

## INTRODUCTION AND SUMMARY

Although thermodynamic data for ferrous oxide are among the most important in extractive metallurgy, adequate values have not been available until quite recently. The older data suffered not only from the usual experimental difficulties but especially from lack of the knowledge that ferrous oxide of stoichiometrical composition does not exist as a single, thermodynamically stable crystalline phase under any circumstances.

This paper reports new experimental data on the heat of formation of ferrous oxide by two methods (combustion calorimetry and solution calorimetry), employing material of unequivocal composition. The results are compared with values obtained from data for the hydrogen reduction, carbon monoxide reduction, and disproportionation reactions of ferrous oxide, and a best value is selected.

A table of heat and free energy of formation values of ferrous oxide to 2,000°K. is given. These values are combined with available data for water, carbon monoxide, and carbon dioxide to obtain theoretical heats and free energies of reduction corresponding to the selected heat of formation. Hydrogen and carbon monoxide reduction equilibria are compared, and the differences in trend with temperature and the percentage utilization of the reductants are considered.

## MATERIALS

The principal materials used in this work are ferrous oxide, iron, magnetite, and anhydrous ferrous chloride.

### Ferrous Oxide

The preparation of ferrous oxide of suitable purity for thermochemical measurements is difficult. The investigations of Jette and Foote<sup>3/</sup> and Darken and Gurry<sup>4/</sup> have shown that the stoichiometric composition (FeO) does not exist as a thermodynamically stable, single-phase, crystalline substance. The maximum iron content of the crystalline ferrous oxide phase found by the former workers corresponds to Fe<sub>0.9480</sub> and by the latter to Fe<sub>0.9530</sub>. The deviation from the 1:1 atomic ratio is attributed to vacant iron spaces in the lattice, rather than to extra oxygen in the interstices. Ferrous oxide is unstable at temperatures below 833°K. with respect to iron and magnetite. To prevent disproportionation, it must be prepared at a higher temperature and quenched rapidly through the range from 833°K. to near room temperature. The rate of disproportionation at room temperature and somewhat above is very low.

3/ Jette, E. R., and Foote, F., A Study of the Homogeneity of Wüstite (FeO) by X-ray Methods: Trans. Am. Inst. Min. and Met. Eng., vol. 105, 1933, p. 276.

4/ Darken, L. S., and Gurry, R. W., The System Iron-Oxygen. I. The Wüstite Field and Related Equilibria: Jour. Am. Chem. Soc., vol. 67, 1945, p. 1398.

The ferrous oxide used in this work was prepared by the method of Blue and Claasen.<sup>5/</sup> Equivalent amounts of magnetite and iron, in separate containers, were heated at constant temperature in a closed system (previously evacuated) in the presence of a few mm. pressure of water vapor. The water vapor oxidizes the iron to produce hydrogen, which, in turn, reduces magnetite and reforms water. The net result is the transfer of oxygen from the magnetite to the iron. As this process continues, the materials in the two containers approach each other in composition.

Three batches of ferrous oxide of about 130 grams each were made. Only the material produced from magnetite was retained for use. The original amounts of magnetite and iron were adjusted, upon the basis of their chemical analyses, to yield products having near the maximum iron content possible for the stable (at preparation temperature) crystalline ferrous oxide phase. A silica-glass outer container was used, and alundum thimbles separated the solid reactants. The temperature of reaction was 1,150°K., and the heating periods were from 4.9 to 9.3 days for the three batches. The batches were quenched by plunging the silica-glass container and its contents at about 950°K. into stirred, iced brine. Careful examination, as indicated below, showed the three batches to be virtually identical.

The final product analyzed 76.60 percent iron, 23.18 percent oxygen (loss in weight on complete reduction by hydrogen), and 0.17 percent silica, leaving 0.05 percent unaccounted for. The iron:oxygen atomic ratio corresponds to  $Fe_{0.947}O$ . The X-ray diffraction pattern contains no lines other than those of ferrous oxide. Tests for metallic iron by the mercuric chloride method of Morris<sup>6/</sup> were negative. The substance was found to be only very slightly magnetic, indicating at most a negligible magnetite residue.

