Equilibria in the PdS–H_2–Pd_4S–H_2S and Pd_4S–H_2–Pd–H_2S Systems[*]

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It is known that in the palladium-sulfur system there are three stable compounds, namely PdS_2, PdS and Pd_4S. The sulfur pressure associated with the dissociation of PdS_2 to PdS has been measured by Biltz and Laar(1), while the thermodynamic properties of the other two compounds are not yet known. The present studies have been undertaken to measure the dissociation pressures of PdS and Pd_4S on the basis of measurements of the equilibrium between a hydrogen-hydrogen sulfide gaseous mixture and a PdS–Pd_4S or Pd_4S–Pd solid mixture. From the experimental results, the free energies of the formation of the three sulfides were calculated.

Experimental

Materials. — PdS was prepared from palladium chloride of a guaranteed reagent. From a 5% hydrogen chloride aqueous solution of palladium chloride, PdS was precipitated by the introduction of gaseous hydrogen sulfide. Pd_4S was not prepared as a pure substance, but was produced in the solid phase in the intermediate state of a reduction of PdS to Pd (or in the sulfidization of Pd to PdS). This compound was identified by X-ray analysis.

Apparatus and Procedures.—A streaming method was employed. The reaction tube is shown in Fig. 1. In the figure, A is a pyrex tube 30 cm. in length and 1 cm. in inner diameter. The right hand portion of the tube is expanded downwards to be charged with the sulfide mixture. B is a pyrex outlet tube 9 mm. in outer diameter and 5 mm. in inner diameter. The heating element is a nichrome resistance furnace. The temperature of the furnace was controlled manually within ±1°C. The temperature was measured by a platinum vs platinum—rhodium thermocouple at

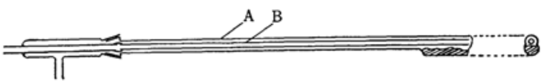

Fig. 1. Schematic diagram of the reaction tube.

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[*] Presented at the 14th Annual Meeting of the Chemical Society of Japan, April, 1961.

1) W. Biltz and J. Laar. *Z. anorg. u. allgem, Chem.*, **228**, 257 (1936).

the outside of the reaction tube. The temperature of the inner space of the reaction tube was proved to be equal to that of the outside by a preliminary test. Hydrogen gas was generated by electrolysis of a potassium hydroxide solution. Oxygen was eliminated by introducing the gas into a heated copper net. The hydrogen thus prepared was found by gas-chromatographic analysis to contain a trace of oxygen and about 2% nitrogen. These impurities were disregarded, since any error due to these minor quantities falls within the normal scattering of experimental results. For the sake of uniform mixing, the gas mixture of hydrogen and hydrogen sulfide was stored before use above vacuum pump oil in a glass vessel. After the reaction, the gas mixture was led into a potassium hydroxide aqueous solution and then gathered in a glass vessel, where the volume of the hydrogen was measured. The amount of hydrogen sulfide in the alkaline solution was determined by iodometric titration. The rate of gas flow appropriate for attaining equilibrium was examined at 625°K. No change in apparent equilibrium composition was detected when the flow rate was changed from 7 to 60 cc./min. Another confirmation of the attainment of equilibrium is given by the fact that the apparent equilibrium compositions of the gaseous mixture were consistent with each other, irrespective of the direction of reaction, as will be seen below.

Results

PdS–Pd_4S System. — The equilibrium was measured over the temperature range of 613 to 795°K. The ratios of the equilibrium partial pressure of hydrogen sulfide to that of hydrogen are summarized in Table I. The reaction is represented by the following equation:

TABLE I. EQUILIBRIUM CONSTANTS OF THE REACTION, $4/3\ PdS+H_2=1/3\ Pd_4S+H_2S$

Temp., °K	P_{H_2S}/P_{H_2}
612	3.68×10^{-2}
613	3.74×10^{-2}
622	3.50×10^{-2}
622	4.40×10^{-2}
622	4.29×10^{-2}
622	4.00×10^{-2}
663	8.94×10^{-2}
678	1.09×10^{-1}
*713	1.53×10^{-1}
731	1.84×10^{-1}
747	2.40×10^{-1}
773	3.28×10^{-1}
788	3.22×10^{-1}
791	3.75×10^{-1}
791	3.13×10^{-1}
*791	3.64×10^{-1}
795	3.08×10^{-1}

