[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE NEW JERSEY ZINC COMPANY (OF PA.)]

Reduction Equilibria of Zinc Oxide and Carbon Monoxide[1]

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Introduction

As a result of the work of Bodenstein and his co-workers[3] it is now universally recognized that the reduction of zinc oxide by carbon does not proceed directly to any appreciable extent, but is the result of two reactions which occur simultaneously at elevated temperatures and which may be formally represented by the equations

$$ZnO(s) + CO(g) = Zn(g) + CO_2(g) \qquad (1)$$

$$C(C, \text{graphite}) + CO_2(g) = 2CO(g) \qquad (2)$$

Equilibrium data for reaction (2) are experimentally known over a considerable range of temperature from the classical work of Rhead and Wheeler; moreover, they can be calculated with even greater accuracy from the very accurate thermodynamic data for graphite and the carbon gases which have been made available in recent years.[4]

Equilibrium data for reaction (1) had been limited to the results obtained by Maier and Ralston[5] in the temperature range 550–850°, although additional results which extend to 1056° have recently been published by Bodenstein,[6] based on the Doctor's Dissertation of W. Falkenberg.[7] It appeared to be of interest to extend the equilibrium data for reaction (1) to the higher temperatures actually used in zinc reduction, and the experiments to be described in this paper were done in the temperature range 900–1100°, using a dynamic method different from that of Maier and Ralston.

Beginning in 1934, a study was made in this Laboratory of the relative rates of reactions (1) and (2), the results of which are being published elsewhere.[8] In these experiments, the extent to which reaction (1) occurred in the above temperature range was so great, even with a time of contact of gas and solid of the order of 0.01 second, as to indicate that equilibrium might be attained if the time of contact could be increased to one or more seconds. Since this could readily be done, equilibrium measurements were begun early in 1935, and were continued at intervals over a two-year period.

This paper describes the experimental method used and the results obtained, and compares these results with those of Maier and Ralston and of Bodenstein, the basis of comparison being a newly revised free energy equation for the reaction which employs up-to-date thermodynamic data for the substances involved.

Experimental Method

The method finally adopted was to pass the desired gas at a slow rate around a precalcined briquet of zinc oxide placed in a silica furnace tube maintained at the desired temperature, the briquet being freely suspended from one arm of a chemical balance. From the known rate of flow of the gas and the observed rate of loss in weight of the briquet, it was possible to calculate the composition of the gas leaving the briquet. On the assumption that equilibrium had been reached, values of the equilibrium constant could be obtained, as defined by the expression

$$K_1 = P_{Zn}P_{CO_2}/P_{CO}$$

There were several advantages to this experimental method. It permitted a determination of the amount of reaction occurring without requiring direct analysis of the equilibrium gas, which cannot be done accurately because of the speed with which the reaction reverses as the gases cool. It also permitted the use of mixed gases, and while the admixture of an inert gas such as nitrogen gave irregular results which had to be rejected, the use of mixtures high in carbon dioxide proved to be essential in order to assure attainment of equilibrium in the limited time available.

The chief disadvantages of the method were that it involved the somewhat inaccurate measurement of the rates of gas flow, that it was not a static equilibrium method, and that the equilibrium could not be approached from both sides.

Apparatus.—The furnace used was a 24-inch long by 12-inch diameter, compensated-wound resistance furnace, provided with a silica reaction tube $1^1/_4$ inches in diameter and 40 inches long, the bottom end of this tube projecting about seven inches below the lower end of the furnace. Immediately above the upper end of the furnace, a $^3/_4$-inch bore silica side tube was sealed onto the reaction tube, wound with resistance wire for heating, and properly insulated. The purpose of this auxiliary heating (to about 900°) was to keep the exit gases hot and prevent excessive blockage of the tube by condensation of zinc or the re-

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(3) M. Bodenstein and F. Schubart, *Metall u. Erz*, **14**, 177 (1917); see also *Z. Elektrochem.*, **23**, 105 (1917); M. Bodenstein, *Trans. Electrochem. Soc.*, **51**, 365 (1927).

(4) See, for example, the references accompanying Table VII; also F. D. Rossini, *J. Chem. Phys.*, **6**, 569 (1938).

(5) C. G. Maier and O. C. Ralston, THIS JOURNAL, **48**, 364 (1926).

(6) M. Bodenstein, *Z. Elektrochem.*, **46**, 132 (1940).

(7) W. Falkenberg, "Dissertation," University of Berlin, 1929.

(8) Am. Inst. Mining & Mech. Eng., Tech. Paper 1295, *Metals Tech.*, 1941.

formation of zinc oxide. The furnace was mounted on a small truck and track to facilitate alignment of the furnace tube with the zinc oxide briquet suspended from the balance arm. The balance used was one of moderate sensitivity from which one pan had been removed.

Figure 1 shows the dimensional arrangement of the reaction tube and accessories, and the location of the experimental briquet. The system of tubes, held in place by rubber stoppers, C, which were thermally insulated by the plugs, D, was arranged so that by passing a slow stream of purified nitrogen into the upper side arm, B, a downward current of gas would be created which would prevent any of the gaseous reduction products from leaving the furnace except through the heated side tube, F. This arrangement was necessary in order to prevent condensation of zinc or zinc oxide on the $^1/_{16}$-inch silica rod, A, by which the specimen briquet, H, was suspended from the balance. K was a baffle used to spread the incoming gas, and J was the refractory protection tube for the platinum–platinum-rhodium thermocouple. A short piece of silica tubing, inserted at F, could be replaced whenever it became seriously clogged with zinc oxide. A hydrogen flame was kept burning at the mouth of this tube to prevent a too rapid formation of rock oxide.

Materials.—The zinc oxide used was a relatively dense ceramic grade material having the following typical analysis, in per cent.: PbO, 0.022; total Fe, 0.015; total S as SO_3, 0.03; insoluble in HCl, 0.16; water soluble salts, 0.12. The oxide was pressed into cylindrical briquets one inch in diameter and two inches long, and these were heated at 1000° for an hour to harden them sufficiently for use. Only a very slight shrinkage occurred during the heat treatment, which may also have reduced the total impurities somewhat. Two such briquets were drilled and mounted end to end for each experiment.

Carbon monoxide was prepared as needed by passing tank carbon dioxide over severely coked low-sulfur coal in an auxiliary furnace maintained at about 1130°. The carbon monoxide was carefully purified, particular attention being paid to removal of traces of sulfur present as carbonyl sulfide. The purified gas contained only traces of hydrogen or hydrocarbons, and about 2% of nitrogen which could not be removed.

Carbon dioxide was used directly from a tank, while the nitrogen was purified by conventional means.

Measurement of Rates of Flow.—The gases were metered by means of the conventional type of capillary flowmeters, which were calibrated at intervals throughout the work. It was realized that the greatest potential source of error in these experiments, one amounting to 3–5% of the measured rate of flow, lay in the calibration and use of these flowmeters, and careful attention was paid to this phase of the work.

Temperature Measurement.—Temperatures were measured as at J, Fig. 1, with a platinum–platinum-rhodium thermocouple which was checked at frequent intervals against two similar couples standardized against samples of copper, aluminum and copper–silver eutectic whose melting points were certified by the U. S. Bureau of Standards. Temperatures were read to within 1° and furnace temperatures were maintained constant to within ±1° by means of a Tagliabue temperature controller.

