entropies thus calculated are given in Table II. Here we estimate that the uncertainty in the experimentally determined part should in all cases be less than 1%. For the extrapolated portion of the entropy it is impossible to make a reliable estimate of the uncertainty, especially in the case of the salts.

In addition to the data given above, we have made one determination of the heat of fusion of $d(l+)$-lactic acid. As is well known, this compound is not stable, showing a decided tendency to form a lactone and an anhydride with the elimination of water. For this reason the fusion was not very sharp; furthermore, having once been fused it was impossible, in the calorimeter, to obtain it again in the completely crystalline state. Nevertheless we believe it to be of some interest to present this preliminary value of the heat of fusion, which was found to be 4030 calories per mole.

TABLE II

ENTROPIES OF THE COMPOUNDS PER MOLE IN CAL. DEGREE^{-1} MOLE^{-1}

Substance	S_{90}	$\Delta S_{90-298.1}$	$S_{298.1}$
Guanidine carbonate	22.31	48.28	70.59
Glutamic acid hydrochloride	18.39	40.94	59.33
Ornithine dihydrochloride	21.31	48.94	70.25
$d(l+)$-Lactic acid	10.43	23.87	34.30
$l(d-)$-Lactic acid	10.26	23.75	34.00

Summary

1. The heat capacity data between 90 and 298.1°K. for five organic compounds have been presented.
2. The entropies of these five compounds at 298.1°K. have been calculated.
3. A preliminary value for the heat of fusion of $d(l+)$-lactic acid has been given.

PASADENA, CALIFORNIA RECEIVED DECEMBER 4, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF METALLURGY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Equilibrium FeO + H_2 = Fe + H_2O at Temperatures up to the Melting Point of Iron

BY JOHN CHIPMAN AND SHADBURN MARSHALL

Equilibria of iron and its lowest oxide with a gas phase containing steam and hydrogen or carbon dioxide and monoxide have been of interest in connection with the reduction of iron ore, the scaling of steel at high temperatures, the behavior of iron catalysts, and the establishment of the water gas equilibrium. Several careful researches on these equilibria have established the free energy of the lowest oxide in the form which occurs in equilibrium with solid iron at temperatures up to about 1360°. Reviews of the literature on this field were included in the papers of Emmett and Shultz[1] and of Chipman and Murphy[2] and need not be repeated here. One noteworthy paper has appeared more recently in which Britzke, Kapustinsky and Schaschkina[3] report measurements extending up to 1225°.

On account of the importance of ferrous oxide in many metallurgical reactions, a determination of its free energy at higher temperatures was undertaken. The plan of this investigation was to establish the equilibrium conditions involving steam, hydrogen, solid iron and liquid oxide over a sufficient range to permit extrapolation to the melting point of iron. At the same time a redetermination below the melting point of the oxide served as a useful check on existing data.

Experimental Method

A weight change method was adopted for the important reason that it permitted a minimum contact of the iron specimen with its support and hence a minimum contamination of either the metallic or non-metallic phase. It proved admirably suited to the problem at high temperatures where the reaction rate was rapid. As shown in Fig. 1 the specimen K was suspended from a balance A mounted directly over the tubular furnace. Commercial hydrogen was passed over platinized asbestos E at 400°, thence through a water saturator C maintained at a controlled temperature in a well-stirred oil-bath and the steam–hydrogen mixture was delivered to the bottom of the furnace. With the furnace at constant temperature, the saturator temperature was adjusted to create a gain or loss in the weight of the specimen, which, when both phases were present in the specimen, indicated respectively oxidizing and reducing conditions. When the saturator temperature was changed slowly and uniformly, it was

---

[1] Emmett and Shultz, THIS JOURNAL, **52**, 4268 (1930); **54**, 3780 (1932).

[2] Chipman and Murphy, *Ind. Eng. Chem.*, **25**, 319 (1933).

[3] Britzke, Kapustinsky and Schaschkina, *Z. anorg. allgem. Chem.*, **219**, 287 (1934).

possible to observe the change from gain to loss of specimen weight or *vice versa* within a very narrow temperature range. The mid-point of this range was taken as the equilibrium point and the constant was computed from the total pressure (barometric) and the known properties of steam.

