Studies of Thermochemical Hydrogen Production. VII. Vapor-Liquid Equilibrium for Sulfur Dioxide-Bromine-Hydrobromic Acid-Sulfuric Acid-Water System

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In order to eliminate SO_2 from HBr gas produced by the reaction between SO_2, Br_2, and H_2O, vapor-liquid equilibrium measurements of the Br_2–H_2SO_4–H_2O system saturated with HBr have been made over a wide range of the constituent concentrations. Experiments were carried out in a semi-flow system at 25 °C under atmospheric pressure. The relative concentration of HBr saturated in the liquid phase decreased from 0.31 to 0.05 [mol]/[mol] with an increase in the relative H_2SO_4 concentration from 0.0 to 0.40 [mol]/[mol]. The solubility of Br_2, as defined by Henry's law constant, varied from 1.1 to *ca.* 150 atm/mol/mol with the above-mentioned decrease in the HBr concentration. The relation between the partial pressure of SO_2 in the gas phase and the composition of the liquid phase was found to be expressed by the following empirical formula: $P_{SO_2}=K\cdot C_{HBr}\cdot C_{H_2SO_4}/C_{Br_2}$, where the value of K is 8×10^{-4} when C is expressed as a relative molar concentration for each species in the liquid phase. The unconverted SO_2 can be effectively removed by bringing the effluent gases from the reactor into contact with a HBr-saturated aqueous solution containing an excess of Br_2.

The research and development of thermochemical hydrogen production from water by the iron-bromine family cycle has previously been carried out by the present authors.[1–3] One of the most feasible iron-bromine thermochemical cycles consists of the following four chemical reactions:

$$SO_2 + Br_2 + 2H_2O \longrightarrow H_2SO_4 + 2HBr \quad (1)$$

$$H_2SO_4 \longrightarrow H_2O + SO_2 + 1/2O_2 \quad (2)$$

$$3FeBr_2 + 4H_2O \longrightarrow Fe_3O_4 + 6HBr + H_2 \quad (3)$$

$$Fe_3O_4 + 8HBr \longrightarrow 3FeBr_2 + 4H_2O + Br_2 \quad (4)$$

Each reaction step has been investigated experimentally on a laboratory scale, and our earlier works have dealt with Reactions 2, 3, and 4.

The reaction between SO_2, Br_2, and H_2O is relatively well known as a usual method for preparing gaseous HBr in a laboratory-scale operation.[4] Recently, equilibrium determinations and reaction kinetic measurements have been carried out by Velzen *et al.*[5] during the course of the development of the electrochemical hybrid-water-splitting cycle, Mark-13, presented by Schuetz *et al.*[6] It has also been confirmed by the present authors that gaseous HBr and concentrated sulfuric acid could be prepared by using a packed column reactor.[7]

One of the problems to be solved, however, is the removal of the small quantity of unconverted SO_2 contained in the HBr gas produced in a flow reactor of SO_2 with Br_2 and H_2O. This is because the HBr gas produced by Reaction 2 is circulated for use in the bromination of Fe_3O_4, *i.e.*, Reaction 4, and the contamination of HBr by SO_2 would cause the formation of $FeSO_4$ as an undesirable side reaction. The continuous operation of the cycle would cause $FeSO_4$ to be accumulated as a by-product, and its thermal decomposition to Fe_2O_3 would be additionally required. On the other hand, the contamination of HBr by Br_2 matters little. The requirement for SO_2-free HBr gas seems to be fulfilled by bringing the effluent HBr gas from the reactor into contact with a HBr-saturated aqueous solution containing an excess of Br_2. Therefore, prior to the kinetic measurements, vapor-liquid equilibrium measurements of the HBr-saturated Br_2–H_2SO_4–H_2O system have been made over a wide range of constituent concentrations.

Some equilibrium data have already been reported by Velzen,[5] but they were confined to the liquid phase with a high concentration of H_2SO_4.