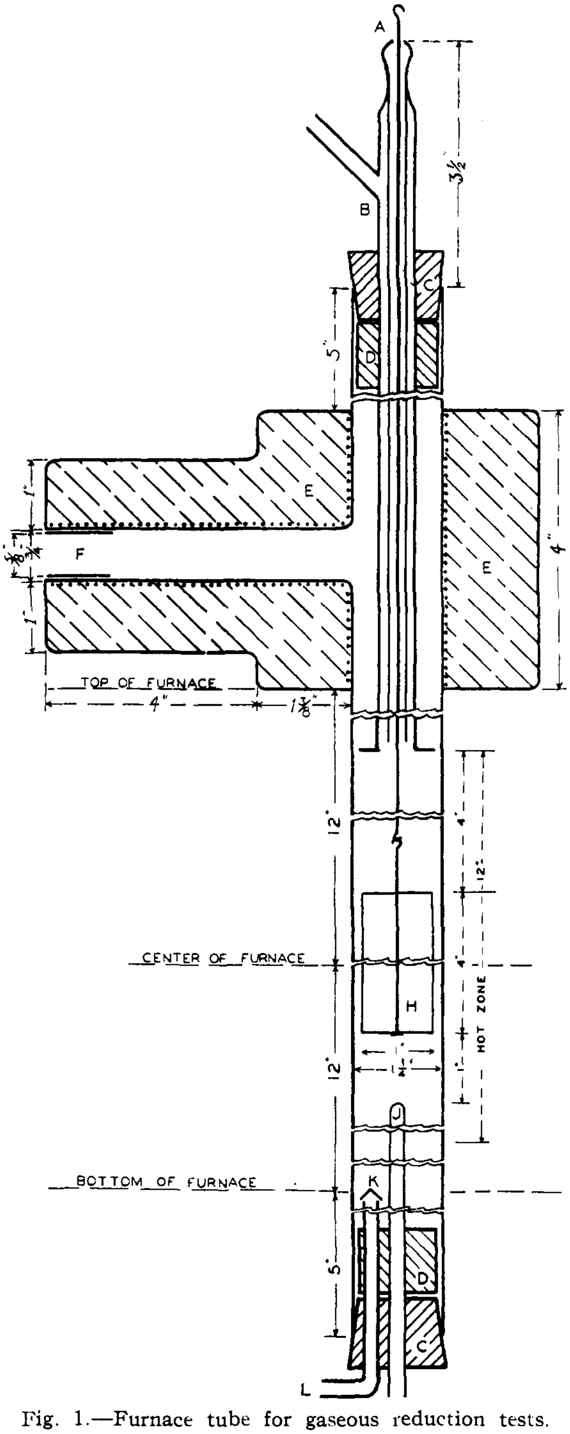

Fig. 1.—Furnace tube for gaseous reduction tests.

Temperature surveys made in an empty furnace tube indicated a central zone 10 to 12 inches long in which the temperature was constant within one or two degrees. The introduction of a briquet and tube assembly, however, resulted in a slight rise in temperature starting at about the middle of a briquet and extending above it for several inches. This was an advantage in one respect, the higher temperature above the briquet preventing any back reaction until the gases were removed from contact with the suspension rod. Because of this effect, and because of the endothermic nature of the reduction reaction, it was necessary to fix the experimental temperatures more accurately than could be done with the control couple located below the briquet. Special experiments were therefore made in which a briquet, mounted on the end of a silica tube, was fixed at its normal position in the furnace. A second couple was placed in this tube and, with the temperature of the control couple being maintained constant as in a normal experiment, a temperature survey was made between the bottom of the briquet and the upper end of the furnace, both when nitrogen was flowing through the furnace and when carbon monoxide or mixtures of carbon monoxide and dioxide were used. The rate of gas flow was 200 cc. per minute in each case.

The temperatures thus measured at the upper end of the briquet were used as the experimental equilibrium temperatures, on the assumption that the stream of gas attained these temperatures and came into chemical equilibrium with the briquet at this point. With the control couple maintained at 900, 1000 and 1100°, the three experimental temperatures finally adopted in this way were 900, 1002 and 1105°, respectively, bearing in mind that the final equilibrium data were selected from experiments in which high initial carbon dioxide concentrations were employed.

TABLE I

REDUCTION OF ZINC OXIDE BY CARBON MONOXIDE

Run no. 261, 4″ ceramic oxide briquet, nominal gas flow 200 cc./min., temperature 1100°, weights removed in steps of 0.05 g. each.

Total time, min.	Time intervals, min.	Rate, grams/min.	Rate mole/min. × 10^3
1.41	0.41	0.122	1.50
1.83	.42	.119	1.46
2.23	.40	.125	1.54
2.60	.37	.135	1.66
3.00	.40	.125	1.54
3.40	.40	.125	1.54
3.80	.40	.125	1.54
4.18	.38	.132	1.62
4.60	.42	.119	1.46
4.97	.37	.135	1.66
5.38	.41	.122	1.50
5.77	.39	.128	1.57
6.15	.38	.132	1.62
6.56	.41	.122	1.50
6.97	.41	.122	1.50
7.34	.37	.135	1.66
7.76	.42	.119	1.46
8.12	.36	.139	1.71
8.50	.38	.132	1.62
8.88	.38	.132	1.62
9.30	.42	.119	1.46
	Average	.127	1.56

Gas analyses	CO, %	CO_2, %	N_2, %
Before run	72.5	24.2	3.3
After run	73.3	23.5	3.2
Average	72.9	23.85	3.25

Barometric pressure, 752.3 mm.
Room temperature 33°.

Description of a Typical Experiment.—While the briquet, freely suspended in the furnace from the balance arm, was coming up to temperature, a stream of nitrogen was passed upward through the furnace while a second stream was admitted through the upper tube as at B, Fig. 1. After a period of thirty to sixty minutes, tests were made to indicate the constancy of the briquet weight. Weight losses were entirely negligible, usually being zero and never being more than one milligram per minute even at the highest temperature.

With the weight of the suspended briquet balanced by weights on the remaining balance pan, the stream of nitrogen was replaced by one of the desired reducing gas, a stop watch was started, a fractional weight was removed from the pan, and the time noted when the pointer again swung past the center mark. This method of timing was found to be preferable to that of watching for equal swings of the pointer on each side of center. The removal of fractional weights was continued until from 15 to 20 readings had been taken, the first two or three readings being discarded since during this time residual nitrogen was being flushed out.

In general, there was no trend in the rate values as an experiment progressed, and the average of the entire set of values was used. There was some fluctuation in the rate values, but since weight losses were cumulative, these fluctuations tended to even out over a series of three or four readings. The method gave the equivalent of an average rate obtained over a period ranging from fifteen minutes to

TABLE II

REDUCTION OF ZINC OXIDE BY CARBON MONOXIDE

Run no. 300, 4″ ceramic oxide briquet, nominal gas flow 200 cc./min., temperature 900°, weights removed in steps of 0.005 g. each.

