All of the experimental results for the methyl halides can be explained by assuming that the primary reaction is $CH_3X + H = CH_3 + HX$.

The reactions with the ethyl halides were too complicated to warrant the proposal of a definite mechanism.

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Gaseous Thermal Diffusion—The Principal Cause of Discrepancies among Equilibrium Measurements on the Systems Fe_3O_4–H_2–Fe–H_2O, Fe_3O_4–H_2–FeO–H_2O and FeO–H_2–Fe–H_2O

BY P. H. EMMETT AND J. F. SHULTZ

When Sainte-Claire Deville[1] in 1870 first determined the ratio of water vapor to hydrogen in equilibrium with Fe–FeO, he pioneered the investigation of a system that up to the present has yielded puzzling and widely varying results. Although the apparatus devised by him and illustrated in principle in Fig. 1B has been used by practically all of the later workers, the experimental equilibrium water vapor–hydrogen ratios for a given temperature cover a considerable range of values, some being as much as 40% higher than others. Recently,[2] using a dynamic rather than a static type apparatus, we obtained experimental results for the equilibrium constants K_1 and K_2 of the reactions

$$\mathrm{FeO} + \mathrm{H_2} = \mathrm{Fe} + \mathrm{H_2O} \qquad K_1 = \mathrm{H_2O/H_2} \tag{1}$$

and

$$\mathrm{Fe_3O_4} + \mathrm{H_2} = 3\mathrm{FeO} + \mathrm{H_2O} \qquad K_2 = \mathrm{H_2O/H} \tag{2}$$

that were consistent among themselves and agreed with the values calculated indirectly from the Fe–C–O system[3] and the equilibrium constant[4] for the reaction

$$\mathrm{CO_2} + \mathrm{H_2} = \mathrm{CO} + \mathrm{H_2O} \qquad K_3 = (\mathrm{H_2O})(\mathrm{CO})/(\mathrm{CO_2})(\mathrm{H_2}) \tag{3}$$

Although there seemed to be little doubt that the flow experiments were correct, no entirely satisfactory explanation could be given for the 40% discrepancy between them and some of the carefully performed static experiments. Inasmuch as the source of error causing this gross uncertainty might be affecting the equilibrium constants not only for the Fe–H–O system but also for other equally important heterogeneous systems, a careful study was undertaken of the static types of apparatus and procedure used in previous experimental studies of the Fe–H–O system.

(1) Sainte-Claire Deville, *Compt. rend.*, **70**, 1105, 1201 (1870); **71**, 30 (1871).

(2) Emmett and Shultz, THIS JOURNAL, **52**, 4268 (1930).

(3) E. D. Eastman, Bur. of Mines Circular 6125 (1929).

(4) Equation 38 from paper of Bryant, *Ind. Eng. Chem.*, **23**, 1019 (1931).

The results of a part of this study have been presented briefly in a recent communication;[5] they seem to show that our previously reported values for K_1 and K_2 obtained by the use of a flow system are essentially correct and that the above-mentioned 40% discrepancy is to be attributed principally to an error caused by thermal diffusion in practically all previous static type experiments on equilibrium in the Fe–H–O system. In the course of the work it was found possible so to modify the usual static Deville type apparatus as to be able to perform static equilibrium experiments that consistently yielded correct values for K_1 and K_2. Accordingly, this apparatus was used in obtaining values of K_4 for the reaction.

$$^3/_4Fe_3O_4 + H_2 = {}^3/_4Fe + H_2O \qquad K_4 = H_2O/H_2$$

The primary purposes of the present paper are, therefore, to present the results of these static equilibrium experiments, to discuss in some detail the thermal diffusion measurements that have been made, and to show how the thermal diffusion factor operates in the usual static type apparatus.

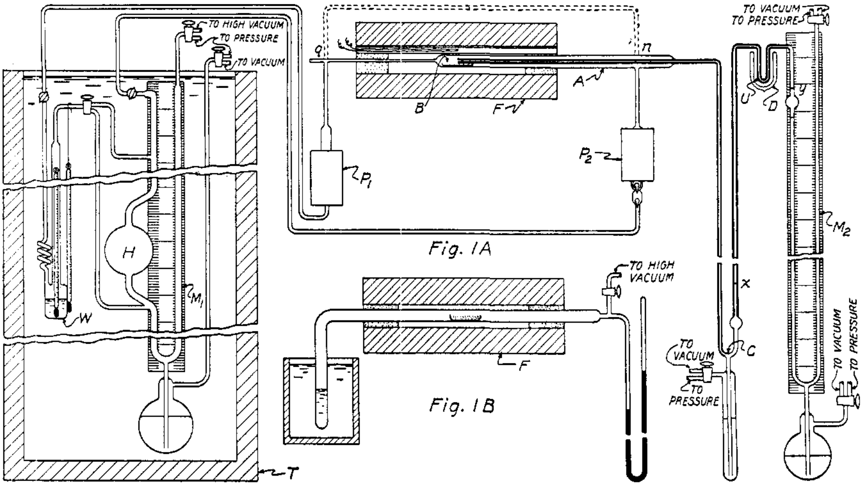

Fig. 1A

Fig. 1B

Fig. 1.