This ferrous oxide is identical with that used by Coughlin, King, and Bonnickson<sup>7/</sup> in high-temperature heat-content measurements and by Todd and Bonnickson<sup>8/</sup> in low-temperature heat-capacity determinations.

### Iron

Electrolytic iron having a purity of 99.96 percent was used in the form of fine mill cuttings. The impurities, expressed in percent, are 0.017 carbon, 0.005 nickel, 0.005 copper, less than 0.005 molybdenum, less than 0.005 cobalt, 0.003 manganese, 0.002 sulfur, 0.001 silicon, 0.001 phosphorus, less than 0.001 chromium, less than 0.001 tin, less than 0.001 vanadium, less than 0.0008 aluminum, less than 0.0005 calcium, and less than 0.0005 magnesium.

### Magnetite

Magnetite was prepared by heating pure ferric oxide in high vacuum for 8 hours at 1,350° C. Analysis gave 72.49 percent iron, as compared with the theoretical 72.36 percent.

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- 5/ Blue, R. W., and Claasen, H. H., Preparation of Wüstite: Jour. Am. Chem. Soc., vol. 71, 1949, p. 3839.
- 6/ Morris, J. P., Determination of Metallic Iron and Oxygen in Sponge Iron: Bureau of Mines Rept. of Investigations 3824, 1945, 31 pp.
- 7/ Coughlin, J. P., King, E. G., and Bonnickson, K. R., High-Temperature Heat Contents of Ferrous Oxide, Magnetite, and Ferric Oxide: Jour. Am. Chem. Soc., vol. 73, 1951, p. 3891.
- 8/ Todd, S. S., and Bonnickson, K. R., Low-Temperature Heat Capacities and Entropies at 298.16°K. of Ferrous Oxide, Manganous Oxide, and Vanadium Monoxide: Jour. Am. Chem. Soc., vol. 73, 1951, p. 3894.

## Anhydrous Ferrous Chloride

Anhydrous ferrous chloride was prepared by the method of Kelley and Moore,<sup>9/</sup> except that the starting material was the electrolytic iron described above. The iron was dissolved in excess hydrochloric acid, and the solution was evaporated to apparent dryness in an atmosphere of carbon dioxide. The material then was heated slowly in vacuum to 250° C. and finally in a stream of dry hydrogen chloride to 550° C. Analysis gave 44.15 percent iron and 55.92 percent chlorine, as compared with the theoretical figures 44.06 and 55.94 percent. Ferric iron was less than 0.02 percent, as determined colorimetrically by the thiocyanate method.

### HEAT OF FORMATION AT 298.16°K.

The heat of formation of ferrous oxide was determined by two methods, combustion calorimetry and solution calorimetry.

### Combustion Calorimetry

The heat of combustion of ferrous oxide was measured with previously described<sup>10/</sup> apparatus and techniques. Fine mill cuttings of electrolytic iron, in the proportion of 1 gram of iron to 1.5 grams of ferrous oxide, were used as a kindling agent, in conjunction with the usual filter-paper fuse ignited by a heated platinum wire spiral. Silica-glass crucibles were used to hold the combustion samples. The combustions were conducted in 30 atm. pressure of oxygen at a calorimeter temperature of 303.16°K. Calibration of the calorimeter was made with National Bureau of Standards benzoic acid, sample 39g.

One of the difficulties encountered in calorimetric combustions of iron and ferrous oxide is that the iron:oxygen ratio of the combustion product varies from run to run. Consequently, it is necessary to group and average the determinations and to make careful chemical analyses of the combined and carefully mixed combustion products for each group.

### Combustions of Iron

A group of three calorimetric combustions of electrolytic iron alone, using 1 g. samples, gave an average heat evolution of 1,555.0 cal. per gram (in vac.) under bomb conditions. The correction for impurities was calculated to be -1.10 cal per gram, using data in the National Bureau of Standards Tables of Selected Values of Chemical Thermodynamic Properties.

