$	−10.61
Entropy of the hypothetical perfect gas at 273.10°K. and 1 atmosphere pressure	45.89 ± 0.1 E. U.

Table VI summarizes the calculation of the entropy of *liquid* deuterium oxide at 298.10°K.

TABLE VI

CALORIMETRIC ENTROPY OF LIQUID DEUTERIUM OXIDE AT 298.10°K.

0–18°K., Debye function, $\theta = 185$	0.135
18–276.92°K., graphical	10.247
Fusion at 276.92°K., $\frac{1501}{276.92}$	5.420
276.92–298.10°K., graphical	1.472
Calorimetric entropy of liquid D_2O at 298.10°K.	17.27 ± 0.05 E. U.

For use in thermodynamical calculations, 0.806 E. U. should be added to the value in Table VI, giving 18.08 E. U., on the basis of Pauling's theory, discussed in a later section.

The Entropy from Spectroscopic Data.—The entropy was calculated from the well-known equation

$$S = 3/2\, R \ln M + 4R \ln T + R/2 \ln I_A I_B I_C - R \ln \sigma + 265.35 + S_{\text{vibrational}}$$

The vibrational fundamentals $\nu_1 = 2784$ cm.$^{-1}$, $\nu_2 = 2666$ cm.$^{-1}$, $\nu_3 = 1179$ cm.$^{-1}$ given by Barker and Sleator[17] and Rank, Larsen and Bordner[18] were used in the calculation of the vibrational entropy. At 273.10°K., this amounts to only 0.02 E. U.

As there exist no experimental values for the moments of inertia of deuterium oxide, a calculation of these was made from the corresponding moments of inertia for hydrogen oxide in the

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[14] Bartholomé and Clusius, *Z. physik. Chem.*, **B28**, 167 (1935).

[15] La Mer and Baker, THIS JOURNAL, **56**, 2641 (1934).

[16] Jacobs, *Trans. Faraday Soc.*, **31**, 813 (1935).

[17] Barker and Sleator, *J. Chem. Phys.*, **3**, 660 (1935).

[18] Rank, Larsen and Bordner, *ibid.*, **2**, 464 (1934).

ground state (non-rigid molecule) given by Freudenberg and Mecke.[19]

In this calculation, it was assumed that the root mean square distance between the D atoms in D_2O was the same as the root mean square distance between the H atoms in H_2O; it was also assumed that the root mean square distance between the O atom and the line connecting the D atoms was the same as the corresponding distance between the O atom and the line connecting the H atoms. Thus

$$I_{A_{D_2O}} = \left[\frac{\dfrac{2DO}{2D + O}}{\dfrac{2HO}{2H + O}}\right] I_{A_{H_2O}} \qquad (1)$$

$$I_{B_{D_2O}} = \frac{D}{H} \times I_{B_{H_2O}} \qquad (2)$$

$I_{C_{D_2O}}$ was calculated assuming that the distance between the D and O atoms in D_2O was the same as the distance between the H and O atoms in H_2O, and that this distance r is determined by the expression

$$I_{C_{H_2O}} = 2Hr^2\left(1 - \frac{1}{9}\cos^2\frac{\alpha}{2}\right)$$

The valence angle α is determined by

$$\tan\frac{\alpha}{2} = \frac{2}{3} \times \sqrt{2\frac{I_{B_{H_2O}}}{I_{A_{H_2O}}}}$$

Then

$$I_{C_{D_2O}} = \frac{D\left(1 - \dfrac{2}{10}\cos^2\dfrac{\alpha}{2}\right)}{H\left(1 - \dfrac{1}{9}\cos^2\dfrac{\alpha}{2}\right)} I_{C_{H_2O}}$$

The following values were obtained for the moments of inertia of deuterium oxide (in g.-cm.^{2}):

$$I_A = 1.790 \times 10^{-40} \qquad I_B = 3.812 \times 10^{-40}$$
$$I_C = 5.752 \times 10^{-40}$$

Then, at 273.10°K. and one atmosphere pressure

$$S_{D_2O} = \frac{3}{2}R\ln 20.0284 + 4\,R\ln 273.10 + \frac{R}{2}\ln(1.790 \times 10^{-40} \times 3.812 \times 10^{-40} \times 5.752 \times 10^{-40}) - R\ln 2 + 265.35 + 0.02 = 46.66 \text{ E. U.}$$

in accordance with the usual custom of neglecting entropy due to nuclear spin. At 298.1°K. and one atmosphere, the spectroscopic entropy for D_2O is 47.46 E. U.

A comparison of this spectroscopic value with the calorimetric entropy given in Table V shows a difference of 0.77 E. U. A corresponding discrepancy of 0.82 E. U. at 298.1°K. was found by Giauque and Stout[4] in the case of hydrogen oxide.

Two explanations of the hydrogen oxide discrepancy have been made. Giauque and Ashley[2] offered an explanation which assumed that the ortho and para states in gaseous water persisted in the solid state at low temperatures. This theory, as pointed out by Giauque and Stout,[4] leads to a calculated discrepancy of 1/3 $R \ln 2 = 0.459$ E. U. for deuterium oxide, as compared to a calculated discrepancy of 1.033 E. U. for hydrogen oxide.

Pauling[3] has offered an alternative explanation which ascribes the discrepancy to the random orientation of the hydrogen bonds in the crystal. His theory leads to a calculated discrepancy of $R \ln 6/4 = 0.806$ E. U. This discrepancy, in Pauling's explanation, is identical for both forms of water.

