be separated in one operation from mixed yttrium group material containing 2% ytterbium.

3. Analysis of the precipitate showed it to be of variable composition approaching the formula $YbSO_4 xH_2O$. It is a very light green crystalline compound. It is soluble in dilute acids with the evolution of hydrogen and in nitric acid with evolution of oxides of nitrogen.

4. The ytterbous ion, Yb⁺⁺, is green.

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[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

EQUILIBRIA IN THE Fe-H-O SYSTEM.

INDIRECT CALCULATION OF THE WATER GAS EQUILIBRIUM CONSTANT

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In a previous paper¹ we have calculated the value of the equilibrium constant for the reaction

 $CO_2 + H_2 \approx CO + H_2O$ $K_1 = (P_{CO})(P_{H_2O})/(P_{CO2})(P_{H_2})$ (1) by combining the equilibrium constants obtained in our experiments² on the two reactions

The values so calculated were found to be in good agreement with those measured directly by Neumann and Köhler.³ Such previous calculations made by Eastman and Evans,⁴ Eastman⁵ and Eastman and Robinson,⁶ respectively, had, however, given values about 40% higher than the directly measured equilibrium constants. The first two of these calculations were based on the reactions

$FeO + H_2 = Fe + H_2O$	$K_4 = P_{\rm H20} / P_{\rm H2}$	(4)
$FeO + CO = Fe + CO_2$	$K_5 = P_{\rm CO_2}/P_{\rm CO}$	(5)
$Fe_{3}O_{4} + H_{2} = H_{2}O + 3FeO$	$K_6 = P_{\rm H2O}/P_{\rm H2}$	(6)
$Fe_3O_4 + CO = 3FeO + CO_2$	$K_7 = P_{\rm CO_2}/P_{\rm CO}$	(7)

The calculations by Eastman and Robinson were made with the help of their own equilibrium data on the reactions

$\mathrm{SnO}_2 + 2\mathrm{H}_2 = 2\mathrm{H}_2\mathrm{O} + \mathrm{Sn}$	$K_8 = P_{\rm H_{2O}}/P_{\rm H_2}$	(8)
$SnO_2 + 2CO = Sn + 2CO_2$	$K_{\rm P} = P_{\rm CO2}/P_{\rm CO}$	(9)

¹ Emmett and Shultz, THIS JOURNAL, 52, 1782-1793 (1930).

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² Emmett and Shultz, *ibid.*, **51**, 3249-3262 (1929).

³ Neumann and Köhler, Z. Elektrochem., 34, 218 (1928).

⁴ Eastman and Evans, THIS JOURNAL, 46, 888 (1924).

⁵ Eastman, Bureau of Mines Information Circular 6125 (1929).

⁶ Eastman and Robinson, THIS JOURNAL, 50, 1106 (1928).

In view of the importance of knowing the correct values for the water gas equilibrium constant, as well as the values for the equilibria involving iron and its oxides, it seemed worth while to attempt to ascertain whether the above-mentioned discrepancy might be due to errors in previous determinations of the equilibria of Reactions 4, 5, 6 and 7.

Examination of the literature has shown that the equilibrium constants that have been obtained for Reactions 5 and 7 differ considerably among themselves but exhibit no regular variations. The most reliable values agree approximately with those chosen by Eastman.⁸ However, values for equilibria involved in Reactions 4 and 6 vary in a somewhat regular manner; they can for the most part be divided into two groups. In Group I are those agreeing with the determinations of Eastman and his co-workers; when combined with equilibrium constants for Equations 5 and 7, they give values for the water gas constant that are 40% or so higher than those directly measured. In the second group are those agreeing approximately with the theoretical curve calculated by combining equilibrium constants of the Fe-C-O system (Equations 5 and 7) and the directly measured value of the constants for Equation 1. A study of the apparatus and procedure employed by these two groups of workers made it seem possible that the values in the first group constitute what might be termed false equilibria in that they may have been influenced by an abnormal consumption of hydrogen by the surface of the iron oxide specimens. Such surface effects had been observed by us during the determination of the equilibrium in Reaction 3. They had also been noted by a number of previous workers.⁷

It seemed that the use of a dynamic rather than a static method would eliminate this source of error. The present paper gives the results of a series of equilibrium measurements obtained by a dynamic method on Reaction 4, at temperatures between 600 and 1000° , and on Reaction 6 at 700 and 800° .

Apparatus and Procedure

The dynamic method used in the present experiments is almost identical with that reported in a previous paper.¹ It consisted essentially in passing steam-hydrogen mixtures over an iron-iron oxide mixture and analyzing the effluent gases for water vapor and for hydrogen. Equilibrium was approached both from the side of reduction and of oxidation.

The apparatus is shown in Fig. 1. It consisted of a saturator, A; a reaction tube, J; an electric furnace, B; and an analytical apparatus, C and D. The saturator consisted of two towers containing glass beads and immersed in a thermostat controllable to $\pm 0.1^{\circ}$. Tank hydrogen, after being freed from oxygen by hot copper, was passed through a flowmeter and mixed with excess steam from a steam boiler; the steam-hydrogen mixture was passed through the thermostated saturator towers.

⁷ Richardson, Vibrans and Bell, Science, 56, 27 (1922); Pease and Cook, THIS JOURNAL, 48, 1199 (1926); Taylor, Chem. Met., 27, 1263 (1922).

