$S_2O_8^=$ and Ag^+ to $Cr_2O_7^=$ and then testing with hydrogen peroxide or diphenylcarbazide. The solution containing Mn^{++} is treated with sodium hydroxide and sodium peroxide to precipitate manganese dioxide, which is then identified by the sodium carbonate–potassium chlorate bead test or with sodium bismuthate in nitric acid.

NEW YORK CITY RECEIVED MARCH 1, 1934

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

Thermodynamic Functions of Nitrous Oxide and Carbon Dioxide[1]

BY LOUIS S. KASSEL[2]

Spectroscopic data have been used to calculate accurate values for the free energies, and in some cases the entropies, heat contents, and specific heats, of nearly all the common diatomic gases. Approximate values have also been obtained for several polyatomic gases, with the neglect of all the anharmonic and interaction terms. The infra-red spectrum of carbon dioxide has now been rather well mapped, and the results have been analyzed quite completely; it should therefore be possible to calculate thermodynamic functions for carbon dioxide with high accuracy. The spectrum of nitrous oxide has received much less attention, but the data amply justify calculation, since the free energy is quite unknown. The simpler case of nitrous oxide will be treated first.

Nitrous Oxide

Plyler and Barker[3] studied the infra-red spectrum of nitrous oxide; their work identifies the three fundamental vibration frequencies and determines roughly the anharmonic and coupling constants. The molecule is definitely linear and unsymmetrical. As was pointed out by Badger and Woo,[4] Plyler and Barker made an error in calculating the moment of inertia, the correct value being 66.1×10^{-40} g. cm.^{2}. Since the rotational stretching terms and the rotation–vibration interactions are not known, the Q-sum for each electronic level factors into one term due to a rigid rotator and one to a group of coupled oscillators. We assume that the lowest electronic state is $^1\Sigma$ and that no others need be considered. The only problem then is to calculate the vibrational factor of the Q-sum.

The vibrational levels are given by

$$E = 1288.7v_1 + 593.0v_2 + 2237.9v_3 - 3.3v_1^2 - 3.1(v_2^2 - l^2/3) - 13.8v_3^2 - 9.8v_1v_2 - 26.7v_1v_3 - 13.3v_2v_3 \text{ cm.}^{-1}$$

where v_1 and v_3 are the quantum numbers of the two single valence vibrations, and v_2 and l are the total and azimuthal quantum numbers of the double deformation vibration; the allowed values of l are $\pm v_2$, $\pm (v_2 - 2)$, etc. Using the notation

$$r = e^{-1288.7F} \qquad s = e^{-593.0F} \qquad t = e^{-2237.9F}$$
$$a = 3.3F \qquad b = 3.1F \qquad c = 13.8F$$
$$d = 9.8F \qquad e = 26.7F \qquad f = 13.3F$$
$$g = 3.1F/3 \qquad F = hc/kT$$

the vibrational factor of the Q-sum becomes

$$Q_{\text{vib.}} = \Sigma_{v_1} \Sigma_{v_2} \Sigma_{v_3} \Sigma_l\, r^{v_1}s^{v_2}t^{v_3} \exp.\ (av_1^2 + bv_2^2 + cv_3^2 + dv_1v_2 + ev_1v_3 + fv_2v_3 - gl^2)$$

We now expand the exponential term into a power series and perform the indicated summations. In addition to formulas previously given,[5] we require the first of the following two formulas, which will be useful for other linear molecules also.

$$\Sigma l^2 = (v/3)(v + 1)(v + 2)$$
$$\Sigma l^4 = (v/15)(v + 1)(v + 2)(3v^2 + 6v - 4)$$

where the sums run over alternate integral values of l from $-v$ to $+v$. The significant terms in the result are

$$Q_{\text{vib.}} = RS^2T\{[1 + ar(1 + r)R^2 + 2bs(1 + 2s)S^2 + ct(1 + t)T^2 + 2drRsS + erRtT + 2fsStT - 2gsS^2] + [b^2s(1 + 18s + 33s^2 + 8s^3)S^4 + 2bdrRs(1 + 7s + 4s^2)S^3 + 2bfs(1 + 7s + s^2)S^3tT - 2bgs(1 + 10s + 9s^2)S^4 + d^2r(1 + r)R^2s(1 + 2s)S^2] + [(b^3/3)s(1 + 88s + 718s^2 + 1208s^3 + 473s^4 + 32s^5)S^6]\}$$

where

$$R = 1/(1 - r) \qquad S = 1/(1 - s) \qquad T = 1/(1 - t)$$

In this expression the first bracket contains all the terms from the linear term of the exponential expansion, the second bracket the five largest

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Associate physical chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

[3] Plyler and Barker, *Phys. Rev.*, **38**, 1827 (1931).

