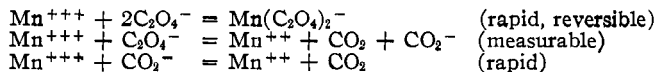


$$\frac{d\rho_{\text{CO}_2}}{dt} = k_1 \frac{(\text{Mn}(\text{C}_2\text{O}_4)_2^-)}{(\text{C}_2\text{O}_4^{2-})}$$

when oxalate ion is in excess, and by the equation

$$\frac{d\rho_{\text{CO}_2}}{dt} = k_2(\text{Mn}^{+++})(\text{C}_2\text{O}_4^-)$$

when oxalate ion is in deficiency and fluoride ion is present to form a complex with manganic ion. This led to the adoption of the following mechanism.



The formula of the manganic oxalate complex ion was found to be $\text{Mn}(\text{C}_2\text{O}_4)_2^-$.

The influence of the ionic strength on the rate was found to be in accord with that predicted using the Brönsted hypothesis.

An explanation was proposed for the formation of peroxides when the reaction takes place in the presence of oxygen.

PASADENA, CALIFORNIA

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

**THE HEAT CAPACITY AND ENTROPY OF CARBON MONOXIDE.
HEAT OF VAPORIZATION. VAPOR PRESSURES OF SOLID
AND LIQUID. FREE ENERGY TO 5000°K. FROM
SPECTROSCOPIC DATA**

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Carbon monoxide gas is one of the simpler diatomic molecules. Spectroscopically the normal level is a $^1\Sigma$ state and it has no other electronic configurations that are appreciably occupied until temperatures far in excess of the 5000°K. limit of our calculations are reached. While nuclear spin should not produce any appreciable effect on the observed behavior of such a molecule, it is of interest to note that the predominant isotopes of both carbon and oxygen are without nuclear spin.

In view of the molecular simplicity it might be expected that the entropy obtained from the band spectrum would agree with that obtained from the ordinary application of the third law. However, this proves not to be the case and it becomes a matter of considerable practical as well as theoretical interest to determine the extent to which similar effects may exist in other molecules. In attempting to find a definite physical explanation for the discrepancy it is desirable to have an accurate quantitative measure of the amount.

It is also our purpose to consider the equilibrium $\text{C}(\text{graphite}) + \frac{1}{2}\text{O}_2 =$

¹ Shell Research Fellow, Academic year 1929-30.

CO, combining thermal data on graphite and the accurately known heat of reaction with spectroscopic data on oxygen and carbon monoxide.

Preparation of Carbon Monoxide.—The carbon monoxide was made by the well-known method of dropping formic acid into concentrated sulfuric acid. The chemically pure reagents were boiled to remove dissolved gases and were later subjected to a vacuum in the closed preparation system. The formic acid was cooled with ice during the latter procedure to prevent too rapid evaporation. The preparation system was evacuated by means of a mercury diffusion pump and found to be vacuum tight before the reagents were introduced. The first portion of the carbon monoxide to be prepared was discarded. The carbon monoxide was passed through a 50% potassium hydroxide solution and then over phosphorus pentoxide. It was then condensed in liquid air and distilled three times; the first and last portions of each distillation being discarded.

Heat Capacity Measurements and Data.—The measurements of heat capacity were carried out in gold calorimeter II described by Giaque and Wiebe.² The method was the same as that given by the above authors and by Giaque and Johnston.³ The discussion of the various factors affecting accuracy and the estimation of the accuracy at various temperatures has been given in the latter paper and applies to the present work. It is believed that the entropy may be computed from the results with an accuracy of two-tenths of one per cent.

Three preparations of carbon monoxide were used in the measurements. These are referred to as I, II and III.

The temperature standard was the copper-constantan thermocouple "W" of Giaque, Buffington and Schulze.⁴ Since the original comparison with the hydrogen gas thermometer it has frequently been checked against the vapor pressure of oxygen. This comparison was repeated in the course of the present experiments and it was found to agree within a few hundredths of a degree at several temperatures in the liquid oxygen range. This is within the limit of the accuracy claimed, namely, 0.05° .

The temperature intervals and warming rates were all measured by means of the gold resistance thermometer. In correcting for the heat effect due to vaporization into the small gas volume above the condensed gas, during a temperature rise, the density of the liquid was taken from the work of Baly and Donnan⁵

$$d_{(1)} = 1.1604 - 0.0045 T$$

As the volume of the solid is not very important in the above correction, it could be estimated with sufficient accuracy by comparison with nitrogen.

² Giaque and Wiebe, *THIS JOURNAL*, **50**, 101 (1928).

³ Giaque and Johnston, *ibid.*, **51**, 2300 (1929).

⁴ Giaque, Buffington and Schulze, *ibid.*, **49**, 2343 (1927).

⁵ Baly and Donnan, *J. Chem. Soc.*, **81**, 907 (1902).

The amount of material was measured by means of the five-liter volumetric apparatus described by Giauque and Johnston.⁸ Between series II and III an accident to the measuring bulb necessitated replacement, which was done with the same precautions described for the previous apparatus. The amount of material was determined as follows:

$$\text{Number of moles} = V \times P \times \frac{D}{M} \times \frac{1}{1 + KT} [1 + \alpha(1 - P)]$$

Gas density at 0°C.

$$D = 1.2504 \text{ g./l.}^{6,7}$$

Molecular weight

$$M = 28.000$$

Coefficient of thermal expansion (0–100°C.)

$$K = 0.003669^8$$

Coefficient of deviation from Boyle's law (per atmosphere) α

$$= -0.0005^9$$

Gravitational acceleration (at Berkeley)

$$= 979.973 \text{ cm./sec.}^{10}$$

The value 4.185 absolute joules equal to 1 calorie (15°) was used in converting the electrical units to calories. The relation 1.00042 absolute joules = 1 international joule was used in calculating the energy.