The reaction chamber was a silica tube, flanged and ground at one end to fit tightly against a similar flanged and ground pyrex glass tube. The two tubes were drawn together by a brass clamp, padded by asbestos washers and were made gas-tight by a layer of de Khotinsky wax over the joint. The other end of the quartz tube was drawn down and sealed to a small quartz tube in order to decrease the dead space between the oxide mixture and the analytical apparatus. The quartz reaction tube was surrounded by a heavy copper jacket for a distance of about 20 centimeters and packed with 85% magnesia into the electric furnace shown in the diagram. The copper cylinder surrounding the reaction tube fitted tightly into the alundum tube upon which the nichrome heating element was wound. It was centrally located in the furnace, being about 15 centimeters from each end.



Fig. 1.-Apparatus.

In all of the final runs temperatures were measured by calibrated Pt-Pt-Rh thermocouples in conjunction with a Type K potentiometer. One couple was placed in a thin quartz thermocouple well in the center of the iron-iron oxide mixture, as shown in Fig. 1. The other Pt-Pt-Rh couple was placed in contact with the outside of the reaction tube. During each run it was moved along the tube to obtain the lengthwise temperature gradient. The gradient along the oxide mass was found to agree with that obtained on the outside couple, and was accordingly measured only a few times. The iron-iron oxide mass was about 5° cooler at each end than in the center. The gradient across the reaction tube was usually only one or two degrees; in a few runs it was as much as five degrees.

In the large number of preliminary experiments, alumel-chromel couples calibrated initially at 100 and 444° were used in conjunction with a portable potentiometer for measuring the temperature of the reaction tube. Unfortunately, during use the thermocouples became very brittle and broke before a final calibration over the range of temperatures used could be made.

The high reactivity desired in these measurements was obtained by using as a source of iron synthetic ammonia catalysts.⁸ Sample A contained 0.5% ZrO₂ and 0.5% Al₂O₃. Sample B was a "pure iron" catalyst containing only 0.15% Al₂O₃.

The analytical apparatus was very similar to that previously described. The gas pipet D was of 250-cc. capacity and was water jacketed in order to eliminate any uncertainty as to its temperature. The weighing tube C was connected to the exit of the reaction vessel by a ground joint. All glass tubing between the thermostat and the reaction tube and at the exit of the reaction vessel was heated electrically to prevent

⁸ Eastman, This Journal, 44, 975 (1922).

condensation of any of the moisture present. Dehydrite was used in the weighing tube to catch any moisture not condensed in the main bulb of the tube. The specially designed gas pipet could be attached by a rubber connection directly to the weighing tube and exerted practically no back pressure in the line.

In carrying out the experiments, approximately 54 g. of the fused Fe₈O₄ was placed in the quartz reaction tube. The latter was packed into the furnace and connected as shown in the diagram. The iron oxide was then reduced completely by hydrogen at approximately 600°. At each furnace temperature at which runs were made the saturator was set at such a temperature as to give a steam-hydrogen mixture intermediate in



Fig. 2.—Variation with 1/T of log K, where $K = (H_2O)/(H_2)$ in equilibrium with FeO–Fe, Fe₃O₄–FeO or Fe₃O₄–Fe. Curve I is calculated by combination of the "best values" for the equilibrium constants of the Fe–C–O system and direct water gas constants as measured by Neumann and Köhler. Curve II is the experimental curve of Eastman and Evans.

composition between that of Curve I and that of Curve II, Fig. 2. Each run consisted in attaching the analytical apparatus to the exit of the reaction tube and determining the weight of water and volume of hydrogen in the exit gas passed during a given time. The composition of the entering gas was carefully checked at each saturator temperature to make certain that the steam-hydrogen mixture entering the reaction tube corresponded closely to that calculated from the temperature of the saturator. In the course of each experiment the following data were taken: temperature of catalyst, as measured by each of the thermocouples; flowmeter reading; temperature of the flowmeter, of the saturator bath, of the condenser surrounding the weighing tube, and of the gas in the pipet; the time of the run; the apparent volume of hydrogen collected; the height of final water level in the pipet above the water level at its exit; barometric pressure; and weight of water collected in the U-tube. The "U"-tube was always first carefully wiped with alcohol and then weighed to constant weight. From these data the exit and entering steam-hydrogen ratios could be calculated. One could also calculate the average composition of the iron-iron oxide mixture in the reaction tube.

When the accumulation of oxide on the iron sample decreased the rate of attainment of equilibrium too greatly, the temperature of the saturator was dropped sufficiently to cause the entering steam-hydrogen ratio to be smaller than that corresponding to Curve I, Fig. 2. Runs were then continued until most of the oxide was removed. Values of K_4 were determined in this way at intervals of 100° from 600° to 1000°, inclusive.

The two series of determinations of equilibria over $FeO-Fe_8O_4$ were carried out after oxidizing the Fe to FeO by long-continued steaming with a steam-hydrogen ratio a little too-small to produce Fe_8O_4 . This oxidation was continued until the exit steamhydrogen ratio was identical with the entering, indicating that any iron remaining in the sample was covered effectively by a layer of FeO and would therefore have no influence on measurements of the FeO-Fe₈O₄ equilibrium. Equilibrium values were obtained over FeO-Fe₈O₄ at 700 and 800°.

Results

In Table I are averaged the results of a number of preliminary experiments on the Fe-FeO system. The temperatures are those measured by the alumel-chromel couple at the center of the mass of iron-iron oxide.

