Assuming that zinc and cadmium vapors are perfect monatomic gases, standard free-energy equations have been derived for volatilization, sublimation and fusion.

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REDUCTION EQUILIBRIA OF ZINC OXIDE AND CARBON MONOXIDE[1]

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For several years past, the Bureau of Mines at its Berkeley Station intermittently has studied metallic oxides. The great importance of the reduction equilibria of metallic oxides, especially in metallurgical operations, makes it highly desirable that these materials be studied systematically. Satisfactory determinations of free energy of formation of the heavy metal oxides are especially to be sought; for if these be known, the data treated thermodynamically should suffice for many utilitarian needs.

Zinc oxide is among the most interesting and important from this point of view. Not only are accurate equilibria measurements highly desirable because in this case theoretical results may be directly applied to metallurgical practice, but also the new use of zinc oxide as catalyst for methanol formation, etc., gives the problem of its reduction equilibria considerable general chemical interest.

Experimental Difficulties

In the temperature range through which zinc oxide is appreciably reduced by gases such as carbon monoxide or hydrogen, that is, above about 400°, the rate of reduction is moderately fast. This fact, combined with the relatively high vapor pressure of zinc in the temperature range of reduction, makes adequate sampling of gas, without change of composition from those concentrations in equilibrium with solid oxide and metal vapor, an extraordinarily difficult experimental problem.

The most ambitious past attempt to measure actual reduction equilibria of zinc oxide is undoubtedly to be found in the experiments of Bodenstein.[2] His experiments fall into two groups, in the first of which he attempted to measure the temperature of reduction of zinc oxide by carbon at various pressures by means of thermal and weight variations of mixtures of zinc oxide and charcoal during heating. In later experiments zinc oxide and graphite were heated in a silica chamber sealed by a lead trap. This

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[1] Published by permission of the Director of the Bureau of Mines.

[2] Bodenstein, *Z. Elektrochem.*, **23**, 105 (1917).

apparatus was a static one, with the criterion of equilibrium the constancy of external pressure required to keep the trap levels constant.

Bodenstein realized the incorrectness of the first measurements, for by calculating the heat of reaction from these results a totally absurd value was obtained as compared to thermal calculation from heats of formation.

In calculating the later results, Bodenstein assumed the partial pressure of zinc vapor in his system to be either half the total pressure (from the stoichiometric relationships of the reaction) when this was less than the vapor pressure of zinc, or equal to the vapor pressure of zinc when half the total pressure was greater than the vapor pressure. The matter of the solubility of zinc in lead is dismissed with the casual statement that zinc is but slightly soluble in lead. However, reference to the freezing-point curves of Heycock and Neville,[3] Arnemann,[4] and Spring and Romanoff,[5] indicates that at 596°, the lowest temperature of Bodenstein's later measurements, the solubility of zinc in lead is about 14% by weight, whereas at 795, the highest temperature used, the solubility is about 27%. The cubic content of the charge container was approximately 20 cc., so that even a minute amount of lead would have sufficed to dissolve the zinc content of the vapor without the formation of a zinc-rich phase. Even if such a new phase had appeared, the vapor pressure of zinc therein would still be low, for the solubility of lead in zinc is approximately 4% at the lower temperature, and 15% at the higher. Under these circumstances, Bodenstein's failure to define the zinc partial pressure must constitute a serious criticism of the results obtained. Had zinc itself been used for the trap material, or had the mass of lead used been given, some estimate might be made of the actual zinc pressures at equilibrium, but actually there does not seem to be any method of even approximately calculating the results, even though the vapor pressures of zinc-lead solutions are measured.

The experiments of Fulton,[6] who passed known mixtures of carbon monoxide and dioxide over zinc and attempted to observe the temperature of oxidation, may be dismissed without serious consideration, since the equilibrium curve which he drew did not even slope in the correct direction for an endothermic reaction.