The corrected value, 1,553.9 cal. per gram, corresponds to 86,785 cal. per gram atom of iron, evolved under bomb conditions, or  $\Delta U_B = -86,785$ . Three corrections are necessary to convert from the latter value to the corresponding value for standard state conditions, namely, the correction of 1 atm. fugacity of oxygen, the correction to a constant pressure process, and the correction to 298.16°K.

Analysis of the combined combustion products of this group for total iron and oxygen (loss in weight on complete reduction by hydrogen) gave a composition corresponding to  $FeO_{1.310}$ . In other words, 0.655 mole of oxygen had reacted with 1 gram-atom of iron. The X-ray diffraction pattern contained only lines attributable to

9/ Kelley, K. K., and Moore, G. E., The Specific Heats at Low Temperatures of Anhydrous Chlorides of Calcium, Iron, Magnesium, and Manganese: Jour. Am. Chem. Soc., vol. 65, 1943, p. 1264.

10/ Humphrey, G. L., The Heats of Formation of  $TiO$ ,  $Ti_2O_3$ ,  $Ti_3O_5$ , and  $TiO_2$  from Combustion Calorimetry: Jour. Am. Chem. Soc., vol. 73, 1951, p. 1587.

magnetite. However, a magnetic test showed that a small slightly magnetic (or non-magnetic) fraction also was present. These results are interpreted as indicating that the combustion product is largely magnetite with some ferrous oxide as a separate phase.

The correction to unit fugacity of oxygen is obtained from the coefficient of energy change of oxygen with pressure,  $-1.56$  cal. per mole per atm.,<sup>11/</sup> and the amount of oxygen consumed in the reaction. The result is  $-31$  cal. per gram-atom of iron burned.

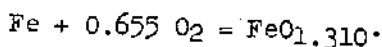
The correction to a constant pressure process is obtained from the relationship

$$\Delta H = \Delta U + RT\Delta n,$$

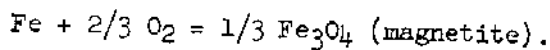
in which  $\Delta H$  is the heat associated with the constant-pressure process,  $\Delta U$  is the heat associated with the constant-volume process,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $\Delta n$  is the number of moles of gaseous products minus the number of moles of gaseous reactants (in this instance,  $-0.655$ ). This correction is  $-395$  cal. per gram-atom of iron burned.

The correction from  $303.16^\circ$  to  $298.16^\circ\text{K}$ . is estimated as  $-4$  cal. per gram-atom of iron burned, from heat-capacity data given by Kelley.<sup>12/</sup>

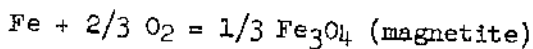
The net result of applying these corrections is  $\Delta H_{298.16} = -87,220$  cal. for the reaction



This result, as well as those to be obtained subsequently, will be corrected to a common basis corresponding to the reaction



Data obtained by Darken and Gurry,<sup>13/</sup> when corrected to  $298.16^\circ\text{K}$ ., yield  $-21,920$  cal. as the heat of oxidation of  $\text{FeO}_{1.056}$  to  $\text{FeO}_{1.333}$ . Values in the National Bureau of Standards Tables,<sup>14/</sup> calculated to the same basis, give  $-21,710$  cal. Using the mean value,  $-21,820$ , and interpolating linearly, it is computed that  $-1,810$  cal. would be evolved in further burning the product to  $\text{FeO}_{1.333}$ . Thus, the heat of the reaction



becomes  $\Delta H_{298.16} = -89,030$  cal., or the heat of formation of  $\text{Fe}_3\text{O}_4$  is  $\Delta H_{298.16} = -267,100$  cal. per mole, from the present measurements. This value will be employed in correcting subsequent data for the iron used as kindler in burning ferrous oxide.

<sup>11/</sup> Rossini, F. D., and Frandsen, M., The Calorimetric Determination of the Intrinsic Energy of Gases as a Function of the Pressure. Data on Oxygen and its Mixtures with Carbon Dioxide to 40 Atmospheres at  $28^\circ\text{C}$ .: Nat. Bureau of Standards Jour. Res., vol. 9, 1932, p. 733.

<sup>12/</sup> Kelley, K. K., Contributions to the Data on Theoretical Metallurgy. XI. Entropies of Inorganic Substances. Revision (1948) of Data and Methods of Calculation: Bureau of Mines Bull. 477, 1950, 147 pp.