			ΤA	BLE I				
PRELIMINARY I	Equilibrium	Data	FOR	REACTION	4 in	H_2O-H_2-Fe	-FeO (System
Temp., °C.				600	700	800	900	1000
Runs 40–329	K	$= H_2$	O/H_2	0.343	0.41	3 0.493	0.591	0.679
No. of runs avera	ged			6	40	38	19	11

In Tables II, III, IV, V and VI are given the data obtained in the final runs. In Cols. 3 and 4 are the inlet and exit steam-hydrogen ratios corresponding to the temperatures listed in Col. 2. In Col. 5 of each table are the equilibrium values corrected for convenience to 600, 700, 800, 900 and 1000°, respectively. The temperatures recorded in Col. 2 are the averages between the hottest point indicated by the outside couple and the coolest portion of the sample indicated by the inside couple.

TABLE II

Equilibriu	M DATA FOR RE	action 4 at 600°	
Temp., t°C.	Entering H2O/H2	Exit H_2O/H_2 = K_4 for $t^\circ C$.	K ₄ corrected to 600°C.
587	0.51	0.313	0.324
589	.51	.306	.315
590	.51	. 322	.331
625	. 51	.354	. 333
621	. 51	.350	.332
619	. 51	.350	.334
581	.21	.299	.315
622	.21	.361	.342
597	.21	.345	.348
599	.21	.341	.342
		Ave	erage .332
	EQUILIBRIUN Temp., <i>t</i> °C. 587 589 590 625 621 619 581 622 597 599	EQUILIBRIUM DATA FOR RH Temp., Entering 1°C. 1140/Hz 587 0.51 589 .51 590 .51 625 .51 621 .51 619 .51 581 .21 622 .21 597 .21 599 .21	EQUILIBRIUM DATA FOR REACTION 4 AT 600° Temp., Entering Exit $H_{2}O/H_{3}$ i°C. $H_{2}O/H_{3}$ = X_{4} for i°C. 587 0.51 0.313 589 .51 .306 590 .51 .322 625 .51 .354 621 .51 .350 581 .21 .299 622 .21 .361 597 .21 .345 599 .21 .341

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T 110 10 T T T	TABLE	III
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Equilibrium Data for Reaction 4 at 700°					
Run	Temp., t°C.	Entering H2O/H2	Exit H_2O/H_2 = K_4 for $t^{\circ}C$.	K₄ corrected to 700°	
345^{a}	710	0.21	0.437	0.424	
346^{a}	706.5	.21	. 433	.427	
356	706	. 51	.428	. 423	
357	707	. 51	.432	.426	
358	725	.51	.441	. 420	
359	715	. 51	.437	.424	
360	702.5	.21	.420	.418	
361	698	.21	.418	. 420	
362	699	.21	.416	.417	
			Ave	erage .422	

^a These values were obtained on Sample B. The other values were all obtained on Sample A. TABLE IV

	Equilibrium	DATA FOR RE	action 4 at 800°	
Run	Temp., I°C.	Entering H ₂ O/H ₂	Exit H_2O/H_2 = K_4 for $t^{\circ}C$.	K₄ corrected to 800°
332ª	807	0.20	0.519	0.513
333ª	805	.20	.478	.474
334^{a}	805	.20	. 500	.496
336ª	795	.20	.498	.503
337ª	817	.20	. 504	.490
365	816	.67	.511	.498
366	818.5	.67	.517	.502
367	817	.67	.514	.500
369	817	.20	.519	.502
370	818	.20	.515	.500
371	814	.20	.504	.509
			Av	rerage .499

^a These values were obtained on Sample B. The other values were all obtained on Sample A.

TABLE	V
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Equilibrium Data for Reaction 4 at 900°					
Run	Temp., /°C.	Entering H2O/H2	Exit H_2O/H_2 = K_4 for $t^{\circ}C$.	K _i corrected to 900°	
380	899	0.77	0.599	0.600	
381	900	.77	.595	.595	
382	886	.77	.576	.586	
383	917	.77	.623	.610	
390	902	.39	.595	. 593	
391	901	.39	.598	. 597	
392	899	.39	. 590	.591	
			Av	erage .594	

In Tables VII and VIII are recorded the few equilibrium values obtained at 700 and 800° for Reaction 6. The temperatures in these runs were measured with the alumel-chromel couples and were accordingly subject to the above-discussed uncertainties.

TABLE VI

Equilibrium Data for Reaction 4 at 1000 $^{\circ}$					
Run	Temp., t°C.	Entering H2O/H2	Exit H_2O/H_2 = K_4 for $t^{\circ}C$.	K ₄ corrected to 1000°	
384	979	0.91	0.646	0.662	
385	986	.91	.656	.667	
386	1020	.91	.69 2	.677	
387	1013	.40	.683	.673	
388	1014	.40	.683	.672	
389	1015	.40	.677	.665	
			Av	erage .669	

TABLE	VII

A	Approximate Equilibrium Data for Reaction 6 at 700°					
Run	Temp., t°C.	Entering H2O/H2	Exit H_2O/H_2 = K_4 for $t^{\circ}C$.	K4 corrected to 700°		
307	702	0.98	1.176	1.152		
308	702	.98	1.288	1.264		
309	697	.98	1.110	1.146		
319	709	1.35	1.266	1.158		
320	705	1.35	1.264	1.200		
321	700	1.35	1.166	1.166		
			Ave	erage 1.181		