The heat capacity results are given in Table I.

TABLE I
HEAT CAPACITY OF CARBON MONOXIDE
Molecular weight 28.000

T, degrees absolute	ΔT	C_P , calories per degree per mole	Series
14.36	2.640	1.637	I
16.94	2.153	2.458	I
19.37	2.328	3.268	I
21.93	2.213	3.976	I
24.31	2.172	4.573	I
26.64	2.284	5.114	I
29.01	2.345	5.681	I
31.56	2.696	6.272	I
39.85	3.001	8.111	I
44.21	3.403	9.055	I
44.71	2.293	9.089	III
47.90	3.837	9.888	I
48.34	4.427	9.937	III
52.34	3.909	11.01	I
55.07	4.775	11.73	III
56.82	4.901	12.71	I
59.04	3.025	13.61	III
61.55	Transition		
63.47	2.209	12.02	II
64.55	3.570	12.16	III
66.02	2.569	12.30	I
68.09	Melting Point		

⁶ Moissan, *Compt. rend.*, **102** (1886).

⁷ Rayleigh, *Proc. Roy. Soc. (London)*, **A62**, 204 (1897).

⁸ Regnault, *Ann. chim.*, **5**, 52 (1842).

⁹ Schlatter, Thesis, Geneva, 1923.

¹⁰ Sternewart, Landolt, Börnstein and Roth, "Physikalisch-chemische Tabellen," Berlin, 1923.

TABLE I (Concluded)

T, degrees absolute	ΔT	C_p , calories per degree per mole	Series
70.02	2.227	14.42	I
72.17	3.804	14.43	II
75.47	2.623	14.48	II
75.80	4.577	14.39	I
78.78	3.890	14.41	II
79.06	4.566	14.48	I
80.61	4.829	14.50	I
83.39	3.877	14.40	I
84.66	2.716	14.45	I

Series I, 2.7594 moles. Series II, 2.8414 moles. Series III, 2.5830 moles.

The heat capacity of carbon monoxide has been measured by Eucken¹¹ and by Clusius.¹²

The results of Clusius agree quite well with the present investigation, the largest deviations being below 20°K. and near the boiling point. The average deviation is about 3%. However, the algebraic deviation is only about 0.1%, showing agreement as to total energy input over the region. The earlier work of Eucken does not agree as well.

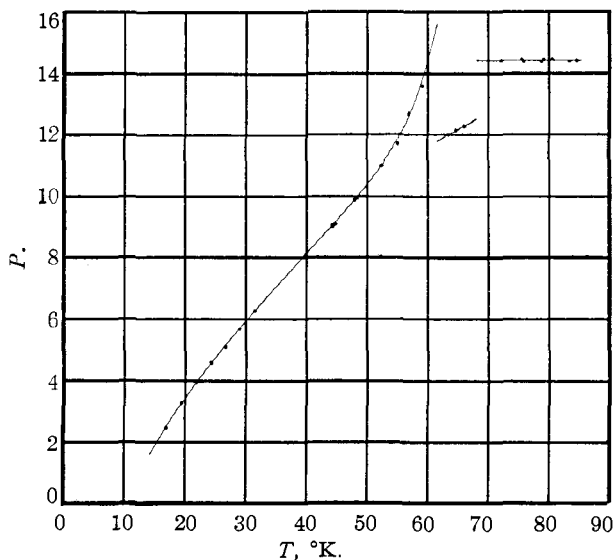


Fig. 1.—Capacity of carbon monoxide in calories per degree per mole.

The results given in Table I are shown graphically in Fig. 1.

Transition and Melting Point Temperatures.—The transition and melting point temperatures were investigated with various percentages trans-

¹¹ Eucken, *Ber.*, **18**, 4 (1916).

¹² Clusius, *Z. physik. Chem.*, [B] **3**, 41 (1929).

formed. The transition temperature was observed over a period of nineteen hours, the melting point for eighteen hours with preparation I and for sixteen hours with preparation II. The data are collected in Table II.

TABLE II
TRANSITION AND MELTING POINT TEMPERATURES OF CARBON MONOXIDE

Transition temperature			Melting point temperature		
Percentage transformed	T, °K.	Series	Percentage transformed	T, °K.	Series
15	61.55	III	3	68.09	I
45	61.55	III	3	68.07	I
45	61.55	III	20	68.09	II
80	61.55	III	55	68.09	II
80	61.56	III	85	68.09	II
Average	61.55 ± 0.05		Average	68.09 ± 0.05	

In Table III the data of previous observers have been collected.