<sup>13/</sup> Work cited in footnote 4.

<sup>14/</sup> National Bureau of Standards Tables of Selected Values of Chemical Thermodynamic Properties, Ser. I, Table 47-1: June 30, 1949.

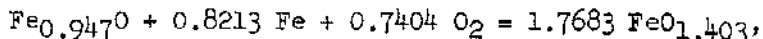
The above result for the heat of formation of magnetite agrees well with -267,000 cal. per mole, as given in the National Bureau of Standards Tables;<sup>15/</sup> and with -267,800 cal. per mole, obtained from Darken and Gurry's<sup>16/</sup> measurement at 1,523°K. after correcting to 298.16°K.

Combustions of Ferrous Oxide-iron Mixtures

The first group of two calorimetric combustions of ferrous oxide-electrolytic iron mixtures was made with the masses, 1.50031 grams (corrected for the silica content) of ferrous oxide and 0.99902 gram of iron. The results are 2,174.60 and 2,173.92 cal. for the mixture, the mean being 2,174.26 cal. Correction for impurities in the iron reduces the mean to 2,173.16 cal.

The combined combustion products of this group were analyzed for total iron and oxygen and found to correspond to the composition FeO<sub>1.403</sub>. The X-ray diffraction pattern contained only lines attributable to magnetite and hematite, and a magnetic test also showed the presence of two phases. The product is interpreted, therefore, as a mixture of magnetite and hematite.

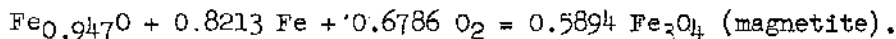
Conversion of the above result to the basis of 1 mole of Fe<sub>0.947</sub>O (mol. wt. = 68.89) yields ΔU<sub>B</sub> = -99,785 cal. for the over-all reaction



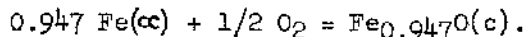
under bomb conditions.

Corrections to standard-state conditions, made as explained above, involve -35 cal. to convert to unit fugacity of oxygen, -446 cal. to convert to a constant-pressure process, and +3 cal. to convert to 298.16°K. The net result is ΔH<sub>298.16</sub> = -100,260 cal. for the over-all reaction as written.

To convert to the common basis of FeO<sub>1.333</sub> (or Fe<sub>3</sub>O<sub>4</sub>, magnetite) as the final product, Darken and Gurry<sup>17,18/</sup> data and the National Bureau of Standards Tables<sup>19/</sup> are used again. Data of the former, when corrected to 298.16°K., yield -9,220 cal. for the heat of oxidation of FeO<sub>1.333</sub> to FeO<sub>1.500</sub> (i.e., magnetite to hematite), whereas data from the latter source give -9,250 cal. The mean is -9,240 cal. Linearly interpolating for our 2-phase product of composition FeO<sub>1.403</sub> shows that a correction of +6,850 cal. must be applied to convert to magnetite as the final product. (It is to be emphasized that this correction, and others made in similar fashion, involves only differences of data in the literature. This is not the same as assuming actual specific values for magnetite and hematite). The result is ΔH<sub>298.16</sub> = -93,410 cal. for the over-all reaction



Application of the previously found heat of formation of Fe<sub>3</sub>O<sub>4</sub> (magnetite), ΔH<sub>298.16</sub> = -267,100 cal., leads to ΔH<sub>298.16</sub> = -64,020 cal. per mole as the heat of formation of Fe<sub>0.947</sub>O,



<sup>15/</sup> Work cited in footnote 14.

<sup>16/</sup> Work cited in footnote 4.

<sup>17/</sup> Work cited in footnote 4.

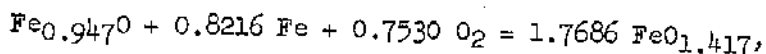
<sup>18/</sup> Darken, L. S., and Gurry, R. W., The System Iron-Oxygen. II. Equilibrium and Thermodynamics of Liquid Oxide and Other Phases: Jour. Am. Chem. Soc., vol. 68, 1946, p. 798.