O'Harra[7] repeated the experiments of Fulton, obtaining a greater number of points, and showed that Fulton's curve should actually have been drawn to indicate an increasing concentration of carbon dioxide at high temperatures. It is probable, however, that the results of this method

[3] Heycock and Neville, *J. Chem. Soc.*, **71**, 394 (1897).

[4] Arnemann, *Metall u. Erz*, **7**, 201 (1910).

[5] Spring and Romanoff, *Z. anorg. Chem.*, **13**, 29 (1897).

[6] Fulton, *Trans. Am. Inst. Mining Met. Eng.*, **60**, 293 (1919).

[7] O'Harra, "Oxidation of Zinc Vapor by Carbon Dioxide," Bur. Mines, *Tech. Paper*, **336** (1924).

suffer from the same difficulty as Bodenstein's thermal measurements, that is, what is being measured is a reaction rate, the results being determined largely by the sensitivity of the method. O'Harra says of his curve, "It may give approximately the equilibrium conditions of the reaction, but as equilibrium was approached from one direction only, it is perhaps doubtful whether the curve shown....gives accurately the true equilibrium conditions."

Tsutomu Maeda[8] passed carbon monoxide over zinc oxide in a boat maintained at an elevated temperature in a porcelain tube. Since the construction of the apparatus was apparently such that the concentration of zinc vapor could probably not be definitely fixed or estimated, and since no attempt was made to "freeze" the reaction compositions, it is doubtful whether these results are safe for the calculation of equilibrium.

Present Experimental Method

Preliminary experiments indicated not only that it was impossible to cool gas mixtures of carbon monoxide, carbon dioxide and zinc vapor with sufficient rapidity to prevent change of composition during sampling, but also that in the temperature range through which reduction of zinc oxide by carbon monoxide takes place readily, the amount of carbon dioxide was in general less than 1% by volume, despite the fact that O'Harra's results would indicate concentrations of about 5%. The latter fact also precludes any attempt to measure pressure changes due to volume relationships in the reaction $ZnO(s) + CO(g) = Zn(g) + CO_2(g)$, for the amount of reduction in a static system would be too small to enable accurate measurement by ordinary manometric means.

The problem of a true sample seemed at first a hopeless one, until it occurred to us that if the equilibrium gases were passed through a good solvent for zinc metal, at the same temperature as the equilibrium mass, sufficiently rapid absorption of the zinc might occur so that a negligible change during removal of the gas might result. Molten lead and, more satisfactorily, molten tin, were found to have this property, at least in part. Gases which are neutral to zinc are of course reducing to both these metals. After the removal of zinc vapor, the gases obviously may be cooled as desired without change of composition.

The apparatus actually used is shown diagrammatically in Fig. 1.

Two gas chambers, A, A', of approximately 300cc. capacity were used as reservoirs of dry gas, collected over mercury. The outlet B, of chamber A was connected by a de Khotinsky seal C, to the silica reaction chamber D. The continuation of B into D was of capillary tubing, reaching nearly to the bottom of D, which was filled with an intimate mixture of c. p. zinc shavings (electrolytic) and c. p. zinc oxide. The outlet of D, through the tin bubbler E, was made as short as possible, so that both D and E occupied a uniform temperature zone of an electric tube furnace F. A small bulb G, in the outlet tube from E, served to prevent the plugging of the outlet by spattering droplets of

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[8] Maeda, *Bull. Inst. Phys. Chem. Res. (Japan)*, **2**, 350 (1923); *C. A.*, **17**, 3124 (1923)

metal. The outlet tube was connected at C′ (de Khotinsky joint) with a small glass trap H, containing a droplet of mercury. The rate of passage of gas through the apparatus was controlled by observation of the bubbling through H. The receiving chamber A′ was used to collect gas, and had outlets to the atmosphere, to the analytical apparatus at J, and a return circuit to the container A through K.

The silica part of the apparatus, after being filled, was dehydrated by the passage of a slow stream of dry air at 300° for a period of several hours. During this period the tin in the trap had been allowed to solidify on the side of E to permit passage of the gas stream. After A had been connected onto the apparatus, it was filled with carbon monoxide (in some cases carbon dioxide) from a container (not shown), over concd. sulfuric acid. After the system had been brought to the desired temperature, a 300cc. sample of gas was passed alternately from A through the apparatus to A′, and back through K, until portions withdrawn for analysis showed constant composition of gas.