TABLE III
SUMMARY OF AVAILABLE TRANSITION AND MELTING POINT TEMPERATURE DATA

Transition Temperature	
T, °K.	
60.4	(1916) Eucken ¹¹
61.51	(1929) Clusius ¹²
61.55 ± 0.05	This research
Melting Point	
62	(1877) Cailletet ¹³
66	(1885) Olszewsky ¹⁴
74	(1885) Von Wroblewsky ¹⁵
67.3	(1916), Eucken ¹¹
68.22	(1929) Clusius ¹²
68.06	(1931) Verschoyle ¹⁶
68.09 ± 0.05	This research

Purity of Carbon Monoxide.—One of the best methods of estimating an impurity which is soluble in a liquid but insoluble in the solid phase is by calorimetric observation of the premelting effect. The short temperature range of the solid modification stable at the melting point was a slight handicap to this method in the case of carbon monoxide. However, no abnormal rise is apparent in the last point observed below the melting point. The evidence is sufficient to determine that the impurity is not greater than one-thousandth of one mole per cent. The constancy of the melting point confirms the purity although this method is greatly inferior in sensitivity to the premelting method.

Heats of Fusion and Transition.—The heats of fusion and transition were measured by starting the energy input a little below the transition or

¹³ Cailletet, *Compt. rend.*, **85**, (1877).

¹⁴ Olszewsky, *ibid.*, **100**, 350 (1885).

¹⁵ Von Wroblewsky, *Wien. Ber.*, **90** (1885).

¹⁶ Verschoyle, *Trans. Roy. Soc. (London)*, **A230**, 189 (1931).

fusion temperature, and ending a little above. A correction was made for $\int C_P dT$. The results are given in Table IV with those of other observers.

TABLE IV
HEATS OF FUSION AND TRANSITION OF CARBON MONOXIDE
Molecular weight 28,000

ΔH transition, Calories per mole	
152.3	Series III
150.4	Series I
151.3 \pm 1	(1931) Average this research
144.1	(1916) Eucken ¹¹
151.2	(1929) Clusius ¹²
ΔH fusion	
199.6	Series III
199.7	Series I
199.7	Series II
199.7 \pm 0.2	(1931) Average this research
224.1	(1916) Eucken ¹¹
198.2	(1929) Eucken (corrected by Clusius) ¹²
201.5	(1929) Clusius ¹²

It may be noticed that the two determinations of the heat of transition differ by an amount far beyond the ordinary limit of our calorimetric error. This point will be considered later.

Vapor Pressures of Solid and Liquid Carbon Monoxide.—Vapor pressures were measured on the same material used in Series II of the calorimetric measurements but not at the same time as it was undesirable to have the manometer volume connected during calorimetric measurements. The apparatus was essentially the same as that described by Giauque, Johnston and Kelley.¹⁷ A Gaertner cathetometer with an accuracy of 0.05 mm. of mercury was used to compare the large diameter manometer with a standard meter.

The results have been represented by equations 1 and 2. For solid carbon monoxide from the transition point at 61.55° to the melting point at 68.09°

$$\log P_{(\text{cm.})} = -\frac{425.1}{T} + 7.82259 - 0.0075960 T \quad (1)$$

For liquid carbon monoxide

$$\log P_{(\text{cm.})} = -\frac{477.3}{T} + 11.23721 - 0.064129 T + 2.5911 \times 10^{-4} T^2 \quad (2)$$

In addition an equation was calculated for the vapor pressure of the solid stable below 61.55°K. This was done with the assistance of the various calorimetric data, including the heat of vaporization to be given below. In correcting the measured heat of vaporization to the value which would be obtained for evaporation to a dilute gas the thermodynamic equation

¹⁷ Giauque, Johnston and Kelley, *THIS JOURNAL*, **49**, 2367 (1927).

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P$$

was combined with Berthelot's equation.

The heat of sublimation of the solid stable at or below 61.55°K. was found to be 1963 calories per mole at 61.55°K. The heat capacity of the solid can be represented very roughly but with sufficient accuracy from 20° to the transition point by

$$C_P = -1.25 + 0.24 T$$

These several data yield the equation, for solid carbon monoxide below 61.55°K.

$$\log P_{(om.)} = -\frac{418.2}{T} + 4.127 \log T + 1.47365 - 0.02623 T \quad (3)$$

TABLE V
VAPOR PRESSURE OF CARBON MONOXIDE

T , °K. observed	P int. cm. observed	ΔP		Remarks
		obs.-calcd.	obs.-calcd.	
60.24	1.998	0.010	~0.03	Solid
61.55	2.819			Transition point
	2.810			Transition point
	2.807			Transition point
	2.808			Transition point
	2.810			Transition point
Average	2.811 \pm 0.005	0.000	0.00	Transition point
62.22	3.275	-.017	.02	Solid
63.30	4.230	.006	-.01	Solid
64.31	5.283	.008	.01	Solid
65.28	6.546	.013	-.01	Solid
66.12	7.769	-.015	.01	Solid
67.02	9.325	-.019	.01	Solid
68.09	11.529			Melting point
	11.531			Melting point
	11.531			Melting point
Average	11.530 \pm 0.005	0.000	0.00	Melting point
69.101	13.651	-.020	.009	Liquid
69.892	15.558	.008	-.003	Liquid
70.690	17.641	-.007	.003	Liquid
72.227	22.364	.040	-.012	Liquid
73.246	25.971	.045	-.012	Liquid
73.860	28.325	.014	-.003	Liquid
74.586	31.347	-.003	.001	Liquid
75.434	35.229	.014	-.003	Liquid
76.351	39.784	-.025	.005	Liquid
77.267	44.859	.002	-.000	Liquid
78.110	49.934	.008	-.001	Liquid
78.948	55.406	-.002	.000	Liquid
79.858	61.871	-.012	.002	Liquid
81.102	71.689	.020	-.002	Liquid
82.032	79.747	-.001	.000	Liquid
83.132	90.206	-.001	.000	Liquid

One observation on the vapor pressure of this modification was made, namely, $P = 1.998$ cm. at 60.24°K . The observed and calculated values are included in Table V. The temperatures at which observations were made on the liquid are given to 0.001 degree as they are relatively consistent to better than 0.01 degree. The principal error appears to be in the pressure measurements, the increase in ΔT , observed-calculated, at the lower temperature, being due largely to this source.