* From sulfidization side

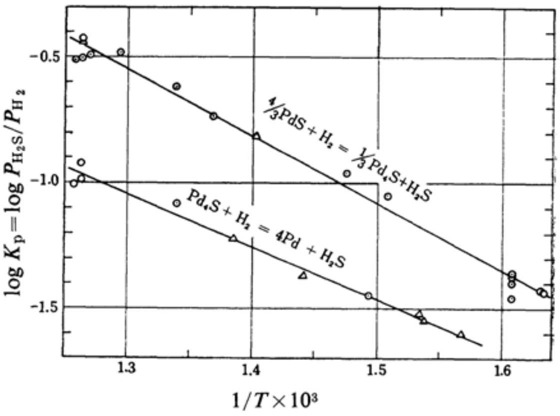

Fig. 2. Logarithm of the equilibrium constants plotted against reciprocal temperature.

$$\frac{4}{3}PdS+H_2=\frac{1}{3}Pd_4S+H_2S,\ K_p=P_{H_2S}/P_{H_2} \quad (1)$$

The logarithms of equilibrium constants are plotted against the reciprocal temperature in Fig. 2. By the least-aquare method, the following equation was derived for the standard free energy change of this reaction:

$$\Delta G^0=(12200\pm300)-(13.4\pm0.5)T$$
$$(\pm130\ \text{cal./mol. at } 613\sim798°\text{K}) \quad (1')$$

Pd_4S–Pd System.—The temperatures of the measurements ranged from 638 to 795°K. The equilibrium constants, defined below, are shown in Table II and in the lower portion of Fig. 2.

TABLE II. EQUILIBRIUM CONSTANTS OF REACTION, $Pd_4S+H_2=4Pd+H_2S$

Temp., °K	P_{H_2S}/P_{H_2}
*638	2.50×10^{-2}
*650	2.83×10^{-2}
*652	3.01×10^{-2}
670	3.57×10^{-2}
*694	4.27×10^{-2}
*722	6.00×10^{-2}
746	8.29×10^{-2}
791	1.03×10^{-1}
791	1.20×10^{-1}
795	9.87×10^{-2}

* From sulfidization side

From these values, the free energy equation can be derived as follows:

$$Pd_4S+H_2=4Pd+H_2S,\ K_p=P_{H_2S}/P_{H_2} \quad (2)$$
$$\Delta G^0=(9600\pm400)-(7.7\pm0.6)T$$
$$(\pm90\ \text{cal./mol. at } 638\sim795°\text{K}) \quad (2')$$

In Eqs. 1′ and 2′, the figures after the ± sign denote the standard deviations.

Discussion

Combining Eqs. 1 and 2 with that of the thermal dissociation of hydrogen sulfide, one can calculate the dissociation pressures of these two sulfides. Within the temperature range of this experiment, the free energy change associated with the dissociation of hydrogen sulfide is given by[2]:

$$H_2S = H_2 + \frac{1}{2}S_2 \tag{3}$$

$$\Delta G^0 = 21200 - 11.3T \tag{3'}$$

Therefore,

$$\frac{3}{8}PdS = \frac{2}{3}Pd_4S + S_2 \tag{4}$$

$$\log P(\text{atm.}) = -14600/T + 10.8 \tag{4'}$$

$$2Pd_4S = 8Pd + S_2 \tag{5}$$

$$\log P(\text{atm.}) = -13500/T + 8.3 \tag{5'}$$

and

$$2PdS_2 = 2PdS + S_2 \tag{6}$$

$$\log P(\text{atm.}) = -7330/T + 8.45 \tag{6'}$$

Here, the temperature equation for PdS_2 was calculated from the data of Biltz and Laer's measurement at three temperatures.

Next, on the basis of Eqs. 4, 5 and 6, the free energies of the formation of Pd_4S, PdS and PdS_2 are:

$$4Pd + \frac{1}{2}S_2(g.) = Pd_4S \tag{7}$$

$$\Delta G^0 = -30800 + 19.0T \tag{7'}$$

$$Pd + \frac{1}{2}S_2(g.) = PdS \tag{8}$$

$$\Delta G^0 = -32800 + 23.3T \tag{8'}$$

$$Pd + S_2 = PdS_2 \tag{9}$$

$$\Delta G^0 = -49700 + 41.7T \tag{9'}$$

The standard free energies of the formation of these sulfides at 298°K cannot be obtained because of a lack of knowledge about their heat contents.

Summary

Equilibrium measurements were carried out by a streaming method on the systems of palladium sulfides and of hydrogen-hydrogen sulfide gaseous mixtures. From the results, the dissociation pressures of PdS and Pd_4S were calculated, and the free energies of the formation of PdS_2, PdS and Pd_4S from palladium metal and sulfur diatomic gas were obtained.

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[2] K. K. Kelley, *Bur. Mines Bulletin*, No. 406 (1937).