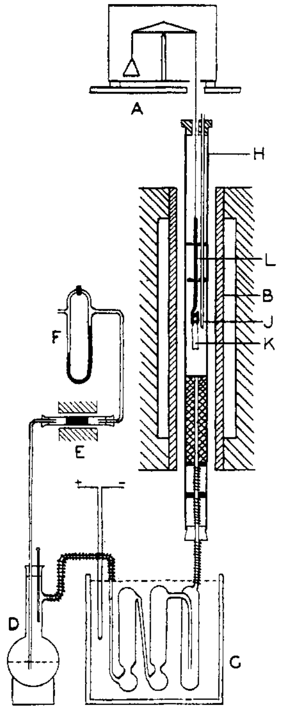

Fig. 1.—Arrangement of apparatus: A, balance; B, globar heating element; C, saturator; D, preliminary saturator; E, platinized asbestos; F, flow meter; H, impervious alumina tube; J, thermocouple protection tube; K, specimen; L, alundum rod.

The iron employed in this study was obtained in the form of rolled carbonyl iron sheet 1.2 mm. thick. This material was cut into strips 3 cm. wide and annealed in dry hydrogen inside a previously annealed Armco iron tube at 1200° for one hundred hours. After this treatment it was found to contain 0.002% oxygen; the annealing was therefore repeated after which the oxygen content was below 0.001%. The strips were cold rolled to 0.27 mm. thickness. Specimens were sheared to the desired size and cleaned in hot hydrochloric acid before use. Several pieces of the annealed strip were analyzed and the following results were the highest that were found: C below 0.005%; S below 0.004%; Si below 0.008%; Mn below 0.003%; Cu, 0.004%; P, 0.002%; Ni, 0.031; O, 0.001; N, nil.

The heating element B, Fig. 1, was a silicon carbide (Globar) tube 5 cm. inside diameter and 55 cm. long. Power was supplied by a motor generator controlled by a variable resistance in the field circuit. By hand regulation it was possible to maintain temperatures constant within ±2° up to 1600°.

Inside the heating element was placed a slightly longer tube H of impervious alumina (Alfrax 2 B). The platinum–platinum–10% rhodium thermocouple was mounted inside a small porcelain tube J (McDanel) which was inserted from the top. Cemented to this tube were two alumina disks which acted as radiation shields. For the same purpose the lower part of the tube was filled with a refractory insulating brick (K-30) the topmost piece of which extended well into the zone of uniform temperature. Between brick and disk was a distance of some 15 cm. within which no temperature differences could be detected by movement of the thermocouple. As further evidence of uniformity it was found in observations through the top of the furnace using blue furnace glasses that objects within this zone could not be distinguished. Specimens of iron 5 cm. long used in melting point determinations showed incipient melting uniformly over their entire length.

Before the first experiment the thermocouple was calibrated at the melting points of copper and nickel by an immersion method and at that of palladium (1555°) by the wire method. After expt. 4 and again after expt. 8 it was checked at the copper and palladium points. Finally, after use at the highest temperature and after several determinations of the melting point of iron, it was rechecked at the palladium point and again after the last run at the nickel and palladium points. In all of these tests the couple agreed with the standard tables within 1° and accordingly all temperatures were read from the table without correction.

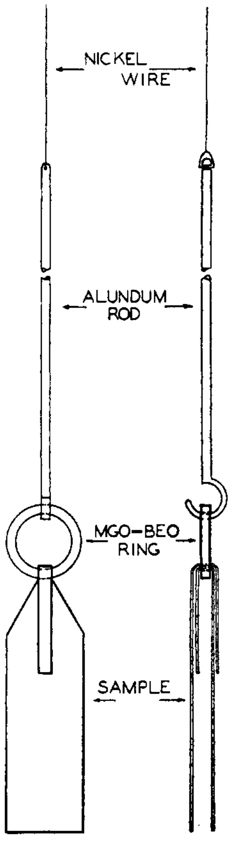

Fig. 2.—Method of suspending sample.