The vapor pressure of carbon monoxide has been measured by Clusius and Teske¹⁸ and their data have been compared with our equations in Table VI.

TABLE VI
VAPOR PRESSURE OF CARBON MONOXIDE

Data of Clusius and Teske Compared with Equations 1 and 2

T , °K. observed	P , int. cm. observed	ΔP obs.-calcd.	ΔT obs.-calcd.	Remarks
60.336	2.041	-0.042	+0.07	Solid
60.616	2.083	- .151	+ .25	Solid
61.455	2.459	- .279	+ .41	Solid
61.985	3.083	- .033	+ .05	Solid
63.974	4.465	- .453	+ .45	Solid
64.348	5.519	+ .179	- .15	Solid
64.892	6.099	+ .090	- .07	Solid
65.967	7.755	+ .215	- .13	Solid
66.201	7.965	+ .051	- .03	Solid
67.171	9.888	+ .255	- .13	Solid
67.373	9.963	- .076	+ .04	Solid
68.213	11.708	- .108	+ .05	Solid
69.735	15.184	+ .023	- .01	Liquid
70.801	17.811	- .146	+ .05	Liquid
71.457	19.795	- .077	+ .03	Liquid
72.338	22.830	+ .135	- .04	Liquid
73.350	26.430	+ .112	- .03	Liquid
73.409	26.521	- .021	+ .01	Liquid
73.994	28.745	- .108	+ .03	Liquid
74.690	31.518	- .285	+ .07	Liquid
74.710	31.897	+ .006	- .00	Liquid
74.778	32.144	- .056	+ .01	Liquid
75.558	35.650	- .160	+ .03	Liquid
75.631	36.180	+ .015	- .00	Liquid
76.004	37.995	- .024	+ .00	Liquid
76.325	39.691	+ .019	- .00	Liquid
76.449	40.783	+ .457	- .08	Liquid
76.574	40.878	- .006	+ .02	Liquid
77.497	46.482	+ .286	- .05	Liquid
77.499	46.492	+ .283	- .05	Liquid
78.265	51.062	+ .154	- .02	Liquid
78.828	54.620	+ .024	- .00	Liquid
79.696	60.666	- .022	+ .00	Liquid
79.967	62.418	- .278	+ .04	Liquid

¹⁸ Clusius and Teske, *Z. physik. Chem.*, [B] 6, 135 (1929).

While the average deviation is very much greater than in the present work, the results are well represented by our equations. In fact, equation 1 represents the data of Clusius and Teske for the liquid range with a slightly smaller average deviation than was obtained with their own equation.¹⁹

From equation 1 the boiling point was found to be $81.61 \pm 0.05^\circ\text{K}$. The boiling point data of several observers are summarized in Table VII.

TABLE VII
BOILING POINT OF CARBON MONOXIDE

$T, ^\circ\text{K}$.	Observer
80	(1885) Von Wroblewsky ²⁰
83	(1885) Olszewsky ¹⁴
81.8	(1902) Baly and Donnan ⁵
81.66	(1919) Von Winning (corrected to Leiden scale) ¹⁸
81.62	(1929) Clusius and Teske ¹⁸
81.62	(1931) Verschoyle ¹⁶
81.61 ± 0.05	This research

Heat of Vaporization of Carbon Monoxide.—The entropy of vaporization contributes roughly one-half of the total entropy for the simple gases. For this reason it is very desirable to have a direct and accurate determination of this quantity. The experimental method has been described previously.^{2,3}

The results are given in Table VIII, which also includes the value given by Eucken and that calculated from our vapor pressure determinations. The latter method is in general inferior to the directly determined value due to uncertain correction for gas imperfection at the higher pressures and to increasing error in dP/dT at low pressures.

¹⁹ Since this paper was written our attention has been called to some very accurate vapor pressure measurements by Verschoyle [*Trans. Roy. Soc. (London)*, **A230**, 189 (1931)]. The equation given by Verschoyle does not represent his values in the liquid range, the discrepancy undoubtedly being due to some typographical error. However, we have compared his results from the melting point to 82.2° with our Equation 2. The agreement is extraordinarily good. The maximum deviation is 0.02° and the average deviation 0.01° . However, Verschoyle's results, which extend to a pressure of 143 cm., are not very satisfactorily represented by our Equation 2 above the boiling point. Below the melting point the agreement is not as good. Although Verschoyle's results extend to 54.21°K ., he apparently failed to notice the transition at 61.55°K . and represents all of his results on the solid states by a single equation. Near the transition temperature Verschoyle's temperatures are about 0.06° higher than the present work. Below 61.55°K ., Verschoyle's results do not agree well with our equation 3 obtained with the assistance of the calorimetric data. At 54.2°K ., his results are 0.12° lower than those given by Equation 3. However, our one observation on this crystal modification at 60.24° is only 0.03° lower than Verschoyle's results in this region.