Equilibrium Constants for the Fe–H–O System

The final form of the static apparatus used in the present experiments and shown in Figure 1A was a modified Deville type. It consisted essentially of a 2-cm. quartz tube, A, containing a sample of the metal–metal oxide in boat B packed into a well insulated furnace F, and connected by quartz to Pyrex seals to Pyrex tubing leading to a water bulb W, and a 14-mm. mercury manometer M contained in the thermostat T. The latter was equipped with a glass front and was constructed according to specifications previously described.[6] P_1 and P_2 were all-glass circulating pumps by which the water vapor–hydrogen mixture in the reacting system could be circulated in either a clockwise or counter-clockwise direction[7] over the boat B. The actual rate of gas circulation

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(5) Emmett and Shultz, THIS JOURNAL, **54**, 3780 (1932).

(6) Tremearne, *Ind. Eng. Chem., Anal. Ed.*, **2**, 426 (1930).

(7) Porter, Lind and Bardwell, *Ind. Eng. Chem.*, **18**, 1086 (1926).

effected by them in the present low pressure experiments was not accurately measured; at one atmosphere pressure, however, the pumps were capable of circulating 50 to 75 cc. of gas per minute against a pressure head of 2–3 mm. of water. The apparatus could be evacuated through the manometer M by a high vacuum pump. The exit pressure on the manometer was measured regularly by an attached McLeod gage not shown in the drawing. By the use of a telescope the pressure differences between the two arms of the manometer M were read on a carefully calibrated brass scale placed immediately behind the manometer arms. Bulb H of about 500 cc. capacity permitted the volume of the gas mixture being circulated over the solid phases to be changed to suit the particular experiment being carried out.

The first form of our static apparatus on which a majority of the experiments summarized below were carried out is not shown in the diagram but it differed from the final form in only a few minor details. Thus, the furnace was arranged vertically instead of horizontally, the oxide–metal charge being supported by a thin platinum gauze placed on the constriction between the 15-mm. quartz reaction tube and the 3-mm. quartz tubing projecting out of the lower end of the furnace. Furthermore, in the original apparatus the water bulb but not the mercury manometer was thermostated.

In the first apparatus we determined the temperature of the charge by two calibrated Pt–Rh thermocouples in conjunction with a type K Leeds and Northrup potentiometer. One of these was placed in a thin quartz shield in the center of the charge, the other directly opposite it but on the outside of the quartz reaction vessel. Since these experiments demonstrated the absence of an appreciable cross temperature gradient in the furnace, the inner thermocouple was omitted in the final set-up shown in Fig. 1A. Care was taken in this latter apparatus, however, to place the boat B directly opposite the thermocouple used.

Each tank of hydrogen used was analyzed for nitrogen. The amounts of gas consumed in an experiment were so regulated that the 0.1 to 0.2% nitrogen present in some of the tanks of hydrogen caused no measurable error in the final readings.

The oxide samples used were as follows.

Sample A was Fe_2O_3 No. 6, described in a previous paper.[8] It contained 0.12% of sodium hydroxide as impurity. It was reduced *in situ* to Fe_3O_4.

Sample B was a doubly promoted fused Fe_3O_4 used in preparing Fe synthetic ammonia catalysts.[9] It contained 0.35% Al_2O_3 and 0.08% K_2O.

Sample C was Fe_2O_3 No. 4, previously described[8] and contained 1.55% Al_2O_3. It was reduced *in situ* to Fe_3O_4.

Sample D was a pure Fe_2O_3 sample reduced to Fe_3O_4 at 400° by a 0.2:1 water vapor–hydrogen mixture.

Samples E and F were pure Fe_2O_3 samples reduced to Fe_3O_4 at 700° in a 1.8:1 water vapor–hydrogen mixture.

Sample G was pure Fe_2O_3 reduced at 700° by a 0.425:1 water vapor–hydrogen mixture.

The Fe_2O_3 used in samples B, E, F and G was prepared by drying ferric hydroxide precipitated from ferric nitrate solution by ammonium hydroxide.

The apparatus used in the reduction of samples D, E, F and G consisted of a 5-cm. quartz tube packed into a furnace and connected on the one end by a ground joint to a source of water vapor and hydrogen. Water vapor from a steam boiler, together with pure hydrogen from a flow meter, was passed through heated connecting tubes to two thermostated bead towers in series and then to the quartz reaction tube. The thermostat varied only ±0.1° during the preparation of a sample.

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[8] Emmett and Miss Love, *J. Phys. Chem.*, **34**, 41 (1930).

[9] Larson and Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925).

In carrying out the static experiments, two or three preliminary oxidation or reduction runs were made when necessary to ensure the presence of both solid phases. Any possible surface effects that might result from an insufficient amount of one phase were thereby avoided.

