JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 67 MAY 8, 1945 NUMBER 5

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE SCHOOL OF APPLIED SCIENCE]

Equilibrium between Solid Ferrous Chloride and Gaseous Hydrogen Sulfide at Intermediate Temperatures

BY JAMES J. LUKES,[1] CARL F. PRUTTON AND DAVID TURNBULL

Introduction

During an investigation of the joint action of hydrogen sulfide and hydrogen chloride on iron the equilibrium established between ferrous chloride and gaseous hydrogen sulfide was studied in the temperature range between 340 and 460°. It was first assumed that the reaction between these substances could be represented by the equation

$$FeCl_2(s) + H_2S(g) \longrightarrow FeS(s) + 2HCl(g) \quad (1)$$

However, preliminary work showed that, in addition to hydrogen chloride and hydrogen sulfide, hydrogen was present in the equilibrium gas mixture. Evidence has been presented in the literature which indicates that in this system hydrogen might result from one of the reactions[2]

$$2FeCl_2 + 2HCl \longrightarrow 2FeCl_3 + H_2 \quad (2)$$

$$FeS + H_2S \longrightarrow FeS_2 + H_2 \quad (3)$$

$$FeS + xH_2S \longrightarrow FeS_{1+x} + xH_2 \quad (4)$$

At lower temperatures considerable hydrogen may be formed according to (2) since Jellinek and Koop[2] found $K_p = 5.92 \times 10^2$ for this reaction at 273°. Allen and co-workers[3] found that the dissociation pressures of pyrite (FeS_2) are less than the sulfur pressures produced by dissociation of hydrogen sulfide in the temperature range 500–565° and therefore reaction (3) will occur under these conditions. Many investigations[4] have shown that sulfur may be added to ferrous sulfide to form a series of solid solutions of the general composition FeS_{1+x} in which the sulfur may be present in excess of the stoichiometric ratio by as much as 15%.

It is the purpose of this paper to show the probable reaction which leads to the presence of hydrogen in the equilibrium mixture from the reaction of ferrous chloride with hydrogen sulfide and to report the equilibrium constants for the resulting over-all reaction in the temperature range 340 to 460°.

Experimental

Materials.—Ferrous chloride was prepared by passing pure, dry hydrogen chloride over reagent grade iron wire in a quartz tube at 1000°. It was condensed in the cool portion of the tube outside of the furnace and collected in a quartz capsule sealed to the tube. This capsule was then sealed off and put aside until ready for use. Ferrous chloride prepared by the above method contained 99.7% by weight of the theoretical amounts of iron and chlorine and less than 0.01% of ferric chloride.

Hydrogen sulfide, with a manufacturer's guarantee of 99.7% purity, was dried over phosphorus pentoxide, liquefied and then distilled. Hydrogen sulfide purified by this method was absorbed by solid potassium hydroxide to the extent of 99.9% and had no detectable effect on pure dry mercury after contact with it for over a month.

In establishing the mechanism of the reaction, it was necessary in certain determinations to admit hydrogen chloride or hydrogen in the initial gas mixture. Pure hydrogen chloride was prepared from sulfuric acid and sodium chloride and purified by liquefaction followed by distillation. Hydrogen was purified by passing the gas of 99.5% purity over heated copper to remove oxygen and then over phosphorus pentoxide to remove water.

Apparatus and Procedure.—All experiments were made in the apparatus shown diagrammatically in Fig. 1. Reaction bulb B, having a volume of 175 ml., was heated to the desired temperature by means of an electrical furnace A, which consisted of a heavy steel core, uniformly wound with nichrome wire and insulated with magnesia. A maximum temperature differential of 1.2° existed along the nine-inch central section of the furnace and the reaction bulb was embedded in steel plugs in order to establish temperature uniformity within the bulb. Temperature was held constant to within ±1° by means of a Leeds and Northrup micromax controller connected to a three-junction chromel–alumel thermocouple near the heating elements.

B was connected to the mercury manometer E through

---

[1] Taken from the thesis submitted by James J. Lukes in partial fulfillment of the requirements for the Ph.D. degree. Present address: Standard Oil Company, Whiting, Indiana.

