light. The history, then, is of importance as well as the constants in judging the purity of acetophenone.

Density.—The density of the pure solvent at 25°, determined with a pycnometer (with the usual corrections for reducing the values to the vacuum basis, the apparent weight of 1 cc. of water being taken as 1.00400 g.), compared to water at 4° was found to be 1.02382 ± 0.002%. This agrees exactly, to the limit of their experimental error, with the value calculated from the interpolation equation of Dutoit and Friederich: $d_t = 1.0267 - 0.0_38467\,(t - 21.6) - 0.0_6596\,(t - 21.6)^2$; or $d^{25°}_{4°} = 1.0238$. It will be remembered that these authors recrystallized their acetophenone to a constant freezing point differing from ours. The impurity left, for the most part, would be water, which would have little effect on their values since it was found to have very little on ours, although ours were carried out to another decimal place. To be of value as a criterion of purity, the densities would have to be determined far more precisely than ours, but as we were interested in the density in our work only as a means of changing weight-normal concentrations to volume-normal, more accurate determinations were not made.

Summary

A large quantity of acetophenone has been purified by a method involving the slow recrystallization of the substance in the dark and in the absence of moisture, and the following constants have been determined: freezing point = 19.655° ± 0.002°; specific conductance, at 25° = 6.43×10^{-9} mho; density at 25° compared to water at 4° = 1.02382 ± 0.002%.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

EQUILIBRIA INVOLVING THE OXIDES OF IRON

BY E. D. EASTMAN AND R. M. EVANS

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In a previous paper[1] various uncertainties in the existing data relating to the systems, iron:hydrogen:oxygen and iron:carbon:oxygen, have been pointed out and fully discussed. The work described in the present paper was undertaken in order to remove some of the more important of the uncertainties concerning the equilibria expressed by the following equations.

$$FeO + H_2 = Fe + H_2O; \quad K_1 = (H_2O)/(H_2) \qquad (1)$$
$$Fe_3O_4 + H_2 = 3FeO + H_2O; \quad K_2 = (H_2O)/(H_2) \qquad (2)$$
$$FeO + CO = Fe + CO_2; \quad K_3 = (CO_2)/(CO) \qquad (3)$$
$$Fe_3O_4 + CO = 3FeO + CO_2; \quad K_4 = (CO_2)/(CO) \qquad (4)$$

In particular it was our purpose (1) to investigate the nature of the solid phases in the iron:hydrogen:oxygen system; (2) to measure the equilib-

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[1] Eastman, THIS JOURNAL, **44**, 975 (1922).

rium constants for the reactions in this system, after careful study of the errors affecting the measurements, in the hope of establishing trustworthy values of them; and (3) to secure such data in the carbon system as might be necessary to justify confidence in the results of comparisons of the equilibrium data in the two systems through the values which may be calculated from them of the constant for the water gas reaction,

$$CO_2 + H_2 = CO + H_2O;\ K_5 = (CO)\ (H_2O)/(CO_2)\ (H_2) \qquad (5)$$

Solid Phases in the Iron: Hydrogen: Oxygen System

Our work in this part of the problem consisted in the study, at a temperature of 772°, of the composition of the gas in equilibrium with solid phases varying in (average) composition from nearly pure iron to nearly pure ferro-ferric oxide. In determining equilibrium gas compositions we used the method devised by Deville,[2] and since used by nearly all other workers in this field. In principle, this method consists in allowing water vapor maintained at constant pressure by contact with liquid water at a fixed and known temperature to react with iron in a closed tube at a constant high temperature. From measurements of the total pressure after equilibrium is established the pressures of hydrogen are then obtained by subtracting the known vapor pressure of water. Variation in composition of the solid was accomplished by successive heatings in a stream of water vapor in the apparatus, starting with pure iron. The increase in weight of the sample was determined after each treatment, and the composition of the solid calculated.

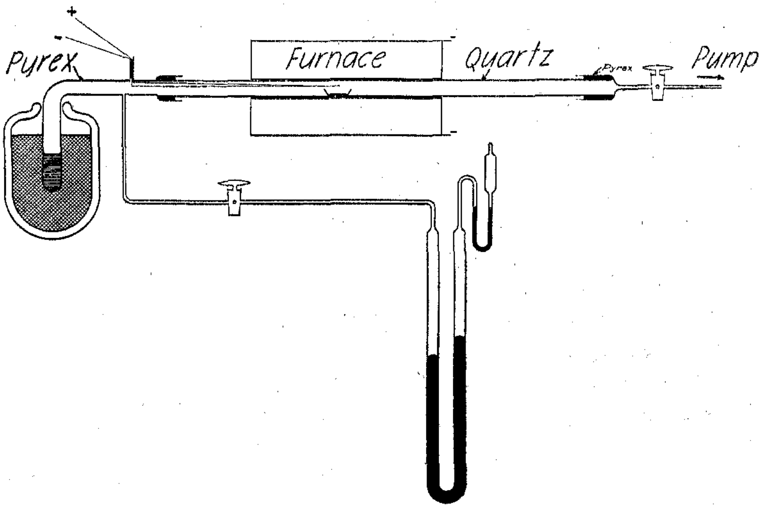

Fig. 1.—Apparatus.