The saturator C was of a type which previously had been used in several investigations and had been found by thorough tests to give complete saturation of the gas. As indicated in Fig. 1, the hydrogen was given a preliminary wetting in a simple bubbler D which was held at approximately the temperature of the saturator. The latter consisted of two towers filled with glass beads and distilled water and a third empty tower which was used as a safeguard against entrainment of spray. The three towers, which were sealed together in an all-glass unit, were immersed in a well-stirred oil-bath whose temperature was controlled by hand regulation of bare wire heating coils. Temperatures were read to 0.01° by means of a four-junction copper-constantan thermocouple which was calibrated over the range used by comparison with a standard resistance thermometer. The e. m. f. of this couple and of that used in the furnace were read with an L. and N. "portable precision" potentiometer.

Several methods of mounting the specimen were tried but that shown in Fig. 2 was the only one that could be used at the highest temperatures. A thin alundum rod ground to the desired size from a larger piece extended from the hot zone to a point near the top of the furnace where it hung from the nickel wire which was suspended from the balance arm. The lower end of the rod was fashioned into a hook which supported a ring of magnesia or beryllia. The iron specimen was cut to such a shape that one end of it could be inserted through the ring and bent downward in an inverted U. Two such pieces were inserted from opposite sides and provided a total surface area of 28 sq. cm. and a weight of 3 g.

In carrying out a series of determinations the specimen was brought to a desired temperature under reducing conditions and the ratio of water vapor to hydrogen was then increased until oxidation began. It was found that the point at which a weight increase was first noted corresponded to a gas composition distinctly on the oxidizing side of equilibrium. The tendency of the metal to exhibit this passivity was quite variable and showed no definite relation to the previous preparation of the surface. In some cases oxidation began promptly and proceeded slowly and in some of the earlier runs this was confused with the equilibrium point. In one extreme case the specimen was exposed to a slightly oxidizing atmosphere at 1360° for thirty-two minutes before oxidation began. When it started suddenly, the specimen gained 0.35 g. in weight in ten minutes.

After an oxide coating had been obtained the saturation temperature was decreased until reduction was noted, then alternately increased and decreased so as to approach equilibrium slowly from each side. The record of one such determination is reproduced in Table I. Here the atmosphere has been changed from oxidizing to reducing and back to oxidizing, passing twice through the equilibrium which must correpond quite closely to the two observations indicated.

In illustration of the method of computation, the average of the two points of Table I will be used, namely, 1510° and a saturator temperature of 77.49°. The barometric pressure was 756.3 mm. (cor.) and the water vapor pressure 320.6 mm., from which P_{H_2O}/P_{H_2} is 0.734. This is the ratio at the saturator temperature which must be corrected for the deviation of water vapor from ideal gas behavior. This correction, which amounts to only 0.8 to 1.0%, was computed from the specific volume of saturated water vapor[4] and was applied to all data. The value of K corresponding to the ratio above is 0.742.

TABLE I

RECORD OF EXPERIMENT 13c

Time	Furnace temp., °C.	Saturator temp., m. v.	Oxygen, g.	Observations
4:31	1509			
4:32		12.749	0.265	Oxidizing
4:33		.753	.267	Oxidizing
4:34		.756	.268	Oxidizing
4:35	1509	.753	.270	Oxidizing
4:36		.746	.271	Oxidizing
4:37		.745[a]	.272	Oxidizing
4:38	1509	.738	.271	Reducing
4:39		.735	.271	Reducing
4:40		.734	.270	Reducing
4:41		.732	.269	Reducing
4:42	1510	.735	.268	Reducing
4:43		.736	.267	Reducing
4:44	1511	.742[a]	.267	Constant
4:45		.746	.267	Constant
4:46	1510	.750	.268	Oxidizing
4:47		.756	.269	Oxidizing

[a] Observations nearest equilibrium.

Results

A summary of all experiments is contained in Table II. The fifth column gives the approximate increase in weight of the specimen at the time of the equilibrium measurement. The last column indicates the manner in which the equilibrium gas composition was estimated, RO signifying that it was during a change from reducing to oxidizing conditions. It will be noted that many of the points constitute duplicate determinations in which the approach has been from both sides.