The results of the present static equilibrium experiments are shown in Tables I, II and III; they were obtained by circulating water vapor–

TABLE I

EQUILIBRIUM DATA FOR THE SYSTEM Fe_3O_4–H_2–Fe–H_2O AS MEASURED IN A STATIC TYPE APPARATUS

Run	Sample	Temp., °C.	Initial H_2O/H_2	P_{total}, mm.	P_{H_2O}, mm.	P_{H_2}, mm.	$K_4 = P_{H_2O}/P_{H_2}$	K_4 corrected to 400, 500 and 550, resp.
43	A	401	0.111	136.4	13.38	123.0	0.108	0.107
92	B	408	.237	120.6	12.51	108.1	.115	.105
167	B	399	∞	128.0	13.05	115.0	.114	.115
168	B	401	.097	138.5	13.05	125.5	.104	.103
169	B	399	.212	129.2	13.05	116.2	.112	.113
202	C	401.5	.090	155.7	14.22	141.5	.100	.098
							Average for 400°	.107
44	A	502.5	.143	76.6	13.38	63.2	.211	.209
45	A	499	.161	77.4	13.47	63.9	.210	.210
47	A	502.5	∞	25.6	4.58	21.0	.218	.215
48	A	503.5	∞	24.8	4.58	20.2	.226	.222
96	B	501.5	∞	71.2	12.51	58.7	.213	.211
100	B	500.5	∞	74.6	13.17	61.4	.214	.214
101	B	502	.446	74.0	13.21	60.8	.217	.215
104b	B	500.5	.220	75.4	13.47	61.9	.217	.216
105	B	499.5	.207	76.0	13.47	62.5	.215	.215
170	B	502	∞	74.7	13.17	61.5	.214	.212
176	B	500.5	∞	75.2	13.25	62.0	.214	.213
179	B	500.5	.325	75.9	13.59	62.3	.218	.217
181	B	500	∞	75.9	13.68	62.2	.220	.220
182	B	502	.182	77.5	13.86	63.6	.218	.216
204	C	499.5	.133	83.7	14.26	69.4	.206	.207
256a	D	500	.255	100.0	17.50	82.5	.212	.212
258b	D	504	.229	97.2	17.50	79.7	.219	.214
							Average for 500°	.214
80	B	550	∞	54.8	12.19	42.6	.286	.286
81	B	549.5	∞	54.4	12.19	42.2	.289	.290
87	B	549.5	∞	54.8	12.23	42.6	.287	.288
88	B	550	∞	55.4	12.27	43.1	.284	.284
89	B	551.5	.210	55.8	12.27	43.5	.282	.280
172	B	551.5	∞	60.3	13.17	47.1	.279	.277
173	B	553	.350	59.5	13.21	46.3	.286	.282
174	B	550	.397	60.4	13.25	47.2	.281	.281
175	B	550	∞	60.5	13.25	47.3	.280	.280
178	B	550	∞	61.2	13.47	47.7	.282	.282
180	B	550.5	∞	62.1	13.68	48.4	.283	.282
205	C	550	.216	65.7	14.31	51.4	.279	.279
							Average for 550°	.283

TABLE II

EQUILIBRIUM DATA FOR THE SYSTEM Fe_3O_4–H_2–FeO–H_2O AS MEASURED IN A STATIC TYPE APPARATUS: SAMPLE E; P_{H_2O}, 17.50 MM.

Run	Temp., °C.	Initial H_2O/H_2	P_{total}, mm.	P_{H_2}, mm.	$K_4 = P_{H_2O}/P_{H_2}$	K_4 corrected to 600, 700, 800°, resp.
279b	599	0.393	58.4	40.9	0.428	0.432
280	599	.660	55.0	37.5	.467	.471
281	598.5	.421	56.0	38.5	.454	.459
282	601	.507	54.2	36.7	.477	.473
283	599	.454	55.0	37.5	.467	.471
					Average for 600°	.461
268	701	.479	32.2	14.7	1.190	1.18
269a	699.5	.714	32.4	14.9	1.175	1.18
269b	700.0	1.224	32.4	14.9	1.175	1.18
270	699.5	0.854	32.6	15.1	1.158	1.16
271a	699.5	1.400	32.4	14.9	1.175	1.18
272	700.5	0.686	33.0	15.5	1.128	1.12
273	700.5	1.549	32.4	14.9	1.175	1.17
274	700.5	0.936	33.0	15.5	1.128	1.12
					Average for 700°	1.16
275	802.5	1.356	24.8	7.3	2.396	2.35
276	802.5	1.011	24.8	7.3	2.396	2.35
277	801.0	3.181	24.8	7.3	2.396	2.37
278	802.5	7.000	24.8	7.3	2.396	2.35
					Average for 800°	2.35

TABLE III

SUMMARY OF EQUILIBRIUM DATA FOR THE SYSTEM FeO–H_2–Fe–H_2O MEASURED IN A STATIC TYPE APPARATUS

Temp., °C.	$K_1 = P_{H_2O}/P_{H_2}$ By oxidation	 By reduction	 Average of static runs	 By flow expts.[a]
600	0.334 (5)	0.334 (1)	0.334 (6)	0.332
700	.420 (27)	.418 (14)	.419 (41)	.422
800	.508 (6)	.496 (8)	.501 (14)	.499
900	.623 (4)	.576 (3)	.603 (7)	.594
1000	.682 (2)	.675 (3)	.678 (5)	.669