TABLE VIII APPROXIMATE FOUL IPPLIEM DATA FOR REACTION 6 AT 800°

III I KOMIMITE EQUILIBRIUM DAIN FOR HUMEIION UM 600							
Run	Temp., t°C,	Entering H2O/H2	Exit H_2O/H_2 = K_4 for $t^{\circ}C$.	K ₄ corrected to 800°			
310	802.5	0.98	2.462	2.432			
314	800	2.64	2.390	2.390			
315	800	2.64	2.362	2.362			
322	802.5	1.35	2.363	2.333			
323	802.5	1.35	2.367	2.337			
325	800	2.63	2.350	2.350			
326	800	2.63	2.372	2.372			
			Av	erage 2.368			

326 800 2.63 2.372 2.372 Average 2.368 In a number of the preliminary experiments the space velocity was lowered. No change in the exit ratio of steam to hydrogen was thereby produced. This constancy in composition of the exit gas at different rates of flow is further evidence that true equilibrium was being attained. All

runs listed in Tables II to VI were made with an inlet hydrogen flow of about 23 cc. per minute.

The accuracy of the above equilibrium data depends upon the accuracy with which three measurements were made, the temperature of the ironiron oxide, the volume of hydrogen passing through the reaction tube during a certain time, and the weight of water vapor passing in the same period of time.

The volume of hydrogen and the weight of water obtained per unit time were measured with considerable accuracy. The measurement of the 250 cc. of hydrogen could not, it seems, involve an uncertainty of more than ± 0.5 cc. or 0.2%; this represents the summation of possible errors in reading the pressure, temperature and volume of gas in the pipet. Assuming an uncertainty of ± 1 mg. in the weight of water obtained in each run, the total maximum errors that it seems might have been entailed in individual experiments in the analysis of the exit gas would accordingly range from $\pm 1.9\%$ at 600° to $\pm 1.1\%$ at 1000° for the Fe-FeO system, and from $\pm 0.5\%$ at 800° to $\pm 0.7\%$ at 700° in the FeO-Fe₃O₄ system.

In the experiments in which Pt-Pt-Rh thermocouples were used, together with a Type K potentiometer, the uncertainty in the temperature corresponding to a particular equilibrium value should not exceed $\pm 6^{\circ}$ at 600 and 700°, $\pm 7^{\circ}$ at 800 and 900° and $\pm 9^{\circ}$ at 1000°. The temperature at any particular portion of the reaction tube is known more accurately than this. A temperature uncertainty of this amount, however, results from the impossibility of ascertaining precisely which portion of the metal oxide mass determines the measured equilibrium value in a given run. The temperature uncertainty in the two series of runs on the FeO-Fe₃O₄ system, and in the preliminary runs on the Fe-FeO system is harder to estimate. The consistency of the values in the latter runs and their general agreement with those of the final runs would indicate that the temperatures measured with the alumel-chromel couples are probably correct to within $\pm 10^{\circ}$.

When the above-mentioned errors are taken into consideration, the values of K_4 at 600, 700, 800, 900 and 1000° are 0.332, 0.422, 0.499, 0.594 and 0.669, respectively, each value being correct to ± 0.012 unit. The values of K_6 at 700 and 800° are approximately 1.18 and 2.37, respectively. The above errors are estimated maximum errors that might exist in any one experiment. The probable errors calculated from the above data are of course very much smaller.

It will be noted in the above data that there is no difference between the values obtained with iron oxide, Sample A, and those obtained with Sample B. This observation was also apparent in the runs summarized in Table I. This indicates that the small content of Al_2O_3 or ZrO_2 does not materially affect the free energy of the iron samples.

In the above experiments the oxygen content of the samples was varied over wide limits with no influence on the equilibrium constant obtained. At one point equilibrium values taken from the high steam-hydrogen side remained constant, while the percentage of oxygen in the iron sample increased steadily from about 0.4 to about 5%. The first two runs after freshly oxidizing or reducing the sample were omitted in the above averages in order to exclude any possible surface effect from the final equilibrium values.

Discussion of Results

Logarithms of the values of K_4 and K_6 observed by various workers are plotted against 1/T in Fig. 2. Curve I was calculated by combining the "best values" chosen by Eastman⁸ for the equilibria in Reactions 5 and 7 with the directly measured values of the water gas equilibrium of Reaction 1 as measured by Neumann and Köhler.³ Curve II is one drawn by Eastman and Evans as being representative of their own values for the equilibria of Reactions 4 and 6. It is to be observed that the results of Eastman and Evans, of Schreiner and Grimmes9 and of Wöhler and Günther¹⁰ agree fairly well with each other and with Curve II, but are about 40% higher than values lying along Curve I. The results of Van Groningen are said to be in agreement with these workers too, though his dissertation has not been available to us. The results of Wöhler and Prager,¹¹ Wöhler and Balz,¹² Chaudron,¹³ Deville¹⁴ and Preuner¹⁵ lie, for the most part, between the two curves. The values obtained by the last three workers agree more closely with Curve I than with Curve II, though they are somewhat erratic. Finally, it will be noted, the values obtained in the present experiments are in excellent agreement with Curve I and are consistent with the maximum values of K_4 fixed by the experiments of Krings and Kempkens¹⁶ and of Ferguson.¹⁷

Because of the importance of knowing the correct values for the equilibria of Reactions 4 and 6 and of gas-solid equilibria in general, it has seemed worth while to examine carefully the procedure and apparatus employed by the various above-mentioned workers with a view of ascertaining a possible cause of the large discrepancies that exist in the present equilibrium data.

