

oxide employed in the measurements described in the two preceding sections of this paper. This value may be converted to 298.16°K. by use of the heat content data for ferrous oxide obtained by Coughlin, King, and Bonnicksen^{25/} and the tables of Kelley^{26/} for iron and oxygen. The result is $\Delta H_{298.16} = -63,080 - 16,320$ (ferrous oxide, 1,523° to 298.16°K.) + 10,660 (iron, 298.16° to 1,523°K.) + 4,960 (oxygen, 298.16° to 1,523°K.) = -63,780 cal. per mole.

The rounded value, $\Delta H_{298.16} = -63.8$ K. cal. per mole, is adopted as the best value of the heat of formation of ferrous oxide by this method. The carbon monoxide reduction equilibria reported by Sambongi^{27/} for liquid ferrous oxide are not considered for the present purpose.

Hydrogen Reduction Equilibria

Hydrogen reduction equilibria of crystalline ferrous oxide have been measured by Britzke, Kapustinsky, and Schaschkina;^{28/} Chipman and Marshall;^{29/} Emmett and Schultz;^{30/} Iwase and Sano;^{31/} and Sibata and Kujirai.^{32/} The results of the last four mentioned investigations are in good agreement on the average. Those of the first deviate appreciably from the others. For the derivation of the heat of formation of ferrous oxide, the results of Chipman and Marshall and Emmett and Schultz are adopted here as best. Consideration of data for the liquid range of ferrous oxide is deferred to a later section of this paper.

The calculations are shown in table 2. Column (1) gives the temperatures. Column (2) gives the measured values of $K = \frac{P_{H_2O}}{P_{H_2}}$. Column (3) gives the corresponding values of $\frac{\Delta F^0}{T} = -R \ln K$. Column (4) gives values of the entropy of reaction at T, obtained from the entropies at 298.16°K.^{33,34/} and entropy increments

^{25/} Work cited in footnote 7.

^{26/} Kelley, K. K., Contributions to the Data on Theoretical Metallurgy. X. High-Temperature Heat-Content, Heat-Capacity, and Entropy Data for Inorganic Compounds: Bureau of Mines Bull. 476, 1949, 241 pp.

^{27/} Sambongi, K., On the Reduction Equilibria of Iron Oxides: Japan Sci. Rev., Eng. Sci., vol. 1, 1950, p. 63.

^{28/} Britzke, E. V., Kapustinsky, A. F., and Schaschkina, T. I., Die Affinität von Metallen zu Sauerstoff. Über das Gleichgewicht zwischen Eisen und Wasserdampf: Ztschr. anorg. Chem., vol. 219, 1934, p. 287.

^{29/} Chipman, J., and Marshall, S., The Equilibrium $FeO + H_2 = Fe + H_2O$ at Temperatures up to the Melting Point of Iron: Jour. Am. Chem. Soc., vol. 62, 1940, p. 299.

^{30/} Emmett, P., and Schultz, J. F., Gaseous Thermal Diffusion - The Principal Cause of Discrepancies among Equilibrium Measurements on the Systems $Fe_3O_4-H_2-Fe-H_2O$, $Fe_3O_4-H_2-FeO-H_2O$, and $FeO-H_2-Fe-H_2O$: Jour. Am. Chem. Soc., vol. 55, 1933, p. 1376.

^{31/} Iwase, K., and Sano, K., A Statical Method of Investigation of the Oxidation and Reduction Equilibria of Iron by Water Vapor: Professor Kōtarō Honda Anniversary Volume, 1936, p. 465.

^{32/} Sibata, Z., and Kujirai, M., Measurements of the Equilibrium Reaction, $H_2O + D_2 = D_2O + H_2$, and Its Statistical and Thermodynamical Calculations: Jour. Chem. Soc. Japan, vol. 61, 1940, p. 1199.

^{33/} Work cited in footnote 8.