[2] Jellinek and Koop, *Z. physik. Chem.*, **145A**, 305 (1928).

[3] Allen, Crenshaw, Johnston and Larsen, *Am. J. Sci.*, **33**, 189 (1912).

[4] Hägg and Sucksdorf, *Z. physik. Chem.*, **22B**, 444 (1933).

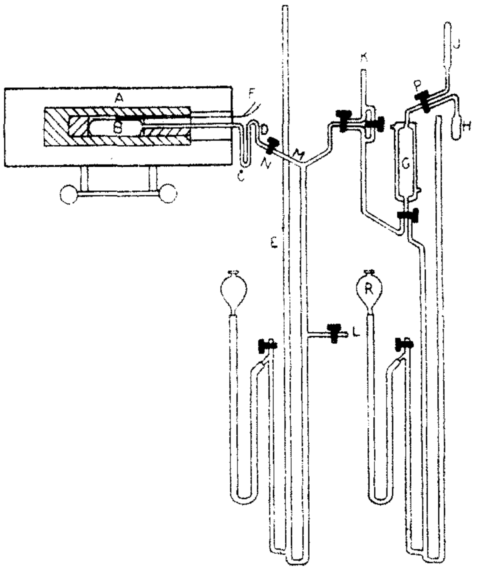

Fig. 1.—Apparatus for equilibrium study.

capillary tubing. A calibrated platinum–platinum plus 10% rhodium thermocouple, whose potential was determined with a Leeds and Northrup type K potentiometer, was used to measure bulb temperature. Manometer readings were made with a calibrated Gaertner cathetometer and were reproducible to ±0.1 mm.

In order to check the accuracy of pressure and temperature measurements, the bulb was filled at a known pressure with nitrogen at 60° and heated to 430°. After corrections were made for gas imperfection and thermal expansion of the reaction bulb, the calculated pressure was 0.09% lower than the measured pressure at 430°.

A Cenco Hyvac pump connected at K was used to evacuate the system (to 0.003–0.005 mm. of mercury). A McLeod gage and gas purification train was connected to the system at L.

Prior to equilibrium measurements the capsule containing ferrous chloride was introduced into the reaction bulb and the bulb was then evacuated. With stopcock N closed the capsule was broken in the evacuated bulb which was then placed in the furnace and sealed to the system at M. With the bulb at room temperature hydrogen sulfide was admitted at L to a given pressure. The bulb and its contents were now heated to a definite temperature which was held constant until equilibrium was established. Four days were usually required for equilibrium to be reached. Since the same total final pressure was obtained whether the temperature under investigation was approached by cooling from a higher temperature or by heating from a lower temperature, it may be assumed that equilibrium was established.

After equilibrium had been reached the gas mixture was withdrawn into the evacuated gas measuring bulb G where the pressure and temperature were determined. The mixture was then forced into bulb H containing potassium hydroxide, which had been thoroughly outgassed at 300° under vacuum. After absorption was complete the residual gas was returned to G and its pressure measured. To test the residual gas for hydrogen it was passed into bulb J containing copper oxide heated to 280–300°. A visible condensate forming at this time on the cooler walls of the tubes leading to J indicated that water was produced in the reaction. When the pressure in J became constant it was cooled and the final pressure measured. These pressures were found to be in all runs only a few millimeters above the vapor pressure of water. When correction was made for the vapor pressure of water it was found in most experiments that from 3 to 5 molar per cent. of the equilibrium gas mixtures had reacted with the copper oxide and that the residual gas after absorption in bulb J in excess of water vapor amounted to less than 0.1 molar per cent. of the equilibrium mixture in all determinations. It is reasonable to assume that the gas which was not absorbed by potash but which reacted with copper oxide was hydrogen.

As a further check upon the gas concentrations found by pressure measurements, chemical analyses for chloride and sulfide were run on the potassium hydroxide in bulb H after absorption. Chloride was determined potentiometrically and sulfide was oxidized by bromine to sulfate and determined as barium sulfate. Corrections were applied for the sulfide and chloride found in the original potassium hydroxide.