[a] See Emmett and Shultz, THIS JOURNAL, 52, 4268 (1930). Numbers in parentheses show number of runs averaged.

hydrogen mixtures in a counter-clockwise direction over an Fe–FeO, FeO–Fe_3O_4 or Fe–Fe_3O_4 sample through bulb W and back again to the reaction tube until over three successive fifteen-minute periods no pressure change occurred. Since comparatively few equilibrium data for the Fe-Fe_3O_4 system are available in the literature, Table I gives all of the completed experiments made on reaction 4. The only counter-clockwise runs omitted are those in which equilibrium was approached so slowly that a steady state could not be obtained during a single work day and those that were irregular because of temporary failure of the circulating pumps. A plot of the total pressure as a function of time yielded curves that left no uncertainty as to whether or not the circulating pumps had been functioning properly throughout a run. The table is practically self-explanatory. The pressures recorded in column 5 are the final ones read on manometer M, when a steady state had been reached. The vapor pressures of water are those given in the "International Critical Tables" for the observed temperatures which were read to 0.05° on a calibrated thermometer included in the reaction system and projecting into the water in bulb W. The hydrogen pressures of column 6 are the values of column 4 minus those of column 5. The average values of K_4 are 0.107, 0.214 and 0.283 at 400, 500 and 550°, respectively.

In Table II are shown all of the counter-clockwise experiments performed in the final static apparatus on the system Fe_3O_4–H_2–FeO–H_2O. These show constant reproducible H_2O/H_2 equilibrium ratios averaging 0.461, 1.16 and 2.35 at 600, 700 and 800°. They were obtained over sample E which was prepared by reducing Fe_2O_3 to Fe_3O_4 at 700° with a stream of 1.8:1 water vapor–hydrogen.

The runs on the Fe–FeO system were too numerous to be presented in detail. A summary of them is presented in Table III.

The averages of the values of K_2 and K_1 obtained in the present static experiments differ by less than 2% from those of our former flow experiments.[2] Thus, in the FeO–Fe_3O_4 system the flow and static results are, respectively, 1.18 and 1.16 at 700°, and 2.37 and 2.35 for 800°. The values for flow and static experiments in the Fe–FeO system are shown in columns 7 and 8, Table III.

The experimental errors involved in the static runs are small. Possible error in obtaining the absolute temperatures of the samples (±2°), in making each pressure reading (±0.2 mm.), and in reading the temperature of the water-bath (±0.05°), would mean maximum uncertainties of about ±0.004 in the individual values of K_4, ±0.003 for 600°, to 0.012 for 1000° in the values of K_1, and ±0.014, ±0.04 and ±0.13 in the values of K_2 at 600, 700 and 800°.

The experimental results presented in Tables I to III are for those runs in which counter-clockwise circulation was employed, the water vapor–hydrogen mixture passing quickly from the metal oxide sample through the small diameter quartz tube to water bulb W. It was invariably found, however, that if circulation in the opposite direction was employed so that the water vapor–hydrogen mixture passed from the metal–oxide sample along the *large diameter* quartz tube to the cool part of the apparatus, values of K_1, K_2 and K_4 were much higher than those shown and rather erratic. Thus at 700° the value of K_1 with clockwise circulation varied from 0.46 to 0.58. In fact many of the values obtained by clockwise circulating agreed well with those shown along curve 2, Fig. 2, being 30 to 40% higher than our own flow results or counter-clockwise static experiments. The results of these clockwise circulation experiments were at first baffling; however, they furnished a clue that led eventually to the phenomenon of thermal diffusion as the explanation not only of our own observations but of the many erroneously high values of K_1 and K_2 reported by various workers.

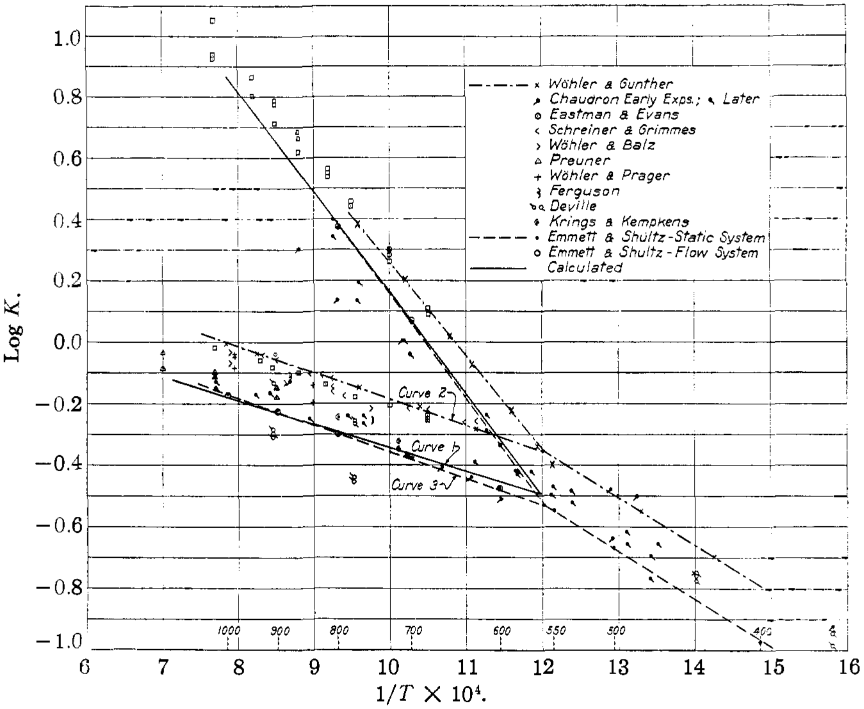

Fig. 2.