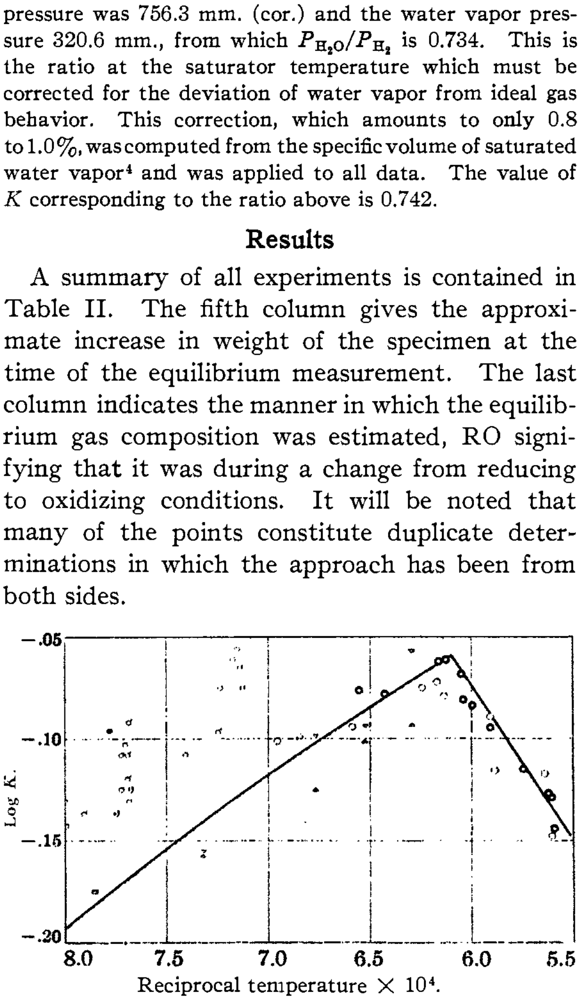

Fig. 3.—Experimental values of log (P_{H_2O}/P_{H_2}): ◯, preliminary and approximate results; O, results considered most dependable; ☐, Emmett and Shultz; △▽, scaling and non-scaling, Jominy and Murphy; ♂, Britzke, *et al.*

The points are plotted in Fig. 3, in which the more precise experiments are designated by larger circles. Data of other investigators within the range are included for comparison. Since certain results appear to deserve greater weight than others, a brief discussion of each experiment is in order. Experiment 2 must be regarded as a preliminary run without great precision; expt. 3 was more carefully conducted and should have yielded satisfactory results. The one result of 4 appears dependable; the support failed before a second point could be obtained. A similar occurrence prevented a satisfactory check in expt. 5. In the sixth run the equilibrium point was

---

(4) Landolt-Börnstein, "Tabellen," Vol. II, pp. 1318–1323.

traversed in only one direction, and for this reason the results cannot be given great weight.

It was noted that some of the samples when removed from the furnace bore evidence of diffusion of iron oxide into the magnesia support. Although the specimen was in contact with its support over only a very small area, it seemed possible nevertheless that some contamination of the iron oxide might occur. The effect of such contamination was investigated by Schenck, Franz and Willeke[5] who found that the equilibrium point was very greatly affected by all of the common refractory oxides except beryllia. Accordingly a tube of this oxide was fabricated and cut into rings which were used to support the specimens in the later experiments.

The results of expt. 8 did not differ from those in which a magnesia support was used. Experiments 9 to 12 were made to determine the melting points of iron and its oxide. During 12, two equilibrium points were observed, but these must be ruled out for the reason that a crack was found in the alumina tube after the completion of the run and neither the time of occurrence nor the effect of the crack is known. Experiment 13 was conducted after a careful survey of the possible causes of minor discrepancies in the earlier runs and its results are considered the most dependable of the series.

TABLE II

SUMMARY OF EQUILIBRIUM DATA

Expt.	Temp., °C.	K	Oxygen g.	Observations	Support
2a	1165	0.792	0.08	RO	MgO
b	1188	.797	.08	OR	
c	1246	.806	.10	OR, RO	
d	1358	.834	.04	OR, RO	
3a	1253	.840	.06	OR, RO	MgO
b	1350	.867	.01	OR, RO	
c	1386	.831	.02	OR, RO	
4	1421	.804	.07	OR, RO, OR	MgO
5a	1501	.764	.06	OR	MgO
6a	1510	.706	.05	OR	MgO
b	1427	.766	.06	OR	
c	1420	.814	.10	OR	
8a	1395	.825	.09	OR, RO	BeO
b	1467	.766	.15	RO, OR	
c	1514	.717	.12	RO, OR, RO, OR	
12a	1329	.847	.15	OR, RO	BeO
b	1348	.849	.08	OR, RO	
13a	1283	.835	.41	OR, RO	BeO
b	1360	.870	.33	RO, RO, OR	
c	1380	.855	.22	OR, RO	
d	1505	.747	.24	RO, OR	
e	1510	.742	.26	OR, RO	