Details concerning the experimental arrangements and procedure will

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[2] St. Clair Deville, *Compt. rend.*, **70,** 1105, 1201 (1870); **71,** 30 (1871).

be understood from the following statements, and from the diagram in Fig. 1.

The samples investigated consisted initially of about 1 g. of iron. The sample in each run was contained in a boat placed in a quartz glass tube 2 cm. in diameter and 70 cm. long in the center of a resistance furnace. The quartz glass tube was joined by water-cooled seals of de Khotinsky cement to Pyrex tubes leading to the water reservoir, manometer and pump. A calibrated platinum-platinumrhodium thermocouple, with one junction directly over the boat, was used to measure temperatures in the tube. The thermocouple readings were made with a portable potentiometer and were accurate to 2°. By hand regulation of the furnace, the temperature was kept constant within 5° during runs. The water in the reservoir was maintained at 0° by immersion in an ice-bath. The inside diameter of the manometer tubing was 2 cm. The levels of the mercury in the manometer were read to 0.05 mm. by means of a cathetometer.

Of the possible sources of error which were experimentally studied one which had to be guarded against with great care was found to be the evolution, during runs, of occluded gases from the walls of the heated tube. This evolution was followed in blank runs and found to become inappreciable only after long periods of heating. To reduce the errors from this source the tube was always carefully baked, while evacuated, before each set of equilibrium measurements, at temperatures above those to be used in the actual run. From the time required to obtain equilibrium and the approximately known rate of evolution of gas from the tube under the conditions of the experiments, we could be sure that errors larger than those from other sources did not enter.

To test the possible influence of variations in the method of preparation of the iron, we used samples prepared by reduction of purified ferric hydroxide with hydrogen and carbon monoxide, respectively, at about 1000°, and by electrolysis of ferrous ammonium sulfate with a mercury cathode, the mercury being subsequently removed by heating strongly in a vacuum. The three preparations proved to be identical so far as our measurements were concerned.

Experiments were made with porcelain, alundum and platinum boats as containers. Of these materials porcelain proved most satisfactory, reacting with the charges to only an insignificant extent. The platinum boat gained in weight very appreciably during runs, and the alundum was completely permeated, apparently by iron, and could not be used.

The approach to equilibrium in the experiments could be followed by the rate of change in pressure. The time required for essential constancy in pressure depended largely on the degree of oxidation of the iron. Thus, at 772°, and with samples containing from 0 to 10% of oxygen, the rate was very rapid, the time required ranging from less than 30 minutes to about 45 minutes. With samples containing between 10% and 20% of oxygen the time required increased to as much as five hours. This was due, undoubtedly, to the fact that considerable sintering of the surface of the solids took place during the continued heating, which retarded the diffusion of the gases into the lower layers of the material. Again, when the sample contained about 20% of oxygen and the second oxidation, from FeO to Fe_3O_4, had begun to take place on the solid, the reaction again came quickly to equilibrium. Finally, the oxidation of the last of the FeO to Fe_3O_4 proceeded very slowly indeed. One of two devices was used to confirm the fact that the constancy of pressure truly corresponded to the equilibrium condition. When the solid phase was nearly pure iron or ferrous oxide and the reaction rapid, it was possible to approach the equilibrium from both directions by reaching equilibrium at a given temperature both by cooling from a slightly higher temperature and by heating from a slightly lower one. An increase in temperature is marked by a decrease in the equilibrium pressure of hydrogen. Thus the equilibrium was first measured starting with an excess of water vapor and then with an excess of hydrogen, the one case corresponding to oxidation of the solid phases and the other to reduction. When the reaction was slower, a slightly different scheme was used. When the pressure had become constant at 772°, the temperature was raised by not more than 25° and the pressure was found to drop. This drop could occur only when equilibrium had been very nearly established since the change of the equilibrium pressure with the temperature is only about 0.01 mm. per degree.

The apparatus was designed to permit rapid convection currents, in order to insure the rapid saturation and mixing of the hydrogen and water vapor. The evidence was good that this object had been attained. To test whether the convection currents had an appreciable effect upon the temperature of the surface of the water in the reservoir (and so upon the vapor pressure) we worked in some cases with solid ice present in the reservoir itself and found the same results as without it.

The numerous data obtained in these experiments will not be given in detail. It will suffice for the present purpose to present the final results graphically in a composition diagram. In Fig. 2, the percentage of hydrogen in the gas in equilibrium with the solids in each experiment is plotted as ordinate against the corresponding percentage of oxygen in the solid phase as abscissas. The points of Series A, B and C in this figure were obtained with iron prepared by reduction of ferric oxide with hydrogen, and with porcelain boats as containers. Series D and E were made with the same iron, but with platinum boats. Points of two other series, F and G, corresponding to electrolytic iron and iron from reduction of ferric oxide with carbon monoxide, respectively, are not shown in the figure as the solid compositions were inaccurate although the gas compositions were in good agreement with the other series in the horizontal portions of the curve. The error in the gas compositions is of the order of 1% in the individual determinations. The error in the solid compositions is not large at low oxygen contents in most cases, but increases to

1% or more in the cases of higher oxidation. The solid compositions in Series D (platinum boats) are practically without significance. The general character of Fig. 2 is entirely similar to the diagram obtained by Matsubara[3] in the carbon system, and seems to eliminate the possibility that his results at low oxygen content are seriously in error, since in this part of our work reaction was always rapid and tests of the attainment of equilibrium easily secured.