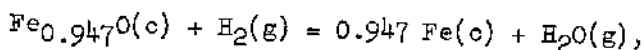
^{34/} Work cited in footnote 12.

above 298.16°K.^{35/} In this connection, it should be noted that the entropy of Fe_{0.9470} at 298.16°K., as reported by Todd and Bonnicksen^{33/} of this laboratory, contains an addition of 0.41 cal per deg. per mole to account for the assumed complete randomness of occurrence of vacant iron spaces in the lattice. This was not based upon evidence of any type, but merely appeared the more plausible procedure at the time their paper was written. The calculations conducted for the present report indicate strongly that the lattice is ordered. Consequently, this correction has been omitted as $S_{298.16}^0 = 13.74$ is used. Column (5) gives the heats of reaction at T, obtained by combining results in columns (3) and (4). Finally, column (6) gives the heats of reaction at 298.16°K., obtained from the values in column (5) and heat-content increments above 298.16°K.^{36,37/} No account has been taken of the deviation in the composition of ferrous oxide in these experiments from Fe_{0.9470}.

TABLE 2. - Calculation of heat of reduction of ferrous oxide by hydrogen at 298.16°K.

T, °K.	$K = \frac{P_{H_2O}}{P_{H_2}}$	$\frac{\Delta F^0}{T}$	ΔS	ΔH	$\Delta H_{298.16}$, cal./mole
Data of Chipman and Marshall					
1,438	0.792	0.46	1.80	3,250	5,780
1,461	.797	.45	1.77	3,240	5,840
1,519	.806	.43	1.69	3,220	5,940
1,526	.840	.35	1.64	3,040	5,770
1,556	.835	.36	1.61	3,070	5,880
1,623	.867	.28	1.50	2,890	5,830
1,631	.834	.36	1.50	3,030	5,990
1,633	.870	.28	1.50	2,910	5,880
				mean	5,860
Data of Emmett and Schultz					
873	.334	2.18	2.10	3,740	5,830
973	.419	1.73	2.05	3,680	5,820
1,073	.501	1.37	2.28	3,920	5,860
1,173	.603	1.01	2.18	3,740	5,770
1,273	.678	.77	2.13	3,690	5,810
				mean	5,820

The mean value of the heat of the reaction,



at 298.16°K. from the two sets of data is $\Delta H_{298.16} = 5,840$ cal. per mole. Joining this value with the heat of formation of gaseous water,^{38/} leads to $\Delta H_{298.16} = -63,640$ cal. per mole as the heat of formation of ferrous oxide, which is rounded to $\Delta H_{298.16} = -63.6$ K. cal. per mole.

^{35/} Work cited in footnote 26.

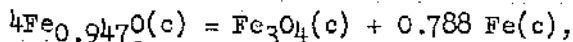
^{36/} Work cited in footnote 7.

^{37/} Work cited in footnote 26.

^{38/} Work cited in footnote 14.

Disproportionation Reaction of Ferrous Oxide

Knowledge of the disproportionation reaction,



and the entropies of its constituents may be employed to obtain the heat of formation of ferrous oxide. The work of Darken and Gurry^{39/} (their table XII) shows that ferrous oxide of composition $\text{Fe}_{0.9470}$ begins to disproportionate on cooling to 873°K. under equilibrium conditions. It is known also that disproportionation is complete at 833°K. under equilibrium conditions. For the present purpose, no significant error will be made in using the mean of these temperatures, 853°K., in the calculations that follow.

From the work of Todd and Bonnickson,^{40/} as amended in the previous section, and the compilation of Kelley,^{41/} the entropy of the above reaction is $\Delta S_{298.16} = -14.85 + 1.0$ cal. per deg. This value may be converted to the corresponding result at 853°K. by use of the tables of Coughlin, King, and Bonnickson^{42/} and Kelley.^{43/} The result is $\Delta S_{853} = -14.85 + 6.05 (0.788 \text{Fe}, 298.16^\circ \text{ to } 853^\circ) + 49.70 (\text{Fe}_3\text{O}_4, 298.16^\circ \text{ to } 853^\circ) = -52.20 (4\text{Fe}_{0.9470}, 853^\circ \text{ to } 298.16^\circ) = -11.3$ cal. per deg.

Taking $\Delta F_{853}^0 = 0$, it follows that $\Delta H_{853} = -11.3 \times 853 = -9,640$ cal. for the heat of the disproportionation reaction at 853°K. This value is converted to the corresponding result for 298.16°K. by the reverse of the process followed above for ΔS . The result is $\Delta H_{298.16} = -9,640 - 3,330 (0.788 \text{Fe}, 853^\circ \text{ to } 298.16^\circ) - 27,590 (\text{Fe}_3\text{O}_4, 853^\circ \text{ to } 298.16^\circ) + 27,900 (4\text{Fe}_{0.9470}, 298.16^\circ \text{ to } 853^\circ) = -12,660$ cal.