The two lines of Fig. 3 were drawn to conform as nearly as possible to the best experimental points (expts. 3, 4, 8, 13) and to intersect at the melting point of the oxide 1369°. The slightly curved line below the melting point represents the equation which will be deduced in a later section. Attention is called to the rather extended scale upon which log K is plotted and the smallness of the heat of reaction, two factors which combine to render clearly visible the curvature occasioned by a change in heat capacity of only 2.2 calories per degree. It may be noted also that the greatest deviations from the lines do not exceed 0.02 unit in log K, while the mean deviation of all the points tabulated is only 0.0086 unit or 0.04 calorie per degree in the free energy. The uncertainty in the four best runs is somewhat less than this. The straight line above the melting point is expressed by the equation:

$$\log K = 1583/T - 1.021 \qquad (1)$$

Melting Point of Ferrous Oxide.—The lowest oxide of iron does not have the stoichiometric composition required by the formula FeO but instead has a somewhat higher oxygen content and is stable over a range of compositions. This solid solution, which is called "wüstite," has been the subject of a number of investigations among which may be mentioned those of Pfeil[6] and of Jette and Foote.[7] They have shown that the iron-rich extremity of the solid solution field is of the constant composition 76.8% iron and it is the solid solution of this composition which is taking part in the reaction under study.

The melting point of "wüstite" has been variously recorded between 1350 and 1380°. During the course of our expt. 12, an amount of oxide corresponding to about 0.4 g. of oxygen was built up on the specimen at a temperature of 1360° and under slightly oxidizing conditions. The temperature was raised about 1° per minute until a sudden loss of weight indicated the melting and dripping of the highly fluid liquid. This occurred at 1370°. A second specimen, which was coated with oxide equivalent to 0.6 g. of oxygen was heated through the same range at a rate of 0.3° per minute. The oxide dripped off at 1369°.

---

(5) Schenck, Franz and Willeke, *Z. anorg. allgem. Chem.*, **184**, 1 (1929).

(6) Pfeil, *J. Iron Steel Inst. (London)*, **123**, 237 (1931).

(7) Jette and Foote, *Trans. Am. Inst. Mining Met. Engrs.*, **105**, 276 (1933).

Another method of estimating the melting point is by the intersection of the two experimental lines shown in Fig. 3. The best lines drawn through the points of expt. 13 meet at 1365°. The direct determination is considered the more dependable and accordingly the lines of Fig. 3 are drawn to intersect at 1369°. This is to be compared with 1370° found by Tritton and Hanson[8] and 1380 ± 5° reported by Bowen and Schairer.[9]

Melting Point of Iron.—Discrepancies in the published values of the melting point of iron may be due in part to impurities in the metal. Oxygen is seldom reported in analyses of iron, yet it is normally present and is generally an important impurity in vacuum-melted iron. From its solubility in liquid iron it may be calculated that its effect on the melting point may be as large as about 10°, exact calculation being impossible in the absence of dependable data on the solid solubility.

The furnace used in the equilibrium study was well adapted to a determination of the effect of oxidation upon the melting point. We did not wish to carry out a determination in dry hydrogen for fear that reduced silicon from the refractories might be transported to the specimen. Accordingly measurements were made in hydrogen containing a limited amount of water vapor, and in a mixture approaching the equilibrium ratio. In neither case was there an appreciable change in the weight of the specimen until the melting point was reached when a drop of metal weighing one to two grams melted off. There was evidence of uniform melting over the entire length of the specimens.