The data shown in Fig. 2 clearly establish the existence of solid solutions in the composition ranges 0.0–5.0% and 20–24% oxygen, and in a range of unknown limit above 27% oxygen. Only two of the above limits are sufficiently defined by our results to permit estimates of the compositions of the saturated solutions. Taking the values 5.0% and 24.3% oxygen, we find about 18 mole per cent. as the solubility both of ferrous oxide in iron and of ferroferric oxide in ferrous oxide at 772°.

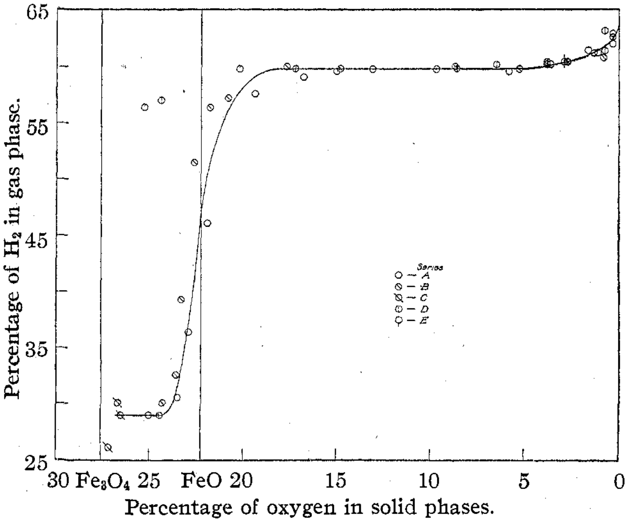

Fig. 2.—Composition diagram for the system Fe:H:O at 772°.

Equilibrium Constants in the Iron: Hydrogen: Oxygen System

When a sufficient knowledge of the range of solid solutions had been gained from the preceding work, the equilibrium constants for Reactions 1 and 2 were determined at various temperatures between 678° and 1039° and a temperature–equilibrium-constant diagram constructed from the results.

Using a sample of iron containing 8.6% oxygen, which Fig. 2 shows to consist of two phases, the equilibrium pressure of hydrogen was determined

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[3] Matsubara, *Trans. Am. Inst. Mining Met. Eng.*, preprint No. 1051, issued with Mining and Metallurgy, Feb., 1921.

as before at 772° and then in like manner at the other temperatures, from which the values of K_1 were directly obtained as the ratios $(H_2O)/(H_2)$ in each case. The tests of equilibrium employed in this work were the constancy in pressure, and the method of approach to the final condition alternately from a higher and a lower temperature, as previously described. But since a long time was required for the completion of this series of measurements and some of the work was done at rather high temperatures, an added precaution was taken to eliminate errors from the liberation of occluded gases. It was possible to follow the increase in pressure due to occluded gases quite closely by repeating the measurements at 772° from time to time during the course of the series, since the value of the constant was known with considerable accuracy at 772° from the preceding work, and the reaction involved was rapid at this temperature. The gains of such readings over the original value for the pressure at 772° constituted corrections to the results obtained at the other temperatures which amounted in the largest case to 6% in the total pressure. The final values of the equilibrium constants at the various temperatures were obtained with about the same accuracy as at 772°, since these corrections were so small and since the values increased quite regularly. The truth of this was further confirmed at 865° by twice measuring the equilibrium pressure immediately after evacuating the apparatus and before any correctoin for occluded gases was necessary. The results thus obtained at this temperature checked within 0.05 mm. in the pressure of hydrogen with two determinations made in the usual way, notwithstanding the fact that in one case almost the maximum correction of 0.55 mm. was made and that in another the solid had been oxidized from 8.6 to 14.8% of oxygen by the continued evacuation in the presence of water vapor. The time required for the establishment of equilibrium in this series varied with the temperature from less than 15 minutes at 1022° to at least four hours at 678°.

The direct observations and the calculated values of K_1 in each experiment are shown in Table I. In the first column of this table the series to which the experiment belonged is indicated. Experiments B-6 to B-10 in this case comprise one continuous series of measurements, B-11 to B-19 another. B-20 and B-22 are individual measurements. Readings at 772° were repeated after B-6, B-10, B-11 and B-17. The second column of the table shows the temperature, and the third indicates the side of approach to equilibrium. Col. 4 contains observed values of the total equilibrium pressure, Col. 5 the corrections for evolved gas discussed above, and Col. 6 the corrected values of total pressure. In the seventh column is given the partial pressure of hydrogen at equilibrium. The last column contains the resulting values of K_1. The composition of the solid phase in these experiments varied between 8.6% and 14.8% of oxygen. The pressure of water vapor in all cases was taken as 4.58 mm. We estimate that the error attaching to the individual determinations of the constant may be about 3%.