Although the amounts of hydrogen sulfide and hydrogen chloride found in the equilibrium mixture by chemical analysis checked the amounts calculated from pressure measurements within experimental error, the latter was considered more accurate and equilibrium constants were thus calculated from pressure measurements. This calculation was made in the following manner. Let

P^0_{HCl}, $P^0_{H_2S}$, $P^0_{H_2}$ be partial pressures of the designated gases at the reaction temperature before any reaction has taken place.

P_{HCl}, P_{H_2S}, P_{H_2} be partial pressures of the designated gases at equilibrium.

P be the final total pressure at equilibrium

then

$$P_{HCl} = 2(P - P^0_{H_2} - P^0_{H_2S}) - P^0_{HCl}$$

Initial partial pressures of hydrogen and hydrogen chloride appear in the above expressions since in some experiments measured amounts of these gases were added in the starting mixture. Corrections were made in the calculations for bulb expansion and for the low temperature of the capillary tubing, C.

Discussion

Table I summarizes the equilibrium pressures of the various gases at various temperatures resulting from the reaction of hydrogen sulfide with ferrous chloride. This table shows that partial pressures of hydrogen chloride and hydrogen sulfide calculated from chemical analyses were in good agreement (within 2–3%) with those calculated from pressures measurements. Observations made on the rate of attainment of equilibrium suggested that hydrogen was formed by a very slow reaction. After temperature equilibrium was established in the reactor the reaction proceeded quite rapidly and in about five hours the total pressure became nearly constant. At this point the pressure could be reproduced by heating the reaction mixture up 10° and then cooling to the initial temperature. Nevertheless the total pressure drifted up very slowly and became constant only after a period of four days had elapsed since the start of the reaction. This slow pressure increase amounted in all to about 15 mm. and was attributed to the slow formation of hydrogen by one of the reactions (2), (3) or (4).

It does not appear that hydrogen could have been formed by reaction (2) since no trace of ferric chloride was ever detected by analytical means in the cool portions of the connecting capillary C. Due to its high volatility any ferric chloride formed would have distilled into this capillary at the temperatures of the investigation. Furthermore, addition of a considerable pressure of hy-

TABLE I

SUMMARY OF EQUILIBRIUM PRESSURES AND CONSTANTS FOR THE REACTION BETWEEN FERROUS CHLORIDE AND HYDROGEN SULFIDE

Temp., °C.	Initial pressures in atmospheres			Equilibrium pressures, atmospheres: From pressure measurements			From chemical analysis		$K_p = P_{H_2}^{0.14}(P_{HCl})^2/P_{H_2S}^{1.14}$
	H_2S	HCl	H_2	H_2S	HCl	H_2	H_2S	HCl	
343.7	0.780	...	...	0.456	0.567	0.041	...	...	0.502
351.3	1.030	...	0.088	.627	.709	.137	...	...	.649
352.8	0.820	0.232	...	.557	.692	.033	...	0.701	.579
367.1	.880	...	...	.451	.748	.055	0.446	0.759	.925
383.4	.774	.857	...	.619	1.129	.020	...	1.111	1.268
392.3	.745	...	.429	.330	0.739	.474	.317	0.748	1.746
392.9	.758	...	...	.300	.803	.056	.296	.812	1.702
411.5	.624	...	...	.196	.748	.054	...	.762	2.393
432.9	.366	.513	...	.156	.876	.029	.158	.886	3.864
455.6	.767	...	...	.133	1.080	.105	.136	1.074	...

drogen initially did not materially depress the amount of hydrogen formed in the reaction (see temperatures 351.3 and 392.3 in Table I) as would be expected if hydrogen were formed by reaction (2).

Next to be considered is the possibility that hydrogen was formed by reaction (3). If this were the case then at equilibrium the ratio P_{H_2}/P_{H_2S} should be constant. Table II shows the value of this ratio at several temperatures for different initial pressures of hydrogen.