Total time, min.	Time intervals, min.	Rate, grams/min.	Rate, mole/min. × 10^3
3.98	1.95	0.0026	0.0319
6.02	2.04	.0025	.0307
8.10	2.08	.0024	.0295
10.20	2.10	.0024	.0295
12.05	1.85	.0027	.0332
14.27	2.22	.0024	.0295
16.18	1.91	.0026	.0319
18.20	2.02	.0025	.0307
20.13	1.93	.0026	.0319
22.07	1.94	.0026	.0319
24.12	2.05	.0024	.0295
26.18	2.06	.0024	.0295
28.20	2.02	.0025	.0307
30.35	2.15	.0023	.0282
32.32	1.97	.0025	.0307
34.37	2.05	.0024	.0295
36.45	2.08	.0024	.0295
38.48	2.03	.0025	.0307
40.68	2.20	.0023	.0282
42.75	2.07	.0024	.0295
	Average	.0025	.0303

Gas analysis	CO, %	CO_2, %	N_2, %
Before run	34.1	64.3	1.6

Barometric pressure, 753.6 mm.
Room temperature, 27°.

an hour, but it had the advantage of proving, by the constancy of successive values, that no pieces of the briquet had broken off during the experiment.

At the close of the experiment, the briquet and suspension rod were removed from the furnace, and the rod was examined closely for the deposition of any zinc or zinc oxide. Occasionally a very small amount of "philosopher's wool" was found at a point about four inches above the briquet, but its weight was entirely negligible.

To illustrate the type of results obtained, two sets of experimental data are given in Tables I and II. The first of these represents a rapid reaction at high temperature, the second a very slow reaction rate obtained with a carbon monoxide–carbon dioxide mixture at 900°. The use of higher concentrations of carbon dioxide at 900° resulted in rates so slow that the balance swings could not be timed accurately.

Control Experiments.—Numerous preliminary experiments were done in order to determine the possibilities of the method and to eliminate various possible sources of error. The results of these will be described in general terms.

1. **Rate of Gas Flow.**—Attempts were made to obtain a true value of the equilibrium constant by extrapolating to zero rate of flow the values obtained with gas flows ranging from 300 to 25 cc. per minute of pure carbon monoxide, but the values of the equilibrium constant at the slowest rates of flow were abnormally large. By inserting a silica capillary tube to the upper surface of the briquet and slowly withdrawing a gas sample during a run it was found that, at slow rates of flow, nitrogen from the stream entering at the top of the furnace was able to diffuse to the briquet surface. Such dilution with nitrogen should permit a relative increase in the amount of reaction over that occurring with pure carbon monoxide. Further careful tests of this kind showed that no dilution by nitrogen at the upper surface of the briquet occurred at 900° with a gas flow of 100 cc. per minute, or at 1000 or 1100° with a flow of 200 cc. per minute. These minimum rates of flow were, therefore, observed in the final experiments.

2. **Use of Mixed Gases.**—Tests made with mixtures of carbon monoxide and carbon dioxide showed that these mixtures behaved as would be expected from the law of mass action. The effect of the addition of carbon dioxide is to decrease the number of carbon monoxide molecules which must react to produce equilibrium, such decrease being relatively greater than the decrease in the concentration of carbon monoxide molecules produced by dilution with carbon dioxide, thus correspondingly increasing the likelihood of attaining equilibrium.

The addition of nitrogen to the carbon monoxide has the opposite effect, that is, it slightly decreases the chance of reaching equilibrium. In spite of this it seemed that the use of carbon monoxide–nitrogen mixtures should be tried. Anomalous results were obtained, in the sense that dilution of the carbon monoxide with 10% nitrogen was nearly as effective as dilution with 50% nitrogen in decreasing the amount of reaction. Similar experiments with helium–carbon monoxide mixtures were made, with similar results. Adsorption of the inert gas on the briquet surface would

TABLE III

CALCULATION OF ZnO–CO EQUILIBRIUM CONSTANTS AT 900°

Total gas flow, cc./min. cor. to N. T. P.	Initial gas compn., %			Atm. press., mm.	Wt. loss of briquet, g./min.	Calcd. exit gas compn., %				K_1 cor. to 760 mm.
	CO	CO_2	N_2			Zn	CO_2	CO	N_2	
271.7	96.7		3.3	757.4	0.0711	6.72	6.72	83.49	3.07	0.00539
271.7	96.4		3.6	758.2	.0722	6.82	6.82	83.01	3.35	.00559
179.4	97.4		2.6	747.0	.0484	6.91	6.91	83.76	2.42	.00560
180.0	97.6		2.4	745.5	.0485	6.91	6.91	83.95	2.23	.00558
180.0	97.4		2.6	750.6	.0489	6.96	6.96	83.66	2.42	.00572
180.0	97.3		2.7	750.1	.0477	6.80	6.80	83.88	2.52	.00544
181.2	97.1		2.9	750.6	.0476	6.74	6.74	83.82	2.70	.00535
180.6	97.6		2.4	755.1	.0486	6.90	6.90	83.97	2.23	.00563
91.2	99.4		0.6	751.8	.0245	6.89	6.89	85.67	0.55	.00548
91.2	97.9		2.1	750.1	.0246	6.93	6.93	84.20	1.94	.00563
90.9	97.9		2.1	748.0	.0249	7.02	7.02	84.02	1.94	.00578
91.9	97.3		2.7	752.8	.0254	7.09	7.09	83.53	2.29	.00596
180.2	92.7	4.95	2.35	747.0	.0336	4.87	9.58	83.31	2.24	.00550
181.7	91.95	5.4	2.65	750.1	.0311	4.50	9.66	83.31	2.53	.00515
185.4	72.35	25.25	2.4	745.5	.0107	1.57	26.43	69.64	2.36	.00585
189.2	71.0	26.3	2.7	750.6	.0105	1.51	27.41	68.43	2.65	.00598
185.8	45.25	53.3	1.45	750.6	.0039	0.571	53.57	44.42	1.44	.00680[a]
186.2	44.6	52.6	2.8	755.1	.0038	.563	52.87	43.78	2.79	.00676[a]
92.0	47.05	51.1	1.85	748.0	.0021	.613	51.41	46.14	1.84	.00672[a]
92.9	47.3	50.85	1.85	754.4	.0020	.590	51.15	46.44	1.82	.00645[a]
178.2	34.45	64.1	1.45	752.8	.0024	.370	64.24	33.95	1.44	.00693[a]
178.4	33.9	64.3	1.8	754.0	.0022	.336	64.42	33.45	1.76	.00642[a]
177.2	34.1	64.3	1.6	753.6	.0025	.382	64.44	33.59	1.59	.00727[a]
									Average	0.00676 ± 0.0002

[a] These values only used in obtaining final average given.