Table I

Equilibrium Data Concerning Reaction 1

Series	Temp. °C.	Reaction O = oxidation R = reduction	Obs. press. Mm. of Hg	Corr. Mm. of Hg	Total press. Mm. of Hg	Hydrogen press. Mm. of Hg	K_1
Fig. 2	772	..	...	....	11.40	6.80	0.67
B-6	725	O	12.30	−0.25	12.05	7.45	.62
B-7	678	O	12.75	− .25	12.50	7.90	.58
B-8	678	R	13.10	− .25	12.85	8.25	.55
B-9	725	R	12.35	− .25	12.10	7.50	.61
B-10	678	O	13.00	− .25	12.75	8.15	.56
B-11	818	R	11.30	− .40	10.90	6.30	.73
B-12	865	R	10.85	− .40	10.45	5.85	.78
B-13	909	R	10.50	− .45	10.05	5.45	.84
B-14	952	R	10.25	− .50	9.75	5.15	.89
B-15	909	O	10.60	− .55	10.05	5.45	.84
B-16	865	O	11.00	− .55	10.45	5.85	.78
B-17	818	O	11.45	− .60	10.85	6.25	.73
B-18	1022	R	10.00	− .60	9.40	4.80	.96
B-19	952	O	10.45	− .60	9.85	5.25	.87
B-20	865	O	10.50	.00	10.50	5.90	.78
B-21	865	R	10.45	.00	10.45	5.85	.78

The equilibrium constant of Reaction 2 was first measured using exactly the same experimental procedure as for Reaction 1, except that the solids consisted of mixtures of the phases of higher oxidation. The equilibrium pressures of hydrogen corresponding to Reaction 2 are, however, very much lower than those in (1), resulting in much larger uncertainties in the values of the constant. For example, it was necessary to work at temperatures below about 850° in order to keep the possible errors below 10%. A second series of runs was therefore made in which the ice-bath of the preceding experiments was replaced by a water-bath. The temperature in the water reservoir (and thus the vapor pressure) was determined by means of a calibrated mercury thermometer immersed in it. Before beginning this series, the apparatus was heated for 72 hours to drive out most of the occluded gases. Accumulation of errors from this source was prevented also by evacuating after every two or three measurements.

All of the experimental data obtained concerning Reaction 2 are contained in Table II. The significance of the column headings in this table is the same as in Table I, except that the corrections for occluded gases and the corrected total pressures in the latter are replaced by the values of the water-vapor pressures, determined from the temperature readings. Two different samples of oxides, prepared by heating iron in a stream of water vapor, each containing about 26.7% of oxygen, were used in these measurements.

TABLE II

EQUILIBRIUM DATA CONCERNING REACTION 2

Series	Temp. °C.	Reaction O = oxidation R = reduction	Total press. Mm. of *Hg*	Water vapor press. Mm. of *Hg*	Hydrogen press. Mm. of *Hg*	K_2
Fig. 2	772	..	6.45	4.58	1.85	2.5
C-3	725	O	7.15	4.58	2.55	1.8
C-4	865	R	5.60	4.58	1.00	4.6
C-5	678	O	8.20	4.58	3.60	1.3
C-6	865	R	5.60	4.58	1.00	4.6
C-8	725	O	7.10	4.58	2.50	1.8
C-9	678	R	8.40	4.58	3.80	1.2
C-10	865	R	5.70	4.58	1.10	4.2
H-1	772	R	24.55	18.10	6.45	2.8
H-2	678	R	28.80	16.30	12.50	1.3
H-3	725	R	24.90	16.40	8.50	1.9
H-4	772	R	22.60	16.45	6.15	2.7
H-5	818	R	21.30	16.55	4.75	3.5
H-6	865	R	20.25	16.65	3.60	5.6
H-7	818	R	20.40	15.90	4.50	3.5
H-8	772	O	21.90	16.00	5.90	2.7
H-9	725	O	24.50	16.30	8.20	2.0
H-10	909	R	19.30	16.45	2.85	5.8
H-11	952	R	20.20	17.45	2.75	6.3
H-12	909	O	20.90	17.55	3.35	5.2
H-13	909	R	20.35	17.50	2.85	6.2
H-14	865	O	21.20	17.55	3.65	4.8
H-15	818	O	22.40	17.65	4.75	3.7
H-16	1022	R	20.00	17.85	2.15	8.3
H-17	952	O	20.70	17.90	2.80	6.4
H-18	865	R	21.00	17.25	3.75	4.6
H-19	1022	R	19.45	17.30	2.15	8.0
H-20	818	O	22.55	17.45	5.10	3.4
H-21	909	R	19.95	17.05	2.90	5.9
H-22	952	R	19.50	17.10	2.40	7.1
H-23	818	O	21.95	17.20	4.75	3.6
H-24	952	R	19.55	17.15	2.40	7.2
H-25	1022	R	19.30	17.60	1.70	10.4

The accuracy of the individual determinations of K_2 is thought to be about 3 or 4% at the lowest temperatures employed. At the higher temperatures, where the equilibrium pressures of hydrogen are low, the uncertainty of measurement amounts to 10% or more. There is some indication also that at the higher temperatures the error from the evolution of gas from the heated tube was not completely eliminated, or else that another possible error, to be discussed, entered to an increasing extent. When the water reservoir in experiments like these is maintained at 0°, the density relations are such as to prevent the formation (by contact with the circulating gases or through radiation) of a warmer layer or film of liquid water at the surface of the reservoir. At temperatures above 4° this is not the case. In the last experiments described above, therefore, the temperature at the surface of the water, which fixed the vapor pressure, may have been slightly higher than the measured temperature below the surface. Such an effect would be greater, the higher the furnace temperature and may have become appreciable at the higher temperature in our work. If so, it would lead to low values of K_2. For these reasons we do not give great weight to the values of K_2 determined above about 865°, but believe that more nearly correct values might be obtained by extrapolation from the lower temperatures.