TABLE II

K_p VALUES CALCULATED UPON ASSUMPTION THAT HYDROGEN IS FORMED BY REACTION (3)

Temp., °C.	$P^0_{H_2}$, atm.	$K_p = P_{H_2}/P_{H_2S}$	K_p from thermodynamic data
351.3	0.088	0.2190	0.110
352.8	.000	0.0594	.108
392.3	.429	1.436	.061
392.9	.000	0.188	.061

At the lower two temperatures and at the upper two temperatures the ratios diverge by a far greater amount than can be accounted for by the small temperature differences. Furthermore this ratio differs markedly from K_p values, shown in the last column of Table II, calculated from thermodynamic data listed by Kelley.[5] Thus, if equilibrium had been established in the system, the presence of hydrogen could not have been due to reaction (3).

If it is assumed that hydrogen was formed by reaction (4) then $1 + x$ in the formula FeS_{1+x} should be given by $(A + B)/A$ where A is the amount of the initial hydrogen sulfide which was involved in the formation of hydrogen chloride and B is the amount of the initial hydrogen sulfide which was involved in the formation of hydrogen. Table III lists the values of these ratios calculated from the experimental data at various temperatures and they deviate very little from the average value of 1.14.

Constancy of these values of $1 + x$ for the

TABLE III

AMOUNTS OF HYDROGEN SULFIDE GOING TO FORM HYDROGEN AND HYDROGEN CHLORIDE IN THE REACTION OF HYDROGEN SULFIDE WITH FERROUS CHLORIDE

Temp., °C.	A Pressure of initial HCl formation, atm.	B H_2S involved in H_2 formation, atm.	$(A + B)/A = 1 + x$
343.7	0.283	0.0407	1.14
351.3	.355	.0494	1.14
352.8	.230	.0330	1.14
367.1	.374	.0553	1.15
383.4	.136	.0193	1.14
392.3	.370	.0454	1.12
392.9	.401	.0563	1.14
411.5	.375	.0541	1.15
432.9	.136	.0195	1.14
455.6	.530	.1046	1.20

various determinations furnishes convincing evidence that hydrogen is formed in this system according to reaction (4). It was observed that the sulfides formed in this reaction were attracted by a strong alloy magnet, which would be expected since solid solutions of sulfur in ferrous sulfide are known to be magnetic. Further confirmation of this mechanism is offered by the work of Roberts,[6] who found a limiting composition of $FeS_{1.14}$ for solid solutions of sulfur in ferrous sulfide at 300° Haraldsen[7] found a limiting composition of $FeS_{1.15}$ at 330°.

In view of this evidence it appears that the equilibrium in the system under investigation is reached by an initial rapid reaction (1), which is virtually completed in a few hours, followed by a slow reaction (4) which requires several days to go to completion. In order to represent the overall equilibrium in the system equations (1) and (4) may be combined to give

$$FeCl_2(s) + 1.14H_2S(g) \longrightarrow FeS_{1.14}(s) + 2HCl(g) + 0.14H_2(g) \quad (5)$$

K_p values for this reaction, $K_p = P^2_{HCl}P^{0.14}_{H_2}/P^{1.14}_{H_2S}$, are collected in Table I. When $\log_{10}K_p$ is plotted against $1/T$ a straight line is obtained as is

---

[5] Kelley, Bur. of Mines Bull., **406**, 21 (1937).

[6] Roberts, THIS JOURNAL, **57**, 1034 (1935).

[7] Haraldsen, *Z. anorg. Chem.*, **246**, 195 (1941).

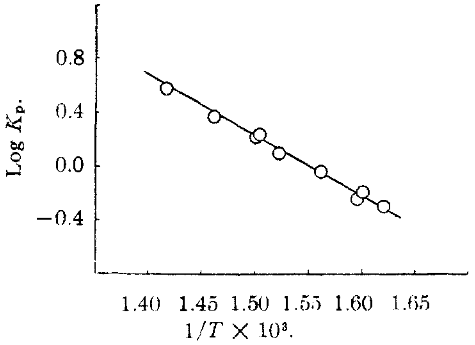

Fig. 2.—Plot of log K_p *vs.* $1/T$ for the reaction: $FeCl_2(s) + 1.14H_2S(g) \rightarrow FeS_{1.14}(s) + 2HCl(g) + 0.14H_2S(g)$.

shown in Fig. 2. This line may be represented by the equation

$$\log_{10}K_p = -(4{,}320/T) + 6.71$$

From this we find that the heat of reaction (5), ΔH, assumed to be constant with temperature, is 19,800 calories.