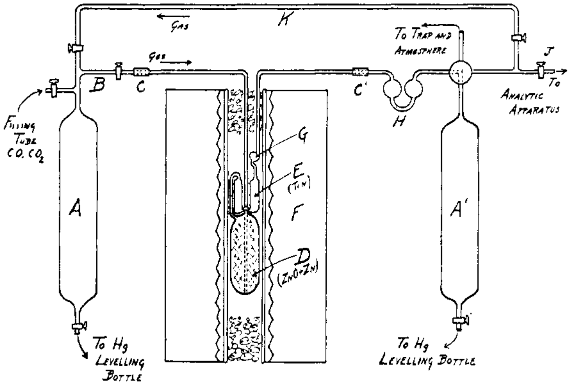

Fig. 1.

The analytical apparatus for the determination of carbon dioxide and carbon monoxide comprised modifications of the Peterson-Palmquist apparatus described by Anderson,[9] using a long vertical capillary instead of the short horizontal one described, and omitting the copper cooling coil. The carbon dioxide apparatus, the buret of which had been carefully calibrated with mercury, was sensitive to 0.0001% of carbon monoxide, and was probably accurate to better than 0.01%. The chief source of inaccuracy in the present case is due to the fact that carbon monoxide is the residual gas, and there is a slight tendency for the synthesis of formate in the caustic absorbent. The total volume of sample used for an analysis was about 30 cc., permitting ten analyses to be made during a determination.

For the estimation of carbon monoxide, a similar apparatus was built, with a lower chamber in the buret (since the gas was nearly 100% pure) and for absorption four absorption pipets, graded in size, containing acid cuprous chloride. The sensitivity of the monoxide apparatus was about 0.01%, and results could be checked to about 0.1%. Although the method of analysis for carbon monoxide is inherently less accurate than that for carbon dioxide, because of the unsatisfactory nature of the absorbent medium, considerable errors in carbon monoxide content do not markedly affect the value of the equilibrium constant. A number of other methods of analysis for carbon monoxide were tried, including the iodine pentoxide method, absorption in ammoniacal cuprous chloride, absorption in a suspension of cuprous oxide in sulfuric acid, etc.,

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[9] Anderson, This Journal, **35**, 162 (1913).

but none were found as satisfactory as the acid cuprous chloride both in point of view of time and completeness of absorption.

Temperatures were determined by thermocouples in direct contact with D and E, the temperature scale of the couples being fixed by the method of Roberts.[10] The temperature difference between D and E was usually considerably less than 5°—mean temperatures were chosen for calculation.

The carbon monoxide was made from c. p. formic acid and c. p. concd. sulfuric acid. After it had been washed with concd. caustic alkali solution, it was stored over concd. sulfuric acid, and before it was used it was again washed with concd. caustic alkali solution, and finally dried through two rather long phosphorus pentoxide tubes in series, before admission to A.

Experimental Results

In all, some 25 experiments were carried out in the apparatus described above. Of these, seven were failures, without quantitative results, mostly due to manipulative errors, in that the tin from the trap was accidentally sucked into the reaction chamber, although some failed because a droplet of tin became lodged in the outlet tube, freezing in the cooler portion and shutting off the passage of gas. Several were made at temperatures higher than could be handled by the apparatus, for the amount of distilled zinc which could be absorbed by the tin was distinctly limited.