TABLE IV

CALCULATION OF ZnO–CO EQUILIBRIUM CONSTANTS AT 1000°

Total gas flow, cc./min. cor. to N. T. P.	Initial gas compn., %			Atm. press., mm.	Wt. loss of briquet, g./min.	Calcd. exit gas compn., %				K_1 cor. to 760 mm.
	CO	CO_2	N_2			Zn	CO_2	CO	N_2	
361.1	98.0		2.0	753.9	0.185	12.40	12.40	73.46	1.74	0.0207
361.1	98.8		1.2	753.6	.187	12.49	12.49	73.97	1.05	.0209
269.0	97.5		2.5	746.8	.157	13.85	13.85	70.15	2.15	.0268
269.9	96.7		3.3	748.5	.159	13.95	13.95	69.26	2.84	.0277
179.4	97.8		2.2	741.7	.116	15.11	15.11	67.91	1.87	.0328
178.2	98.3		1.7	749.3	.111	14.64	14.64	69.26	1.46	.0305
178.8	97.8		2.2	750.1	.118	15.38	15.38	67.38	1.86	.0346
177.6	98.2		1.8	750.1	.105	14.00	14.00	70.45	1.55	.0274
178.2	97.6		2.4	743.0	.110	14.52	14.52	68.90	2.06	.0299
178.8	97.3		2.7	741.2	.111	14.60	14.60	68.49	2.31	.0303
180.6	92.2	5.15	2.65	741.7	.0969	12.88	17.34	67.45	2.33	.0323
180.7	91.3	5.55	3.15	741.2	.0937	12.49	17.34	67.41	2.76	.0313
185.3	72.1	25.95	1.95	749.3	.0449	6.26	30.59	61.33	1.82	.0308
190.9	69.45	28.15	2.40	743.0	.0410	5.59	32.17	59.99	2.29	.0293
183.6	47.45	51.45	1.1	750.1	.0206	3.00	52.91	43.03	1.06	.0364[a]
183.3	45.56	53.05	1.35	750.1	.0198	2.89	54.41	41.36	1.34	.0375[a]
177.3	47.25	51.15	1.6	759.5	.0179	2.71	52.47	43.27	1.55	.0329[a]
176.2	44.30	53.35	2.35	738.4	.0170	2.59	54.55	40.56	2.30	.0338[a]
174.4	22.7	76.6	0.7	762.5	.00712	1.11	76.86	21.34	0.69	.0401
172.8	21.05	77.55	1.4	757.7	.00514	0.813	77.73	20.07	1.39	.0314[a]
170.5	19.7	78.40	1.9	738.4	.00519	.832	78.59	18.71	1.87	.0339[a]
172.0	21.35	77.95	0.7	750.3	.00549	.872	78.14	20.29	0.70	.0332[a]
175.2	7.4	92.1	.5	751.8	.00214	.335	92.12	7.034	.51	.0434
175.6	6.95	92.25	.8	751.8	.00235	.367	92.28	6.563	.79	.0510
175.2	7.35	92.15	.5	760.7	.00200	.314	92.17	7.020	.50	.0412[a]
177.1	7.2	92.05	.75	748.8	.00184	.285	92.06	6.895	.76	.0375[a]
									Average	0.0353 ± 0.0025

[a] These values only used in obtaining final average given.

TABLE V

CALCULATION OF ZnO–CO EQUILIBRIUM CONSTANTS AT 1100°

Total gas flow, cc./min. cor. to N. T. P.	Initial gas compn., %			Atm. press., mm.	Wt. loss of briquet, g./min.	Calcd. exit gas compn., %				K_1 cor. to 760 mm.
	CO	CO_2	N_2			Zn	CO_2	CO	N_2	
181.2	100.0			750.3	0.2105	24.24	24.24	51.52		0.1125
181.2	100.0			744.5	.2075	23.98	23.98	52.05		.1082
182.4	99.6		0.4	755.6	.205	23.63	23.63	52.42	0.32	.1059
180.0	98.0		2.0	749.3	.209	24.24	24.24	50.01	1.51	.1158
180.0	97.4		2.6	746.8	.211	24.40	24.40	49.23	1.97	.1188
175.9	96.8		3.2	750.6	.208	24.57	24.57	48.44	2.42	.1231
176.4	96.5		3.5	752.3	.214	25.05	25.05	47.29	2.61	.1314
181.4	91.1	5.25	3.65	749.3	.193	22.66	26.72	47.79	2.83	.1249
177.5	90.85	5.40	3.75	750.6	.182	22.03	26.24	48.81	2.92	.1169
182.8	72.75	24.45	2.80	751.8	.119	15.18	35.92	46.51	2.39	.1159
178.4	72.90	23.85	3.25	752.3	.127	16.40	36.33	44.55	2.72	.1323
185.6	45.10	52.90	2.0	746.8	.0578	7.90	56.62	33.64	1.84	.1307[a]
182.2	46.35	50.50	3.25	750.1	.0594	8.24	54.58	34.29	2.89	.1295[a]
175.5	48.25	50.30	1.45	755.4	.0563	8.12	54.34	36.21	1.33	.1212[a]
173.6	22.70	76.45	0.85	747.5	.0197	3.03	77.17	18.98	0.82	.1212[a]
174.4	23.00	76.10	.9	748.0	.0195	2.99	76.82	19.32	.87	.1170[a]
176.2	8.25	91.60	.15	747.3	.00679	1.050	91.69	7.12	.14	.1329[a]
176.9	8.35	91.20	.45	747.5	.00676	1.042	91.28	7.220	.46	.1295[a]
									Average	0.1260 ± 0.006

[a] These values only used in obtaining final average given.

account for the results obtained, but this seems highly improbable, and no other explanation could be found. It was finally decided to exclude all results obtained with mixtures containing inert gases, even though those obtained with from 30 to 50% of nitrogen in the initial gas were in fair agreement with the equilibrium values finally adopted.

3. **Tests for Attainment of Equilibrium.**—Several different methods were used in attempts to obtain independent evidence that equilibrium was being attained. Some were inconclusive while others, which cannot be described for lack of space, indicated that equilibrium was at least being very closely approached, if not actually attained, in spite of the short reaction time available.

Experimental Results

The experimental results obtained at 900, 1002, and 1105° are given in Tables III, IV, and V, respectively. Conventional methods were used in arriving at the rates of gas flow given in column 1 of these tables. The rates of loss in weight of the briquets, given in column 6, are each averages of at least 15 individual measurements. The loss of zinc oxide in moles per minute is equal to the moles per minute of zinc vapor and of carbon dioxide formed, and of carbon monoxide disappearing, permitting the calculation of the final gas compositions.

The apparent equilibrium constant thus obtained must be corrected to the true value for a pressure of one atmosphere by multiplying by $P/760$, where P is the experimental barometric pressure. The values of K_1 which are marked "a" are those which were used in arriving at the final average value at each temperature. The remaining values were discarded either as representing a failure to reach equilibrium or, as in the case of three values obtained at 1002°, because they appeared to be inexplicably large.

The results obtained at each temperature are plotted in Fig. 2 as a function of the concentration of carbon dioxide in the gas. For comparison, Maier's[9] equilibrium values, calculated from his 1930 free energy equation, are indicated. There is evident at all three temperatures a trend toward increasing values of K_1 with increasing concentration of carbon dioxide in the initial gas. This may be explained by assuming that true equilibrium is closely approached only when the amount of reaction necessary to reach equilibrium has been greatly decreased by the addition of large amounts of carbon dioxide. On this basis, the final values of K_1 were obtained by considering only those experiments in which 50% or more of carbon dioxide was initially present. Also evident at the two higher temperatures is the tendency for the values of K_1 to pass through a local minimum at about 75% of initial carbon dioxide. No satisfactory explanation for this effect was found, and these values were, therefore, included in the final averages. The experimental values for K_1 finally adopted are, in atmospheres: 0.0068 at 900°; 0.0357 at 1002°; 0.126 at 1105°.