From the results, which are given in Table III, we may extrapolate in both directions to obtain the melting point of oxygen-free and of oxygen-saturated iron. According to Fig. 3 the equilibrium ratio at 1524° is 0.724. Extrapolation to this ratio on the one hand and to zero on the other gives, for the melting point of oxygen-saturated metal, 1524°, and for that of pure iron, 1535°. The latter agrees well with the average of previous determinations,[10] while the former is in agreement with the temperature 1523° reported by Bowen and Schairer[9] for oxidized iron.

TABLE III

MELTING POINT OF IRON

Expt.	Barometer, mm.	Saturator temp., °C.	P_{H_2O}/P_{H_2} (cor.)	M. p., °C.
9	755.9	26.0	0.034	1534.0
10	755.9	27.3	.037	1534.3
11a	756.0	76.12	.674	1524.4
11b	756.0	75.93	.666	1524.4
Extrapolated			.000	1534.7
Extrapolated			.724	1523.6

Thermodynamic Treatment.—The results reported here, together with published information at lower temperatures, include data on all of the allotropic forms of iron. Thermal data on the metal are summarized in Table IV. The sources of these data have been cited in a previous paper[2] and the only change that seems necessary is a revised equation for the heat capacity of gamma iron, bringing this into agreement with the data summarized by Austin.[11] It may be remarked that the heat effect of the α–β change, which is spread over a considerable temperature range, is lumped at one temperature for the sake of simplicity and without significant loss of accuracy. On the basis of Table IV the difference in free energy of the several forms may be expressed by the equations

$$Fe(\alpha) = Fe(\gamma);\quad \Delta F^\circ = 110 - 3.65T \ln T + 0.00283T^2 + 22.347T \quad (2)$$

$$Fe(\beta) = Fe(\gamma);\quad \Delta F^\circ = 2160 + 2.30T \ln T - 0.00057T^2 + 17.430T \quad (3)$$

The specific heat at low temperatures of an impure ferrous oxide containing 77.24% iron was determined by Millar[12] and that of a similar (probably identical) material at high temperatures by White.[13] The solid oxide which was present in our equilibrium studies was the iron-saturated solid solution "wüstite" which, according to Jette and Foote,[7] has a constant composition of 76.8% iron. These materials were doubtless sufficiently alike to permit the use of the observed specific heats in the present calculation without correction for impurities. The two sets of specific heat data may be represented by the linear equation, $c_p = 0.1663 + 0.000029T$. Now in applying this to our data it must be borne in mind that we are not dealing with a simple compound FeO but with a phase in which the average oxygen atom is combined with approximately 0.95 iron atom. The free energy calculated directly

---

(8) Tritton and Hanson, *J. Iron Steel Inst. (London)*, **110**, 90 (1924).

(9) Bowen and Schairer, *Am. J. Sci.*, **24**, 177 (1932).

(10) Cleaves and Thompson, "The Metal Iron," McGraw-Hill Book Co., Inc., New York, N. Y., 1935, p. 133.

(11) Austin, *Ind. Eng. Chem.*, **24**, 1225 (1932).

(12) Millar, THIS JOURNAL, **51**, 215 (1929).

(13) White, *ibid.*, **55**, 1047 (1933).

from the equilibrium constant is that corresponding to the formation or reduction of 69 g. of this phase containing 16 g. (23.2%) of oxygen and 53 g. (0.95 g. atom) of iron. For brevity this amount of this phase will be designated "FeO (wüstite)." The corresponding heat capacity is listed in Table IV.

The heat capacities of the two gases are taken from recent calculations based upon spectroscopic data.[14,15] They may be represented with sufficient accuracy for present purposes by the two linear equations of Table IV which are designed to cover the range 298–1700°K.

TABLE IV

THERMAL DATA ON THE REACTING SUBSTANCES

Substance	Molal heat capacity cal. mole⁻¹ degree⁻¹	Heat of phase changes, cal.
Fe(α)	$3.90 + 0.00680T$	$\alpha \rightarrow \beta$; $\Delta H_{1033} = 470$
Fe(β)	9.85	$\beta \rightarrow \gamma$; $\Delta H_{1183} = 218$
Fe(γ)	$7.55 + 0.00114T$	$\gamma \rightarrow \delta$; $\Delta H_{1673} = 110$
Fe(δ)	9.85	
FeO(wüstite)	$11.47 + 0.00200T$	
H_2(g)	$6.57 + 0.00074T$	
H_2O(g)	$7.09 + 0.00270T$	