Thermal Diffusion as a Factor in Equilibrium Measurements on the Fe–H–O System.—According to the theory of thermal diffusion worked out by Chapman[10] and by Enskog[11] and verified for certain gas mixtures by a number of workers,[12] if two gases of different molecular weights such as water vapor and hydrogen are placed in a tube one end of which is heated while the other remains cold, the ratio of the heavy gas to the light gas rapidly becomes and remains larger in the cold end of the tube than in the hot end. It seemed probable that in accordance with this theory the water vapor–hydrogen ratio in the "cold end" of a Deville type apparatus would be higher than in the "hot end." Furthermore, calculations made by equations developed by Chapman showed that assuming the molecules of

(10) Chapman, *Proc. Roy. Soc.* (London), **93**, 1 (1916); *Phil. Trans. Roy. Soc.*, **217**, 115 (1917); *Phil. Mag.*, **48**, 602 (1924).

(11) D. Enskog, *Physik. Z.*, **12**, 538 (1911); *Ann. Physik*, **38**, 742 (1912).

(12) For a complete bibliography on thermal diffusion see Ibbs and Grew, *Proc. Phys. Soc.*, **43**, 142 (1931).

water vapor and of hydrogen to be elastic spherical shells of diameters[13] 2.29 and 1.36 Å., respectively, the possible thermal separation that could occur is about twice as great as the largest observed discrepancies.

In order to prove that this thermal diffusion factor actually does account for the large observed discrepancies in Fe–H–O equilibrium data the apparatus shown in Fig. 1A was so modified as to permit an actual determination of the water vapor–hydrogen ratios to be made simultaneously in the hot and cold ends of tube A. The Pyrex tube between pump P and furnace F was sealed off at q; then a connecting line from q to n was inserted as shown by the dotted line in Fig. 1A. This permitted the water vapor–hydrogen mixture to be circulated across the cold end of A. By diffusion this gas mixture could penetrate the hot portion of tube A and reach the metal–oxide sample. Finally a 1-mm. quartz capillary tube was fastened by a quartz–Pyrex seal to a 0.2-mm. capillary tube and sealed into tube A as shown in Fig. 1A. This capillary was then connected through a mercury cut-off C to a gas buret and another manometer M_2 as shown.

By lowering the mercury in C a sample of water vapor–hydrogen from the "hot end" of the quartz reaction tube could be collected in the buret between the marks x and y, at a pressure p_1. By circulating the gas sample back and forth through the capillary U surrounded by liquid air in the Dewar flask D the water vapor could be frozen out, leaving hydrogen at pressure p_2'. The water vapor–hydrogen ratio is equal to $(p_1-p_2)/p_2$, where p_2 is the value of the hydrogen pressure, corrected for the slight pressure change caused by cooling the gas in "U." The volume of the capillary immersed in liquid air was ordinarily only a few hundredths of a cc. out of a total buret volume of about 4 cc., so the correction to p_2' was small. In making an actual analysis it was customary first to remove and pump out the small amount of gas from the sampling capillary down to the gas buret about five minutes before the regular analysis was taken. This increased somewhat the accuracy of the analytical determinations by making the gas sample taken for analysis more nearly the composition of the gas mixture actually present at the moment of sampling in the hot part of the reaction tube.

A comparison of the composition of the water vapor–hydrogen mixture in the hot and the cold ends of the reaction tube is shown in Table IV. Columns 3 and 4 give the water vapor–hydrogen ratios calculated by reading the total pressure in A on manometer C and noting the temperature of the water in bulb W; the analytical results are shown in columns 5, 6 and 7. Although the observational errors were necessarily rather large, this method of analysis proved quite satisfactory. Assuming an accuracy of ±0.2 mm. in each pressure reading on the manometer M_2 used in the analytical determinations, there might be a maximum error in any one

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[13] Jeans, "Dynamic Theory of Gases," p. 327.

water vapor–hydrogen analysis from 3 to 5%, depending upon the partial pressures of hydrogen and water vapor in the sample chosen.

