[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS]

Equilibrium in the System SnO_2–H_2–Sn–H_2O. Indirect Calculation of the Values of the Water Gas Equilibrium Constants

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

In previous publications[1] we have shown that thermal diffusion by creating a difference between the composition of a water vapor–hydrogen mixture in the hot end and that in the cold end of a reaction tube has been responsible for many of the experimental values for the equilibrium constants in the Fe–H–O system being as much as 40% too high. It seemed very probable that the same phenomenon had caused the values of K_1 obtained by Eastman and Robinson[2] for the reaction

$$\frac{1}{2}SnO_2 + H_2 = \frac{1}{2}Sn + H_2O \qquad K_1 = H_2O/H_2$$

to be similarly in error. We have, accordingly, redetermined the value of K_1 using the apparatus and procedure that has previously been shown to eliminate thermal diffusion errors in determining values of the equilibrium constants for the Fe–H–O system.[3] The sample of SnO_2 used was prepared by dissolving C. P. tin in nitric acid, heating the resulting stannic acid to expel the moisture and finally igniting it in air to 500 or 600°. The 3-g. SnO_2 sample was partially reduced *in situ* before the final experiments.

Results

The experimental results are shown in Table I. The total pressures (column 4) were read on a mercury manometer. The partial pressure of water vapor as obtained from the "International Critical Tables" for the

TABLE I

EQUILIBRIUM MEASUREMENTS ON THE SYSTEM SnO_2–H_2–Sn–H_2O

Run	Temp., °C.	Initial H_2O/H_2	P_{total}, mm.	$K_1 = P_{H_2O}/P_{H_2}$	K_1 corr. to 600, 700, 750 and 800°C., resp.
26	650.5	0.837	38.4	1.61	1.61
27	650.0	5.51	37.2	1.76	1.76
38	650.0	0.757	38.4	1.61	1.61
29	651.0	2.097	37.8	1.68	1.67
				Average for 650°	1.66
17	700.5	0.837	34.4	2.21	2.20
18	701.5	0.952	34.2	2.25	2.23
19	700.5	∞	34.2	2.25	2.24
20	700.0	0.603	34.6	2.17	2.17
21	700.5	∞	34.2	2.25	2.24
				Average for 700°	2.22

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

(2) Eastman and Robinson, *ibid.*, **50**, 1106 (1928).

(3) The apparatus is that shown in Fig. 1A of a preceding article on the Fe–H–O system by Emmett and Shultz, THIS JOURNAL, **55**, 1376 (1933); the procedure was identical with that there described.

TABLE I (*Concluded*)

Run	Temp., °C.	Initial H_2O/H_2	P_{total} mm.	$K_1 = P_{H_2O}/P_{H_2}$	K_1 corr. to 600, 700, 750 and 800°C., resp.
22	751.0	0.578	32.0	2.85	2.84
23	749.5	0.619	32.0	2.85	2.86
24	750.5	∞	32.2	2.79	2.78
25	749.5	∞	32.0	2.85	2.86
				Average for 750°	2.84
12	799.5	7.18	30.4	3.54	3.55
13	800.0	0.653	30.6	3.44	3.44
14	799.5	0.734	30.4	3.54	3.55
15	800.0	∞	30.4	3.54	3.54
16	799.5	∞	30.4	3.54	3.55
				Average for 800°	3.53

temperatures of the thermostated water bulb included in the reaction system was 23.7 mm. in all runs. The hydrogen pressures used in calculating K_1 are the differences between the total pressures in the system and the partial pressures of water vapor.

If the temperature of the metal oxide sample is considered accurate to ±2°, that of the water-bath to ±0.05°, and the pressure readings to ±0.2 mm., the total uncertainty that might exist as to the value of K_1 given by any one experiment would be ±0.06 unit at 650° C., ±0.09 at 700, ±0.13 at 750 and ±0.18 at 800°. The probable errors calculated from the runs shown in Table I are of course very much smaller.