The data of the remaining 18 determinations are summarized in Table I. In all of these except the last three, there was no detectable deposit of zinc

TABLE I

SUMMARY OF EXPERIMENTAL DATA FOR THE REACTION

$ZnO(s) + CO(g) = Zn(g) + CO_2(g)$

Expt.	Run	No. of cycles gas passed	Total time Hrs.	No. analyses of CO_2 = cycles; at equil.	% CO_2	±A. d. of m.	Temp., °C.	Ratio $\times 10^3$ P_{CO_2}/P_{CO}
1	25	6	10.7	3	0.0532	0.0007	552.2	0.547
2	24	5	7.0	4	.0759	.0016	594.0	0.781
3	20	5	9.0	3	.1165	.0009	657.4	1.198
4	19	6	12.0	5	.1140	.0069	660.1	1.173
5	21	6	14.8	4	.1483	.0032	693.2	1.526
6	22	4	14.3	3	.1707	.0022	715.1	1.758
7	16	3	9.0	3	.2354	.0027	742.0	2.425
8	12	6	10.5	5	.3085	.0041	756.2	3.180
9	11	6	8.3	3	.2618	.008	760.3	2.698
10	9	7	8.1	6	.2438	.017	761.5	2.511
11	23	5	15.3	4	.2532	.0018	762.8	2.609
12	13	5	11.2	3	.3610	.0021	799.8	3.725
13	2	11	12.8	4	.3560	.019	800.2	3.675
14	3	9	11.2	6	.3542	.0047	801.1	3.655
15	1	11	13.0	final	.3765	...	805.0	3.780
16	14	6	13.0	5	.5515	.0054	836.2	5.702
17	5	6	6.3	5	.5307	.032	840.7	5.488
18	4	8	8.7	7	.5392	.024	846.6	5.575

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[10] Roberts, *Phys. Rev.*, [2] **23,** 386 (1924).

above the tin in the cooler parts of the outlet tube, indicating that the zinc vapor had been satisfactorily absorbed. In the last three a slight deposit was formed. Of these 18, No. 15 (Run 1) was made with a lead trap, and starting from 100% carbon dioxide, No. 13 (Run 2), tin trap, started with 5.60% carbon dioxide, 94.4% carbon monoxide (on the carbon dioxide side of equilibrium), and No. 17 (Run 5), lead trap, started with 0.518% of carbon dioxide, which had been estimated from previous results to be near the equilibrium concentration. All other experiments were made with the tin trap, and monoxide containing only traces of dioxide. The results of these experiments from the dioxide side justified confidence that the apparatus would work satisfactorily from either side; moreover, it was evident that either tin or lead would serve for the trap and that no marked effect of the trap material was in evidence. Because of the greater speed in attaining equilibrium with monoxide, since the equilibrium is near the 100% monoxide side, no further work with dioxide was done, particularly as the adjustment of the dioxide content of pure carbon monoxide to near the estimated equilibrium concentration was a tedious and time-consuming job. The greater solubility of zinc in tin, as compared to lead, was the reason for the continued use of this metal.

Thermodynamic Treatment of Results

In setting up the standard free-energy equations for the data above, the notation and method of Lewis and Randall[11] were used. This consists in plotting the equation $\Sigma = -R\,ln\,K + \Delta\Gamma_0\,ln\,T + {}^1/_2\Delta\Gamma_1 T + {}^1/_6\Delta\Gamma_2 T^2 \cdots$ against the reciprocal temperature. If the data are accurate, the procedure must lead to a line without curvature, whose slope is ΔH_0. The value I of the integration constant of the free-energy equation as calculated for each point is the difference between Σ and computed values of $\Delta H_0/T$.

In the reaction, $ZnO(s) + CO(g) = Zn(g) + CO_2(g)$, the specific heats of carbon monoxide, carbon dioxide and zinc (monatomic gas) have been taken as the values given by Lewis and Randall. For data on the specific heat of zinc oxide we are indebted to Drs. Arthur L. Day and W. P. White, of the Geophysical Laboratory, through whose courtesy the following data are made available.

TABLE II

SPECIFIC HEAT OF ZINC OXIDE

Col.	1	2	3	4
Temp. range, °C.	25–700	25–900	25–1100	25–1300
Mean C_p per ZnO	11.693	11.929	12.156	12.369

The material used by Dr. White was a pure crystalline zinc oxide obtained from the New Jersey Zinc Company.