From the heat of the disproportionation reaction at 298.16°K. and the heat of formation of magnetite; $\Delta H_{298.16} = -267,400$ cal. per mole (adopted previously), it follows that the heat of formation of $\text{Fe}_{0.9470}$ is $\Delta H_{298.16} = -63,680$ cal. per mole, which is rounded to $\Delta H_{298.16} = -63.7$ K. cal. per mole. The ± 1.0 cal. per deg. uncertainty in $\Delta S_{298.16}$ for the disproportionation reaction places the error in this heat value at about ± 0.9 K. cal. per mole.

Discussion

Table 3 lists the results obtained for the heat of formation of $\text{Fe}_{0.9470}$ by the five methods. These values have a spread of 0.7 K. cal. per mole, which is not exorbitant. The directly determined values (that is, the present measurements) are the highest and lowest in the group. Both results depend upon complex and difficult experimentation, and that from solution calorimetry suffers in accuracy from the uncertainty in the heat of formation of ferrous chloride (see table 1). The least accurate value in the group is the one based upon data for the disproportionation reaction. The neglect (of necessity) of deviations in composition from $\text{Fe}_{0.9470}$ in treating the hydrogen reduction equilibria should not produce an appreciable error, as Darken and Gurry^{44/} have shown that the heat of formation of ferrous oxide per gram atom of oxygen is substantially constant over the composition range $\text{Fe}_{0.9480}$ to $\text{Fe}_{0.8620}$.

^{39/} Work cited in footnote 4.

^{40/} Work cited in Footnote 8.

^{41/} Work cited in footnote 12.

^{42/} Work cited in footnote 7.

^{43/} Work cited in footnote 24.

^{44/} Work cited in footnote 4.

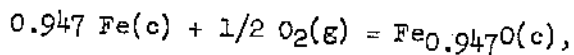
TABLE 3. - Heat of formation of $\text{Fe}_{0.9470}$ at 298.16°K .

Method	$\Delta H_{298.16}, \text{K. cal./mole}$
(1) Combustion calorimetry (measurements in this paper)	-64.0
(2) Solution calorimetry (measurements in this paper)	-63.3
(3) Carbon monoxide reduction equilibria (literature data) ...	-63.8
(4) Hydrogen reduction equilibria (literature data)	-63.6
(5) Disproportionation reaction (literature data)	-63.7

It appears that the best choice for the present is $\Delta H_{298.16} = -63.8 \pm 0.2 \text{ K. cal. per mole}$, which is about the mean of all the values.

HEAT AND FREE ENERGY OF FORMATION FUNCTIONS

For the reaction

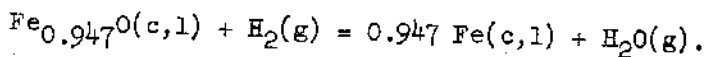


the value $\Delta H_{298.16} = -63.8 \pm 0.2 \text{ K. cal. per mole}$ was adopted in the preceding section. The entropy of $\text{Fe}_{0.9470}$, $S_{298.16}^0 = 13.74 \text{ cal. per deg. per mole}$ and the entropies of iron and oxygen, listed by Kelley,^{45/} lead to $\Delta S_{298.16} = -16.91 \pm 0.2 \text{ cal. per deg. per mole}$. From these values and the heat content and entropy increment tables of Coughlin, King, and Bonnickson^{46/} for $\text{Fe}_{0.9470}$ and Kelley^{47/} for iron and oxygen, the isothermal heat and free energy may be calculated at high temperatures. The results appear in table 4, values being listed at even 100° -intervals and at transition and melting points of iron and ferrous oxide. It is believed that these values will be reasonably adequate for other compositions of the ferrous oxide phase in the high iron region. As was mentioned previously, Darken and Gurry^{48/} found the heat of formation per gram-atom of oxygen combined to be quite insensitive to composition in the range $\text{Fe}_{0.9480}$ to $\text{Fe}_{0.8620}$ at $1,523^\circ\text{K}$.