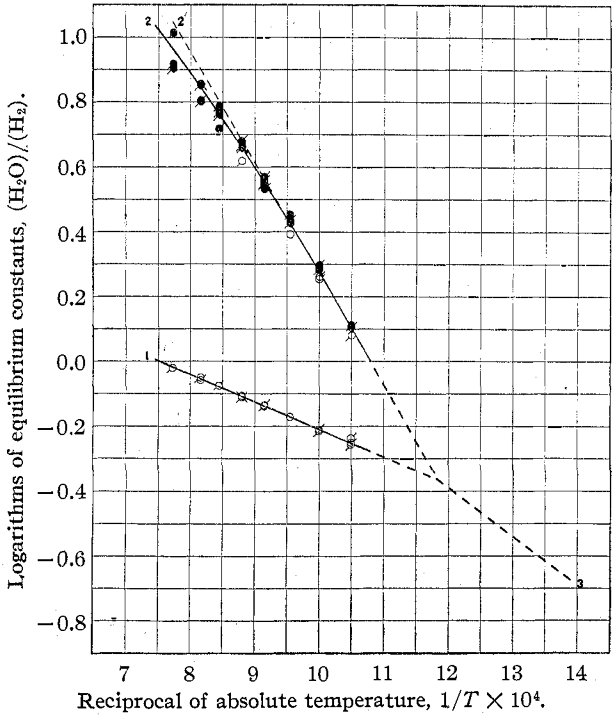

Fig. 3.—Equilibrium constants and temperature in the system, Fe:H:O.

The values of K_1 and K_2 contained in Tables I and II are shown graphically in Fig. 3. The common logarithms of the constants are plotted in this figure as ordinates against the reciprocals of the absolute temperature as abscissas. The strokes attached to the circles representing the experimental points indicate the direction from which equilibrium was approached. Two or more strokes represent multiply-determined points. The solid circles correspond to Series H for K_2, in which the higher vapor pressures of water were used. Curves 1 and 2 in this figure are drawn as most representative of the experimental values of K_1 and K_2, respectively. Their extrapolations to lower temperatures intersect at about 570°. This is the transition temperature below which ferrous oxide is unstable with respect to ferroferric oxide and iron. Curve 3 in the figure is that calculated for the constants in the reaction

$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O; \quad K_6 = (H_2O)/(H_2) \tag{6}$$

The dotted curve marked 2′ in the figure results from linear extrapolation of the low temperature values of K_2 and, as previously explained, we believe lies somewhat nearer the true values of these constants than does Curve 2.

At the present time there exist, in addition to our results, four relatively recent sets of determinations of K_1. Our values of K_1 are in very good agreement at all temperatures with those determined by Schreiner and Grimnes,[4] and by Wöhler and co-workers.[5] Wöhler and Günther quote results by van Groningen,[6] the details of which have not been available to us, but which appear to be in virtually exact agreement with ours. The work of Chaudron,[7] though it was formerly[1] regarded as more reliable than the earlier work because of the known character of the solid phases used in it, appears to have been affected by some of the errors previously discussed. It disagrees, by amounts far larger than the necessary error of measurement, with all of the other recent values.[8]

Our values of K_2 are in agreement, within the combined experimental error, with the previously measured ones of Wöhler and Günther,[5] and van Groningen.[6] Chaudron's[7] figures again differ widely from all of these.

What we regard as the best values of K_1 and K_2 at present available are shown at regular temperature intervals in Table III. The values of K_1 there given are taken from Curve 1 in Fig. 3, which we believe closely represents the true values of this constant. In the determination of K_2 the experimental difficulties are somewhat greater, and the limits of error

[4] Schreiner and Grimnes, *Z. anorg. Chem.*, **110,** 311 (1920).

[5] Wöhler and Prager, *Z. Elektrochem.*, **23,** 199 (1917). Wöhler and Balz, *ibid.*, **27,** 406 (1921). Wöhler and Günther, *ibid.*, **29,** 276 (1923).

[6] van Groningen, *Dissertation,* Delft, 1921.

[7] Chaudron, *Ann. chim.*, **16,** 221 (1921).