For comparison: Boiling point, 81.62° (V.), 81.61° (C. and G.).
Triple point temperature, 68.06° (V.), 68.09° (C. and G.).
Triple point pressure, 11.486 cm. (V.), 11.531 cm. (C. and G.).

²⁰ Von Wroblewsky, *Compt. rend.*, **100**, 979 (1885).

TABLE VIII
HEAT OF VAPORIZATION OF CARBON MONOXIDE

ΔH at 760 mm. in cal./mole	Moles of CO evaporated	Molecular weight 28.000	Time in minutes	Remarks
1443.4	0.22487		36	Series II
1444.1	.21939		46	Series I
1444.8	.21934		46	Series I
1442.6	.21913		46	Series I
1442.8	.21979		46	Series I
1443.6 \pm 1.0 average	This research			
1414	Eucken (1916) ¹¹			
1434	From vapor pressure equation 2, assuming a Berthelot gas			

The 1434 value for the heat of vaporization obtained from the vapor pressure measurements is of course to be given no weight in comparison with the calorimetric value. This calculation, however, increases the justification for assuming that Berthelot's equation represents the behavior of carbon monoxide. This will be assumed later in connection with the effect of gas imperfection on the entropy.

The Entropy of Carbon Monoxide.—The entropy calculation is summarized in Table IX. A Debye function with $h\nu/k = 79.5$ was used to extrapolate to the absolute zero.

TABLE IX
CALCULATION OF ENTROPY OF CARBON MONOXIDE

0–11.70°K. Debye extrapolation $h\nu/k = 79.5$	0.458
11.70–61.55 Graphical	9.632
Transition 151.3/61.55	2.457
61.55–68.09 Graphical	1.228
Fusion 199.7/68.09	2.933
68.09–81.61 Graphical	2.611
Vaporization 1443.6/81.61	17.689
Entropy of carbon monoxide gas at boiling point	37.01 \pm 0.1
Correction for gas imperfection assuming Berthelot gas	0.21
Entropy corrected to the ideal state	37.2 E. U.

The 0.21 E. U. correction for gas imperfection was calculated by combining Berthelot's equation with the thermodynamic equation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \text{ yielding}$$

$$\Delta S_{\text{correction}} = R \frac{27 T_0^3 P}{32 T^3 P_0}$$

The critical data were taken from the review of such data given by Pickering²¹

$$T_0 = 134.1^\circ\text{K. } P_0 = 35 \text{ atmospheres}$$

²¹ Pickering, *Sci. Papers Bur. Standards*, 21, 608 (1926).

The correction to the ideal state is necessary in order that comparison may be made with the entropy which will now be calculated from the band spectrum of carbon monoxide.

The entropy is given by the expression

$$S^\circ = \frac{3}{2} R \ln M + \frac{5}{2} R \ln T - R \ln P - \frac{5}{2} R - 7.267 + R \ln Q + RT \frac{d \ln Q}{dT} \quad (4)^{22}$$

$$Q = \sum p e^{-\epsilon/kT} \text{ over all quantum levels}$$

The energy levels of carbon monoxide may be represented by the expressions

$$\epsilon_{\text{rotation}} = [B_0 + \alpha(v + 1/2)]m^2 + [D_0 + \beta(v + 1/2)]m^4$$

$$\epsilon_{\text{vibration}} = \omega_e(v + 1/2) + \omega_e X_e (v + 1/2)^2$$

Birge²³ has recalculated the data of Snow and Rideal²⁴ and gives $B_e = 1.853$, $\alpha = 0.020$, $D_e = 5.418 \times 10^{-6}$, $\beta = -6.918 \times 10^{-8}$, $\omega_e = 2167.4$, $\omega_e X_e = -12.70$. Mulholland²⁵ has expressed Q as a simple series in terms of B for rigid molecules. Giauque and Overstreet²⁶ have given an expression which is suitable for non-rigid molecules.

$$Q = e^{\frac{hc}{kT} \left(\frac{B}{4} + \frac{D}{16} \right)} \cdot \frac{kT}{Bhc} \left[1 + \frac{B}{12} \left(\frac{hc}{kT} \right) - \frac{2D}{B^2} \left(\frac{kT}{hc} \right) + \frac{12D^2}{B^4} \left(\frac{kT}{hc} \right)^2 + \dots \right] \quad (5)$$

This avoids the considerable labor involved in summing the individual Boltzmann factors for the rotational levels.

From the above expression for Q and the derivative of its logarithm used in equation 4, the entropy of carbon monoxide is calculated and given in Table X. The values for all natural constants are those given in the "International Critical Tables."

TABLE X
COMPARISON OF EXPERIMENTAL AND SPECTROSCOPIC ENTROPIES OF CARBON MONOXIDE

T, °K.	Spectroscopic	Experimental	
		Actual gas	Corrected to ideal state
81.61	38.318	37.0 ± 0.1	37.2 E. U.
298.1	47.313	46.2

The "experimental" value given for 298.1°K. was obtained by adding the calculated increase in column 2 to 37.2.

It is clear from the discrepancy between the spectroscopic and experimental values that some random situation remains in the solid state at liquid hydrogen temperatures. This is in addition to the small amount considered by the Debye extrapolation.