In the temperature range 1183–1642°K. the change in heat capacity in the reaction is $-3.77 + 0.00104\ T$. The free energy equation is then:

$$\text{FeO(wüstite)} + H_2(g) = 0.95\ \text{Fe}(\gamma) + H_2O(g)$$
$$\Delta F^\circ = \Delta H_0 + 3.77T \ln T - 0.00052T^2 + IT \quad (4)$$

The evaluation of ΔH_0 and I will be done graphically by means of a "sigma plot." For this purpose the equation corresponding to the above is:

$$\log K = -\Delta H_0/4.575T - 1.897 \log T + 0.0001137T - I/4.575 \quad (5)$$

from which the log K and the two terms originating in ΔC_p are grouped as "Σ." In order to include available data below 910° an additional term must be included which is found from Equations 2 and 3. Including this term, sigma is defined by the equation

$$\Sigma = \log K + 1.897 \log T - 0.0001137T - 0.95(F_\gamma - F_\alpha)/4.575T \quad (6)$$

Values of Σ are plotted against reciprocal temperature in Fig. 4. The data include for comparison the older work of Eastman and Evans,[16] which is now known to have suffered the unsuspected error of thermal separation of the gases in the static system employed.

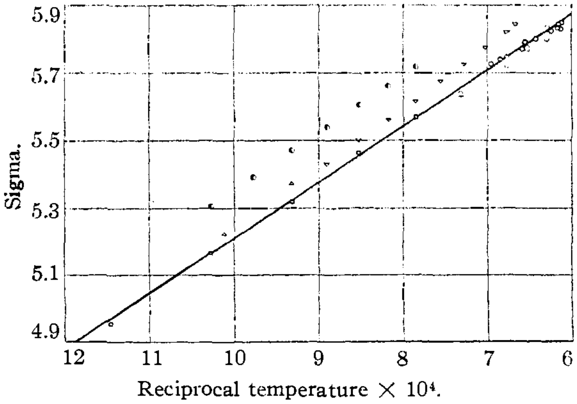

Fig. 4.—Experimental values of *sigma* of equation (6). ○, Authors; □, Emmett and Shultz; ◠ ◡, Jominy and Murphy; △, Krings and Kempkens; ▽, Britzke, *et al.*; ◐, Eastman and Evans.

The straight line is drawn through our results and those of Emmett and Shultz.[1] The limiting oxidizing and reducing compositions of Jominy and Murphy[17] are in very good agreement with the line. Data of Krings and Kempkens[18] and of Britzke and co-workers[3] (points shown are at round temperatures) form a consistent series which, however, is in disagreement with our results.

The straight line of Fig. 4 is represented by the equation

$$\Sigma = -1653/T + 6.863 \quad (7)$$

from which the free energy change in Reaction 4 is

$$\Delta F^\circ = +7562 + 3.77T \ln T - 0.00052T^2 - 31.398T \quad (8)$$

At temperatures within the range of stability of alpha iron, Equations 2 and 8 combine to give

$$\text{FeO(wüstite)} + H_2(g) = 0.95\ \text{Fe}(\alpha) + H_2O(g) \quad (9)$$
$$\Delta F^\circ = 7457 + 7.24T \ln T - 0.00321T^2 - 52.628T$$

The free energy and heat of formation of wüstite from the elements at 25° may be obtained from the solution of Equation 9 and Rossini's[19] recently published functions for water vapor. The results are

$$0.95\ \text{Fe}(\alpha) + {}^1/_2O_2 = \text{FeO(wüstite)}$$
$$\Delta H^\circ_{298} = -63{,}380 \text{ cal.}$$
$$\Delta F^\circ_{298} = -58{,}420 \text{ cal.}$$

The corresponding value for the entropy of wüstite is 14.06 units. It is not easy to compare these results with calorimetric determinations since the latter have been based upon the erroneous assumption of a simple stoichiometric compound. Roth and his co-workers[20] report 64.2 kilocalories as the heat of formation of FeO

---

[14] Gordon, *J. Chem. Phys.*, **2**, 65, 549 (1934).

[15] Davis and Johnston, THIS JOURNAL, **56**, 1045 (1934).