[4] Badger and Woo, THIS JOURNAL, **54**, 3523 (1932).

[5] Kassel, *Phys. Rev.*, **43**, 364 (1933).

quadratic terms and the third bracket the single largest cubic term; this cubic term is not actually used in the calculations, since it is quite small. The factor RS^2T is just the harmonic contribution to the Q-sum, and we have therefore isolated within the braces the exact correction factor due to anharmonic and coupling terms. It is a simple matter to differentiate this factor twice with respect to $(1/T)$; the factor and its derivatives may then be evaluated at several temperatures and the anharmonic contributions to the various functions obtained. Table I gives F/T, H and C_p up to 1500°K. at intervals of 50°, which permit interpolation by second differences. It has not seemed worth while to tabulate the entropies; $S_{298.1} = 56.941$ including a spin entropy of $R \ln 9 = 4.366$.

TABLE I

THERMODYNAMIC FUNCTIONS FOR N_2O INCLUDING NUCLEAR SPIN

T, °K.	$-(F° - E_0°)/T$	H	C_p
250	47.927	1859.0	8.687
298.1	49.257	2290.6	9.251
300	49.306	2308.2	9.272
350	50.513	2785.1	9.790
400	51.592	3286	10.246
450	52.574	3809	10.656
500	53.479	4351	11.029
550	54.319	4911	11.363
600	55.107	5488	11.673
650	55.847	6079	11.961
700	56.547	6683	12.221
750	57.212	7300	12.459
800	57.845	7928	12.678
850	58.451	8568	12.879
900	59.032	9216	13.064
950	59.590	9873	13.233
1000	60.127	10539	13.389
1050	60.644	11213	13.534
1100	61.145	11893	13.661
1150	61.627	12579	13.790
1200	62.096	13272	13.904
1250	62.549	13969	14.011
1300	62.990	14672	14.110
1350	63.418	15381	14.203
1400	63.834	16093	14.290
1450	64.239	16810	14.373
1500	64.634	17530	14.449

The most reliable specific heat measurements on nitrous oxide are those of Eucken and Lüde.[6] As Table II shows, the agreement with the calculated values is quite good, although at the highest temperature it is beyond Eucken's estimated error of 0.5%.

TABLE II

SPECIFIC HEAT OF NITROUS OXIDE

T, °K.	C_p, obs.	C_p, calcd.
271.6	8.910	8.948
287.4	9.149	9.131
389.5	10.034	10.154

The heat of formation of nitrous oxide at 20° has been reported as −19,500 cal.$_{15}$ by Awbery and Griffiths,[7] and as −19,740 cal.$_{15}$ by Fenning and Cotton.[8] These determinations almost certainly supersede all earlier measurements; we shall adopt the average value, −19,620 cal.$_{15}$. Combining the results of Table I with the values previously calculated for nitrogen by Giauque and Clayton,[9] and by Johnston and Davis,[10] and with values for oxygen calculated by Johnston and Walker,[11] we obtain $\Delta E_0° = 20{,}429$ cal. for the formation of 1 mole of gaseous nitrous oxide. Table III gives a few values for the equilibrium constant of this reaction, and shows the equilibrium concentrations of nitrous and nitric oxides in air, assumed to contain 78.03% nitrogen and 20.99% oxygen. It is clear that no appreciable amount of nitrous oxide would be formed at any temperature.