REDUCTION EQUILIBRIA

Hydrogen Reduction

The results in table 4, when combined with similar data for gaseous water,^{49/} lead to heat and free-energy values for the reaction



^{45/} Work cited in footnote 12.

^{46/} Work cited in footnote 7.

^{47/} Work cited in footnote 24.

^{48/} Work cited in footnote 4.

^{49/} Work cited in footnote 14: Ser. III, table of June 30, 1948.

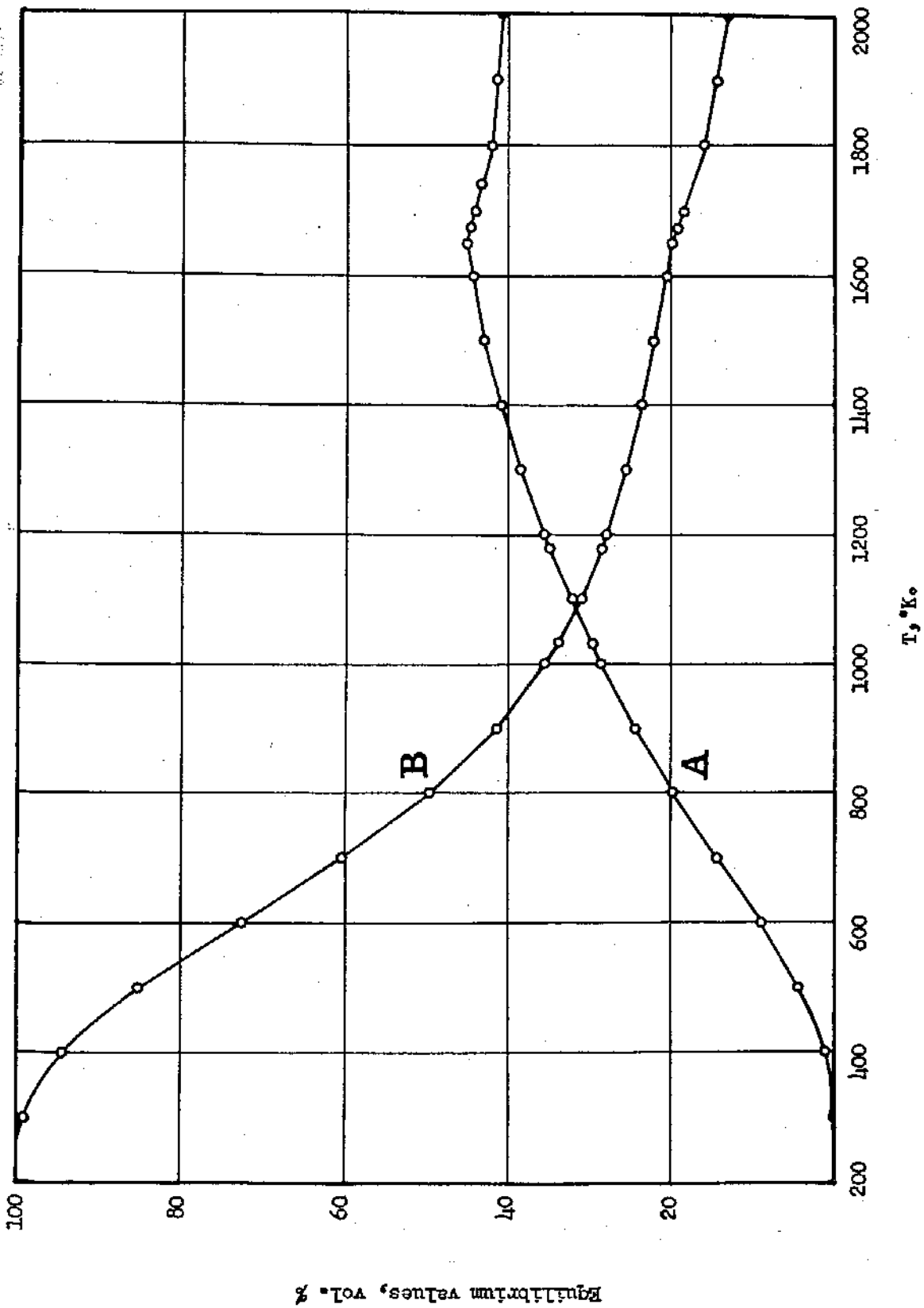


Figure 1. - Equilibrium percentages of water and carbon dioxide in hydrogen and carbon monoxide reductions of ferrous oxide: Curve A, water; curve B, carbon dioxide.