The errors that may exist in the experimental determination of the equilibrium constant are of two kinds: (1) those resulting from incorrect observation of the temperature during a run, or faulty measurement of the partial pressure of water vapor or of hydrogen in the gaseous mixture at the end of an experiment; (2) those due to failure to obtain true equilibrium between the steam-hydrogen mixture and the solid phases indicated in Equations 4 and 6.

It seems very unlikely that the first type of error could be the entire cause of the above-mentioned discrepancies. In most cases the tempera-

- ¹¹ Wöhler and Prager, *ibid.*, 23, 199 (1917).
- ¹² Wöhler and Balz, *ibid.*, **27**, 406 (1921).
- ¹³ Chaudron, Compt. rend., 159, 237 (1914); Ann. chim. phys., 16, 221 (1921).
- ¹⁴ Deville, Compt. rend., 70, 1105, 1210 (1870); 71, 30 (1871).
- ¹⁵ Preuner, Z. physik. Chem., 47, 385 (1904).
- ¹⁶ Krings and Kempkens, Z. anorg. allgem. Chem., 183, 225 (1929).
- ¹⁷ Ferguson, J. Wash. Acad. Sci., 13, 275 (1923).

⁹ Schreiner and Grimmes, Z. anorg. Chem., 110, 311 (1920).

¹⁰ Wöhler and Günther, Z. Elektrochem., 29, 276 (1923).

ture of the sample was probably known with reasonable accuracy. The partial pressure of water could be in error only to the extent that there was any inaccuracy in measuring the temperature of the water in the thermostated bulb attached to the reaction tube in static experiments, or inaccuracy in determining the weight of water passing the iron samples per unit time in the experiments made by a dynamic method. No large uncertainties seem to have existed in either of these measurements. The principal error in measuring the partial pressure of hydrogen in static experiments arises from possible evolution of inert gas from the walls of the reaction tube of the metal sample during a run, or from possible leaking of air into the apparatus. Either occurrence would cause the total pressure and hence the apparent partial pressure of hydrogen to be too high; this would lower the apparent value of the equilibrium ratio of steam to hydrogen. Although this might explain some of the discrepancies between the various static experiments, it could not possibly account for the results of some of the static experiments being 40% higher than those obtained by the present dynamic method.

It has seemed to us that the cause of the discrepancy is of the second type. A careful consideration of the experiments of the various principal workers makes it appear probable that in the experiments performed by the static Deville method a false equilibrium has been measured—an equilibrium that differs from true equilibrium because of an abnormal consumption of hydrogen by a "surface oxide" present to a greater or less extent in all the static experiments carried out. Before discussing the work of the various authors it will be well to define what is meant by the "surface effect" here referred to.

Several instances are recorded in the literature in which the passage of a steam-hydrogen mixture over a freshly oxidized metal has resulted for a brief period in an exit steam-hydrogen ratio much higher than that corresponding to equilibrium with the massive metal-metal oxide phases. Conversely, passage of a steam-hydrogen mixture over freshly reduced metal surfaces has resulted in such an evolution of hydrogen that the effluent gas has for a short time possessed much less steam than corresponded to the normal equilibrium. Thus, Richardson, Vibrans and Bell noted the evolution of hydrogen in excess of equilibrium requirements when they passed steam over iron freshly reduced from iron oxide. Almquist and Black¹⁸ and Emmett and Brunauer¹⁹ have observed the definite formation of oxide on iron synthetic ammonia catalysts by ratios of steam to hydrogen much below equilibrium. Pease and Cook⁷ noted excessive hydrogen consumption in passing steam-hydrogen mixtures over

¹⁸ Almquist and Black, This Journal, 48, 2814 (1926).

¹⁹ Emmett and Brunauer, *ibid.*, **52**, **26**82 (1930).

freshly formed nickel oxide. The present authors¹ have called attention to similar phenomena in their study of the equilibria in Reactions 2 and 3. The effect is particularly observable in this latter system. In Fig. 3 is reproduced a diagram taken from the last mentioned paper. It clearly

570⁶ 140 2040 100 60 80 0 Time, min. Fig. 3.-Typical curves showing the effect of surface oxide on the CO₂-CO equilibrium value over a cobalt-cobalt oxide mixture. The three series of runs shown were taken immediately after oxidation of the cobalt surface to CoO. The entering CO_2 -CO ratios in the 570, 515 and 450° runs shown were 102, 194 and 324, respectively.

shows the manner in which such an effect can raise the ratio of CO_2/CO to a value much in excess of equilibrium if the surface of the oxide concerned is completely oxidized The oxidation of the surface metal atoms by a gaseous oxidizing agent or reduction of the surface atoms of a metal oxide by a reducing gas thus appears to proceed with a greater decrease in free energy than does the oxidation of the massive metal to oxide or reduction of the normal oxide to massive metal. There are at present no data defining precisely the thickness of the "surface" to which such abnormal phenomena are restricted. A11 quantitative evidence available is, however, consistent with this "surface effect," being limited for the most part to the few outer layers of atoms of the metal or oxide.