TABLE III

FORMATION OF NITROUS OXIDE IN AIR AT ATMOSPHERIC PRESSURE

T, °K.	$[N_2O]/[N_2][O_2]^{1/2}$	N_2O, %	NO, %
300	6.87×10^{-19}	2.5×10^{-17}	3.70×10^{-14}
1000	6.87×10^{-9}	2.5×10^{-7}	3.59×10^{-3}
1500	1.98×10^{-7}	5.1×10^{-6}	0.134

Although nitrous oxide is very unstable with regard to the elements, it is very stable compared to ammonium nitrate. Using data in Lewis and Randall, we estimate

$$N_2O(g) + 2H_2O(l) = NH_4NO_3(aq)$$
$$\Delta F°_{298} = 43{,}000 \text{ cal.}$$

Thus 100,000 atm. N_2O would be in equilibrium with 10^{-18} M NH_4NO_3.

Carbon Dioxide

The infra-red and Raman spectra of carbon dioxide have been studied with considerable precision.[12,13,14,15,16] Following a suggestion of

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[6] Eucken and Lüde, *Z. physik. Chem.*, **5B**, 413 (1929).

[7] Awbery and Griffiths, *Proc. Roy. Soc.* (London), **A141**, 1 (1933).

[8] Fenning and Cotton, *ibid.*, **A141**, 17 (1933).

[9] Giauque and Clayton, THIS JOURNAL, **55**, 4875 (1933).

[10] Johnston and Davis, *ibid.*, **56**, 271 (1934).

[11] Johnston and Walker, *ibid.*, **55**, 172 (1933).

[12] Barker, *Astrophys. J.*, **55**, 391 (1922).

[13] Martin and Barker, *Phys. Rev.*, **41**, 291 (1932).

[14] Adams and Dunham, *Pub. A. S. P.*, **44**, 243 (1932).

[15] Dickinson, Dillon and Rasetti, *Phys. Rev.*, **34**, 582 (1929).

[16] Langseth and Nielsen, *Z. physik. Chem.*, **19B**, 427 (1932).

Fermi,[17] Dennison[18] and Adel and Dennison[19] have given a detailed theoretical interpretation of the unusual characteristics of these spectra. The molecule is linear and symmetrical; it would be expected to have one symmetrical valence vibration, ν_1, and one unsymmetrical one, ν_3; in addition, there would be a double bending vibration ν_2, with a subsidiary quantum number l measuring the angular momentum about the figure axis. The frequencies ν_2 and ν_3 would appear in the infra-red spectrum; ν_1 would occur in the infra-red only in combination bands, but would be the strongest line in the Raman spectra. It is found, however, that the Raman spectra contains a strong doublet, and that the infra-red also will not fit such a simple scheme. Fermi showed that the experimental results were those to be expected for the case that $\nu_1 \cong 2\nu_2$, and the complete working out of the theory by Adel and Dennison gave a highly satisfactory agreement with every detail of the observations. It turns out that each set of levels with the same values of l and of $V = 2V_1 + V_2$ goes over into an equal number of levels which are, in the first approximation, linear combinations of the simple levels. There are thus two levels which are partly (0200)[20] and partly (1000); both levels are excited in the Raman effect, due to their (1000) nature; both are excited in the infra-red spectrum by absorption from (0100), because both are to some extent (0200). This interaction thus gives a richer spectrum than would otherwise be found. It also produces large shifts in position for the levels; thus the two levels formed from (0200) and (1000) have a separation of 102.6 cm.$^{-1}$, although $\nu_1 - 2\nu_2$ is only 14.1 cm.$^{-1}$.

Since the molecule is symmetrical, alternate rotational levels are missing when $l = 0$. When $|l| > 0$ all values of $J \geqq |l|$ are allowed, but for each J only $+l$ or $-l$ has the correct symmetry.[21] The first approximation to the rotational energy is $(h^2/8\pi^2 I)(J^2 + J - l^2)$. The corresponding Q-sum is less than that for a simple rigid rotator with the same moment of inertia. At the lower temperatures this effect outweighs the anharmonic corrections; the specific heat is below the harmonic oscillator-rigid rotator approximation up to 700°K., and the heat content up to 1000°K., while the free energy is still below at 1500°K.

As a result of the resonance degeneracy, the calculations are more than usually complicated. It is necessary to treat each value of $V - |l|$ as a separate problem, setting up new series and summing independently. It proves convenient also to treat each value of V_3 separately, since ν_3 is so large that term by term summation is easier than use of the series.