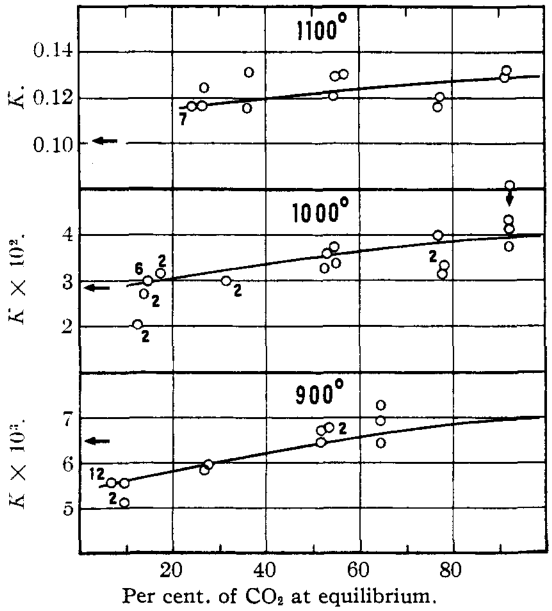

Fig. 2.—Showing dependence of equilibrium constant K on the carbon dioxide content of the gas. For convenience in plotting, final rather than initial carbon dioxide concentrations are shown. The horizontal arrows indicate values of K calculated from Maier's 1930 equation.

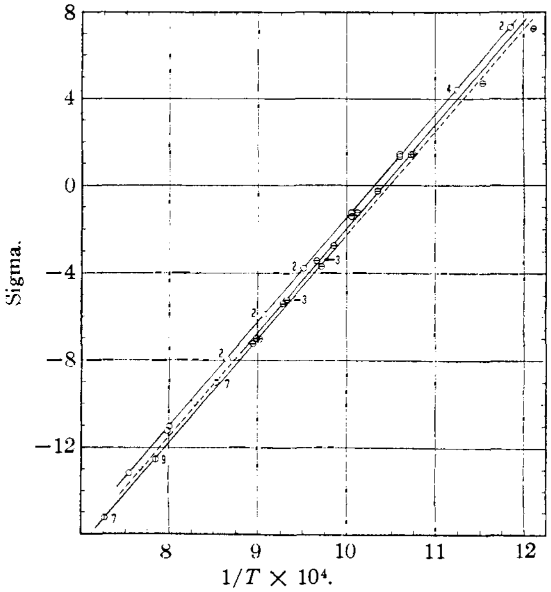

Fig. 3.—Sigma function plot of equilibrium data: O, Bodenstein, left-hand line, slope 47650; ⊖, Maier and Ralston, middle line, slope 47571; ⦶, Truesdale and Waring, right-hand line, slope 47534.

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(9) C. G. Maier, *U. S. Bur. of Mines Bull.*, **324**, p. 44 (1930).

Since, as will be indicated in the following discussion, the adopted average values probably represent minimum values of K_1, it seems worth while to call attention to the maximum values of K_1 obtained by extrapolation of the curves of Fig. 3 to 100% of initial carbon dioxide. These values are: at 900°, 0.007; at 1002°, 0.039; at 1105°, 0.130.

Discussion of Results

Assuming that the rejection of all values of K_1 from experiments involving less than 50% initial carbon dioxide is justified on the basis of failure to attain equilibrium, then, with one exception, the errors arising from experimental technique or from the manner of handling the data are such as to give final values of K_1 which are too low rather than too high. The exception is the error involved in the calibration and use of the flowmeters, undoubtedly the largest single experimental error but one which should affect the results about equally in either direction. Thus, the abnormally high, discarded values of K_1 obtained at 1002° might be attributed to this source. But the flowmeter error cannot be given as the cause of the consistently low results obtained with 75% of carbon dioxide in the initial gas, since it would be necessary to assume that both flowmeters consistently delivered decreased amounts of gas in these cases and not in others.

Comparison of our data with the values calculated from Maier's equation, as in Fig. 2, indicated strongly that the higher the temperature employed, the more closely equilibrium was being approached. This is in line with the results obtained in this Laboratory, which indicate that, in the temperature range under discussion, the reaction *rate* approximately doubles for each 100° rise in temperature, while the amount of reaction required to bring the initial gas to equilibrium does not increase in as large a proportion. In fact, it seemed doubtful that in our experiments at 900° equilibrium had been attained in any case, probably because of the slow reaction rate and because of our inability to employ more than 65% of carbon dioxide in the initial gas.

More conclusive experimental evidence for doubting the attainment of equilibrium at 900° was obtained by using the same experimental method to study the reduction of zinc oxide by hydrogen, a reaction which was known to be much faster and in which, therefore, the chance of reaching equilibrium was better. For the reaction $ZnO + H_2 = Zn + H_2O$, the equilibrium constant is given as $K_2 = p_{Zn} \cdot p_{H_2O}/p_{H_2}$. Dividing K_2 by K_1, there is obtained an expression for the equilibrium constant of the water-gas reaction: $CO_2 + H_2 = CO + H_2O$, where $K_3 = K_2/K_1 = p_{CO} \cdot p_{H_2O}/p_{CO_2} \cdot p_{H_2}$. Values for K_3 as a function of temperature can now be calculated with extraordinary accuracy from appropriate thermodynamic data, and failure to obtain satisfactory agreement with such values by the above combination of experimental data would indicate that values of K_1 or K_2, or both, were in error.

Equilibrium experiments for the hydrogen reduction reaction have been done at 900°, but have not been completed at the two higher temperatures. At present, all that can be said is that values of K_3 obtained from these experiments at 900° were too large, indicating that values for K_1 were too small or, what seems improbable, that values for K_2 were too large as a result of some unforeseen experimental error which caused an apparently excessive amount of reaction.

Comparison of Theoretical and Experimental Equilibrium Data.—There are available for comparison the experimental equilibrium data for reaction (1) published by Maier and Ralston, by Bodenstein, and by the writers. Each set of data was obtained by an independent method, and, while these data do not differ widely, they are not in so good agreement as might be desired. At the time these investigators performed their experiments, their estimated accuracy was as great as that with which high temperature equilibrium values could be calculated from the then available thermodynamic data. As a result of recent revisions of most of the necessary thermodynamic data, equations expressing the free energy and the equilibrium constant of the reaction as functions of the temperature have attained an accuracy which is believed to equal or exceed that of the experimental data. Such equations will, therefore, be used as the basis for comparing the various experimental results.

