

INFLUENCE OF GASEOUS THERMAL DIFFUSION ON EQUILIBRIUM MEASUREMENTS ON THE Fe-O-H SYSTEM

Sir:

In a previous publication [THIS JOURNAL, 52, 4268 (1930)] the authors have pointed out that equilibrium constants for the reaction $\text{FeO} + \text{H}_2 = \text{Fe} + \text{H}_2\text{O}$ reported by various authors [see Eastman and Evans, THIS JOURNAL, 46, 888 (1924)] for static systems are about 40% higher than those obtained by a flow system. Furthermore, the flow system values are in good agreement with the constants calculated indirectly with the help of known Fe-C-O equilibrium data and equilibrium constants for the reaction $\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$. Up to the present no conclusive explanation of the cause of the discrepancy has been presented. It is the purpose of the present letter to point out a source of error that seems to explain the high $\text{H}_2\text{O}-\text{H}_2$ ratio obtained in previous static experiments for both the Fe-H-O system and other metal-metallic oxide systems such as Sn-SnO₂.

It has long been recognized [S. Chapman, *Phil. Trans. Roy. Soc.*, 217A, 115-147 (1918)] that if a mixture of two gases of different molecular weights such as $\text{H}_2\text{O}-\text{H}_2$ or CO_2-H_2 is placed in a tube one end of which is hot and the other cold, the ratio of the heavy gas to the lighter gas will rapidly become and remain larger in the cold portion of the tube than in the hot portion because of thermal diffusion. The purely static experiments on Fe-H₂O-FeO-H₂, SnO₂-H₂-Sn-H₂O or similar equilibria permit this diffusion factor to come into play; the $\text{H}_2\text{O}-\text{H}_2$ ratios obtained in such experiments are always those existing in the part of the apparatus that is at about room temperature and not necessarily in the hot part of the reaction tube. Accordingly $\text{H}_2\text{O}-\text{H}_2$ ratios determined in static experiments for heterogeneous equilibria will in general be higher than the true steam-hydrogen ratios existing in the hot end of the reaction tube in contact with the metal-metal oxide sample, unless some continuous and rapid circulation of the gas mixture is effected.

Preliminary calculations of the maximum difference in the "hot end" and "cold end" $\text{H}_2\text{O}-\text{H}_2$ ratios for the temperature differences existing in the above equilibrium experiments have been made using formulas developed by Chapman (*loc. cit.*). The results indicate that the thermal diffusion factor may easily account for the observed high $\text{H}_2\text{O}-\text{H}_2$ values of the static experiments. To establish definitely that at least in the case of the Fe-H-O system thermal diffusion actually does account for the high $\text{H}_2\text{O}-\text{H}_2$ values, the authors have set up a standard Deville type static apparatus and arranged to analyze samples of the steam-hydrogen mixture taken by a quartz capillary from the hot part of the reaction tube adjacent to the Fe-FeO or FeO-Fe₃O₄ samples. Simultaneously the usual "cold end" steam-hydrogen ratios were determined by observing the total pressure in the system and the temperature of the water thermostat regulating the

vapor pressure of water in the cold part of the apparatus. The average results obtained for the Fe-H-O system may be summarized as follows:

Furnace temp., °C.	Solid phases	Steam-hydrogen ratio			
		In "cold end" (by pressure readings)	In "hot end" by analysis	In static expts. of Eastman and Evans	In flow expts. of Emmett and Shultz
700	Fe-FeO	0.57	0.41	0.584	0.422
800	Fe-FeO	.71	.48	.706	.499
900	Fe-FeO	.82	.55	.822	.594
1000	Fe-FeO	.97	.67	.937	.669
700	FeO-Fe ₃ O ₄	1.50	1.19	1.45	1.181
800	FeO-Fe ₃ O ₄	3.18	2.35	2.98	2.372

The obvious agreement between the "cold end" values (column 3) and the previous static results (column 5) on the one hand, and the "hot end" analysis (column 4) and the previous flow results (column 6) on the other, seems to show definitely that the principal cause of discrepancy between the various steam equilibrium constants for the Fe-H-O system is the factor of thermal diffusion. Since the magnitude of the steam-hydrogen ratios in the Sn-H₂O-H₂-SnO₂ system is about the same as for the Fe-FeO-H₂O-H₂ system, it is evident that the same diffusion factor will also account for the static experiments on the Sn-H-O system in which the steam-hydrogen equilibrium ratios are apparently about 40% high [THIS JOURNAL, 50, 1106 (1928)].

BUREAU OF CHEMISTRY AND SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

P. H. EMMETT
J. F. SHULTZ

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A FILM WHICH ADSORBS ATOMIC H AND DOES NOT ADSORB H₂

Sir:

We report the following brief study, which we shall discontinue for the present, because of its bearing on the subject of "activated adsorption."

A lamp had two pure tungsten filaments and one filament of Elinvar wire which contained 35% nickel and 12% chromium, the remainder being probably iron. The lamp was sealed to a vacuum system having liquid-air traps, and the Elinvar filament heated to a bright red heat in vacuum for fifteen minutes. The amount of metal thus evaporated was too small to be visible on the walls or to produce a change in resistance of the wire. Pure hydrogen was then admitted at a pressure of 0.250 mm. and one of the tungsten filaments was lighted at 2700°K., at which temperature 3.5% of the hydrogen molecules which strike a tungsten surface are dissociated. The hydrogen disappeared at an exponential rate, decreasing from 210 cu. mm. to 170 cu. mm. in 6.5 minutes.

The lamp was next evacuated and torched at about 450° for ten minutes,