[16] Eastman and Evans, THIS JOURNAL, **46**, 888 (1924).

[17] Jominy and Murphy, *Ind. Eng. Chem.*, **23**, 384 (1931).

[18] Krings and Kempkens, *Z. anorg. allgem. Chem.*, **183**, 225 (1929); **190**, 313 (1930).

[19] Rossini, *Bur. Standards J. Research*, **22**, 407 (1939).

[20] Roth, Umbach and Chall, *Arch. Eisenhüttenw.*, **4**, 87 (1930).

and Millar[12] reports its entropy as 12.7 ± 2.0 units.

At temperatures above the melting point of the oxide, there are no data on either its heat capacity or its composition. And since the heat effect at the gamma–delta transformation is quite small, the equilibrium involving solid iron and molten oxide may be represented by the following simple equation in which "FeO(l)" represents a quantity of the liquid oxide containing 16 g. of oxygen

$$FeO(l) + H_2 = Fe(\gamma \text{ or } \delta) + H_2O$$
$$\Delta F^\circ = -7240 + 4.67T \qquad (10)$$

The heat of fusion of wüstite is found from the two free energy equations to be 10,000 calories per mole. Here the "mole" contains 16 g. of oxygen but only 53 g. of iron below the melting point and an undetermined amount in the liquid. The calculated heat thus includes the effect of any change in composition of the oxide. It may be pointed out that this is less than half the magnitude of the heat effect calculated from the data of Jominy and Murphy,[17] the discrepancy arising from disagreement in equilibrium data above the melting point of the oxide.

Summary

The equilibrium of iron and its oxide with steam and hydrogen has been investigated in the range 1200–1515°.

Below the melting point of the oxide the new results and those of Emmett and Shultz are expressed by an equation which agrees essentially with the data of Jominy and Murphy.

Above the melting point the value of $K = P_{H_2O}/P_{H_2}$ is given by: $\log K = 1583/T - 1.021$.

The melting point of the equilibrium oxide was found to be 1369°; its heat of fusion 10,000 calories per mole.

The melting points of oxygen-free and oxygen-saturated iron were found to be, respectively, 1535° and 1524°.

CAMBRIDGE, MASSACHUSETTS
RECEIVED OCTOBER 23, 1939

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 723]

An Investigation of the Complex Structure of the O–H Harmonic Bands of Substituted Alcohols, and of the Effect of Temperature on the Relative Intensities of the Multiplet Components

BY LLOYD R. ZUMWALT AND RICHARD M. BADGER

It has been observed that the fundamental and harmonic O–H vibration bands of alcohols and substituted phenols frequently consist of two or more components even in cases of substances which have only one hydroxyl group per molecule.[1,2,3] When this multiplet structure persists under conditions such as to exclude association it has often been attributed to the presence of two or more molecular species with slightly different O–H frequencies. These different species have usually been supposed to represent merely different stable molecular configurations which result from restricted rotation about one or more single bonds.

Such an explanation, however useful in some cases, must be subject to some suspicion and cannot finally be accepted without further tests since in some cases the apparent complexity of the O–H bands is probably due merely to an accidental near superposition of other harmonic or combination bands. In other instances a multiplet band may represent merely a band sequence, as has been shown to be true of the N–H bands of pyrrole.[4]

The criteria by which complex O–H bands due to the presence of several molecular species may be recognized are as follows. First, a similar pattern should be found in fundamental and harmonic regions, but the separations between the components should be roughly proportional to the number of the harmonic. Second, the relative intensities of the components should, in general, be dependent on the temperature, provided of course that equilibrium between the various molecular species is established. Third, the individual bands making up a multiplet should have different rotational structures. Pauling's explanation of the *o*-chlorophenol spectrum[5] stands up under the first two tests. The third criterion seldom can be

---

(1) Wulf and Liddel, THIS JOURNAL, **57**, 1464 (1935).

(2) Badger and Bauer, *J. Chem. Phys.*, **4**, 711 (1936).

(3) Barchewitz and Freymann, *Compt. rend.*, **204**, 1728 (1937).

(4) Zumwalt and Badger, *J. Chem. Phys.*, **7**, 629 (1939).

(5) L. Pauling, THIS JOURNAL, **58**, 94 (1936).