TABLE IV

THERMAL DIFFUSION EXPERIMENTS USING Fe–FeO OR Fe_3O_4–FeO SAMPLES

Run	Temp., °C.	By manometer Initial H_2O/H_2	By manometer Final H_2O/H_2	Initial pressure $P_{H_2O} + P_{H_2}$, mm.	By analysis Final pressure P_{H_2} (corrected), mm.	P_{H_2O}/P_{H_2}
		Fe–FeO System (Sample F)				
284a	700	0.207	0.548	46.0	32.7	0.40
284b	702.5	.559	.548	53.8	38.0	.42
286a	700	.353	.623	97.0	71.2	.36
286b	699	.660	.646	54.4	37.4	.45
288a	800	.269	.708	48.6	32.7	.49
289	801	.744	.708	48.0	32.7	.47
290a	900	.299	.821	49.8	31.5	.58
290b	902	.854	.821	43.0	28.0	.54
290c	899	.854	.821	45.6	29.6	.54
291a	1001	.304	.966	46.0	26.8	.72
291b	1001	1.011	.966	46.2	27.9	.65
291c	1001	1.035	.966	44.0	26.9	.64
		FeO–Fe_3O_4 System (Sample G)				
297a	700	0.193	1.495	27.4	12.1	1.26
297b	700.5	1.521	1.495	26.4	12.1	1.18
297c	699.5	1.521	1.495	35.6	16.5	1.15
298a	800	0.402	3.181	31.6	9.5	2.33
298b	800.5	3.301	3.181	31.6	9.4	2.36
298c	800	3.430	3.181	32.0	9.6	2.33
298d	800	3.430	3.181	30.4	9.0	2.38

TABLE V

SUMMARY OF THERMAL DIFFUSION RESULTS ON Fe–H–O SYSTEM

System	Temp., °C.	Water–hydrogen ratio In "cold end" by manometer	Best values[a] of previous static expts.	In "hot end" by analysis	In flow experiments[b]
Fe–FeO	700	0.57	0.584	0.41	0.422
Fe–FeO	800	.71	.706	.48	.499
Fe–FeO	900	.82	.822	.55	.594
Fe–FeO	1000	.97	.937	.67	.669
FeO–Fe_3O_4	700	1.50	1.45	1.20	1.181
FeO–Fe_3O_4	800	3.18	2.98	2.35	2.372

[a] See Eastman and Evans, THIS JOURNAL, **46**, 888 (1924). [b] See Emmett and Shultz, *ibid.*, **52**, 4268 (1930).

The summary of various experimental results given in Table V can in our opinion leave no reasonable doubt that owing to the action of thermal diffusion the "best values" for K_1 and K_2 obtained by previous static experiments are about 40% high and that our own flow and static experiments are essentially correct. The water vapor–hydrogen ratios given in

TABLE VI

THERMAL SEPARATION OF WATER VAPOR–HYDROGEN MIXTURES AT 400–500°

Temp., °C.	"Cold end" H_2O/H_2	"Hot end" H_2O/H_2	Percentage water vapor In "cold end"	In "hot end"	Difference
499	0.275	0.180	21.6	15.3	6.3
506	.284	.201	22.1	16.7	5.4
502	.285	.215	22.2	17.7	4.5
405	.297	.225	23.0	18.4	4.6
404	.297	.215	23.0	17.7	5.3

column 3 were obtained by an apparatus and procedure identical in all important respects to that used by Eastman and Evans,[14] Schreiner and Grimmes,[15] Wöhler and Günther[16] and van Groningen,[17] in that a water vapor–hydrogen mixture was permitted to diffuse from the cold end of a large diameter tube to the "hot end" of the same tube and there equilibrate with an Fe–FeO or Fe_3O_4–FeO sample. As in their experiments, the water vapor–hydrogen ratio was taken as the ratio of the P_{H_2O} in the thermostated water bulb W to the difference between the total pressure in the apparatus and the P_{H_2O}. These readings of column 3 agree excellently with the "best values" of the above-mentioned previous static experiments given in column 4 and yet are 40% too high. The composition of the water vapor–hydrogen mixture actually present in the hot end of the reaction tube is given in column 5 by the analysis of samples taken directly from the hot end of the apparatus. Our confidence in the essential correctness of the values of K_1 and K_2 obtained by our static and flow experiments rests upon their agreement with each other, with the results of the direct analysis of column 5, Table V, and with the values calculated from the Fe–C–O system with the help of K_3.

The diffusion data also make clear why our static experiments performed in the apparatus shown in Fig. 1A were correct only when the water vapor–hydrogen mixture was circulated in a counter-clockwise direction. When a steady state is attained in a given experiment at say 700° the gas composition in the "hot end" of the reaction tube will be about 0.41 to 0.42, as shown in column 5, regardless of the direction of circulation. Furthermore, the "cold end" water vapor–hydrogen ratio will be much higher, approaching 0.57 or 0.58, if the gas mixing caused by the pump circulation is not too great. It now becomes evident that circulating the gaseous mixture in a counter-clockwise direction to a steady state and taking the usual manometer and temperature readings is in reality merely a means of analyzing the "hot end" H_2O–H_2 mixture, for the linear velocity of the gas passing along the 3-mm. quartz tube toward q is sufficiently high

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

(15) Schreiner and Grimmes, *Z. anorg. allgem. Chem.*, **110**, 311 (1920).

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

(17) Van Groningen, Dissertation, Delft, 1921. Our conclusions relative to Van Groningen's results are based on statements of Wöhler and Günther as the original dissertation was not available to us.

to prevent a change in composition of the gas mixture by thermal diffusion at the 700° to room temperature transition point. The observed water vapor–hydrogen ratio, therefore, will be the one existing in the hot end of A in equilibrium with the Fe–FeO sample. Clockwise circulation to a steady state, on the other hand, merely analyzes the "cold end" steam–hydrogen mixture giving an observed K_1 value of about 0.57 or 0.58, which is approximately 40% higher than that existing in the "hot end" of the apparatus. It thus becomes clear why our own clockwise results gave high water vapor–hydrogen ratios whereas our counter-clockwise experiments gave correct values of K_1, K_2 and K_4.