To represent these data the expression $C_{p(\mathrm{ZnO_s})} = 9.96 + 2.98 \cdot 10^{-3}T -$

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[11] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923.

$3.87 \cdot 10^{-7}T^2$ has been derived, as the mean value of three separate expressions obtained by selecting three sets of three values each, that is, 1,2,4; 1,3,4; and 1,2,3. For the present work a four-term formula was not thought justified by the accuracy of the chemical data.

TABLE III

SUMMARY OF CALCULATED AND DERIVED VALUES FOR THE REACTION

$$ZnO(s) + CO(g) = Zn(g) + CO_2(g)$$
$$\Delta C_p = -4.46 + 3.12 \cdot 10^{-13}T + 22.47 \cdot 10^{-7}T^2$$

No.	$T°$ Abs.	$\frac{1}{T} \times 10^5$	Log $\frac{P_{CO_2}}{P_{CO}}$	Log V.P$_{Zn}$ (at.)	$-R\ ln\ K$	Σ	$\frac{\Delta H_0}{T}$	I
1	825.3	121.17	−3.2620	−2.2546	25.260	− 3.151	57.300	−60.451
2	867.1	115.33	−3.1073	−1.8892	22.878	− 5.660	54.538	−60.198
3	930.5	107.46	−2.9215	−1.3996	19.785	− 8.926	50.822	−59.748
4	933.1	107.17	−2.9307	−1.3810	19.770	− 8.949	50.680	−59.629
5	966.3	103.49	−2.8164	−1.1515	18.168	−10.631	48.939	−59.570
6	988.1	101.20	−2.7550	−1.0112	17.244	−11.605	47.860	−59.465
7	1015.1	98.51	−2.6153	−0.8448	15.843	−13.153	46.587	−59.740
8	1029.3	97.15	−2.4976	− .7688	14.956	−14.069	45.944	−60.013
9	1033.4	96.76	−2.5690	− .7374	15.139	−13.897	45.762	−59.659
10	1034.6	96.65	−2.6002	− .7305	15.250	−13.788	45.708	−59.476
11	1035.9	96.53	−2.5835	− .7229	15.139	−13.899	45.651	−59.550
12	1072.9	93.21	−2.4289	− .5180	13.493	−15.616	44.077	−59.693
13	1073.3	93.16	−2.4347	− .5159	13.510	−15.598	44.060	−59.658
14	1074.2	93.08	−2.4371	− .5111	13.508	−15.602	44.023	−59.625
15	1078.1	92.75	−2.4225	− .4904	13.337	−15.779	43.864	−59.643
16	1109.3	90.15	−2.2440	− .3304	11.787	−17.384	42.630	−60.014
17	1113.8	89.78	−2.2774	− .2781	11.701	−17.476	42.458	−59.934
18	1119.7	89.31	−2.2533	− .2792	11.593	−17.594	42.235	−59.829
Extrap.	298.1				123.848	98.935	158.638	
					Av. I (Omitting 1 and 2)			59.703±0.133

For the given reaction, the specific-heat change then becomes, $\Delta C_p = -4.46 + 3.12 \cdot 10^{-3}T + 22.47 \cdot 10^{-7}T^2$.

In calculating the partial pressure of zinc vapor in the equilibrium apparatus, the vapor pressure of liquid zinc was taken from the expression for $Zn(l) = Zn(g) - RT\ ln\ p = \Delta F°_T = 30{,}540 + 2.24\ T\ ln\ T - 41.760T$, a value based on a critical reëxamination of vapor-pressure data.[12] The activity of the liquid zinc is taken at unity.

Table III shows the calculated values of the various quantities, used in the computation of the integration constant of the free-energy equation. The plot of Σ *vs.* $1/T$ from which the value of ΔH_0 was derived, is shown in Fig. 2. It is evident that the data, with the exception of the first two points (1 and 2 in the table), fit a straight-line curve fairly well. The points 1 and 2 represent concentrations of carbon dioxide of less than 0.1%, and it is probable that in the presence of residual carbon monoxide, a high percentage error may exist in the analysis of gas for these points.