[8] Ferguson [*J. Wash. Acad. Sci.*, **13,** 275 (1923)] publishes results of experiments by a dynamic method which he interprets as supporting Chaudron's values of K_1, and as disproving the existence of solutions of ferrous oxide in iron. In our opinion these experiments are indecisive because sufficient variation in the gas composition and time of exposure of iron to the gas stream was not made. So far as we can see there is nothing to prevent the conclusion that in each experiment at 750° the gas stream was in equilibrium with a single solid phase of variable oxygen content; that further exposure would have produced no further change in the composition of the solid phases in these experiments; and that solid solution to the extent of at least 6% oxygen is indicated. If this is correct, the values obtained in these experiments, had they been carried (by further increase in the proportion of water vapor in the gas) to the point where two solid phases appeared, would have fallen nearer to ours than to Chaudron's.

wider than for K_1. We believe, therefore, that more representative values of this constant may be obtained by averaging the data of the several closely agreeing observers than from the work of any one. In Fig. 4 we reproduce Curves 2 and 2′ of Fig. 3, together with the curves representing the final results of Wöhler and Günther (Curve 1) and van Groningen (Curve 3). Curve 4 has been drawn as the one most likely to give "best values," and from it the figures for K_2 in Table III are taken.

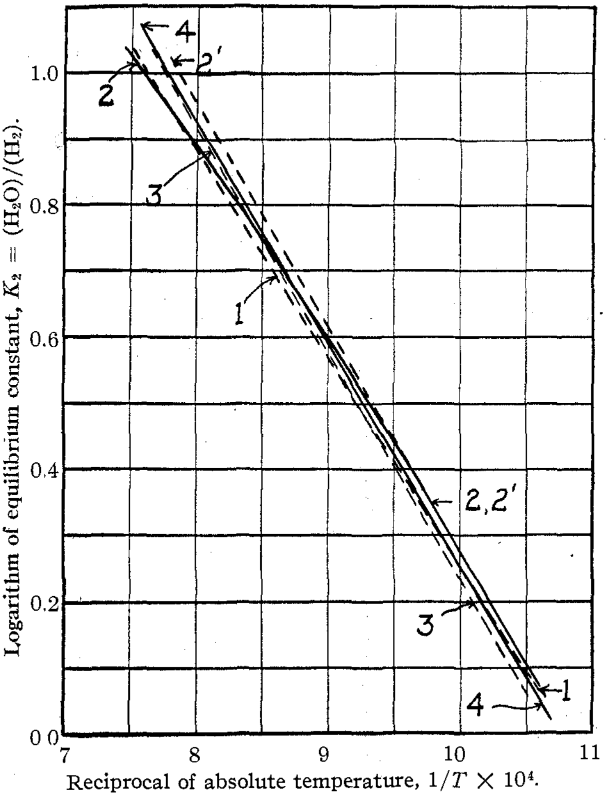

Fig. 4.—Equilibrium constant and temperature in the $FeO:Fe_3O_4:H_2:H_2O$ system. (1) Wöhler and Günther. (2,2′) Eastman and Evans. (3) van Groningen. (4) "Best Values."

Table III

"Best Values" of Equilibrium Constants, $(H_2O)/(H_2)$

Temp., °C	700	750	800	850	900	950	1000
Fe:FeO system, K_1	0.584	0.645	0.706	0.765	0.822	0.879	0.937
$FeO:Fe_3O_4$ system, K_2	1.45	2.11	2.98	4.16	5.50	7.08	9.12

Equilibrium Constants in the Iron: Carbon: Oxygen System

In the previous paper[1] it was pointed out that the agreement between the various determinations of the constant for Reaction 3 is very fair and we have thought it unnecessary to add further to the numerous data concerning this equilibrium. In the values for K_4 for the reaction between ferroferric oxide and carbon monoxide, however, the same consistency does not seem to prevail at all temperatures. The agreement of the various observers is very satisfactory at about 800°, but considerable divergence is found at other temperatures. It seemed to us that the true course of the temperature-equilibrium constant curve for this reaction might be conveniently established with sufficient accuracy by a few measurements in the higher temperature range. We therefore conducted a number of experiments for this purpose between 818° and 1039°.

The apparatus used consisted of a quartz glass tube of about 300cc. capacity connected to a source of carbon monoxide and carbon dioxide, vacuum pump and gas analysis apparatus. Temperature control was the same as in the previous work; the thermocouple, however, was enclosed in a protecting tube in these experiments. The solid sample used was that previously used for the determination of K_2 in Series H. Mixtures of carbon monoxide and dioxide of nearly the equilibrium composition were admitted into the reaction tube. Samples were drawn off and analyzed for monoxide and dioxide after two and four hours, respectively. In no case was the discrepancy between the two analyses greater than the error in the analysis. In order to approach the equilibrium from both directions the gas mixtures were made up first with an excess of one gas and then with an excess of the other.

The results in the order obtained are shown in Table IV. The first column of this table shows the temperature of the run, the second and third columns show the quantities of carbon monoxide and carbon dioxide, respectively, found in the gas samples in the two-hour runs, and the fourth and fifth columns the same for the four-hour runs. In the last column, the calculated values of K_4 are shown. The possible error in the individual values of K_4 is 5%, on the average, over the range of temperatures studied.