<sup>19/</sup> Work cited in footnote 14.

A second series of two calorimetric combustions of ferrous oxide-electrolytic iron mixtures was made using the masses, 1.50055 grams (corrected for the silica content) of ferrous oxide and 0.99955 gram of iron. The heat results are 2,203.87 and 2,209.07 cal. for the mixture, the mean being 2,206.47 cal. Correction for impurities in the iron reduces the mean to 2,205.37 cal.

The combined combustion products of this group were analyzed, and the composition was found to correspond to  $\text{FeO}_{1.417}$ . The X-ray diffraction and magnetic test gave the same results as for the previous group.

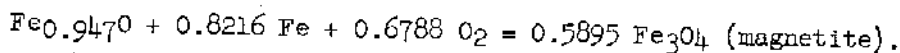
Conversion to the basis of 1 mole of  $\text{FeO}_{0.9470}$  yields  $\Delta U_B = -101,249$  cal. for the over-all reaction



under bomb conditions.

Correction to standard state conditions involves -35 cal. to convert to unit fugacity of oxygen, -454 cal. to convert to a constant pressure process, and +3 cal. to convert to 298.16°K. The result is  $\Delta H_{298.16} = -101,730$  cal. for the above-written, over-all reaction.

Correction to magnetite as the final product, made as explained previously, is +8,220 cal., so that  $\Delta H_{298.16} = -93,510$  cal. for the over-all reaction



Again applying the heat of formation of magnetite,  $\Delta H_{298.16} = -63,950$  cal. per mole is obtained as the heat of formation of  $\text{FeO}_{0.9470}$ .

Comparison of the results of the two groups shows a difference of only 70 cal. or 0.11 percent in the heat of formation of ferrous oxide. This illustrates the necessity for, and great dependence upon, the chemical analyses of the combustion products. The original combustion heats differ by nearly 1.5 percent, but this difference is almost perfectly compensated by the difference in degree of oxidation of the combustion products. The rounded, mean value  $\Delta H_{298.16} = -64.0$  K. cal per mole is adopted as the heat of formation of  $\text{FeO}_{0.9470}$  by this method. A consideration of the possible accumulation of errors leads to the estimate of  $\pm 0.5$  K. cal. as the uncertainty in this result.

#### Solution Calorimetry

In solution calorimetry involving ferrous oxide,  $\text{FeO}_{0.9470}$ , account must be taken of the deviation of composition from stoichiometric  $\text{FeO}$ . In dissolving in any nonoxidizing acid,  $\text{FeO}_{0.9470}$  will produce both ferric and ferrous ions (in the molal ratio of 0.106 to 0.841). Unless this fact is recognized incorrect results will be obtained.

The solution calorimeter used in this work was described previously.<sup>20,21/</sup> The solvent was 20.1 percent by weight hydrofluoric acid, and the calorimeter was operated at 60° C. The amount of  $\text{FeO}_{0.9470}$  dissolved was 1.702 grams in 940.1 g. of the acid. The quantities of all other substances were stoichiometrically equivalent to this amount of  $\text{FeO}_{0.9470}$ .

<sup>20/</sup> Torgeson, D. R., and Sahama, Th. G., A Hydrofluoric Acid Solution Calorimeter and the Determination of the Heats of Formation of  $\text{Mg}_2\text{SiO}_4$ ,  $\text{MgSiO}_3$ , and  $\text{CaSiO}_3$ : Jour. Am. Chem. Soc., vol. 70, 1948, p. 2156.

<sup>21/</sup> King, E. G., Heats of Formation of Crystalline Calcium Orthosilicate, Tricalcium Silicate, and Zinc Orthosilicate: Jour. Am. Chem. Soc., vol. 73, 1951, pp. 656-658.

The scheme employed in obtaining the heat of formation of  $\text{FeO}_{.9470}$  is shown in table 1. The first five reactions were measured in the present work. The final solution obtained after conducting reactions (1) and (4) consecutively is identical with that obtained after conducting reactions (2), (3), and (5) consecutively. The substances were dropped from  $25^\circ \text{C}$ . into the calorimeter at  $60^\circ \text{C}$ . Gelatin capsules were used to contain the substances. Correction for the heat of solution of gelatin was measured in separate experiments.