TABLE VI

MOLAR HEAT CAPACITY EQUATIONS

Equations of the form $C_p = a + b \times 10^{-3} T - c \times 10^{5} T^{-2}$

Substance	a	b	c	Temp., range, °K.	Est. max. % deviation
CO	6.60	1.20	...	273–2500	2
CO_2	10.34	2.74	1.955	273–1200	2
Zn(g)	4.97	(ideal gas)			0
ZnO(s)	11.40	1.45	1.824	273–1573	1

TABLE VII

HEATS AND FREE ENERGIES OF FORMATION

Reaction	$\Delta H_{298.1}$	$\Delta F^0_{298.1}$	Reference
$C(C, \text{graphite}) + {}^1/_2O_2(g) = CO(g)$	-26394 ± 31	-32787 ± 32	b
$C(C, \text{graphite}) + O_2(g) = CO_2(g)$	-94030 ± 11	-94238 ± 14	c
$CO(g) + {}^1/_2O_2(g) = CO_2(g)$	-67636 ± 29	-61451 ± 29	d
$H_2(g) + {}^1/_2O_2(g) = H_2O(g)$	-57798 ± 10	-54638 ± 11	e
$H_2(g) + {}^1/_2O_2(g) + H_2O(l)$	-68318 ± 10	-56693 ± 11	b
$H_2O(l) = H_2O(g)$	$+10520 \pm 3$	$+2055 \pm 1$	b, f
$Zn(s) + {}^1/_2O_2(g) = ZnO(s)$	-83250 ± 50	$-76073(\pm 50?)$	a, g, h
$Zn(s) = Zn(g)$	$+31189(\pm 10?)$	$+22692(\pm 10?)$	i
$ZnO(s) + CO(g) = Zn(g) + CO_2(g)$	$+46803(\pm 50?)$	$+37314(\pm 50?)$	(derived)

[a] These results are supported by the values obtained by Dietrich and Johnston[j] on the zinc hydroxide electrode. [b] F. D. Rossini, *J. Research Natl. Bur. Standards*, **22**, 407 (1939) (Research Paper 1192). [c] F. D. Rossini and R. S. Jessup, *ibid.*, **21**, 491 (1938) (R. P. 1141). [d] F. D. Rossini, *ibid.*, **6**, 37 (1931) (R. P. 260). [e] F. D. Rossini, *ibid.*, **6**, 1 (1931) (R. P. 259). [f] N. S. Osborne, H. F. Stimson and D. C. Ginnings, *ibid.*, **23**, 197 (1939) (R. P. 1228). [g] C. G. Maier, G. S. Parks and C. T. Anderson, THIS JOURNAL, **48**, 2564 (1926). [h] C. G. Maier, *ibid.*, **52**, 2159 (1930). [i] K. K. Kelley, *U. S. Bur. Mines Bull.* **383**, p. 108 (1935). These values for the vaporization of zinc depend upon unpublished data by R. Overstreet at the University of California. [j] H. G. Dietrich and John Johnston, THIS JOURNAL, **49**, 1419 (1927).

Derivation of the Free Energy Equation.—The equations for the molar heat capacities are given in Table VI. After a careful study of available data, these equations were all taken from the compilation by Kelley,[10] whose work must be consulted for a detailed discussion of the derivation of these equations from the original data of various investigators. The temperature range for which the maximum departure from experimental data does not exceed that estimated by Kelley is also given. The specific heats of the gases, including zinc vapor, are very accurately known from spectroscopic data. The data from which the heat capacity equation for zinc oxide was obtained are probably accurate to 1%.

The accuracy of the values for the standard heats and free energies of formation of all the substances involved in evaluating these quantities for reaction (1) has been greatly increased in the past few years, largely through the work of Rossini and others at the United States Bureau of Standards. Table VII gives the values of $\Delta H_{298.1}$ and $\Delta F^0_{298.1}$ for the necessary reactions, and references are made to the sources of the data. The values for the formation and vaporization of water are required in order to obtain similar values for the formation of zinc oxide from electrode potential and heat of solution measurements. The values for reaction (1) are the algebraic sums of the values for the components involved.

Particular attention is called to the value of $\Delta F^0_{298.1}$ for the formation of zinc oxide as given in Table VII. On the basis of electrode potential measurements this value should have been -76063 cal./mole, accompanied by Maier's estimated error of ± 150 calories. This would have led to a value for the reduction reaction of $\Delta F^0_{298.1} = 37304$ cal./mole. But by employing the relationship $\Delta F^0 = \Delta H - T\Delta S$, a value for the reduction reaction of $\Delta F^0_{298.1} = 37314$ is obtained. Since, as will be shown, all of the required entropies and heats of formation are more accurately known than is the free energy of formation of zinc oxide, it seemed best to make the necessary adjustment in the latter quantity to bring all of the data into agreement. Therefore, in Table VII the free energy of formation of zinc oxide is given as -76073 cal./mole. Maier's estimated error for this quantity seems unnecessarily large,[11] and the writers have therefore arbitrarily assigned to this quantity a probable error of 50 calories, and have applied the same estimated error to the corresponding value for the reduction reaction. The remaining estimates of error given in Table VII are those of the authors referred to, with the exception of the estimated error in the data for the sublimation of zinc, which was made by the writers.

The values of the entropies, $S_{298.1}$, for the required substances are as follows: for $CO_2(g)$, 51.091 ± 0.01; for $CO(g)$, 47.321 ± 0.01; for $Zn(g)$, 38.46 ± 0.01; for $ZnO(s)$, 10.4 ± 0.1 entropy units. The estimated error of 0.1 unit

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(10) K. K. Kelley, *U. S. Bur., Mines Bull*, **371** (1934).

(11) An error of 100 calories in the free energy of formation of zinc oxide corresponds to an error of 0.002 volt in the determination of the potential of a suitable cell. Maier's apparent error in such measurements was less than 0.0002 volt, yet he regarded such apparent accuracy as fortuitous and assigned a larger error to his data.

in the entropy of zinc oxide is the largest of the four, yet it corresponds to a possible variation of only 30 calories in the calculated free energy value. The values for carbon dioxide and monoxide are those selected by Rossini,[12] the former being based on the data of Rossini and Jessup[13] and of Kassel,[14] while the latter is based on the data of Clayton and Giauque,[15] Kassel[16] and Johnston and Davis.[17] The values for zinc vapor and zinc oxide are those given by Kelley.[18,19]

Using the data of Tables VI and VII, and employing the familiar method of Lewis and Randall, there is obtained by integration and the evaluation of constants the free energy equation

$$\Delta F^0 = 47557 + 6.194\, T \log T - 0.045 \times 10^{-3}\, T^2 + 0.0655 \times 10^5\, T^{-1} - 49.747\, T \quad (3)$$

In this equation $\Delta H_0 = 47557$ and the remaining integration constant $I = -49.747$. From this equation, and the relation

$$\Delta F^0 = -RT \ln K = -4.575\, T \log K$$

values of K_1 were calculated at a series of temperatures of interest and are given in Table VIII, where K_1 is expressed in atmospheres.

TABLE VIII

VALUES OF FREE ENERGY AND EQUILIBRIUM CONSTANT CALCULATED FROM FREE ENERGY EQUATION FOR THE REACTION

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

T, °K.	ΔF^0	$-\log K_1$	K_1
973.1	17121	3.84574	1.427×10^{-4}
1073.1	14270	2.90664	1.240×10^{-3}
1173.1	11443	2.13213	7.377×10^{-3}
1273.1	8638	1.48306	3.288×10^{-2}
1373.1	5853	0.93172	1.170×10^{-1}

Evaluation of Experimental Data.—Again following the method of Lewis and Randall, the sigma function is defined by the relation

$$\Sigma = \Delta H_0/T + I$$

Substituting this in equation (3) there is obtained

$$\Sigma = -4.575 \log K_1 - 6.194 \log T + 0.045 \times 10^{-3}\, T - 0.0655 \times 10^5\, T^{-2} \quad (4)$$

If values of Σ are plotted against $1/T$, true equilibrium data for the reaction should give a series of points lying on a straight line of slope ΔH_0 and of intercept I.