The difference between the two values is roughly $R \ln 2$. We believe that

²² Giauque, THIS JOURNAL, 52, 4808 (1930).

²³ Birge, Personal communication.

²⁴ Snow and Rideal, Proc. Roy. Soc. (London), A125, 462 (1929).

²⁵ Mulholland, Proc. Cambridge Phil. Soc., 24, 280 (1928).

²⁶ Giauque and Overstreet, THIS JOURNAL, 54, 1731 (1932).

the discrepancy arises as follows. If we consider a molecule with two or more otherwise equivalent positions occupied by isotopes of a given element, it is found that such a molecule enters a crystal lattice without any particular isotopic preference. However, it is true that at extremely low temperatures the almost negligible but nevertheless real energy differences between the possible arrangements will become comparable with kT and thus the crystal will attain perfect order on *reversible* approach to the absolute zero. It is evident even when the positions are occupied by different elements that, unless the crystal lattice has a sufficiently strong preference for a certain arrangement to impose an energy difference much larger than kT , the several possible orientations will exist. It is suggested that this is the case in solid carbon monoxide. This seems more probable when one considers the similar atomic sizes and that it has frequently been assumed that carbon monoxide has an electron structure similar to nitrogen. A discussion of this point has been given by Lewis.²⁷

The electron structure, symmetrical in nitrogen, would of course be somewhat deformed by the differing charges on the carbon and oxygen kernels. Nevertheless, it seems entirely reasonable to assume that the polarity thus induced is insufficient to fix the carbon and oxygen atoms in definite positions at the temperature where the solid is formed. It appears that orderly arrangement in the above respect occurs in carbon monoxide below the temperatures investigated or, what is still more probable, that rearrangement to equilibrium is not easily possible in the solid. In this connection it may be recalled that two determinations of the heat of transition given in Table IV differed by an amount considerably beyond the ordinary limit of error. While no definite conclusion is possible, the difference could be attributed to a different degree of approach to equilibrium in the solid stable below 61.55°K . Unfortunately the experiments were concluded before the calorimetric calculations yielded this information. It would be interesting to hold carbon monoxide at various temperatures below 61.55° for considerable periods of time to investigate this effect.

The amount of entropy corresponding to a complete lack of discrimination between the carbon and oxygen ends of the molecule is $R \ln 2 = 1.38 \text{ E. U.}$ The fact that the observed discrepancy is somewhat smaller, namely, 1.1 E. U. , indicates also that some approach to order has been made and that inability to obtain equilibrium is a factor.

The above type of difficulty, while possible only in certain special cases, is perhaps the most perplexing feature that has been encountered in the practical application of the third law of thermodynamics. It is perplexing because it is by no means obvious how we are to know when it exists. The crystal under investigation may appear perfect to our present powers of

²⁷ Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co., New York, 1923, p. 126.

observation, including x-rays and yet the effect may be present. Certain types of organic molecules would appear to be susceptible to this effect.

The Free Energy of Carbon Monoxide.—From the expression²²

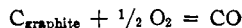
$$\frac{F^\circ - E_0^\circ}{T} = -\frac{3}{2} R \ln M - \frac{5}{2} R \ln T + R \ln P + 7.267 - R \ln Q$$

and the band spectra data previously given, the values of $(F^\circ - E_0^\circ)/T$ have been calculated. The value of R was taken as 1.9869 calories per degree per mole. The results are given in Table XI. The values given in heavy type have been directly calculated. The others have been interpolated by means of a difference plot making use of the Einstein harmonic oscillator function.

TABLE XI

$(F^\circ - E_0^\circ)/T$ FOR CARBON MONOXIDE					
$T, ^\circ\text{K.}$	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	$T, ^\circ\text{K.}$	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	$T, ^\circ\text{K.}$	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$
250	39.138	1200	50.199	3100	57.773
298.1	40.361	1250	50.502	3200	57.832
300	40.405	1300	50.793	3300	58.083
350	41.476	1400	51.347	3400	58.328
400	42.404	1500	51.867	3500	58.566
450	43.224	1600	52.356	3600	58.798
500	43.959	1700	52.819	3700	59.024
550	44.624	1800	53.259	3800	59.245
600	45.233	1900	53.678	3900	59.461
650	45.791	2000	54.077	4000	59.671
700	46.317	2100	54.458	4100	59.867
750	46.806	2200	54.824	4200	60.077
800	47.264	2300	55.176	4300	60.274
850	47.696	2400	55.513	4400	60.466
900	48.106	2500	55.838	4500	60.655
950	48.495	2600	56.152	4600	60.839
1000	48.867	2700	56.455	4700	61.020
1050	49.221	2800	56.748	4800	61.197
1100	49.560	2900	57.031	4900	61.372
1150	49.886	3000	57.307	5000	61.542

Before considering the reaction



it is necessary to obtain the $(F^\circ - E_0^\circ)/T$ for graphite. The values for oxygen have been tabulated by Johnston and Walker.²⁸

The calculation for graphite was made graphically, using the heat capacity data collected in the "I. C. T." These data extend only to 2400°K. and are not as accurate as might be desired. However, it can be seen, by analogy with other substances, that the heat capacity curve given by the available data is not likely to be much in error. The values ob-

²⁸ Johnston and Walker, have kindly allowed us to use their data in advance of publication.

tained are given in Table XII. The values for graphite have been expressed to 0.001 unit although this is considerably beyond the absolute accuracy of the heat capacity data. This is in accordance with the free energy convention which thus allows accurate differences to be obtained.