It is not certain whether the composition $FeS_{1.20}$ calculated at 456° is in error or whether the solubility of sulfur at this temperature is sufficiently large to account for this composition. $\log_{10}K_p$ calculated from this run is not plotted in Fig. 2.

Acknowledgment.—The authors gladly acknowledge many helpful discussions with Professor S. H. Maron of the Chemistry Department and Professor R. L. Barrett of the Department of Geology and Mineralogy.

Summary

An experimental study has been made of the equilibrium relationships existing between solid ferrous chloride and gaseous hydrogen sulfide at intermediate temperatures. For the temperature interval of 620–706°K., pyrrhotite (a solid solution of sulfur in FeS) is formed rather than ferrous sulfide. Equilibrium constants were determined for the reaction: $FeCl_2(s) + 1.14H_2S(g) = FeS_{1.14}(s) + 2HCl(g) + 0.14H_2(g)$. In the temperature interval the relation $\log_{10}K_p = (-4{,}320/T) + 6.71$ was found between K_p and T.

CLEVELAND, OHIO RECEIVED JANUARY 27, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Equilibrium Relationships between Fluid Interfaces: the System Methylene Iodide–Water–Air[1]

BY WILLIAM FOX

Material relating to the equilibrium relationships between interfaces at their mutual edge has been included in most discussions of capillary phenomena since the earliest considerations of the subject.

For the condition where three phases meet at a common edge and one of the phases is a solid it has long been stated[2] that

$$T_{31}\cos\theta + T_{12} = T_{23} \qquad (1)$$

where T is defined as the superficial tension of the interface acting on the mutual edge in a direction parallel to the respective interface (2 refers to the solid phase). Equation 1 is generally recognized as a fundamental equation of capillarity, but its use has never been experimentally justified.

For the condition where all three phases are fluids, it has been believed by many[3] that "If the three fluids can remain in contact with one another, the sum of any two of the quantities (referring to the tensions of the interfaces) must exceed the third, and by Neumann's rule the directions of the interfaces at the common edge must be parallel to the sides of a triangle, taken proportional to T_{12}, T_{23}, T_{31}. If the above-mentioned condition be not satisfied, the triangle is imaginary, and the three fluids cannot rest in contact, the two weaker tensions, even if acting in full concert, being incapable of balancing the strongest."

Where "pure" fluid phases were concerned, Rayleigh[4] has argued that from the hypothesis of Thomas Young "We are thus led to the important conclusion, so far as I am aware hitherto unnoticed, that according to this hypothesis Neumann's triangle is necessarily imaginary, that one of the three fluids will always spread upon the interface of the other two."

From Laplace, Rayleigh concludes that "According to Laplace's hypothesis, then, three fluids cannot rest in contact, but the case is altered if one of the bodies be a solid."

Those who attempted to investigate experimentally the utility of the relationships that might exist between three fluid interfaces at an edge of contact, were faced with difficulties in-

---

(1) Dissertation submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University. This material was included in paper number 16, delivered before the Division of Physical and Inorganic Chemistry at the 108th meeting of the American Chemical Society, New York, N. Y., September 12, 1944.

(2) Thomas Young, "Works," by Peacock, Vol. I, p. 464 (1855). Terminology is that used by Lord Rayleigh.[4]

(3) (a) Article on Capillary Action, 11th edition of Encyclopedia Brittanica. Article by J. C. Maxwell, revised by Lord Rayleigh. The quotation included here is Lord Rayleigh's. (b) See also Franz Neumann, Vorlesungen über die Theorie der Capillarität, pp. 161–163, B. G. Teubner, Leipzig, 1894.

(4) Lord Rayleigh, "Scientific Papers," Vol. III, pp. 414, 416.