When the experiments of different workers are considered from the standpoint of the above-described surface effect, some interesting correlations appear.

Eastman and Evans, Schreiner and Grimmes, and Wöhler and Günther used almost identical apparatus and procedure, and obtained values that are in good

agreement with each other but are, in general, some 40% higher than those corresponding to Curve I in Fig. 2. The method used consisted in permitting water vapor from a thermostated water bulb to come in contact with samples of finely divided iron or iron oxide held in a quartz tube at some definite temperature. Equilibrium was said to have been reached when the total pressure indicated on an attached manometer



became constant. These workers approached equilibrium from the reduction side by then merely increasing the temperature 25 or 50° after having obtained equilibrium from the oxidation side, and permitting the initially low steam-hydrogen ratio to adjust itself to the higher temperature. The samples of iron used were completely reduced in hydrogen initially and introduced into the quartz reaction tube as metallic iron. Evacuation of the apparatus was then carried out with the iron sample heated to free the apparatus from inert gases and decrease the pressure to that of the water vapor from the thermostated water bulb. In some of the experiments in which it was desirable to use a sample of known oxygen content, the iron samples were partially oxidized by continued evacuation until they were converted partially to oxide. In none of the experiments of these three authors was any mention made of approaching equilibrium from the reduction side by adding a large excess of hydrogen.

From this brief description of the procedure followed by these workers it will be apparent that at the start of every experiment mentioned by them iron samples had already been subjected to considerable exposure to steam. Hence each particle of iron must have been oxidized to some depth before the beginning of an experiment. Furthermore, in these experiments the final volume of hydrogen at equilibrium was of the order of only 2 or 3 cc. (S. T. P.) according to calculations based upon the internal volume of the apparatus and the final pressure of hydrogen present. It would seem, accordingly, that conditions were in each instance favorable for the operation of the "surface effect" mentioned above. The small volume of hydrogen in contact with a completely oxidized iron oxide surface would, in accordance with all of the above-mentioned instances, be expected to be partially consumed, thus resulting in a steam-hydrogen ratio much in excess of the true equilibrium value. The method used in approaching equilibrium from the hydrogen side would merely shift this surface effect to another temperature but still leave conditions suitable for it to be operative.

In marked contrast to the above-mentioned work is that of Deville, of Chaudron and of Preuner. They, in general, used a static apparatus similar to that of the first group of workers. However, the procedure employed was such as to eliminate partially the above-mentioned surface effect in at least some of their experiments. Deville and Preuner actually added excess hydrogen to the apparatus and observed the equilibrium resulting from the reduction of an iron oxide sample. Chaudron, in changing from the system FeO-Fe₃O₄ to the system Fe-FeO added excess hydrogen to the apparatus and after reduction evacuated it with the sample of iron cold. Any runs made immediately after such reduction without intervening evacuation with the sample hot should likewise not have been subject to a marked surface effect. Insufficient description of the exact procedure used by these three workers is given, however, to permit one to conclude definitely whether all of the discrepancy between this second group of workers and the first group is due to the influence of the surface effect, or is due in part to errors of Type 1.

Several interesting observations may be made in regard to the work of Deville and of Preuner.

Deville originated the static apparatus subsequently used by most workers in metal-metal oxide-steam-hydrogen equilibrium measurements. He obtained values at only two temperatures in the range covered by our own experiments, namely 907 and 767°, the boiling points of zinc and cadmium. His results at these temperatures are shown in Fig. 2. At 767° it will be noted that the four equilibrium values obtained by Deville fall distinctly into two groups. The two upper values obtained from the oxidation and reduction sides with the water-bath temperature at 15 and 15.4°, respectively, are in perfect agreement with each other, but differ greatly from two lower values obtained with the water-bath supposedly at 0°. No temperature measurements were made of the water in the inner bulb in the experiments of Deville, the temperature being assumed to be that of the surrounding water-bath. It is interesting to note that the four values at 767° are brought into perfect agreement by assuming that the water in the bulb attached to the reaction tube was at 4° instead of 0° . Since at 4° water has its maximum density, it does not seem improbable that in his experiments the water bulb was located at the bottom of an unstirred icebath where the temperature might easily have been 4°. Similarly at 907° the three low values were obtained with the water bulb immersed in an icebath, whereas the two upper values were obtained with the temperature of the water-bath at 15°. In this case, however, an assumed temperature of about 3° would be necessary to bring the two groups of results into agreement. It seems highly probable that this error in the temperature of the water-bath in the runs at 767 and 907° may have caused the discrepancies in his own experiments at these temperatures.

Preuner, working with a Deville type apparatus at temperatures of 900, 1025 and 1150° , obtained equilibrium values for Reaction 4. He, like Deville, took precautions to approach the equilibrium from the reduction side by actually introducing an excess of hydrogen and observing the pressure decrease. In Fig. 2 the higher of the values obtained by Preuner at each temperature are those in which equilibrium was approached from the high steam-hydrogen side. Those obtained from the reduction side are on an average only 5 to 10% above Curve I.