Experimental

The experiments were carried out in a semi-flow system at 25 °C under atmospheric pressure. The apparatus shown in Fig. 1 is composed of a cylindrical vessel 4 cm in diameter and 13 cm in height and equipped with a HBr-gas dispersion tube (ball filter No. 1), three PTFE tubes 1.0 mm in inner diameter for the addition of Br_2 and sulfuric acid and for the withdrawing of a liquid-phase sample, and a magnetic stirrer. The vessel was immersed in a water bath thermostatted at 25 °C.

After the liquid had been saturated with HBr, given quantities of Br_2 and 98 wt% sulfuric acid were introduced into the agitated liquid phase. Simultaneously, HBr gas was passed in at a rate of 50 ml/min. The outlet gas was led to a sampling cell of a derivative spectrophotometer (Yanagimoto Co. Ltd., Type UO-2) for the quantitative analysis of Br_2 as well as of the SO_2 evolved by the oxidation of HBr with H_2SO_4. Figure 2 shows examples of the variation in the Br_2 and SO_2 concentrations in the gas phase

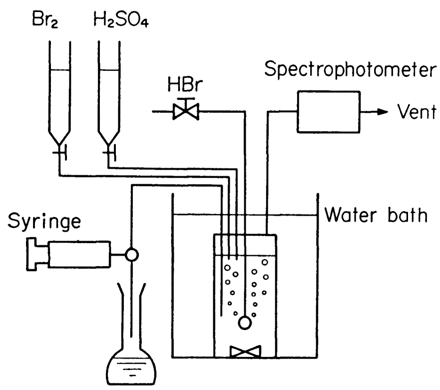

Fig. 1. Experimental appparatus for equilibrium determinations.

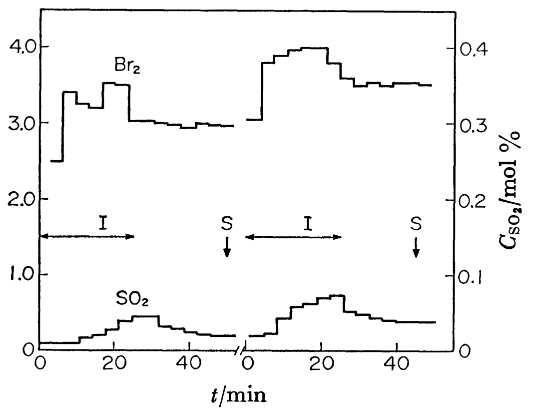

Fig. 2. Variation of Br_2 and SO_2 concentrations in gas phase.
I: Injection of sulfuric acid, S: sampling of liquid phase and determination of gas phase and liquid phase compositions.

monitored alternatively at regular intervals of 3.5 min. After about 20 min, when both the Br_2 and SO_2 concentrations had reached an equilibrium condition, the feed of the HBr gas was stopped, and the composition of the gas phase, considered to consist of only HBr, Br_2, and SO_2, was determined. At the same time, a sample of the liquid phase was taken out by using a syringe, and a weighed aliquot was diluted with a large excess of water in a volumetric flask. The composition of the liquid phase, consisting of HBr, H_2SO_4, Br_2, and H_2O, was calculated by determining the free Br_2, the total acidity, and the sulfuric-acid content. Thus, a given volume of the liquid-phase sample was taken and analyzed for Br_2 iodometrically, after which the total acid content was determined by titration with an NaOH solution. Another sample was analyzed for H_2SO_4 as follows: hydrogen bromide was oxidized by adding nitric acid. After the resulting Br_2 and the excess HNO_3 had been evaporated in a water bath, the remaining sulfuric acid was titrated. Then the HBr content was determined by subtracting the H_2SO_4 content from the total acid content.

Results and Discussion

Experiments were carried out on the liquid phase in concentrations of H_2SO_4 ranging from 0.0 to 80 wt% and in concentrations of Br_2 up to 10 wt%. The equilibrium data at 25 °C under atmospheric pressure are shown in Table 1. The content of SO_2 dissolved in the liquid phase was neglected, since the partial pressure of SO_2 evolved in the gas phase was very low. Moreover, the solubility of SO_2 in these liquid phases can be estimated to be small from the solubility data in sulfuric acid,[8] in a mixture of hydrochloric and sulfuric acids,[9] and in a mixture of hydrobromic and sulfuric acids.[5]