TABLE 1. - Reaction scheme for obtaining heat of formation of  $\text{FeO}_{.9470}$

Measured Reactions <sup>1/</sup>		
Reaction		$\Delta H$ , cal.
(1) $\text{FeO}_{.9470}(\text{c}, 25^\circ) + 2\text{H}^+(\text{sol}, 60^\circ) =$ $0.841 \text{Fe}^{++}(\text{sol}, 60^\circ) + 0.106 \text{Fe}^{+++}(\text{sol}, 60^\circ) + \text{H}_2\text{O}(\text{sol}, 60^\circ)$		$-26,840 \pm 60$
(2) $0.788 \text{FeCl}_2(\text{c}, 25^\circ) = 0.788 \text{Fe}^{++}(\text{sol}, 60^\circ) + 1.576 \text{Cl}^-(\text{sol}, 60^\circ)$		$-14,590 \pm 40$
(3) $0.053 \text{Fe}_3\text{O}_4(\text{c}, 25^\circ) + 0.424 \text{H}^+(\text{sol}, 60^\circ) =$ $0.053 \text{Fe}^{++}(\text{sol}, 60^\circ) + 0.106 \text{Fe}^{+++}(\text{sol}, 60^\circ) + 0.212 \text{H}_2\text{O}(\text{sol}, 60^\circ)$		$-3,290 \pm 40$
(4) $1.576(\text{HCl} \cdot 5.806 \text{H}_2\text{O})(\text{l}, 25^\circ) =$ $1.576 \text{H}^+(\text{sol}, 60^\circ) + 1.576 \text{Cl}^-(\text{sol}, 60^\circ) + 9.150 \text{H}_2\text{O}(\text{sol}, 60^\circ)$		$4,880 \pm 30$
(5) $9.938 \text{H}_2\text{O}(\text{l}, 25^\circ) = 9.938 \text{H}_2\text{O}(\text{sol}, 60^\circ)$		$5,710 \pm 50$
(6) = $-(1) + (2) + (3) = (4) + (5)$ $0.788 \text{FeCl}_2(\text{c}, 25^\circ) + 0.053 \text{Fe}_3\text{O}_4(\text{c}, 25^\circ) + 9.938 \text{H}_2\text{O}(\text{l}, 25^\circ) =$ $\text{FeO}_{.9470}(\text{c}, 25^\circ) + 1.576 (\text{HCl} \cdot 5.806 \text{H}_2\text{O})(\text{l}, 25^\circ)$		$9,790 \pm 100$
Values from Literature <sup>1/</sup>		
(7) $0.788 \text{H}_2(\text{g}, 25^\circ) + 0.788 \text{Cl}_2(\text{g}, 25^\circ) + 9.150 \text{H}_2\text{O}(\text{l}, 25^\circ) =$ $1.576 (\text{HCl} \cdot 5.806 \text{H}_2\text{O})(\text{l}, 25^\circ)$		$-59,480 \pm 80$
(8) $0.788 \text{Fe}(\text{c}, 25^\circ) + 0.788 \text{Cl}_2(\text{g}, 25^\circ) = 0.788 \text{FeCl}_2(\text{c}, 25^\circ)$		$-64,540 \pm 400$
(9) $0.159 \text{Fe}(\text{c}, 25^\circ) + 0.106 \text{O}_2(\text{g}, 25^\circ) = 0.053 \text{Fe}_3\text{O}_4(\text{c}, 25^\circ)$		$-14,170 \pm 20$
(10) $0.788 \text{H}_2(\text{g}, 25^\circ) + 0.394 \text{O}_2(\text{g}, 25^\circ) = 0.788 \text{H}_2\text{O}(\text{l}, 25^\circ)$		$-53,830 \pm 8$
(11) = $(6) - (7) + (8) + (9) + (10)$ $0.947 \text{Fe}(\text{c}) + 1/2 \text{O}_2 = \text{FeO}_{.9470}$		$-63,270 \pm 440$

<sup>1/</sup> The symbols in parentheses following chemical formulas have the following meanings: temperatures are  $^\circ \text{C}$ .; c = crystalline; l = liquid; g = gas; sol = in solution.