On this basis the standard free-energy equation for the reaction $ZnO(s) + CO = Zn(g) + CO_2$ becomes $\Delta F°_T = 47{,}290 + 4.46\,T ln T - 1.56 \cdot 10^{-3}T^2 - 3.745 \cdot 10^{-7}T^3 - 59.703T$. $\Delta F°_{298} = +36{,}920$.

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[12] Maier, THIS JOURNAL, **48**, 356 (1926).

Since the value of ΔH_0 of formation of carbon monoxide, carbon dioxide and zinc vapor from solid zinc are known, these results may be considered an indirect determination of the heat of formation of zinc oxide. From Lewis and Randall[13] $\Delta H_0(CO) = -26{,}600$, $\Delta F^\circ_{298} = -32{,}510$; $\Delta H_0(CO_2) = -94{,}110$, $\Delta F^\circ_{298} = -94{,}260$.

From Maier's[12] recalculation of the vapor-pressure data of zinc, ΔH_0-Zn(g) = $+31{,}515$; $\Delta F^\circ_{298} = +22{,}885$. By combination of these data with the above reduction-equilibrium data, $\Delta H_0(ZnO) = -83{,}285$; $\Delta F^\circ_{298}(ZnO) = -75{,}785$; and for the reaction $Zn(s) + 1/2\ O_2 = ZnO(s)$, $\Delta H = -83{,}285 + 1.61T - 0.26\cdot10^{-3}T^2 - 1.29\cdot10^{-7}T^3$; $\Delta H_{298} = -82{,}830$. $\Delta F^\circ_T = -83{,}285 - 1.61T \ln T + 0.26\cdot10^{-3}T^2 + 0.645\cdot10^{-7}T^3 + 34.23T$.

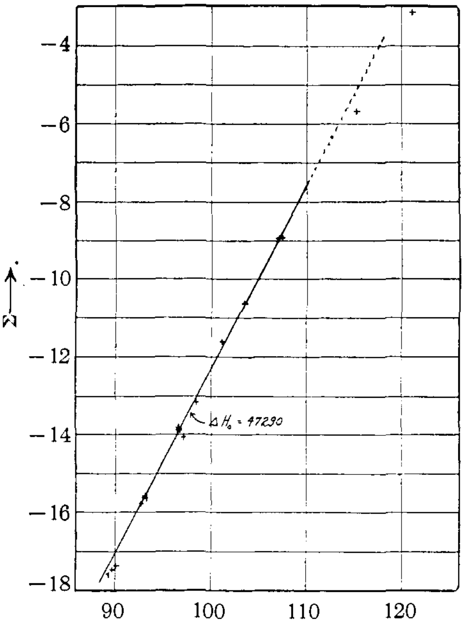

Fig. 2.—Sigma function plot $ZnO_{(s)} + CO = Zn_{(g)} + CO_2$.

Thomsen's[14] value of the heat of formation of zinc oxide was 85,430, obtained from his own measurements of the heat of solution of metallic zinc in sulfuric and hydrochloric acids, combined with Marignac's value for the solution of zinc oxide in sulfuric acid, and Favre and Silbermann's[15] value for hydrochloric acid. Thomsen's value of the heat of solution of zinc was, however, inaccurate, as was shown by Richards, Rowe and Burgess,[16] who obtained for the reaction, $Zn + 2HCl\cdot200H_2O = ZnCl_2\cdot aq. + H_2$, $\Delta H_{291} = -36{,}600$, whereas the older value of Thomsen was $-34{,}210$ cal., representing a difference of 2390 calories.

If the values of Thomsen[17] for the heat of *neutralization* of zinc hydroxide, $Zn(OH)_2 + 2HCl\ aq. = ZnCl_2\ aq. + 2H_2O$; $\Delta H_{291} = -19{,}483$, be accepted, this latter result of Thomsen's may be combined with Mixter's[18] for the reaction, $ZnO + H_2O = Zn(OH)_2$; $\Delta H = -2400$, and with the further

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[13] Ref. 11, p. 576.