Figure 3 contains the sigma function plots for the data of Bodenstein, of Maier and Ralston, and of the writers, based on the calculations summarized in Table IX. All of Bodenstein's data were used in locating the line through his points on the graph, while only the "best" data of Maier and Ralston were considered in locating the corresponding line. The third line corresponding to our own values at 1002 and 1105°, omitting the 900° point, also passes through points from experiments 8, 16, 17, 18 of Maier and Ralston which Maier[20] later chose to reject. The basis for this selection will be discussed later.

The slopes of these three lines, carefully measured on the original 21- by 24-inch plot were, in the order named, 47650, 47571, and 47534. The remarkably close agreement of these values is very gratifying, none of them differing by as much as 100 calories from the theoretical value of 47557 calories per mole. On the assumption that the theoretical value is the most accurate of the four, it was used throughout in calculating values of I from the three sets of experimental data. This arbitrarily alters certain values of I slightly, but the change thus produced is small as compared with the differences in the values of I for the three sets of data.

Before the results shown in Table IX and Fig. 3 can be discussed further, a brief description of the experimental methods used by the earlier investigators must be given.

The data published by Bodenstein resulted from experiments done under his direction by Wilhelm Falkenberg at the University of Berlin in 1929, and it was through the kindness of Professor Bodenstein that the writers obtained a copy of Dr. Falkenberg's thesis late in 1937. A few errors which appeared in the data as published in the thesis were noted by the writers and have been corrected in the recent paper by Professor Bodenstein.

The chief difficulty encountered in determining equilibria in the reaction under discussion is that of preventing the reversal of the reaction, which occurs as the gases leave the hot zone of the furnace, from influencing the experimental results. Bodenstein avoided this by using only initially pure carbon monoxide, passing it slowly over zinc oxide in a silica furnace tube, so that the total

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(12) Reference (*b*), Table VII, this paper.

(13) Reference (*c*), Table VII, this paper.

(14) L. S. Kassel, THIS JOURNAL, **56**, 1838 (1934).

(15) J. O. Clayton and W. F. Giauque, *ibid.*, **54**, 2610 (1932); *ibid.*, **55**, 5071 (1933).

(16) L. S. Kassel, *J. Chem. Phys.*, **1**, 576 (1933).

(17) H. L. Johnston and C. O. Davis, THIS JOURNAL, **56**, 271 (1934).

(18) Reference (*i*), Table VII, this paper.

(19) K. K. Kelley, *U. S. Bur. Mines Bull.*, **350** (1932), p. 43. The value of 10.43 entropy units given in this Bulletin was rounded off in the revised edition (*Bull.*, **394**) to read 10.4 ± 0.1 e. u.

(20) C. G. Maier, reference 9, page 23.

TABLE IX

CALCULATION OF Σ AND I FROM THE EQUATION

$\Sigma = \Delta H_0/T + I = -4.575 \log K - 6.194 \log T + 0.045 \times 10^{-3}\, T - 0.0655 \times 10^{5}\, T^{-2}$ ($\Delta H_0 = 47557$)

Expt.	Temp., °C.	$1/T$ (°K.) × 10^4	$-\text{Log } K_1$	Σ	I
			Maier and Ralston		
1	552.3	12.117	5.5204	7.2180	−50.4068[a]
2	594.1	11.533	4.9970	4.6933	−50.1542[a]
3	657.5	10.746	4.3173	1.3978	−49.7070
4	660.1	10.717	4.3082	1.3489	−49.6179
5	693.3	10.349	3.9641	− 0.3175	−49.5342
6	715.1	10.120	3.7602	− 1.3090	−49.4367
7	742.1	9.851	3.4535	− 2.7831	−49.6315
8	756.3	9.715	3.2516	− 3.7434	−49.9450[a]
9	760.4	9.676	3.2989	− 3.5375	−49.5537
10	761.6	9.665	3.3233	− 3.4289	−49.3927
11	762.9	9.653	3.2992	− 3.5425	−49.4493
12	799.9	9.321	2.9399	− 5.2786	−49.6065
13	800.3	9.316	2.9425	− 5.2677	−49.5718
14	801.2	9.308	2.9400	− 5.2813	−49.5474
15	805.1	9.275	2.9052	− 5.4500	−49.5591
16	836.3	9.015	2.5669	− 7.0727	−49.9453[a]
17	840.8	8.978	2.5777	− 7.0340	−49.7307[a]
18	846.7	8.931	2.5248	− 7.2899	−49.7631[a]
				Average	−49.551 ± 0.066
			Bodenstein		
1	571	11.848	5.5824	7.4426	−48.9029
2	571	11.848	5.5515	7.3012	−49.0443
3	615	11.261	4.9674	4.4951	−49.0588
4	616	11.249	4.9506	4.4153	−49.0815
5	671	10.593	4.3111	1.3315	−49.0456
6	722	10.050	3.7716	− 1.2752	−49.0700
7	722	10.050	3.7378	− 1.4298	−49.2246
8	778	9.515	3.2544	− 3.7855	−49.0360
9	831	9.058	2.8225	− 5.8909	−48.9680
10	883	8.651	2.3942	− 7.9713	−49.1129
11	935	8.278	1.9850	− 9.9590	−49.3267
12	977	8.000	1.7672	−11.0452	−49.0908
13	1056	7.541	1.3317	−13.1924	−49.0551
14	980	7.981	1.7260	−11.2399	−49.1951
15	883	8.651	2.3950	− 7.9677	−49.1093
16	831	9.058	2.8280	− 5.8657	−48.9428
17	778	9.515	3.2549	− 3.7832	−49.0337
18	671	10.593	4.3360	1.4454	−48.9317
19	616	11.249	4.9600	4.4583	−49.0385
20	616	11.249	4.9508	4.4162	−49.0806
				Average	−49.067 ± 0.068
			Truesdale and Waring		
(7)	900	8.524	2.1701[c]	− 9.0351	−49.5727[b]
(9)	1002	7.842	1.4486[c]	−12.5549	−49.8491
(7)	1105	7.256	0.8996[c]	−15.2702	−49.7776
				Average	−49.813 ± 0.036

[a] Omitted from average. Average of remaining 12. [b] Omitted from average. Average of remaining 2. [c] Average values of $-\log K$ for number of experiments indicated in column 1. Average value of I for experiments 8, 16, 17, 18 of Maier and Ralston, and experiments at 1002° and 1105° of Truesdale and Waring.......... −49.835 ± 0.078.

zinc collected outside the furnace, whether as metal or re-formed oxide, was equivalent to the total carbon dioxide present at equilibrium in the effluent gas. The total volume of gas used was found by oxidizing the residual carbon monoxide to the dioxide and absorbing all of the effluent carbon dioxide in a soda lime tube. Subtraction from this of the carbon dioxide equivalent to the zinc gave the total carbon monoxide present at equilibrium, thus completely specifying the composition of the gas leaving the reaction chamber. Space is not available to describe additional details of the ingenious experimental method, but it seems clear to the writers that the equilibrium temperatures were accurately measured and that ample time had been allowed for the attainment of equilibrium.