Our experimental results are summarized in Table II. The values obtained by static and by dynamic experiments of Eastman and Robinson[2] are included for comparison, as also are the values of K_1 calculated from the values of K_2 for the reaction

$$\frac{1}{2}SnO_2 + CO = \frac{1}{2}Sn + CO_2 \qquad K_2 = CO_2/CO$$

together with the value of the constant K_3 [4] for the reaction

$$H_2 + CO_2 = CO + H_2O \qquad K_3 = \frac{(CO)(H_2O)}{(CO_2)(H_2)}$$

In Fig. 1 are plotted our data (curve 2) as well as those of Eastman and Robinson obtained by static experiments (curve 3) and by dynamic experiments (curve 4). Curve 1 shows the equilibrium water vapor–hydrogen ratio calculated indirectly with the assistance of the Sn–C–O data of Eastman and Robinson and values of the water gas constant K_3.

Discussion and Conclusion

As can be seen in Fig. 1, curves 1 and 2 agree approximately with each other, but represent values of K_1 about 25% lower than those obtained in the static experiments of Eastman and Robinson (curve 3). Furthermore, the difference in composition between the water vapor–hydrogen

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[4] The values of K_3 used were obtained from equation 38 given by Bryant, *Ind. Eng. Chem.*, **23**, 1019 (1931).

mixture corresponding to curve 2 and those corresponding to curve 3 is in approximate agreement with that obtained for comparable water vapor–hydrogen ratios and temperature gradients in the Fe–H–O equilibrium studies. Probably, then, their values of K_1 really show the steady state composition of the water vapor–hydrogen mixture in the cold end of the static apparatus rather than the equilibrium ratio existing in the hot end of the apparatus in contact with $Sn-SnO_2$. Thus, values of K_1 obtained in the static experiments of Eastman and Robinson and shown by curve 3 seem to be about 30% high because of the same thermal diffusion factor responsible for errors in similar studies on the Fe–H–O system.

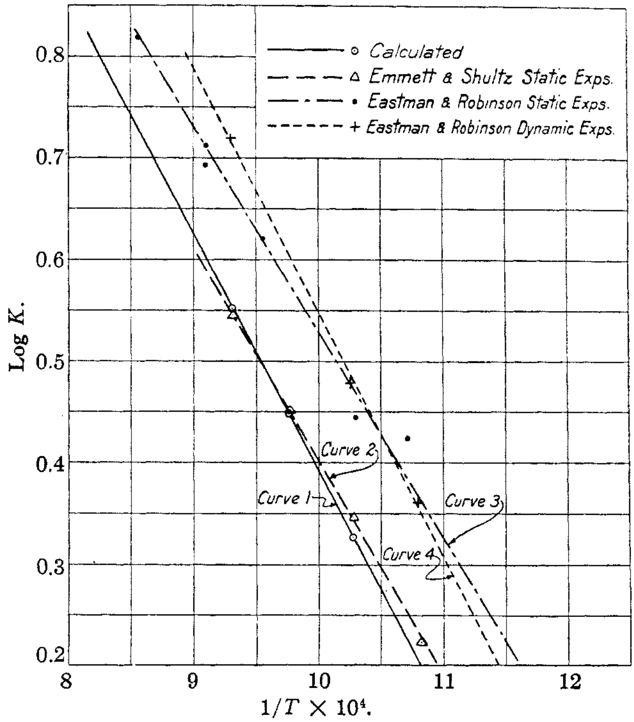

Fig. 1.—Variation with $1/T$ of log K, where $K = H_2O/H_2$ in equilibrium with $Sn-SnO_2$. The calculated values of K represented by curve 1 were obtained by combining the equilibrium data of Eastman and Robinson for the Sn–C–O system with values for the water gas constant K_3 given by free energy equation 38 in the paper of Bryant.[4]

It seems odd, at first, that a dynamic system such as used in obtaining curve 4 could be in error due to thermal diffusion. However, a dynamic or flow system can involve errors due to thermal diffusion as readily as a static system provided the rate of gas passage through the reaction vessel is sufficiently low. In the paper of Eastman and Robinson the rate of gas passage was not given; it might have been small enough to have permitted the water vapor–hydrogen mixture in the cold end of the large diameter inlet tube to have become much larger than that in the hot reaction bulb. At any rate, the 655 and 703° points but not the 809° point in their dynamic experiments can be accounted for by the same amount of thermal diffusion that explains the difference between the curves 2 and 3; the reason for the 809° point being considerably above curve 3 is not clear.