TABLE IV

EQUILIBRIUM DATA CONCERNING REACTION 4

Temp. °C.	Cc. of CO 2-hr. run	Cc. of CO_2 2-hr. run	Cc. of CO 4-hr. run	Cc. of CO_2 4-hr. run	K_4
952	3.60	13.00	..	...	3.61
952	5.35	19.80	4.75	16.45	3.58
1039	4.80	21.90	..	...	4.56
1039	3.45	15.25	3.00	12.80	4.35
952	4.55	17.35	5.70	19.80	3.64
865	5.75	16.80	6.40	16.95	2.78
1039	3.80	16.95	3.70	16.85	4.50
818	9.00	24.40	..	...	2.71
818	9.65	24.75	8.45	20.40	2.49
865	6.00	18.05	6.20	17.05	2.88

The values of K_4 in Table V are shown graphically in Fig. 5, together with the results of the recent work of Matsubara.[3] The agreement of the two sets of data is within the experimental error at all temperatures.

The curve shown in Fig. 5 which best represents these points also agrees with the data of other observers[1] in the middle temperature range, where they agree among themselves. Values of K_4 taken from this curve we believe to be the best now available. A number of them are listed in the last row of Table V. For convenience in reference, the smoothed values of K_3 from the previous paper[1] are given in the second row of this table.

Table V

"Best Values" of Equilibrium Constants, $(CO_2)/(CO)$

Temp., °C.	700	750	800	850	900	950	1000
Fe:FeO system, K_3	0.678	0.608	0.552	0.505	0.466	0.432	0.403
FeO:Fe_3O_4 system, K_4	1.68	2.02	2.40	2.79	3.24	3.67	4.17

Comparison of Results in the Hydrogen and Carbon Systems

If the solid phases in the actual equilibria corresponding to Reactions 1 and 3 may be assumed to be nearly identical in character, the values of K_1 and K_3 may be used to calculate the constant, K_5, of the water: gas reaction. With the same assumptions as to the solid phases, a similar calculation is possible using K_2 and K_4. A comparison of the values of K_5 calculated from these independent sets of equilibrium data is well designed to bring to light any serious errors contained in them.

Using the values of K_1 and K_3 from Tables III and V, respectively, we have calculated K_5 at 50° intervals between 700° and 1000°. The results of these calculations appear in the second column of Table VI. In the third column of this table the values of K_5 are given as calculated from the figures for K_2 and K_4, again taken from Tables III and V. The substantial agreement in the constants so calculated attests the essential correctness of the equilibrium data in the four reactions discussed above, as well as of the calculated values of K_5. As a further test of the latter constants, the values corresponding to them of the integration constant, I, in the free-energy equation for the water: gas reaction have been calculated. The thermal data used in this calculation are those employed by

Table VI

Values of Equilibrium Constant, $K_5 = (CO)\ (H_2O)/(CO_2)\ (H_2)$ and Free Energy Integration Constant, I, for the Water: Gas Reaction

Temp. °C.	K_5 from K_1/K_3	K_5 from K_2/K_4	K_5 by direct measurement	I from K_1/K_3	I from K_2/K_4
700	0.862	0.86 (5)	0.581	−1.32	−1.32
750	1.062	1.04	0.733	−1.29	−1.25
800	1.280	1.24	0.892	−1.26	−1.20
850	1.515	1.49	1.062	−1.24	−1.21
900	1.775	1.70	1.247	−1.24	−1.16
950	2.035	1.93	1.442	−1.23	−1.13
1000	2.325	2.19	1.644	−1.23	−1.11
			Mean	−1.26	−1.20

Lewis and Randall.[9] The resulting values of I are given in the last two columns of Table VI. It will be observed that those obtained from the ferrous oxide-iron systems, in which the equilibrium measurements are most reliable, are remarkably constant, particularly at the higher temperatures. In the results from the ferroferric oxide-ferrous oxide systems a greater variation appears, which is, however, not larger than might be anticipated because of the somewhat larger errors of measurement in these systems. We believe that all of the "internal" evidence now substantiates the fundamental reliability of the equilibrium data in the iron: hydrogen: oxygen and iron: carbon: oxygen systems.

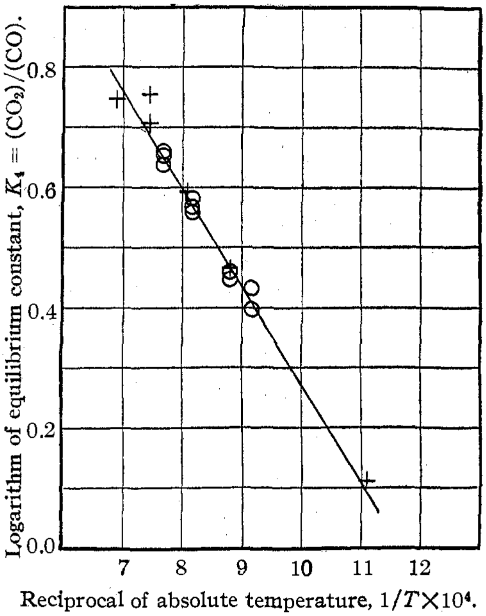

Fig. 5.—Equilibrium constant and temperature in the $FeO:Fe_3O_4:CO:CO_2$ system. + Matsubara. ○ Eastman and Evans. —"Best Values."