TABLE 4. - Heat and free energy of reaction $0.947 \text{ Fe}(c,l) + 1/2 \text{ O}_2(g) = \text{Fe}_{0.947}\text{O}(c,l)$

T, °K.	ΔH , K. cal./mole	ΔF° , K. cal./mole	T, °K.	ΔH , K. cal./mole	ΔF° , K. cal./mole
298.16	-63.8	-58.75	1,300	-63.45	-43.2
400	-63.55	-57.1	1,400	-63.3	-41.7
500	-63.35	-55.5	1,500	-63.15	-40.0
600	-63.15	-53.95	1,600	-63.0	-38.6
700	-63.0	-52.4	1,650	1/-63.95	-37.85
800	-62.95	-50.9	1,650	2/-55.45	-37.85
900	-62.95	-49.4	1,674	3/-55.35	-37.6
1,000	-63.1	-47.85	1,674	4/-55.45	-37.6
1,033	5/-63.4	-47.35	1,700	-55.45	-37.3
1,033	-63.4	-47.35	1,800	-55.2	-36.25
1,100	-63.45	-46.35	1,803	4/-55.2	-36.25
1,179	-63.45	-45.1	1,803	6/-58.7	-36.25
1,179	3/-63.65	-45.1	1,900	-58.5	-35.05
1,200	-63.6	-44.8	2,000	-58.25	-33.8

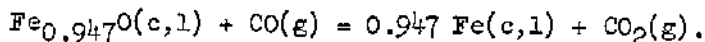
- 1/ Crystalline ferrous oxide.
 2/ Liquid ferrous oxide.
 3/ Gamma iron.
 4/ Delta iron.
 5/ Magnetic inversion; Curie point.
 6/ Liquid iron.

The results of these calculations are given in table 5. Columns (2) and (3) contain the heats and free energies of reaction. Column (4) contains values of the equilibrium constant, $K = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$, and column (5) contains the equilibrium percentage of water in the gas phase for the case in which no gases other than hydrogen and water are present. The values in column (5) also may be interpreted as the maximum theoretical percentage utilization of hydrogen in the reduction of ferrous oxide, under conditions in which the total gas pressure is low enough that fugacity corrections need not be made.

The percentage of water is plotted against temperature in figure 1. It is seen that it increases with temperature to a maximum value at the liquidus temperature of ferrous oxide. The magnitude of the heat of fusion of ferrous oxide is large enough to reverse the sign of the heat of the reduction reaction, and, as a result, the percentage of water decreases at higher temperatures. The shape of the curve in the fusion region is confirmed by the measurements of Chipman and Marshall,^{50/} with which the present calculations agree reasonably well.

Carbon Monoxide Reduction

The results of table 4 also may be combined with data for carbon monoxide and carbon dioxide^{51/} to obtain the heat and free energy of the reaction



^{50/} Work cited in footnote 29.

^{51/} Work cited in footnote 14: Ser. III, tables of Mar. 31, 1949.

TABLE 5. - Data for reaction $\text{Fe}_{0.947}\text{O}(c,l) + \text{H}_2(g) = 0.947 \text{Fe}(c,l) + \text{H}_2\text{O}(g)$