It may be well to point out that if clockwise rather than counter-clockwise gas circulation is employed, our apparatus becomes essentially the same as that used by Wöhler and Balz,[18] Wöhler and Präeger[19] and Chaudron,[20] in that a slow circulation of gas from the "hot end" to the "cold end" of a *large* diameter reaction tube occurs. In agreement with our own clockwise experiments, they obtained erratic values that were from 5 to 40% too high. It seems probable that thermal diffusion also caused the principal errors in their work.

Although the diffusion experiments of Tables IV and V seem to substantiate and prove the correctness of our data on the Fe–FeO and FeO–Fe_3O_4 systems it remained to prove that at 400 and 500° thermal diffusion could account for the rather large differences between our own results on the Fe–Fe_3O_4 system shown on curve 3, Fig. 2, and those of Wöhler and Günther shown on curve 2. However, diffusion experiments on the Fe–Fe_3O_4 system similar to those obtained above for the FeO–Fe and FeO–Fe_3O_4 systems proved impractical because of the slowness with which equilibrium was attained at temperatures of 400 to 500° in the Fe–Fe_3O_4 system. Accordingly, diffusion experiments were performed without a metal–oxide sample in the quartz reaction tube. The apparatus was connected as in our previous diffusion experiments. Sufficient hydrogen was admitted to form "cold end" water vapor–hydrogen ratios shown in column 2, Table VI. After about thirty to sixty minutes circulation of the gas mixture across tube A by the circulating pumps, the analytical values shown in column 3 were obtained.

The differences between the water vapor–hydrogen ratios in columns 2 and 3, Table VI, can be seen to be qualitatively the same as the difference between the 0.107 value for curve 3 and the 0.162 value for curve 2, at 400°; or the 0.214 value for curve 3 and the 0.320 for curve 2, at 500°.

The number of thermal diffusion experiments at 400 and 500° is, however, too small to warrant rigorous quantitative comparisons. Neverthe-

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[18] Wöhler and Balz, *Z. Elektrochem.*, **27**, 406 (1921).

[19] Wöhler and Präeger, *ibid.*, **23**, 199 (1917).

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

less, it may be of interest to point out that the largest observed differences between the cold end water vapor–hydrogen ratios in column 2 and the hot end ratios in column 3 do account quantitatively for the discrepancy between curves 2 and 3 at 400 and 500°. It seems fair to conclude, therefore, that our own values of K_4 shown in Table III are essentially correct whereas those of previous workers are as much as 50% too high because of the thermal diffusion factor.

Discussion

The results of various experimental determinations of K_1, K_2 and K_4 have been plotted in Fig. 2. Of the static experiments, all but the early ones of Deville,[1] Chaudron[21] and Preuner[22] have been discussed and seem to be in error because of thermal diffusion. The experiments of these workers have been considered fully in previous publications;[5,14] various sources of error other than thermal diffusion have already been attributed to them. Consequently, their work need not be discussed here in detail; it will suffice to point out that the experimental results both of Chaudron and Deville probably should have been high because of thermal diffusion, whereas those of Preuner should not have been far in error. As can be seen from Fig. 2, Preuner's results are from about 3 to 16% high; those of Deville, when corrected for various probable sources of error, are 15 to 25% high; and those of Chaudron are from 0 to 40% high. The two or three approximately correct values of K_1 obtained by Chaudron in the 600 to 700° region seem to be either the result of certain errors compensating for the thermal diffusion factor, or of some unexplained detail of procedure stirring the water vapor–hydrogen mixture effectively and eliminating the thermal diffusion error. His results are certainly not sufficiently consistent to be considered valid exceptions to our general conclusions relative to thermal diffusion.

Although our static and flow experiments agree in general with curve 1 obtained indirectly by combining values of K_3 and values for equilibrium constants in the Fe–C–O system, it will be noticed that at 600 and 700° in particular our results seem to be a few per cent. lower and at 900 and 1000° a per cent. or so higher than curve 1. We were at first inclined to attribute this to a combination of possible experimental errors in our own results, and uncertainties in the values of K_3 used in calculating curve 1. Completion of the Fe–Fe_3O_4 experiments, however, has furnished one definite bit of evidence that curve 3 probably represents the value of K_1 and K_2 more accurately than curve 1. Eastman has pointed out that K_4 must be equal to $K_1^{1/4} \cdot K_2^{3/4}$ where K_1 and K_2 are obtained by extrapolation of the equilibrium curves from above the triple point Fe–FeO–Fe_3O_4 down to 400 or 500°. Such extrapolations and calculations

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[21] Chaudron, *Compt. rend.*, **159**, 237 (1914).