From the summary given in Table II the values of K_1 calculated indirectly from the Sn–C–O equilibrium data and the water gas constant K_3 can be seen to agree approximately with our own directly measured values. The agreement is probably within the combined experimental error of our own experiments and those on the Sn–C–O system. The indirectly calculated values of K_1 in column A are based upon the Sn–C–O data of Eastman and Robinson; those in column B on the data of Meyers and Scheffer.[5]

TABLE II

SUMMARY OF EQUILIBRIUM DATA ON THE SN–H–O SYSTEM. VALUES OF $K_1 = H_2O/H_2$

Temp., °C.	Present expts.	Static expts. Eastman and Robinson	Dynamic expts. Eastman and Robinson	Calcd.[a] from water gas constant and Sn–C–O data		
				A	B	C
650	1.66	2.30	2.26	1.59	1.73	1.64
700	2.22	2.97	3.02	2.12	2.30	2.17
750	2.84	3.76	..	2.81	2.95	2.79
800	3.53	4.66	5.19	3.57	3.70	3.50

[a] Column A is based on the Sn–C–O data of Eastman and Robinson; columns B and C on those of Meyers and Scheffer. The Sn–C–O data used in calculating column C have been corrected for possible thermal diffusion errors by the thermal diffusion data of Ibbs and Underwood[6] on carbon monoxide–carbon dioxide mixtures.

It is interesting to note that the indirectly calculated values of K_1 (column C) based upon K_2 values of Meyers and Scheffer that have been corrected for possible thermal diffusion errors[6] agree quite well with our own data. Whether any thermal diffusion errors actually did enter into the Sn–C–O experiments of either Eastman and Robinson or Meyers and Scheffer can of course only be decided by some careful experiments so carried out as to prevent the composition of the CO_2–CO mixture in the hot part of the reaction vessel being different from that in the cold part.

The equilibrium data reported in the present paper remove the last large discrepancy between the directly measured values for the water gas equilibrium constant, K_3, and those calculated indirectly by combining the equilibrium data for various metal–oxide–CO–CO_2 and metal–oxide–

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(5) Maeda [*Bull. Inst. Phys. Chem. Research* (Tokyo), **2**, 330 (1923)] and Fraenkel and Snipischski [*Z. anorg. allgem. Chem.*, **125**, 235 (1922)] have also obtained experimental equilibrium values for the system Sn–C–O. Their work which has been criticized both by Eastman and Robinson and by Meyers and Scheffer has not been used in any calculations in the present paper.

(6) The experimental data of Ibbs and Underwood [*Proc. Phys. Soc.*, **39**, 227 (1927)] on thermal diffusion in carbon monoxide–carbon dioxide mixtures make it possible to calculate the maximum error in the values of K_2 that might have been caused by thermal diffusion in the experiments of Meyers and Scheffer.

H_2O-H_2 systems. In Table III, accordingly, have been summarized the various indirectly calculated and the directly measured values for the water gas equilibrium constants between 400 and 1000°. For comparison the values of the constants obtained from free energy equations 38 and 39 of a recent paper by Bryant[4] have been included. Bryant's equations were formulated from thermal data of various authors for CO, CO_2, H_2O and H_2, together with the 986° directly measured equilibrium value from the work of Neumann and Köhler.[7]

TABLE III

VALUES OF THE WATER GAS EQUILIBRIUM CONSTANT, $K_2 = (CO)(H_2O)/(CO_2)(H_2)$

	Direct measurements		Calculated from equations of Bryant		Calculated[a] from H_2O-H_2 and CO_2-CO equilibria with				
Temp., °C.	Hahn	Neumann and Köhler	Equation 38	Equation 39	Co–CoO	Fe–FeO	FeO–Fe_3O_4	$Sn-SnO_2$ A	$Sn-SnO_2$ B
350		0.041							
400		.080	0.087	0.082					
450		.140	.139	.132	0.137				
500		.200	.205	.197	.207				
550		.290	.292	.281	.297				
600		.410	.394	.378		0.383	0.384		
650		.50	.507	.491		(.488)	(.494)	0.533	0.486
700	0.610	.63	.638	.624		.622	.630	.657	.617
750	.755	.78	.782	.771		(.770)	(.776)	.787	.751
800	.906	.93	.938	.933		.919	.918	.918	.893
850	1.071	1.09	1.11	1.10		(1.11)			
900	1.240	1.29	1.29	1.28		1.315			
950	1.420	1.44	1.48	1.48		(1.50)			
1000	1.606	1.66	1.67	1.68		1.699			