Reaction (1) represents the process of dropping 1 mole of ferrous oxide into the acid, and allowing it to dissolve. Seven measurements of the heat of reaction (1) were made, the following results being obtained:  $-26,880$ ,  $-26,830$ ,  $-26,900$ ,  $-26,690$ ,  $-26,860$ ,  $-26,830$ , and  $-26,890$  cal. The average value is  $-26,840 \pm 60$  cal.

Reaction (2) represents the process of dropping 0.788 mole of anhydrous ferrous chloride into the acid and allowing it to dissolve. Four measurements of the heat of reaction (2) were made. The results are  $-14,590$ ,  $-14,620$ ,  $-14,550$ , and  $-14,580$  cal. The average value is  $-14,590 \pm 40$  cal.

Reaction (3) represents the process of dropping 0.053 mole of magnetite into the final solution obtained after conducting reaction (2). Five measurements of the heat of reaction (3) were made, the results being -3,250, -3,280, -3,340, -3,260, and -3,300 cal. The average value is  $-3,290 \pm 40$  cal.

Reaction (4) represents the process of dropping an accurately prepared and analyzed hydrochloric acid solution (containing 1.576 moles of HCl and  $1.576 \times 5.806 = 9.150$  moles of H<sub>2</sub>O) into the final solution, obtained after conducting reaction (1), and allowing it to mix. Nine measurements of the heat of reaction (4) were conducted. The results are 4,850, 4,840, 4,880, 4,850, 4,960, 4,860, 4,950, 4,850, and 4,880 cal. The average value is  $4,880 \pm 30$  cal.

Reaction (5) represents the process of dropping 9.938 moles of liquid water into the final solution obtained after conducting reactions (2) and (3) and allowing it to mix. It is merely a dilution of the calorimetric solution by water. As heat of dilution enters into many heat of formation measurements by this method, a separate study of it has been made for calorimeter temperatures between 50° and 75° C. It was found that the heat effect per mole of water varies with temperature in a substantially linear manner and that it is relatively insensitive to the amount of water over the pertinent composition range. At 60°, the heat effect in the present instance is  $9.938 \times (575 \pm 5) = 5,710 \pm 50$  cal.

The net result of properly combining reactions (1) to (5) is shown by reaction (6), which constitutes the over-all process for which the heat was measured in the present work.

Reactions (7) to (10) represent, respectively, the heat of formation of the hydrochloric acid used in reaction (4), the heat of formation of the anhydrous ferrous chloride used in reaction (2), the heat of formation of the magnetite used in reaction (3), and the heat of formation of the amount of liquid water necessary for an exact material balance. The heats of reactions (7), (8), and (10) are taken from the National Bureau of Standards Tables<sup>22/</sup> For reaction (9), the mean of the values for the heat of formation of magnetite from the work of Darken and Gurry<sup>23/</sup> ( $\Delta H_{298.16} = -267,800$  cal. per mole) and from the previous section of this report ( $\Delta H_{298.16} = -267,100$  cal. per mole) is adopted.

Proper combination of reactions (6) to (10) results in reaction (11), which represents the formation of ferrous oxide from the elements. The rounded value,  $\Delta H_{298.16} = -63.3 \pm 0.5$  K. cal per mole, is adopted as the final result of this method.

#### Other Methods

##### Carbon Monoxide Reduction Equilibria

Darken and Gurry<sup>24/</sup> have studied carbon monoxide reduction equilibria of ferrous oxide. They derived  $\Delta H_{1523} = -63,080$  cal. per mole as the heat of formation of ferrous oxide of composition Fe<sub>0.9480</sub>, which is virtually identical with the

<sup>22/</sup> Work cited in footnote 14: Tables 10-3 (Mar. 31, 1947); 47-3 (June 30, 1949); 8-1 (June 30, 1947).

<sup>23/</sup> Work cited in footnote 4.

<sup>24/</sup> Work cited in footnote 4.