[22] Preuner, *Z. physik. Chem.*, **47**, 385 (1904).

from curve 1 lead to K_4 values of 0.238 and 0.127 at 500 and 400°, respectively, instead of our experimental values of 0.214 and 0.107. On the other hand, analogous calculations of K_4 from curve 3 yield values in satisfactory agreement with our own experimental results. We are, therefore, inclined to believe that curve 3 represents the Fe–H–O equilibria even more accurately than curve 1 and that the difference between these two curves is due either to slight errors in the present "best values" of the equilibrium constants for the Fe–C–O system or in the values of K_3 or in both.

The question naturally arises as to whether the thermal diffusion factor may not also have influenced the measurements of the CO_2/CO ratios reported for the equilibrium in the Fe–C–O system. Calculations based on the thermal diffusion measurements of Ibbs and Underwood[23] on carbon monoxide–carbon dioxide mixtures do indeed indicate the possibility of considerable errors in the Fe–C–O equilibrium data. Thus if equilibrium with respect to thermal diffusion were established the "cold end" CO_2/CO ratios for the Fe–FeO system might be higher than the "hot end" values by as much as 6.3% at 600° to 7.9% at 1000°. The actual errors in published CO_2/CO data that can be attributed to thermal separation are, however, uncertain for two reasons. In the first place, frequently authors do not state whether the carbon dioxide–carbon monoxide mixture taken for analysis is from the "hot end" or "cold end" of the apparatus. Second, almost all studies of the Fe–CO_2–FeO–CO system have been made at nearly one atmosphere pressure where diffusion is slower and convection currents are likely to cut down considerably the amount of thermal separation occurring between the hot and cold ends of the usual reaction vessel. Only some careful experiments on the Fe–C–O system made in such a way as to avoid any thermal separation of the carbon monoxide–carbon dioxide mixtures can definitely prove whether or not the "best values" for the Fe–C–O system reported by Eastman[3] are free of any thermal diffusion errors.

The apparatus used in the present studies was not well adapted to the determination of the actual and accurate composition of the phases that we have freely spoken of as Fe, FeO and Fe_3O_4. Although the initial composition of the sample and the total amount of oxygen added or removed were always known, it was impossible to say whether the steady state obtained during the one to six hours run employed in the present studies corresponded to equilibrium with the sample as a whole or with only the outer few layers of molecules in the individual solid particles. Experiments extending over much longer equilibration periods would be needed to establish definitely the variation of the water vapor–hydrogen equilibrium ratio with the composition of any solid solutions that might

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(23) Ibbs and Underwood, *Proc. Phys. Soc.*, **39**, 227 (1927).

exist in the iron–oxygen system. The results of Krings and Kempkens,[24] however, make it seem very probable that our Fe phase contained at the most a few tenths of one per cent. of oxygen. The FeO in the present experiments is probably the low oxygen limit of any FeO–O_2 solid solution that may exist.[25] On the other hand, the Fe_3O_4 employed in the FeO–Fe_3O_4 equilibrium experiments was probably the upper limit of any solid solution existing between Fe_3O_4 and small amounts of FeO as it was prepared by passing a 1.8:1 water vapor–hydrogen mixture over Fe_2O_3 at 700°.

The temperature at which the three solid phases, Fe, FeO and Fe_3O_4 can be in equilibrium with a water vapor–hydrogen mixture is about 559° according to the experimental values for K_1, K_2 and K_3, shown along curve 3. This seems definitely lower than the 570° value usually assumed for this point.

In previous publications[5] a tentative explanation for the various discrepancies in Fe–H–O equilibrium studies was made by assuming that a "surface effect" may have been present as a disturbing factor. Our present static experiments, however, have shown that such surface effects cannot account for the consistently high values frequently reported for K_1 and K_2; they may, however, have been factors in the erratic behavior of certain previous experiments, particularly those of Preuner.[22]

No data have appeared in the literature so far relative to the separation of water vapor–hydrogen mixtures that may result for different temperature gradients in consequence of thermal diffusion. The data reported in Tables IV to VI above can in no sense be considered to represent necessarily the maximum thermal separation that may occur in water vapor–hydrogen mixtures as a result of the temperature gradients here existing. It is safe to conclude, however, that within the experimental errors of the present work, they can be considered minimum values for such thermal separation.

Summary

A modified Deville type static apparatus is described by which the equilibrium ratios of water vapor–hydrogen have been found to be 0.334, 0.419, 0.501, 0.603 and 0.678 at 600, 700, 800, 900 and 1000° for the Fe–FeO system; 0.107, 0.214 and 0.283 at 400, 500 and 550° for the Fe–Fe_3O_4 system; and 2.35, 1.16 and 0.461 at 800, 700 and 600° for the FeO–Fe_3O_4 system. Thermal diffusion has been shown to account for previous static values being as much as 40% too high. The change in composition of water vapor–hydrogen mixtures because of thermal diffusion has been measured in the absence of an oxide sample at 400 and 500°. The possible influence of the thermal diffusion factor on the system Fe–C–O has been discussed.

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(24) Krings and Kempkens, *Z. anorg. allgem. Chem.*, **183**, 225 (1924); **190**, 313 (1930).

(25) Ralston, Bull. 296, U. S. Bureau of Mines (1929).