TABLE XII
($F^\circ - E_0^\circ$)/ T FOR GRAPHITE

$T, ^\circ\text{K.}$	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	$T, ^\circ\text{K.}$	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$	$T, ^\circ\text{K.}$	$-\left(\frac{F^\circ - E_0^\circ}{T}\right)$
250	0.403	850	2.325	1800	4.941
298.1	.545	900	2.485	1900	5.172
300	.551	950	2.643	2000	5.394
350	.698	1000	2.798	2100	5.608
400	.854	1050	2.950	2200	5.817
450	1.016	1100	3.099	2300	6.021
500	1.180	1150	3.246	2400	6.218
550	1.345	1200	3.391	2500	6.411
600	1.510	1250	3.534	2600	6.600
650	1.674	1300	3.674	2700	6.783
700	1.838	1400	3.945	2800	6.962
750	2.001	1500	4.206	2900	7.137
800	2.164	1600	4.460	3000	7.309
		1700	4.704		

$$\frac{\Delta F}{T} = -R \ln K = \Delta \left(\frac{F^\circ - E_0^\circ}{T} \right) + \Delta E_0^\circ \tag{6}$$

ΔE_0° is given by the equation

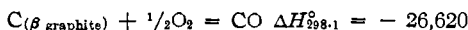
$$\Delta E_0^\circ = \Delta H^\circ - \left[\frac{5}{2} RT + RT^2 \frac{d \ln Q}{dT} \right]_{\text{CO}} + \frac{1}{2} \left[\frac{5}{2} RT + RT^2 \frac{d \ln Q}{dT} \right]_{\text{O}_2} + [H^\circ - E_0^\circ]_{\text{C}} \tag{7}$$

The value of ΔH° was obtained by difference of the heats of combustion of graphite and of carbon monoxide.

For the first of these the value of Roth and Naeser²⁹ was adopted. We have learned from Professor G. S. Parks that a personal communication from Professor Roth states that the graphite weighings were not given on a vacuum basis. The application of the correction for buoyancy leads to a value of 94,240 as the heat of combustion of 12.000 g. of β graphite at 298.1°K.

For the second, the work of Rossini³⁰ gives 67,623 \pm 30 calories as the heat of combustion of carbon monoxide at 298.1°K.

Combining



For carbon monoxide

$$\begin{aligned} \frac{5}{2} RT + RT^2 \frac{d \ln Q}{dT} &= 1480.7 + 590.2 \\ &= 2070.9 \text{ calories at } 298.1^\circ\text{K.} \end{aligned}$$

²⁹ Roth and Naeser, *Z. Elektrochem.*, **31**, 461 (1925).

³⁰ Rossini, *Bur. Standards J. Research*, **6**, 37 (1931).

For oxygen

$$\frac{1}{2} \left[\frac{5}{2} RT + RT^2 \frac{d \ln Q}{dT} \right] = \frac{1}{2} [1480.7 + 589.6]$$

= 1035.2 calories at 298.1°K.

For graphite the "I. C. T." give

$$H^\circ - E_0^\circ = 251.4 \text{ calories at } 298.1^\circ\text{K.}$$

Combining the several values in equation 7, $\Delta E_0^\circ = -27,404$ calories per mole of carbon monoxide.

TABLE XIII
FREE ENERGY OF FORMATION OF CARBON MONOXIDE

$T, ^\circ\text{K.}$	$-\Delta \left(\frac{F^\circ - E_0^\circ}{T} \right)$	$-\frac{\Delta F^\circ}{T}$	$K = [\text{CO}]/[\text{O}_2]^{1/2}$
298.1	18.776	110.705	1.58×10^{24}
300	18.792	110.139	1.19×10^{24}
350	19.182	97.479	2.03×10^{21}
400	19.487	87.997	1.71×10^{19}
450	19.733	80.631	4.21×10^{17}
500	19.933	74.746	2.17×10^{16}
550	20.096	69.921	1.92×10^{15}
600	20.231	65.904	2.54×10^{14}
650	20.339	62.499	4.58×10^{13}
700	20.435	59.584	1.06×10^{13}
750	20.510	57.049	2.95×10^{12}
800	20.570	54.825	9.64×10^{11}
850	20.619	52.859	3.58×10^{11}
900	20.657	51.106	1.48×10^{11}
950	20.687	49.533	6.71×10^{10}
1000	20.713	48.117	3.29×10^{10}
1050	20.732	46.831	1.72×10^{10}
1100	20.747	45.660	9.55×10^9
1150	20.757	44.587	5.57×10^9
1200	20.763	43.600	3.39×10^9
1250	20.766	42.689	2.14×10^9
1300	20.766	41.846	1.40×10^9
1400	20.762	40.336	6.56×10^8
1500	20.751	39.020	3.38×10^8
1600	20.733	37.861	1.89×10^8
1700	20.712	36.832	1.13×10^8
1800	20.688	35.912	7.08×10^7
1900	20.659	35.082	4.66×10^7
2000	20.629	34.331	3.19×10^7
2100	20.599	33.649	2.26×10^7
2200	20.568	33.024	1.65×10^7
2300	20.534	32.449	1.24×10^7
2400	20.500	31.918	9.48×10^6
2500	20.465	31.427	7.40×10^6
2600	20.428	30.968	5.88×10^6
2700	20.392	30.542	4.74×10^6
2800	20.355	30.142	3.87×10^6
2900	20.317	29.767	3.21×10^6
3000	20.279	29.414	2.69×10^6

From this value, the several values of $(F^\circ - E_0^\circ)/T$ and equation 6, $\Delta F^\circ/T$ and K have been computed for the formation of carbon monoxide from the elements. The results are given in Table XIII.