T, °K.	$\Delta H,$ K. cal./mole	$\Delta F^{\circ},$ K. cal./mole	$K = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$	$\text{H}_2\text{O}, \text{ vol.}$ percent
298.16	6.0	4.1	9.55×10^{-4}	0.1
400	5.5	3.55	1.14×10^{-2}	1.15
500	5.05	3.1	4.32×10^{-2}	4.15
600	4.65	2.8	9.70×10^{-2}	8.85
700	4.3	2.5	1.67×10^{-1}	14.3
800	4.05	2.25	2.44×10^{-1}	19.6
900	3.9	2.05	3.20×10^{-1}	24.25
1,000	3.9	1.85	3.96×10^{-1}	28.35
1,033	4.15	1.80	4.20×10^{-1}	29.6
1,033	4.15	1.80	4.20×10^{-1}	29.6
1,100	4.1	1.65	4.70×10^{-1}	31.95
1,179	4.0	1.45	5.36×10^{-1}	34.9
1,179	4.2	1.45	5.36×10^{-1}	34.9
1,200	4.1	1.4	5.51×10^{-1}	35.55
1,300	3.85	1.3	6.24×10^{-1}	38.4
1,400	3.55	1.05	6.89×10^{-1}	40.8
1,500	3.3	.85	7.55×10^{-1}	43.0
1,600	3.05	.75	7.94×10^{-1}	44.75
1,650	2.95	.65	8.18×10^{-1}	45.0
1,650	-4.55	.65	8.18×10^{-1}	45.0
1,674	-4.65	.7	8.05×10^{-1}	44.6
1,674	-4.55	.7	8.05×10^{-1}	44.6
1,700	-4.6	.8	7.87×10^{-1}	44.05
1,800	-4.9	1.15	7.24×10^{-1}	42.0
1,803	-4.9	1.15	7.21×10^{-1}	41.9
1,803	-1.4	1.15	7.21×10^{-1}	41.9
1,900	-1.7	1.3	7.05×10^{-1}	41.35
2,000	-2.0	1.5	6.89×10^{-1}	40.8

The calculations are summarized in table 6. Columns (2) and (3) contain the heats and free energies of reaction. Column (4) contains values of the equilibrium constant, $K = \frac{P_{\text{CO}_2}}{P_{\text{CO}}}$. Column (5) gives the equilibrium percentages of carbon dioxide when no gases other than carbon monoxide and carbon dioxide are present. These results also may be interpreted as the maximum theoretical percentage utilization of carbon monoxide in reduction of ferrous oxide, under conditions in which the total gas pressure is low enough that fugacity corrections need not be made.

The percentage of carbon dioxide also is plotted against temperature in figure 1. It is seen that it decreases continually with increasing temperature. The heat of fusion of ferrous oxide causes a sharp change in slope in the fusion region. The

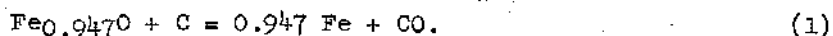
two curves in figure 1 illustrate the adage that carbon monoxide is the better reducing agent at low temperatures and hydrogen at high temperatures. The reducing powers are equal at about 1,085°K.

TABLE 6. - Data for reaction $\text{Fe}_{0.947}\text{O}(\text{c},1) + \text{CO}(\text{g}) = 0.947 \text{Fe}(\text{c},1) + \text{CO}_2(\text{g})$

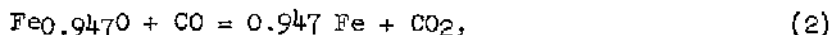
T, °K.	$\Delta H,$ K. cal./mole	$\Delta F^0,$ K. cal./mole	$K = \frac{P_{\text{CO}_2}}{P_{\text{CO}}}$	CO ₂ , vol. percent
298.16	-3.85	-2.7	9.38×10^1	98.95
400	-4.2	-2.25	1.65×10^1	94.3
500	-4.45	-1.75	5.70	85.1
600	-4.65	-1.15	2.62	72.4
700	-4.75	- .55	1.51	60.2
800	-4.8	.00	9.86×10^{-1}	49.65
900	-4.7	.65	7.03×10^{-1}	41.3
1,000	-4.45	1.2	5.47×10^{-1}	35.35
1,033	-4.1	1.4	5.08×10^{-1}	34.7
1,033	-4.1	1.4	5.08×10^{-1}	34.7
1,100	-4.0	1.75	4.47×10^{-1}	30.9
1,179	-3.9	2.15	4.00×10^{-1}	28.55
1,179	-3.7	2.15	4.00×10^{-1}	28.55
1,200	-3.75	2.25	3.86×10^{-1}	27.85
1,300	-3.8	2.8	3.41×10^{-1}	25.45
1,400	-3.85	3.3	3.06×10^{-1}	23.45
1,500	-3.9	3.75	2.83×10^{-1}	22.05
1,600	-3.9	4.3	2.58×10^{-1}	20.5
1,650	-3.9	4.55	2.48×10^{-1}	19.85
1,650	-11.4	4.55	2.48×10^{-1}	19.85
1,674	-11.45	4.8	2.37×10^{-1}	19.15
1,674	-11.35	4.8	2.37×10^{-1}	19.15
1,700	-11.35	5.05	2.24×10^{-1}	18.3
1,800	-11.4	6.0	1.86×10^{-1}	15.7
1,803	-11.4	6.05	1.84×10^{-1}	15.55
1,803	-7.9	6.05	1.84×10^{-1}	15.55
1,900	-8.05	6.8	1.65×10^{-1}	14.15
2,000	-8.1	7.6	1.49×10^{-1}	12.95