Solubility of HBr. The solubility data of the gaseous-phase components of the reaction mixture in the corresponding liquid phase are indispensable for the control of the mass balance of the HBr-producing system. Run No. 1 in Table 1 is an example carried out to determine the solubility of HBr in water. The numerical value obtained, 67.5 wt%, was a little higher than that of 66.0 wt% given by Haase *et al.*[10] The relation between the concentration of HBr and that of H_2SO_4 in the HBr-saturated liquid phase is shown in Fig. 3. The "relative concentration" is defined

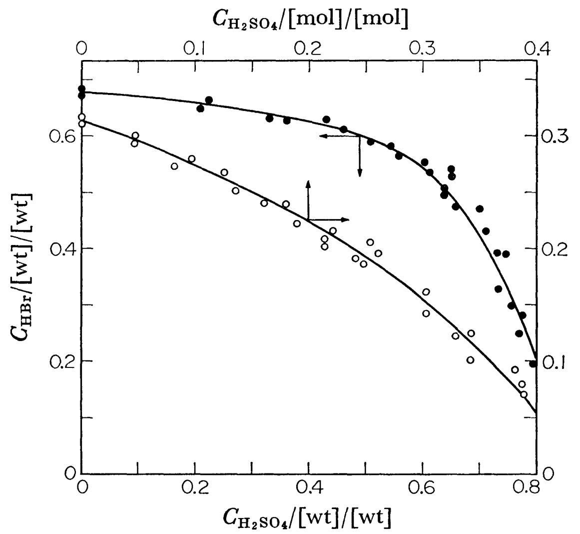

Fig. 3. Solubility of HBr in Br_2-H_2SO_4-H_2O mixture at 25 °C.
C_{Br_2} : 0—10 wt %.

Table 1. Equilibrium determinations for the SO_2-Br_2-HBr-H_2SO_4-H_2O system at 25 °C

Run No.	Liquid phase								Gas phase	
	Br_2		H_2SO_4		HBr		H_2O		Br_2	SO_2
	wt %	mol %	wt %	mol %	wt %	mol %	wt %	mol %	mol %	mol %
1	—	—	—	—	67.5	31.6	32.5	68.4	—	—
2	6.8	1.7	—	—	62.7	30.8	30.5	67.5	1.7	—
3	8.6	2.2	7.8	3.3	54.6	27.8	27.0	66.7	3.2	0.04
4	7.8	2.0	15.8	6.8	48.3	25.2	28.1	66.0	3.8	0.07
5	3.8	1.0	28.7	12.5	39.9	21.0	27.6	65.5	3.5	0.21
6	3.0	0.8	39.2	17.8	31.8	17.4	26.0	64.0	4.6	0.31
7	4.0	1.1	45.6	21.1	25.3	14.2	25.1	63.6	9.6	0.19
8	1.7	0.5	55.0	26.7	20.2	11.8	23.1	61.0	6.9	0.47
9	0.7	0.2	62.7	31.2	14.4	8.6	22.2	60.0	7.0	1.06
10[a]	1.6	0.5	67.7	34.6	9.3	5.7	21.4	59.2	28.0	0.38

a) Also present: liquid bromine insoluble in the liquid phase.

by [mol]/[mol] or [wt]/[wt], where [mol] and [wt] are the concentrations expressed in mol% and wt% respectively. The concentration of HBr saturated in the solution was reduced from 0.31 to 0.05 [mol]/[mol] with an increase in the H_2SO_4 concentration from 0.0 to 0.40 [mol]/[mol].

Henry's law constant (H) is also useful in defining the vapor-liquid equilibrium:

$$H = P_A/X_A \quad \text{(atm/wt/wt or atm/mol/mol)} \tag{5}$$

where P_A is the partial pressure of a gas, A, in the gas phase and where X_A is the concentration of a species, A, in the liquid phase, expressed in a weight fraction or a mole fraction. Figure 4 shows the relation between Henry's law constant for HBr and the H_2SO_4 concentration in the liquid phase. The values of H given by Velzen[5] in the high-H_2SO_4-concentration region were in fair agreement with our data. The presence of Br_2 up to a concentration of 10 wt% had little effect on the solubility of HBr.