If this conclusion is accepted, however, a question immediately arises concerning the water-gas equilibrium itself, since the constants calculated from the iron oxide equilibria do not agree with the directly measured ones. To illustrate this, we have inserted in the fourth column of Table VI the values of K_5 calculated from Lewis and Randall's[9] free-energy equation for the water: gas reaction. This equation depends primarily upon the equilibrium data of Hahn[10] and of Haber and Richardt.[11] The comparison in this way of our data with those of the latter observers, many of which were obtained at temperatures considerably higher than in the iron oxide experiments, of course involves the specific heats of the reacting gases. We believe it unlikely that errors in these quantities are responsible for any large part of the discrepancy between the directly and the indirectly determined values, and believe also that this discrepancy is far greater than the error which may be assigned to the indirect values. A review of Haber's[12] discussion of

[9] Lewis and Randall, "Thermodynamics, and the Free Energy of Chemical Substances," McGraw-Hill Book Co., 1923.

[10] Hahn, *Z. physik. Chem.*, **44,** 513 (1903); **48,** 735 (1904).

[11] Haber and Richardt, *Z. anorg. Chem.*, **38,** 5 (1904).

[12] Haber, "Thermodynamics of Technical Gas Reactions," English translation by Lamb; Longmans, Green and Co., 1908.

the direct determinations does not inspire us with great confidence in them. He points out a source of error which apparently affected the results of Hahn at high temperatures, and may have been operative at all temperatures. Haber's own work was by a method in which a genuine test of the attainment of equilibrium appears to us to be very difficult, and which seems therefore not well suited to the accurate determination of the constant. In view of these facts, and since the study of this reaction through the iron systems is based on values known to correspond closely to equilibrium conditions, and because of the generally greater accuracy of (relatively) low temperature work as compared with high, we have little hesitancy in accepting the values of K_5 as calculated from the iron systems in preference to the direct values.

Complete justification of this position must of course await a redetermination by a direct method of the water: gas constant. It is hoped that such a determination may soon be undertaken. In the meantime it has appeared to us worth while to recalculate the free energies of carbon monoxide and carbon dioxide on the basis of the new results. Taking —1.26, instead of —0.54 as obtained by Lewis and Randall from the earlier data, as the best value now available for I in the free-energy equation for the water: gas reaction, the corresponding integration constants in the equation of Lewis and Randall for the free energy of formation of carbon monoxide and carbon dioxide become —7.48 and —2.30, respectively. The free energies of formation of these substances at 25° are then calculated to be —32300 cal. and —93830 cal., respectively. These free energies thus differ at 25° by 210 and 430 calories from the former values.

Summary

1. The compositions of the gas phase in equilibrium with solid phases varying in average composition between pure iron and ferroferric oxide have been determined at 772° in the system iron: hydrogen: oxygen. The results indicate the existence at this temperature of solid solutions in the composition ranges 0–5% oxygen, 20–24% oxygen, and above about 27% oxygen.

2. Equilibrium constants in the divariant equilibria in this system represented by the equations, $FeO + H_2 = Fe + H_2O$, and $Fe_3O_4 + H_2 = 3FeO + H_2O$ (in which the solid phases are, however, solutions) have been determined between about 657° and 1025°. The sources of error in the measurements have been investigated. The results have been compared with those of other observers, and "best values" tabulated at round temperatures.

3. A series of measurements have been made of the constant of the divariant equilibrium $Fe_3O_4 + CO = 3FeO + CO_2$, between 816° and 1039°, and best values for this constant also tabulated.

4. The values of the equilibrium constants obtained in this paper, together with those discussed in a previous paper for the reaction FeO + CO = Fe + CO_2, have been combined in two independent sets to calculate the constant of the water gas reaction. The values of this constant so calculated are in good agreement with one another at all temperatures, and the values of I in the free-energy equation calculated from them show a satisfactory constancy.

5. The values of the water:gas equilibrium constant and free-energy integration constant calculated from the iron oxide equilibria, while consistent among themselves, are not in agreement with the values directly determined. Reasons have been given for the belief that the latter values are less reliable than the former. Corrections to the free-energy data relating to carbon monoxide and carbon dioxide have been made on the basis of the new results.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE SPECIFIC HEATS OF CERTAIN ORGANIC LIQUIDS AT ELEVATED TEMPERATURES

BY JOHN W. WILLIAMS AND FARRINGTON DANIELS

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It is an interesting fact that the specific heats of gases and solids and their temperature coefficients have been studied much more carefully than those of liquids, although the latter can be measured with greater precision. The reason for this situation is obvious; for solids, and particularly gases, are simpler systems than liquids and their specific heats have been treated mathematically with considerable success. The specific heats of liquids, however, are less amenable to theoretical analysis, for they are complicated by association. When the liquid is heated the complex molecules are broken up and heat is absorbed. This heat is included in many cases as a considerable part of the observed specific heat and prevents the treatment of specific heat as a simple function of the atom.

Before progress can be made in the interpretation of the specific heats of liquids it is necessary to obtain accurate, differential measurements of many liquids over a wide temperature range. Since the heat required to raise the temperature of a liquid includes the energy used in changing from one molecular form to another, irregularities in the specific heat—temperature curves are of particular interest. The whole problem has received new significance since the work of H. B. Baker[1] on dry liquids

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[1] (a) Baker, *J. Chem. Soc.*, 101, 2339 (1912); 121, 568 (1922). (b) Lewis, THIS JOURNAL, **45**, 2836 (1923).