Carbon Reduction

Carbon reduction of ferrous oxide may be represented by



The actual mechanism of this reaction is considered to be



and



in which carbon dioxide acts as a carrier of oxygen from ferrous oxide to the excess carbon in the system. Reactions (2) and (3) combine to give reaction (1) as the over-all result. It is of interest, therefore, to have the heat and free energy values of reaction listed in table 7. These were obtained by combining the results in table 4 with corresponding data for carbon monoxide.^{52/}

It is noted that reaction (1) is not potent below 900°K. At about 1,000°K., the free energy is zero and the corresponding equilibrium partial pressure of carbon monoxide reaches 1 atm. At higher temperatures, the free energy continually becomes more negative and the reaction thermodynamically more potent.

TABLE 7. - Data for reaction $\text{Fe}_{0.947}\text{O}(c,1) + \text{C}(\text{graphite}) = 0.947 \text{Fe}(c,1) + \text{CO}(g)$

T, °K.	$\Delta H,$ K. cal./mole	$\Delta F^{\circ},$ K. cal./mole	T, °K.	$\Delta H,$ K. cal./mole	$\Delta F^{\circ},$ K. cal./mole
298.16	37.4	25.95	1,300	36.25	-11.0
400	37.25	22.05	1,400	35.9	-14.65
500	37.05	18.3	1,500	35.6	-18.25
600	36.8	14.55	1,600	35.25	-21.8
700	36.6	10.85	1,650	35.1	-23.6
800	36.4	7.2	1,650	27.6	-23.6
900	36.3	3.5	1,674	27.5	-24.35
1,000	36.35	-.05	1,674	27.6	-24.35
1,033	36.6	-1.25	1,700	27.55	-25.15
1,033	36.6	-1.25	1,800	27.15	-28.2
1,100	36.55	-3.7	1,803	27.1	-28.3
1,179	36.4	-6.6	1,803	30.6	-28.3
1,179	36.6	-6.6	1,900	30.2	-31.45
1,200	36.55	-7.35	2,000	29.8	-34.7

CONCLUSIONS

The data and calculations of this paper support the following conclusions:

- (1) The best value of the heat of formation of ferrous oxide is $\Delta H_{298.16} = -63.8 \pm 0.2$ K. cal. per mole. This is based upon results obtained from combustion calorimetry, solution calorimetry, hydrogen reduction equilibria, carbon monoxide reduction equilibria, and the disproportionation reaction of ferrous oxide.
- (2) The best correlation of all available data is obtained by the assumption that crystalline ferrous oxide is ordered, that is, that there is no randomness of occurrence of vacant iron spaces in the lattice. Consequently, the entropy of $\text{Fe}_{0.947}\text{O}$ should be taken as $S_{298.16}^{\circ} = 13.74 \pm 0.10$ cal per deg. per mole, as given directly by low-temperature heat-capacity data.
- (3) In hydrogen reduction of ferrous oxide, the maximum theoretical percentage utilization of hydrogen is about 45 percent, occurring at the liquidus temperature of the oxide.
- (4) In carbon monoxide reduction of ferrous oxide, the theoretical percentage utilization of carbon monoxide decreases continually with increasing temperature. Carbon monoxide and hydrogen are equally potent reductants at about 1,085°K.
- (5) Carbon reduction of ferrous oxide is thermodynamically potent at temperatures above 1,000°K., where the theoretical equilibrium partial pressure of carbon monoxide exceeds 1 atm.

^{52/} Work cited in footnote 14: Ser. III, table of Mar. 31, 1949.