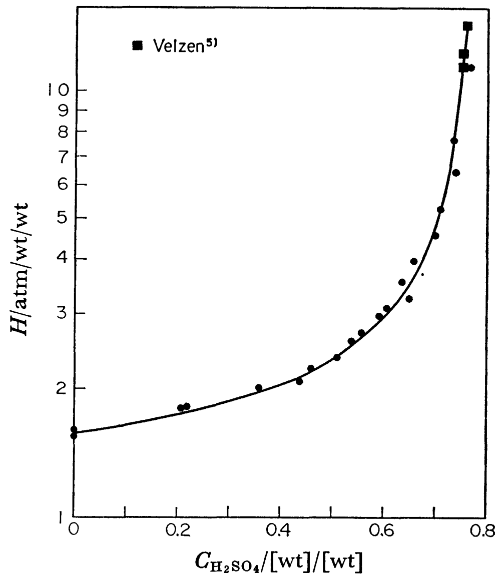

Fig. 4. Relation between Henry's law constant for HBr and concentration of H_2SO_4 in solution at 25 °C.

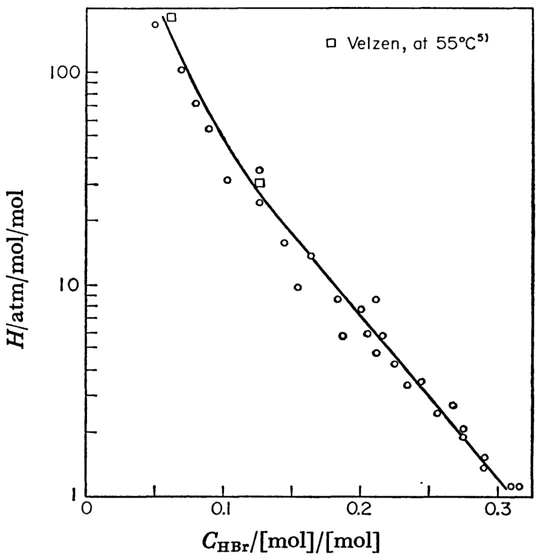

Fig. 5. Relation between Henry's law constant for Br_2 and concentration of HBr in solution at 25 °C. $C_{H_2SO_4}$: 0.40→0.0 [mol]/[mol].

Solubility of Br_2. The solubility of Br_2 in the liquid phase of the reaction mixture depends strongly on the HBr concentration. Figure 5 shows Henry's law constant for Br_2 as a function of the relative HBr concentrations, ranging from 0.05 to 0.31 [mol]/[mol]. The corresponding H_2SO_4 concentrations in the solution can be seen in Fig. 3 to range from 0.40 to 0.0 [mol]/[mol]. It has already been shown by Velzen[5] that the values of H at 23 °C and 55 °C are nearly identical; their values are also in good agreement with our data at 25 °C. It thus appears that the effect of the temperature was negligibly small.

Figure 6 gives the content of Br_2 saturated in the solution of the reaction mixture at a low HBr concentration, *i.e.*, at a high H_2SO_4 concentration. In this case, liquid Br_2 insoluble in the solution was also present, and the partial pressure of Br_2 in the gas phase was equal to that of liquid Br_2, *i.e.*, 0.28 atm at 25 °C, as shown by Run No. 10 in Table 1.

Partial Pressure of SO_2 in the Gas Phase. Since only the equilibrium partial pressure of SO_2 in the gas phase was required for the reaction kinetic measurements and the succeeding design of a reactor unit, the concentration of SO_2 in the solution of the reaction mixture was not determined. The partial pressure of SO_2 evolved in the gas phase in equilibrium with the liquid phase was strongly influenced by both the H_2SO_4 and Br_2 concentrations. It was found that the relation between the partial pressure of SO_2 in the gas phase and the composition of the liquid phase could be expressed by the following empirical formula:

$$P_{SO_2} = K \cdot \frac{C_{HBr} \cdot C_{H_2SO_4}}{C_{Br_2}} \tag{6}$$

where the value of K was *ca.* 7×10^{-4} when C was expressed as a weight fraction or a relative weight concentration for each species in the liquid phase. The validity of this formula (6) is shown in Fig. 7. When C was defined by a mole fraction or a relative molar concentration for each species, the value of K was *ca.* 8×10^{-4}. Figure 8 shows the calculated