One observation not previously mentioned in connection with Preuner's work seems important. Figure 4 is a reproduction of Figure 24 of Preuner's paper. In his article in connection with this figure an experiment is described in which he merely wished to demonstrate the slowness with which a small amount of iron oxide would react with hydrogen at 900° . Water vapor at a pressure of 46.6 mm. was permitted to react in his static apparatus with a sample of completely reduced iron until the pressure had built up to 115 mm. A sufficient amount of hydrogen was then admitted to build up the pressure in the apparatus to about 130 mm. The pressure

quickly dropped to an apparently constant value of about 125 mm. Preuner did not include this value in his equilibrium data, believing apparently that true equilibrium had not been attained. This is the only experiment in which after reaching equilibrium from the oxidation side he introduced hydrogen into the apparatus without further evacuation and resulting oxidation of the sample. As shown in Fig. 2, the equilibrium constant that we have computed from this one experiment agrees well with Curve I. It seems to be added evidence in favor of the validity of Curve I values and is apparently one static experiment in which the above-mentioned surface effect was entirely eliminated.

The values obtained by Wöhler and Prager and by Wöhler and Balz agree much more closely with Curve II, Fig. 2, than with Curve I. The values obtained from the oxidation side are susceptible to the above-mentioned surface effect since evacuation of the reaction vessel and hot sam-



Fig. 4.—Variation with time of the $P_{\rm H20}/P_{\rm H2}$ over a sample of completely reduced iron in a static experiment by Preuner. The experiment is unique among all recorded static experiments on the Fe-H-O system in that after permitting the initially low steam-hydrogen ratio to increase nearly to equilibrium, an excess of hydrogen was added without intervening evacuation. The final steady state pressure shown in this figure corresponds to a value for K_4 in agreement with those of Curve I, Fig. 2.

ple with its attendant oxidation of the surface of the iron was carried out before each run. However, equilibrium was approached from the reduction side by admitting an excess of hydrogen—"sometimes as much as 120 cc."—to an oxidized sample and permitting the pressure to decrease to a constant value. It is not clear why these latter equilibrium values should fail to agree more closely with Curve I.

Any surface effect occurring in a dynamic system is quickly eliminated

by the large amount of steam and hydrogen passing through the reaction tube. Consequently, the equilibrium measurements reported in the present paper should be free from this error. They constitute the first measurements made upon Reaction 4 by a flow system in which the point of equilibrium was determined by analysis of the effluent gas from the reaction tube. The excellent agreement of the experimental points among themselves and with Curve I attests to their probable correctness.

The experiments of Krings and Kempkens and of Ferguson were also made by a flow method. They differ from our own experiments, however, in that the value of the equilibrium constant is deduced from the variation in composition of the iron or iron oxide samples when treated for a number of hours with a given steam-hydrogen mixture. The results of Krings and Kempkens shown in Fig. 2 represent ratios of steam to hydrogen that sufficed to form an appreciable amount of oxide on the iron samples used. Their measurements fix the upper limits to the values of K_4 at the temperatures used. Similar experiments performed with slightly lower steamhydrogen ratios and with iron oxide as a starting material would fix the lower limit for K_4 . Ferguson's measurements unfortunately were made upon a sample of pure electrolytic iron that had been heated in hydrogen for many hours at 900 to 1000°, and that was therefore doubtless extremely inactive and slow to oxidize. At 750°, after six hours exposure of the samples of the iron to streaming mixtures of steam and hydrogen in which the ratios of steam to hydrogen were 0.476, 0.540, 0.568 and 0.595, respectively, the final samples analyzed 99.98, 99.9, 98.0 and 93.6% iron. These experiments of Ferguson definitely indicate that the value for the equilibrium constant for the conversion of Fe into FeO is not greater than 0.568 at 750°, assuming that the 2% oxygen content of this final sample is not present as solid solution. They cannot be considered, however, to contribute information as to the exact value of the equilibrium constant.

It is of course true that the surface effect mentioned and described above can be supposed to affect the equilibrium value only in case the duration of each experiment is insufficient to permit the true equilibrium value characteristic of the mass of iron-iron oxide to be attained. The slowness with which the establishment of true equilibrium throughout the mass of Fe-FeO takes place is evidenced by the fact that, according to the recent work of Krings and Kempkens, when a gas stream containing such a moisture content as to make its steam-hydrogen ratio slightly less than the equilibrium value for Reaction 4 above is passed over a sample of Fe₂O₃, complete reduction at 715° is not obtained for a great many hours. Thus, at the end of eight hundred hours, about 0.6% of oxygen still remained in such a sample.

Eastman and Evans observed that the equilibrium ratio of steam to hydrogen over an iron-iron oxide mixture at 775° decreased rapidly as the

oxygen content of the solid phase fell below 5%. They interpreted this as being an indication that as much as 5% oxygen would dissolve in a sample of iron. However, Krings and Kempkens have recently determined the solubility of oxygen in iron and found it to be of the order of 0.1% or less. Possibly the decrease in the steam-hydrogen ratios in the experiments of Eastman and Evans at these low oxygen contents was the result of enough iron being exposed in the initial sample to eliminate partially the surface error outlined above and to cause the values for the equilibrium steamhydrogen ratio to deviate more and more toward true equilibrium as the percentage of oxygen in the solid phase decreased.

The correlations mentioned in the above discussion are, we believe, significant and must somehow be explained. The tentative explanation here proposed, involving what has been termed "surface effect," seems consistent with most of the known experimental data. However, it cannot be accepted as final until conclusively demonstrated in a series of static experiments in which the exact technique necessary to produce the true equilibrium has been studied in detail. To this end additional experimental work is being undertaken at this Laboratory. An attempt will be made to prove the possibility of obtaining either false equilibrium values or true equilibrium values in a given static apparatus by merely changing one's procedure slightly. Further details as to the nature of this surface effect will accordingly be deferred to a later paper. At that time equilibrium data for steam–hydrogen over Fe–Fe₃O₄ and additional data for the FeO–Fe₃O₄ system will also be presented.