In the case of hydrogen oxide, Giauque and Stout[4] have pointed out that while the discrepancy is quantitatively explained by Pauling's theory, the ortho–para explanation is not absolutely excluded, as a partial attainment of equilibrium between ortho and para forms would lead to a discrepancy somewhat lower than 1.033 E. U. The ortho–para explanation becomes still more improbable for the discrepancy in deuterium oxide, as it predicts a discrepancy of about 0.31 E. U. lower than its measured value. Thus, the agreement between our experimental discrepancy and that calculated by Pauling, together with the similar agreement found by Giauque and Stout for hydrogen oxide, gives strong support to the Pauling theory of random bond orientation.

We are indebted to Professor H. L. Johnston, who suggested the problem to one of us (E. A. L.) and kindly loaned us the pure deuterium oxide used in this investigation, and to Professor W. F. Giauque for the use of the vacuum calorimeter, and for many helpful conversations.

Summary

The heat capacity of solid and liquid deuterium oxide has been determined over their respective ranges from 15 to 298°K.

The melting point has been found to be 276.92°K. The heat of fusion of deuterium oxide is 1501 cal./mole.

The calorimetric entropy of liquid deuterium oxide at 298.1°K. is 17.27 E. U. The value which should be used in thermodynamic calculations is 0.806 E. U. higher, or 1808 E. U., on the basis of Pauling's theory.

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(19) Freudenberg and Mecke, *Z. Physik*, **81**, 465 (1933).

Using our measured heat capacities and the heat of sublimation of deuterium oxide given by Bartholomé and Clusius, we find the calorimetric entropy for $D_2O_{(g)}$ to be 45.89 E. U. at 273.10°K. and one atmosphere pressure. The entropy from spectroscopic data is 46.66 E. U., giving a discrepancy of 0.77 E. U. between the calorimetric and spectroscopic values. This is in good agreement with the theoretical discrepancy 0.806 calculated by Pauling from the assumption of random orientation of the hydrogen bonds in the crystal. This agreement, along with the similar agreement for hydrogen oxide found by Giauque and Stout, is evidence for the correctness of Pauling's theory.

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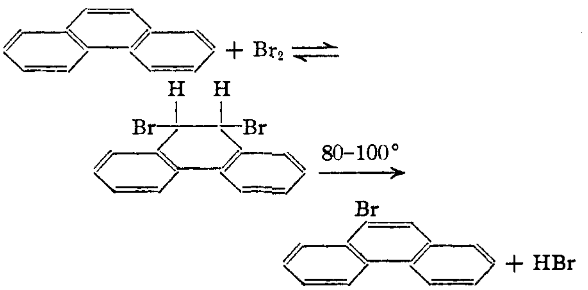
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Study of the Phenanthrene-Bromine Addition Reaction

BY CHARLES C. PRICE

Although it has been recognized since the discovery of phenanthrene[1] that the hydrocarbon forms a crystalline dibromide sufficiently stable to be isolated, the interesting reaction has received but little attention and the dibromide has been studied only as an incidental intermediate in the preparation of 9-bromophenanthrene,[2] loss of hydrogen bromide occurring when the substance is gently heated.



Since the reaction affords a model for the widely considered hypothesis that aromatic substitutions in general involve an addition–elimination mechanism, it was thought that a study of the kinetics of both of the above reactions in the presence and absence of halogenation catalysts might cast some light on the broad problem of substitution. That dibromides can be isolated from phenanthrene and anthracene but not from the other common aromatic hydrocarbons is no indication that these substances are different in kind from the others. It probably is merely a consequence of the greater reactivity of the central nucleus of the tricyclic hydrocarbons and of the stabilization of the dihydrobenzenoid nucleus of the addition product by the terminal, aromatic rings.

It was soon found in preliminary experiments that the reaction between phenanthrene and bromine in non-aqueous solvents is reversible, and that the position of the equilibrium and the rate of its establishment are both measurable by analytical methods. Consequently a study was made of the rate and equilibrium of the first reaction, the original problem being reserved for future investigation.

Analysis for bromine by titration was first tried and found to give approximate but unsatisfactory results, and the final measurements were made by colorimetric analysis for bromine with a Keuffel and Esser spectrophotometer. This proved to be a convenient and reliable method of attack. The experimental deviation of ±5% in the equilibrium constants determined by this method represents an error of only ±0.5% in the determination of the bromine concentration.

The phenanthrene used was a sample from coal tar (Gesellschaft für Teerverwertung) further purified by treatment with maleic anhydride,[3] distillation, and crystallization, m. p. 98.2–98.8°, corr. Pure bromine was prepared according to the directions of Scott,[4] dried over resublimed phosphorus pentoxide, and distilled. The purification of the carbon tetrachloride used as solvent was most satisfactorily accomplished by washing commercial material three times with one-tenth volume of concentrated potassium hydroxide in 50% alcohol at 60°, three times with water, three times with one-tenth volume of concentrated sulfuric acid at 25°, thorough washing with water, a

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(1) Fittig and Ostermayer, *Ber.*, **5**, 933 (1872); *Ann.*, **166**, 361 (1873); Graebe, *Ber.*, **5**, 861, 968 (1872); *Ann.*, **167**, 131 (1873).

(2) Hayduck, *Ann.*, **167**, 181 (1873); Anschütz, *Ber.*, **11**, 1217 (1878); Austin, *J. Chem. Soc.*, **93**, 1763 (1908); Sandqvist, *Ann.*, **398**, 126 (1913); Henstock, *J. Chem. Soc.*, **123**, 3097 (1923); Bachmann, THIS JOURNAL, **56**, 1365 (1934).

(3) Clar, *Ber.*, **65**, 852 (1932).

(4) Scott, *J. Chem. Soc.*, **103**, 847 (1913).