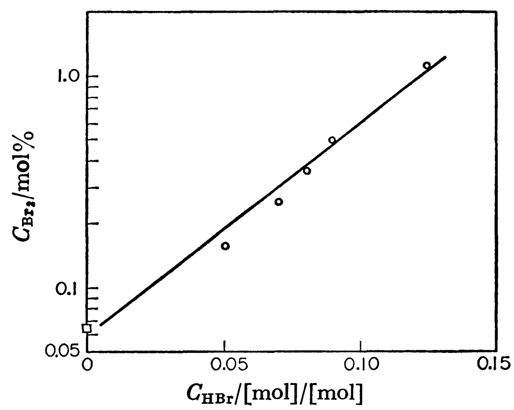

Fig. 6. Solubility of Br_2 in HBr saturated H_2SO_4–H_2O mixtures at 25 °C. $C_{H_2SO_4}$: 0.43→0.34 [mol]/[mol].

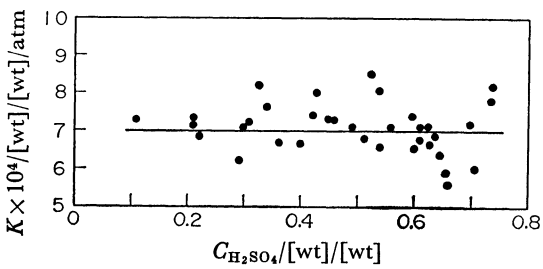

Fig. 7. Validity of empirical formula (6).

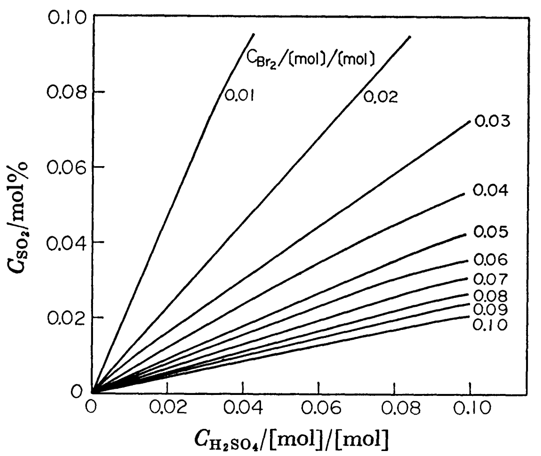

Fig. 8. Calculated equilibrium SO_2 concentration in gas phase as a function of H_2SO_4 and Br_2 concentrations in solution.

equilibrium SO_2 concentration in the gas phase as a function of the relative H_2SO_4 and Br_2 concentrations in the liquid phase.

It can be seen from Fig. 8 that, when HBr contaminated by SO_2 is placed in contact with a HBr saturated aqueous solution of H_2SO_4 and Br_2 at relative concentrations of, for example, 0.03 and 0.07 [mol]/[mol] respectively, the SO_2 content of the gas mixture in equilibrium is reduced to 0.01 mol%. The corresponding relative HBr concentration in the solution obtainable from Fig. 3 was 0.30 [mol]/[mol]; the value of H for Br_2 also obtainable from Fig. 5, was 1.2 atm/mol/mol. Therefore, the Br_2 concentration in the gas phase is expected to amount to 5.9 mol%, since the Br_2 concentration in the solution is calculated to be 4.9 mol%.

Conclusion

As a part of research and development of the thermochemical hydrogen production from water by the iron-bromine family cycle, the vapor-liquid equilibrium for the reaction of SO_2 with Br_2 and H_2O has been investigated. It could be concluded that the development of a continuously HBr-producing process was feasible by combining a packed column reactor with an absorber of unconverted SO_2. The absorbent liquid can be fed into the reactor as a reaction agent when it was condensed into concentrated H_2SO_4. Studies of the reaction kinetics are under way in order to design a practical unit.

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