The Equilibrium Constant for the Water Gas Reaction

The value for the equilibrium constant for Reaction 1 can be calculated readily by combining equilibrium data for the Fe–C–O system of Equation 5 with the values of K_4 obtained in the present experiments. Such a calculation gives water gas constants agreeing with the directly measured values of Neumann and Köhler as closely as do the experimental values determined in the present paper agree with Curve I of Fig. 2. This calculation assumes the accuracy of the data for the Fe–C–O system. In Fig. 5 are shown the data for the Fe–C–O system. Curve I represents the "best values" as chosen by Eastman in his first paper.⁸ The recent experimental values of Schenck and his co-workers²⁰ are also included. Curve II, Fig. 5, represents Eastman's⁸ latest choice of the "best values" for this system.

In Table IX are summarized the values for the water gas equilibrium constants obtained in different ways. Columns 2 and 3 contain those obtained by the direct measurement of $Hahn^{21}$ and of Neumann and Köhler,

²⁰ Schenck, Stahl Eisen, 46, 665 (1926); Z. Elektrochem., 34, 399 (1928); Z. anorg. Chem., 167, 315 (1927); 167, 254 (1927); Schenck and Dingmann, *ibid.*, 166, 113 (1927); 171, 239 (1928).

²¹ Hahn, Z. physik. Chem., 44, 5131 (1903); 48, 735 (1904).

respectively. The values of the water gas equilibrium constant of Reaction 1 calculated by use of the steam-hydrogen and CO₂-CO equilibria with Co-CoO mixtures are shown in Col. 4. Those in Col. 5 were obtained by dividing the value of K_4 from our own Fe-H₂O-H₂-FeO equilibrium data, by K_5 as reported by Eastman. Column 6 contains the indirect



Fig. 5.—Variation with 1/T of log K, where $K = (CO_2)/(CO)$ in equilibrium with FeO-Fe. Fe₃O₄-FeO or Fe₂O₄-Fe.

calculation of Eastman and Robinson based upon their data for Reactions 8 This is the one remaining indirect calculation giving values for the and 9. water gas equilibrium constant that disagree with the directly measured values. The values in Cols. 3, 4 and 5 agree excellently with each other and we believe correspond to the true values of the water gas equilibrium constant over the range of temperature covered.

		TABLE	IX						
WATER GAS EQUILIBRIUM CONSTANTS									
Temp., t°C.	Direct n Hahn	Direct measurements Neumann and Hahn Köhler		Calculated from Fe–FeO system	Sn-SnO2 system				
350		0.041							
400		.080							
450		.140	0.137						
500		.200	.207						
550		.290	.297						
600		.410		0.380					
650		. 50			0.707				
700	0.610	.63		.624	0.882				
750	.755	.78			1.078				
800	.906	. 93		.917	1.294				
850	1.071	1.09							
900	1.240	1.29		1.306					
950	1.420	1.44							
1000	1.606	1.66		1.693					

Summary

1. The value of the equilibrium constant $K_4 = P_{\rm H_2O}/P_{\rm H_3}$ for the reaction FeO + H₂ = Fe + H₂O has been determined by a flow method at 600, 700, 800, 900 and 1000° to be 0.332, 0.422, 0.499, 0.594 and 0.669, respectively.

2. The value of the equilibrium constant $K_6 = P_{\rm H_3O}/P_{\rm H_3}$ for the reaction Fe₃O₄ + H₂ = 3FeO + H₂O has been determined by a flow method at 700 and 800° to be 1.18 and 2.37, respectively.

3. Combination of these values with the "best values" of Eastman for the Fe-C-O system gives values for the water gas equilibrium in good agreement with the water gas values determined directly by Neumann and Köhler.

4. The so-called "surface effect" is presented as a probable reason for the discrepancies between the water gas values as obtained indirectly by other workers and the directly determined values.

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[CONTRIBUTION FROM THE UNIVERSITY OF NORTH CAROLINA]

A STUDY OF THE QUANTITATIVE PRECIPITATION OF CALCIUM OXALATE IN THE PRESENCE OF THE ARSENATE ION

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A study of the quantitative precipitation of calcium oxalate in the presence of the phosphate ion by Dobbins and Mebane¹ showed that the calcium ion could be quantitatively precipitated from a solution containing an excess of phosphate ions. Since the usual method of estimating calcium in calcium arsenate involves the same difficulties met in the phosphate analysis, a similar study was made of the quantitative precipitation of calcium in the presence of the arsenate ion. As the phosphate ion and the arsenate ion are chemically similar, the same method of study was used.

The study was based on the assumption that the so-called tertiary calcium arsenate, which forms on the addition of ammonium hydroxide to the solution, having a much greater solubility product than calcium oxalate would go into solution and thus the calcium oxalate form. Consequently, if the solution be allowed to stand long enough for this metathesis to be complete, it should be possible to precipitate calcium oxalate in the presence of the arsenate ion. In order to determine the most favorable conditions under which to carry out the precipitation, several series of analyses were made to determine the time required for complete

¹ Dobbins and Mebane, THIS JOURNAL, 52, 1469 (1930).