[a] The water vapor–hydrogen ratios and carbon dioxide–carbon monoxide ratios for the Co–CoO calculation, as well as the water vapor–hydrogen ratios for the Fe–FeO, FeO–Fe_3O_4 and $Sn-SnO_2$ calculations, were taken from our equilibrium studies. The $CO-CO_2$ equilibrium data for the Fe–FeO and FeO–Fe_3O_4 systems are the "best value" given by Eastman in Circular 6125, U. S. Bur. of Mines (1929). The $CO-CO_2$ equilibrium data for the $Sn-SnO_2$ system were obtained from the paper of Eastman and Robinson (A) and the paper of Meyers and Scheffer (B). The values inclosed in parentheses involve interpolations in the data on the Fe–H–O system.

The agreement as a whole is very satisfactory; certainly no large errors in the values of the water gas constants between 400 and 1000° now exist. The direct measurements of Hahn[8] are from 2 to 4% lower than the values of K_2 given by equation 39. Those of Neumann and Köhler agree in general decidedly better with equation 38 than with equation 39, as do also the indirect calculations based on equilibria with the Co–CoO system.[9] In the temperature range 600 to 800°, however, indirect calculations based on the Fe–FeO and FeO–Fe_3O_4 systems agree very well with equation 39 but are 2 to 3% lower than the values given by equation 38. It may be

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(7) Neumann and Köhler, *Z. Elektrochem.*, **34**, 227 (1928).

(8) Hahn, *Z. physik. Chem.*, **42**, 705 (1903); **44**, 513 (1903); **46**, 735 (1903).

(9) Emmett and Shultz, THIS JOURNAL, **51**, 3249 (1929); **52**, 892 (1930).

noted in this connection that any errors caused by thermal separation in the carbon dioxide–carbon monoxide mixtures in Fe–C–O equilibrium measurements[10] would cause the values of K_3 calculated from the Fe–C–O and the Fe–H–O data to be low; accordingly the 2 or 3% difference between equation 38 and the values of K_2 thus indirectly calculated might easily be due to such errors in the Fe–C–O data. The direct calculations of K_3 based on our own data for the Sn–H–O system and those both of Eastman and Robinson (A) and Meyers and Scheffer (B) for the Sn–C–O system have been included since it is not possible at present to decide which of the two sets of experimental values of K_2 is the more reliable. It should be noted, however, that as pointed out above the 3 or 4% discrepancy between the values of K_3 in column B and those of equation 38 could be due entirely to thermal diffusion errors in the experiments of Meyers and Scheffer on the Sn–C–O system.

Summary

Values of the equilibrium constant H_2O/H_2 for the reaction $^1/_2\ SnO_2 + H_2 = {}^1/_2\ Sn + H_2O$ have been found to be 1.66, 2.22, 2.84, and 3.53 at 650, 700, 750 and 800°. These values are about 25% lower than the results of previous workers, and when combined with equilibrium data for the Sn–C–O system give values for the water gas constant that agree within a few per cent. with those obtained by direct measurements.

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

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The Recombination of Hydrogen Atoms. I

BY I. AMDUR[1] WITH A. L. ROBINSON

Introduction

The rate of recombination of hydrogen atoms has been measured by Smallwood,[2] Senftleben and Riechemeier[3] and Steiner and Wicke.[4] Kassel[5] has summarized the results of these investigations. It seems fairly certain that the reaction takes place partly on the walls, although Senftleben and Riechemeier and Steiner and Wicke present some evidence to indicate that the wall reaction is not very significant, and partly as a trimolecular gas reaction. Opinion differs as to whether hydrogen atoms or hydrogen

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[1] The material in this paper comprises a portion of a thesis presented by I. Amdur to the Graduate School of the University of Pittsburgh in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1932.

[2] Smallwood, THIS JOURNAL, **51**, 1985 (1929).

[3] Senftleben and Riechemeier, *Ann. Physik*, **6**, 105 (1930).

[4] Steiner and Wicke, *Z. physik. Chem.*, Bodenstein Band, 817 (1931).

[5] Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932, pp. 177–180.