For $V - |l| = 0$ there is no degeneracy, the first order perturbation energy is $(1/2)h\Delta$,[18] and the stabilized wave function[19] is entirely $V_1 = 0$, $V_2 = l$. For $V - |l| = 2$ the two states with first order perturbation energies $h[\pm\sqrt{(V-1)/2}\,\lambda b + \Delta + \ldots]$ have the composition

$$(1/2)[1 \mp (\Delta/\beta)/\sqrt{2V-2}] \quad V_1 = 1, V_2 = V - 2$$
$$(1/2)[1 \pm (\Delta/\beta)/\sqrt{2V-2}] \quad V_1 = 0, V_2 = V$$

The second order perturbation energies for the vibration, and the rotational perturbation energies are functions of V_1 and V_2, so that it is necessary to know the composition of the various actual states. For larger values of $V - |l|$ the levels become more complex and the results will not be given here. The square root terms would be awkward to sum, but fortunately they disappear when we combine the two states which the $\pm$ sign indicates.

It would require too much space to give the details of the various special devices used in the calculations. The results are given in Table IV. Accurate values have been computed only to

TABLE IV

THERMODYNAMIC FUNCTIONS FOR CARBON DIOXIDE

T, °K.	$-(F^\circ - E_0^\circ)/T$	H	C_p
300	43.620	2256.1	8.908
400	45.848	3197.5	9.885
500	47.681	4226.8	10.676
600	49.261	5327.9	11.324
700	50.660	6488.0	11.862
800	51.921	7697.4	12.312
900	53.074	8948.1	12.689
1000	54.137	10233	13.005
1100	55.125	11548	13.27
1200	56.049	12886	13.50
1250	56.490	13564	13.60
1300	56.917	14246	13.69
1400	57.737	15624	13.86
1500	58.513	17017	14.00
1750	60.29	20557	14.3
2000	61.88	24159	14.5
2500	64.64	31500	14.8
3000	67.15	38970	15.0
3500	69.02	46540	15.2

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(17) Fermi, *Z. Physik*, **71**, 250 (1931).

(18) Dennison, *Phys. Rev.*, **41**, 304 (1932).

(19) Adel and Dennison, *ibid.*, **43**, 716 (1933); **44**, 99 (1933)

(20) The quantum state is designated by ($V_1V_2lV_3$).

(21) Dennison, *Rev. Modern Physics*, **2**, 334 (1931).

1500°K. for F/T, and to 1000°K. for H and C_p. At higher temperatures estimated anharmonic corrections have been added to values calculated from the simple Einstein functions, and the results are progressively less reliable as the temperature increases. The exact values of $-(F^\circ - E_0^\circ)/T$ differ from the earlier approximate calculations of Gordon[22] by a maximum of 0.033, which is within that author's intended accuracy. The heat content and specific heat have not been calculated previously.

Table V gives the equilibrium constants for the dissociation of carbon dioxide and the important producer-gas and water-gas reactions. The free energy table of Clayton and Giauque[23] is used for graphite, and the revised table of the same authors for carbon monoxide.[24] The heat content of carbon monoxide, needed in calculating ΔE_0°, is taken from Johnston and Davis.[25] Values for oxygen are those of Johnston and Walker.[11] The free energy of hydrogen up to 2000°K. is from Giauque;[26] the correct free energy above that temperature, and the heat content, are given by Davis and Johnston.[27] The values used for water are those given by the recent exact calculations of Gordon[28] up to 1500°K., and somewhat less accurate estimates[29] at higher temperatures.

Rossini has found the heats of combustion of hydrogen[30] and carbon monoxide[31] to be 68,313 and 67,623 cal., respectively, at 25°. The heat of vaporization of water at that temperature is 10,500 cal./mole.[32] The heat content of saturated water vapor at 25° is only 0.4 cal./mole less than that for the ideal gas, according to a calculation based on the van der Waals equation with $a = 5.47 \times 10^6$ cc.^{2} atm. and $b = 30.55$ cc. It is thus unnecessary to make a correction to ΔE_0°. The heat of combustion of graphite is taken as 94,240 cal.[23] and the heat content used is the "I. C. T." value. Hence we have