The values of K should be accurate to about 5%. At the lower temperatures the error is chiefly in ΔE_0° and at the higher temperatures the uncertainty is almost entirely due to the data on graphite.

In the absence of better information on the heat capacity of carbon above 3000° it seems preferable to omit values above 3000°. However, the values for carbon monoxide have been extended to 5000° and the values for $(F^\circ - E_0^\circ)/T$ of oxygen given by Johnston and Walker²⁸ extend to this temperature. Thus by extrapolation of the data for graphite above 3000°K. a quite reliable calculation of the equilibrium is available.

We wish to thank H. L. Johnston for assisting with the measurements of series I and R. W. Blue for assisting with series II and III.

Summary

The heat capacities of the two crystalline forms of carbon monoxide and the liquid have been measured from 13°K. to the boiling point.

The transition temperature was found to be 61.55°K. \pm 0.05, the melting point 68.09°K. \pm 0.05 and the boiling point 81.61°K. \pm 0.05. From the calorimetric measurements the heat of transition was determined as 151.3 \pm 1 calories per mole, the heat of fusion 199.7 \pm 0.2 and the heat of vaporization 1443.6 \pm 1.0 calories per mole, measured at 760 mm.

From the experimental data the entropy of carbon monoxide gas was calculated to be 37.0 \pm 0.1 E. U. at 81.61°K. Assuming Berthelot's gas equation a correction amounting to 0.2 E. U. for gas imperfection was added, giving 37.2 E. U. This value can be compared to the value calculated for the ideal gas from the band spectrum, 38.318 at 81.61°K.

The observed entropy is low by an amount corresponding approximately to $R \ln 2$. Reasons are given for believing that this is due to lack of discrimination within the crystal lattice for the oxygen and carbon ends of the molecule. It is suggested that this effect may exist in other molecules and that a quantitative correction will be possible in many cases.

The entropy of carbon monoxide gas at 298.1°K. was found to be 47.313 E. U. from the band spectrum data.

The vapor pressure of solid and liquid carbon monoxide was measured and represented by the equations

Liquid 68.09° - 83.13°K.

$$\log P(\text{cm.}) = -\frac{477.3}{T} + 11.23721 - 0.064129 T + 2.5911 \times 10^{-4} T^2$$

Solid 61.55° - 68.09°K.

$$\log P(\text{cm.}) = -\frac{425.1}{T} + 7.82259 - 0.0075960 T$$

Solid below 61.55°K.

$$\log P(\text{cm.}) = -\frac{418.2}{T} + 4.127 \log T + 1.47365 - 0.02623 T$$

The free energy function for carbon monoxide was calculated from spectroscopic data and tabulated to 5000°K. These data were combined with similar data on oxygen and with the available calorimetric data on graphite to give ΔF for the reaction $C_{\text{graphite}} + \frac{1}{2}O_2 = CO$ to 3000°K.

The free energy of formation of carbon monoxide from β graphite and oxygen at 298.1°K. was found to be $\Delta F_{298.1}^{\circ} = -33,000$.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE ACTIVITY COEFFICIENT OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTION FROM BOILING POINT DATA¹

BY BLAIR SAXTON AND RODNEY P. SMITH

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Although the thermodynamic properties of aqueous salt solutions at ordinary temperatures have been extensively investigated, few data are available for the study of these properties at higher temperatures. Measurements of the boiling point elevation of solutions could be used for such a study if sufficient accuracy in the measurement could be attained. Considerable data² have been published on the boiling point elevation of salt solutions. However, due to superheating, variation of pressure, errors of analysis or temperature measurement, the results are not of sufficient accuracy for a calculation of the activity coefficient. It has seemed worth while, therefore, to attempt to design an apparatus for a more accurate determination of the boiling point elevation.

Apparatus

Of the different methods used for the elimination of superheating, the one suggested by Cottrell³ and used by Washburn and Read,⁴ Pearce and Hicks,⁵ and Bancroft and Davis⁶ seems to be the most satisfactory.

The first apparatus, Fig. 1, consisted of a Pyrex tube, A, 43 cm. long and 7.6 cm. inside diameter, over which was sealed a larger tube, B, 28 cm. long, 11.5 cm. inside diameter. A condenser, C, and a small drain tube, D, were sealed into the outer tube, B. A tube, E, for the "cold" junction of the thermocouple was also sealed into the

¹ Part of this paper is from a dissertation submitted by Rodney P. Smith to the Graduate School of Yale University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² For summary of results see "International Critical Tables," Vol. III. p. 324.

³ Cottrell, *THIS JOURNAL*, **41**, 721 (1919).

⁴ Washburn and Read, *ibid.*, **41**, 729 (1919).

⁵ Pearce and Hicks, *J. Phys. Chem.*, **30**, 1678 (1926).

⁶ Bancroft and Davis, *ibid.*, **33**, 591 (1929).