[14] Thomsen, *J. prakt. Chem.*, [2] **11**, 402 (1875).

[15] Favre and Silbermann, *Ann. chim. phys.*, [3] **37**, 437 (1853).

[16] Richards, Rowe and Burgess, THIS JOURNAL, **32**, 1176 (1910).

[17] Thomsen (Burke), "Thermochemistry," Longmans and Co., **1908**, p. 267.

[18] Mixter, *Z. anorg. Chem.*, **92**, 385 (1915).

consideration of Richards' more correct data, a new value of the heat of formation of zinc oxide may be calculated, as follows.

(Mixter) $ZnO + H_2O = Zn(OH)_2$ $\Delta H = -2400$
(Thomsen) $Zn(OH)_2 + 2HCl{\cdot}aq. = ZnCl_2{\cdot}aq. + 2H_2O$ $\Delta H = -19{,}483$
(Sum) $ZnO + 2HCl{\cdot}aq. = ZnCl_2{\cdot}aq. + H_2O$ $\Delta H = -21{,}883$
(Richards) $Zn + 2HCl{\cdot}200\ H_2O = ZnCl_2{\cdot}aq. + H_2$ $\Delta H = -36{,}600$
(Sum reversed) $ZnCl_2{\cdot}aq. + H_2O = ZnO + 2HCl{\cdot}aq.$ $\Delta H = +21{,}883$
(Second sum) $Zn + H_2O = ZnO + H_2$ $\Delta H = -14{,}717$
(Roth)[19] $H_2 + {}^1/_2\ O_2 = H_2O$ $\Delta H = -68{,}380$
Final sum. $Zn + {}^1/_2\ O_2 = ZnO$ $\Delta H_{291} = -83{,}097$

It is felt that this new thermal value for the heat of formation of zinc oxide, which compares favorably with 82,830 derived from the present equilibrium data, is probably more accurate than the older values based on Thomsen's data on the heat of solution of zinc. It is of interest to note that the only fairly recent direct determinations by Thomsen's method are those of DeForcrand[20] who obtained the following values.

ZnO prepared from $Zn(OH)_2$ at 125°C	82,970
from $Zn(NO_3)_2$ at 350°C	83,000
from "rouge blanc"	84,300
by combustion of zinc	84,700

DeForcrand considered that his data showed the polymerization of zinc oxide, but it is important that his determinations were not made on the *same* samples, prepared at high and low temperatures. Experiments carried out in this Laboratory, to be described at some future time, failed to confirm the polymerization theory.

As final check on the calculated value of free energy and heat of formation of zinc oxide, the entropy of zinc oxide may be calculated as follows: $-T\Delta S_{298} = -75{,}785 - (-82{,}830)$; $\Delta S_{298} = -23.62$. Lewis and Randall give S°_{298} for Zn = 9.83, and for ${}^1/_2O_2 = 24.00$. Consequently, S°_{298} for ZnO is calculated to 10.20 entropy units. Preliminary results of low temperature specific-heat work carried out on zinc oxide by Dr. George S. Parks, of Leland Stanford University (personal communication), indicate this to be a not unreasonable figure.

Accuracy of Results

It is somewhat surprising that the method used in these equilibria experiments should have given results as good as these seem to be. The method is obviously limited at high temperatures by the inability to absorb the zinc vapor completely in the tin trap, and at low temperatures by the analytical difficulties of determining very small concentrations of carbon dioxide in the presence of large amounts of carbon monoxide. More-

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[19] Roth, *Z. Elektrochem.*, **26,** 288 (1920). (A critical recalculation of the data of Schuller-Wartha, Thomsen and Mixter.)

[20] DeForcrand, *Ann. chim. phys.*, [7] **27,** 36 (1902).

over at lower temperatures than those used in the present work, reaction rates of reduction become sufficiently slow to present a decided problem, and the maintenance of a definite zinc vapor concentration in the gas phase becomes somewhat difficult.