Twenty equilibrium values were obtained at temperatures from 571 to 1056°. In plotting the derived values in Fig. 3, several of the points lay so close together that they could not be shown separately and had to be averaged. These points are indicated by the accompanying numerals. There seemed to be but one possible location for the line through Bodenstein's points. The data are self-consistent, from which one might conclude that the experimental error was smaller than that experienced by Maier and Ralston and by the writers. As may be deduced from Table IX and Fig. 3, however, Bodenstein's values for the equilibrium constant are consistently smaller than those found by the other workers. In view of the very close approach to equilibrium obtained by the writers in their experiments in which the rates of gas flow were undoubtedly faster than those used by Bodenstein, failure to attain equilibrium cannot be used to explain Bodenstein's lower results. The only alternative is to assume some systematic error in his experiments, but the writers are unable to suggest any probable source of error.

Maier and Ralston obtained their equilibrium data by recirculating carbon monoxide, carbon dioxide, or mixtures of these gases through a heated silica tube containing a mixture of zinc oxide and liquid zinc maintained at the desired temperature. At each passage of the gas the zinc vapor was removed, while still at temperature, by absorption in a bath of molten tin or lead. Recirculation was continued until the CO_2/CO ratio remained constant, as determined by gas analysis. Knowledge of this ratio and of the vapor pressure of zinc at the experimental temperature permitted calculation of the equilibrium constant. The temperature range, 550 to 850°, was held to be limited at the lower end by the accuracy with which traces of carbon dioxide could be determined, and at the upper end by failure to absorb all of the zinc vapor from the gas, thus permitting some conversion of carbon dioxide to monoxide as the gases cooled upon leaving the furnace. The authors estimated their probable experimental errors as totaling 5%.

The six points marked in Table IX are those which were discarded by Maier, the first two because of suspected analytical inaccuracy, and the remaining four apparently because of suspected back reaction, as mentioned above. Inspection of the original data and of Fig. 3 shows, however, that the values for experiments 8, 16, 17, and 18 correspond to relatively larger, rather than smaller, carbon dioxide concentrations than are represented by their selected data; hence, if these four values were discarded for the reason given, such rejection was incorrect.

In drawing the line through the points of Maier and Ralston in Fig. 3, it was caused to pass through the same points as were used by Maier in a similar plot in his 1930 Bulletin.[21] In the final preparation of the figure, however, several of these points lying close together had to be averaged in order to simplify the drawing.

In calculating values of the sigma function from our own data the final average values were used, each point representing from seven to nine individual values. The 900° point was neglected as representing an obvious failure to attain equilibrium. By a coincidence this line falls exactly on the line drawn through Maier's "best" points, thus suggesting incomplete reaction as the source of his numerous lower values. The line drawn through our points corresponding to 1002° and 1105° also passes through, or very close to, four of the points which Maier apparently rejected for an incorrect reason. Obviously all six points on this line are equally correct (or are subject to the same total error).

The line obtained by plotting in Fig. 3 values of sigma calculated from the revised free energy equation lies so close to the one described in the preceding paragraph that it could not be separately drawn on the large-scale graph.

The average values of I calculated for each set of data, all based on the thermodynamically calculated value of ΔH_0, were: for Maier and Ralston, using Maier's selected data, -49.551; for Bodenstein, -49.067; for the two points of Truesdale and Waring, -49.813; for these two points combined with the four incorrectly rejected points of Maier and Ralston, -49.835.

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(21) Reference 9, page 21.

The thermodynamically calculated value of I is -49.747.

The difference between the theoretical value of I and that obtained from Bodenstein's data is such that, if one were to assume his data to be correct, a total error of 203 calories in the separate or combined derived values of $\Delta H_{298.1}$ and $\Delta F^0_{298.1}$ for the reaction would have to be assumed. On the basis of the discussion accompanying Table VII, this large a change does not seem probable. The corresponding figure for the selected data of Maier and Ralston is 58 calories; that for the combined data mentioned in the preceding paragraph, 26 calories, but in the opposite direction.

In spite of the evident care with which the work carried out under Bodenstein's direction was done, it seems difficult to believe that these results can represent true equilibrium values. To accept them would require that all other experimental values, obtained by independent methods, be thrown out on the ground that equilibrium either had been exceeded or, because of systematic errors peculiar to two different experimental methods, appeared to have been exceeded. It is believed, rather, that Bodenstein's data contain a small, undetected systematic error.

If it is true that Maier and Ralston rejected four of their high temperature points for an incorrect reason, then it follows that these points should now be accepted, and all the others rejected as indicating failure to attain equilibrium; all, that is, except the two lowest temperature points which were previously rejected for a legitimate reason. Even these latter two are now in better agreement with the theoretical data than they were originally.

In order to permit comparison of the various sets of equilibrium data in the most familiar way, Table X has been prepared showing the percentage of zinc vapor or carbon dioxide present at equilibrium at each temperature, assuming the reaction to start with zinc oxide and pure carbon monoxide. In making these calculations, ΔH_0 was taken as 47,557, and the values of the integration constant, I, were the average values indicated in Table IX for the work of the respective investigators.

The situation which now exists with respect to our knowledge of the reduction of zinc oxide by carbon monoxide is a particularly happy one. Three different experimental methods have given equilibrium data which are in as good agreement as one ordinarily expects for work at high temperatures. Six of these equilibrium values are in practically complete agreement with highly accurate theoretical values.

TABLE X

EQUILIBRIUM GAS COMPOSITION CALCULATED FROM EXPERIMENTAL AND THEORETICAL DATA, USING INITIALLY PURE CARBON MONOXIDE

	% Zn or CO_2 at equilibrium				% CO at equilibrium, theoretical
Temp., °C.	Bodenstein	M. and R. selected	T. and W. and M. and R.	Theoretical	
700	1.00	1.12	1.21	1.18	97.64
800	2.88	3.24	3.47	3.40	93.20
900	6.73	7.53	8.04	7.88	84.24
1000	13.13	14.54	15.42	15.14	69.72
1100	21.69	23.64	24.82	24.45	51.10

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Summary

Making use of a revised free energy equation for the reaction $ZnO(s) + CO(g) = Zn(g) + CO_2(g)$; $\Delta F^0 = 47557 + 6.194\,T \log T - 0.045 \times 10^{-3}\,T^2 + 0.0655 \times 10^5\,T^{-1} - 49.747\,T$, equilibrium data were calculated which served as the basis for comparing the experimental values of Bodenstein and of Maier and Ralston with those of the authors obtained by a dynamic method and reported in this paper.

Values of the equilibrium constant, expressed in atmospheres, were found by us to be 0.0068 at 900°, 0.0357 at 1002°, and 0.126 at 1105°.

Four of the values obtained by Maier and Ralston between 750° and 850°, and our own average values at 1002° and 1105°, are in practically complete agreement with equilibrium data calculated from the revised free energy equation. The remaining twelve experiments of Maier and Ralston, and our own data at 900°, are believed to be incorrect because of failure to attain equilibrium.

The twenty experiments reported by Bodenstein, though self-consistent, indicate significantly smaller values of the equilibrium constant at all temperatures than were found by the other experimenters. Failure to attain equilibrium is not indicated here, however, and the existence of some systematic experimental error is suggested.

A summary of equilibrium gas compositions based on the various sources of data is given in Table X.

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