Reaction	ΔH_{300}, cal.	ΔE_0°, cal.
$2CO_2 = 2CO + O_2$	135,252	133,513
$CO_2 + C = 2CO$	41,006	39,526
$CO_2 + H_2 = CO + H_2O$	9808	9639

TABLE V

EQUILIBRIUM CONSTANTS INVOLVING CARBON DIOXIDE

T, °K.	K_1	K_2	K_3
300	3.36×10^{-90}	1.63×10^{-21}	1.15×10^{-5}
400	1.53×10^{-65}	5.40×10^{-14}	6.90×10^{-4}
500	9.9×10^{-51}	1.82×10^{-9}	7.71×10^{-3}
600	7.4×10^{-41}	1.90×10^{-6}	3.71×10^{-2}
700	8.4×10^{-34}	2.71×10^{-4}	0.111
800	1.63×10^{-28}	1.11×10^{-2}	0.247
900	2.08×10^{-24}	0.195	0.451
1000	4.00×10^{-21}	1.91	0.719
1100	1.92×10^{-18}	1.23×10^{1}	1.04
1200	3.27×10^{-16}	5.73×10^{1}	1.41
1250	3.13×10^{-15}	1.12×10^{2}	1.60
1300	2.52×10^{-14}	2.09×10^{2}	1.80
1400	1.03×10^{-12}	6.28×10^{2}	2.21
1500	2.57×10^{-11}	1.63×10^{3}	2.63
1750	1.56×10^{-8}	1.06×10^{4}	3.65
2000	1.87×10^{-6}	4.21×10^{4}	4.59
2500	1.42×10^{-3}	2.72×10^{5}	6.08
3000	0.112	8.8×10^{5}	7.08
3500	2.43	....	....

$$K_1 = \frac{(CO)^2(O_2)}{(CO_2)^2} \qquad K_2 = \frac{(CO)^2}{(CO_2)} \qquad K_3 = \frac{(CO)(H_2O)}{(CO_2)(H_2)}$$

in presence of graphite

The calculated values for the water-gas equilibrium are in excellent agreement with the direct measurements of Neumann and Köhler[33] and the indirect determinations of Emmett and Schultz.[34] The constants for the producer-gas reaction agree well with the earlier values of Rhead and Wheeler,[35] but other work, as pointed out by Gordon,[22] indicates a "zero-point" entropy of 0.5 cal./deg. for graphite.

The calculated specific heats agree well with the results of Eucken and Lüde,[6] and up to 2500°K. they fall within 1 cal. of the best experimental values deduced by Eastman.[36] There is little doubt that the calculated values are more nearly correct.

Carbon Monoxide

Thermodynamic functions for carbon monoxide previously given by the author[37] and by Clayton and Giauque[23] are in error due to a confusion of signs of certain spectroscopic constants. Revised values of the free energy have been published by Clayton and Giauque,[24] and of the other functions by Johnston and Davis.[10] Dr. C. W. Montgomery has kindly repeated the calculations at 5000°K., using the author's analytic methods

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(22) Gordon, *J. Chem. Phys.*, **1**, 308 (1933).

(23) Clayton and Giauque, THIS JOURNAL, **54**, 2610 (1932).

(24) Clayton and Giauque, *ibid.*, **55**, 5071 (1933).

(25) Johnston and Davis, *ibid.*, **56**, 271 (1934).

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

(27) Davis and Johnston, *ibid.*, **56**, 1045 (1934).

(28) Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

(29) Gordon, private communication.

(30) Rossini, *Bureau of Standards Journal of Research*, **6**, 1 (1931).

(31) Rossini, *ibid.*, **6**, 37 (1931).

(32) Osborne, Stimson and Fiock, *ibid.*, **5**, 479 (1930).

(33) Neumann and Köhler, *Z. Elektrochem.*, **34**, 227 (1928).

(34) Emmett and Schultz, THIS JOURNAL, **55**, 1390 (1933).

(35) Rhead and Wheeler, *J. Chem. Soc.*, **97**, 2178 (1910).

(36) Eastman, *Bureau of Mines, Technical Paper* 445 (1927).

(37) Kassel, *J. Chem. Phys.*, **1**, 576 (1933).

of summation; his results check the specific heat of Johnston and Davis to 0.002 cal./deg. and the other functions to 0.001 or better.