Over the intermediate temperature range through which a straight-line curve was obtained, the constancy of the calculated values of the integration constant I is somewhat better than for the data of Rhead and Wheeler used by Lewis and Randall for the reaction, $CO + {}^1/_2O_2 = CO_2$.

Considered from the point of view of the technique of equilibria determinations, the present work has taken care of a number of factors which were partly or wholly neglected in previous work. Experimental results were shown to be identical within the experimental error whether the reaction was started from the carbon monoxide or carbon dioxide side. Substitution of lead for tin showed that the trap material did not affect the results in any marked degree. The construction of the apparatus was such that except at the very highest temperatures the equilibrium system had a probable definite zinc vapor concentration corresponding to the vapor pressure of liquid zinc.

Of further factors which might influence the results, there remain the question of the constancy of the solid phase, and the decision as to the degree of "freezing" of the equilibrium mixture actually obtainable by the use of the tin trap. The ordinary method of testing the latter point would have been to vary the rate of passage of gas through the apparatus. Actually some little variation of gas rate ensued in the experiments performed, for it was difficult to maintain an exact rate with the manual adjustments of the present apparatus. Reference to Table I will indicate the range of variation of time and rate of passage. The usual criterion of reproducibility with various rates is not considered entirely conclusive in the present apparatus, however, as results might depend entirely on the small vapor pressure of zinc above the trap material.

Although the results treated thermodynamically do not show reason for doubt of the present data excepting with respect to the heat of reaction already discussed, it was thought desirable to determine, if possible, the free energy of formation of zinc oxide by an entirely different method. Experiments with galvanic cells using a zinc oxide electrode have been made, and furnish corroborative evidence not only as to the free energy of formation, but also as to the constancy of the solid phase. As the data obtained are too extensive for inclusion in the present paper, this part of the work is planned as a later communication.

One observation not previously mentioned with respect to actual behavior of the material during experimentation should not be omitted here. There was a marked formation of elementary carbon in the apparatus during a determination. The carbon was formed *only* in the zinc phase, and not distributed throughout the mass, and may be thought to be due to the reaction, $2CO = C + CO_2$, a reaction which was probably catalyzed at the zinc surfaces in a manner similar to the catalysis of the same reaction at an iron surface, and which tends to go to the right under the experimental conditions. The rate of this reaction was, however, markedly slower than the reduction of zinc oxide by carbon monoxide. It was customary to observe a decrease of about 30 cc. of carbon monoxide of a total volume of 300 cc. in a number of cycles of passage requiring about ten hours' time whereas, starting with pure carbon dioxide, the content of dioxide was decreased to less than 5% in one hour's time. The rate of carbon formation is, therefore, approximately $^1/_{100}$ of the primary reaction investigated, and this is of about the same magnitude as the accidental errors of manipulation and analysis.

We regard the values of heat of reaction and of standard free energy obtained in the present work to be probably correct to within 300 calories.

Summary

Equilibrium data have been obtained for the reaction $ZnO(s) + CO = Zn(g) + CO_2$, over the temperature range 500° to 850°.

A probable error in the older determinations of the heat of formation of zinc oxide is indicated, and a recalculation of thermal data is made which brings the new value in accord with the present work.

Standard free-energy equations are derived for the reduction of zinc oxide by carbon monoxide, and the entropy and free energy of zinc oxide at 25° are calculated.

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THE CATALYTIC EFFECT OF SILVER AMMONIA ION IN THE OXIDATION OF AMMONIA BY PEROXYSULFATES

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Introduction

In a former paper[2] there were presented the results of an investigation on the rate of the oxidation of chromic salts by peroxysulfuric acid ($H_2S_2O_8$), under the influence of silver ion acting as catalyst. The results showed that the rate of the catalyzed reaction is directly proportional to the concentrations both of peroxysulfate ion and silver ion, but independent of the concentration of chromic and hydrogen ions. These facts clearly

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[2] Yost, THIS JOURNAL, **48**, 152 (1926).