Acknowledgment.—The author is very grateful to both Professor D. M. Dennison and Dr. O. K. Rice, each of whom independently corrected an error in the quantum weights for carbon dioxide.

Summary

1. The free energy, heat content and specific heat of nitrous oxide have been calculated up to 1500°K.

2. The heat content and specific heat of carbon dioxide have been computed to 1000°K. and the free energy to 1500°K.; less accurate estimates have been made up to 3500°K. The equilibrium constants for the water-gas and producer-gas reactions have been tabulated from 300 to 3000°K., and that for the dissociation of carbon dioxide to 3500°K.

PITTSBURGH, PA. RECEIVED APRIL 4, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO STATE UNIVERSITY]

The Absorption Spectra of Cobalt Compounds. V. The Cobalt–Ethylenediamine–Halogen Complexes

BY MAURICE L. ERNSBERGER AND WALLACE R. BRODE

In a continuation and extension of previously reported work[1] on compounds of the type $(CoEn_2X_2)X$, this paper presents the absorption spectra of a series of halogen substituted derivatives and the effect on the absorption caused by a change in the halogen substituent. Some of these compounds described have not been previously prepared or had their absorption spectra recorded, and in the case of some of the compounds with recorded absorption spectra, the data available were not satisfactory.

The compounds were prepared according to the methods used by Werner.[2] They react slowly with water and this vitiates to some extent the accuracy of the absorption spectra measurements. By dissolving the compounds in the least possible amount of water and diluting to the desired concentrations with alcohol, solutions were obtained in which the reaction with water was retarded sufficiently to make reliable measurements possible.

The spectra were measured in the visible region by means of a Bausch and Lomb spectrophotometer. In the ultraviolet region measurements were made with a Bausch and Lomb quartz spectrograph using as a light source an underwater spark between tungsten electrodes.[3] The Hilger rotating sectorphotometer system was used.

The compound 1,6-$(CoEn_2I_2)I$ was prepared from $(CoEn_2CO_3)I$. Solid $(CoEn_2CO_3)I$ was treated with concentrated hydriodic acid (44%)

TABLE I

RESULTS OF BAND ANALYSES OF THE ABSORPTION SPECTRA OF SALTS OF THE TYPE $(CoEn_2X_2)X$

Compound	Mean frequency difference	Multiple number	Bands Observed	Bands Calculated	Difference
1,6-$(COEn_2F_2)NO_3$[a]	51.4	10	515	514	− 1
		13	660	668	+ 8
		16	835	823	−12
1,6-$(CoEn_2Cl_2)Cl$	48.5	10	484	485	− 1
		13	635	631	− 4
		16	775	776	+ 1
1,6-$(CoEn_2ClBr)NO_3$	47.0	10	470	470	0
		13	620	611	− 9
(Fig. 1)		16		752	
		(18)	825	822	(−3)[b]
		19		894	
1,6-$(CoEn_2Br_2)Br$	45.6	10	456	456	0
		13	600	593	− 7
		16	740	730	−10
		(18)	820	(821)	+ 1
		19	860	867	+ 7
		22	1010	1003	− 7
1,6-$(CoEn_2I_2)I$	44.8	10	448	448	0
		13		583	
(Fig. 2)		16	720	717	− 3
		19	850	852	+ 2
		22	990	986	− 4
1,2-$(CoEn_2F_2)F$[a]	84.7	7	605	593	−12
		10	835	847	+12
1,2-$(CoEn_2Cl_2)Cl$	79.7	7	558	558	0
		10	800	797	− 3
1,2-$(CoEn_2ClBr)Br$	78.7	7	551	551	0
		10	790	787	− 3
1,2-$(CoEn_2Br_2)Br$	77.9	7	545	545	0
		10	780	779	− 1

[a] Values taken from Gordienko.[1a] [b] Approximate.

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(1) (a) Seibt, Dissertation, Zurich, 1913, p. 53; Gmelin's "Handbuch der anorganischen Chemie," Berlin, 1930, Vol. 58-B, p. 228; (b) Lifschitz, *Z. physik. Chem.*, **105**, 33 (1923).

(2) Werner, *Ann.*, **386**, 1–272 (1912).

(3) Brode, *Bur. Standards J. Research*, **47**, 504–507 (1929).