

# ACTIVITY COEFFICIENT OF SULPHUR IN PYRRHOTITE

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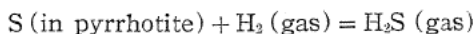
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In order to write the equilibrium constant of chemical reaction including activity of solutions, it is necessary that the activity, or the activity coefficient and the concentration of each component in solutions are made known. In a special case, of course, the activity may be equal to the concentration, but, generally speaking, such an ideality is scarcely ever encountered in actual cases. When a reaction takes place in solid solutions, experimental determination of the activity of each component needs a measurement lasting for many hours on account of slow establishment of chemical equilibrium. Therefore, only a few publications regarding to experimental data of the activity coefficient of a component in solid solutions has been reported in spite of their metallurgical importance.

However, in contrast with the difficulty of experimental determination, the activity coefficient of a component in solid solutions can be also calculated easily by a statistical method without observation of the equilibrium condition.

The purpose of this investigation was not only to determine the activity coefficient of sulphur in pyrrhotite by the experimental measurement, but also to compare these results with those calculated from the statistical method. An experiment was made of the conditions of equilibrium in the reaction between hydrogen gas and sulphur dissolved in pyrrhotite. Chemical equation for this reaction can be written as follows:



## Experimental Details

### 1) Materials

#### a) *Pyrrhotite*

Two kinds of pyrrhotite were used. The one was prepared by reaction of pure hydrogen sulphide on ferric oxide at 450° C for 36 hr, while the other was obtained by the reaction on metallic iron.

Ferric oxide was prepared by ignition of recrystallized cryohydrate of ferric nitrate made from electrolytic iron. Metallic iron was obtained by reduction of thus prepared ferric oxide with hydrogen at 800° C for 5hr.

#### b) *Hydrogen sulphide*

Hydrogen sulphide gas was generated in kipp's apparatus by the reaction of pure synthetic hydrochloric acid on iron sulphide and washed by bubbling the

gas in succession through potassium sulphide solution, hydrochloric acid solution of chromous acetate and hydrochloric acid (1:4), and then dried over calcium chloride and phosphorous pentaoxide.

### c) Hydrogen

Hydrogen obtained by the reaction of pure sulphuric acid (1:5) on electrolytic zinc was purified by passing it through potassium hydroxide solution (1:1), potassium permanganate solution, calcium chloride drier, the heated Pt-asbestos and phosphorous pentaoxide.

## 2) Apparatus

The experimental arrangement was shown in Fig. 1. The total volume of space occupied by the gas throughout the all system was about 600 cc. In the follows description of each part is made:

$F_1$ : a nichrome resistance furnace for heating the reaction tube, of which the range of effective control part is 7 cm with the uniformity of  $\pm 2^\circ\text{C}$  at the experimental temperature.

$F_2$ : a nichrome resistance furnace, connected in series with  $F_1$ , for controlling the temperature of the latter.

A: a reaction tube (2.2  $\times$  50 cm), made of glass, connected to the other part of the apparatus with a ground glass joint.

B: a porcelain boat (1.5  $\times$  2.5  $\times$  8 cm).

T: a trap for condensing hydrogen sulphide.

D: a Dewar's vessel for cooling the trap T by liquid oxygen.

S: a pump circulating the reaction gas throughout the system.

M: a mercury manometer.

R: a mercury reservoir movable by means of connecton.

P: a phosphorous pentaoxide tube.

$G_1, G_2, G_3$ : glass valves able to stop excessive flowing of mercury.

J: almel-chromel thermocouple.

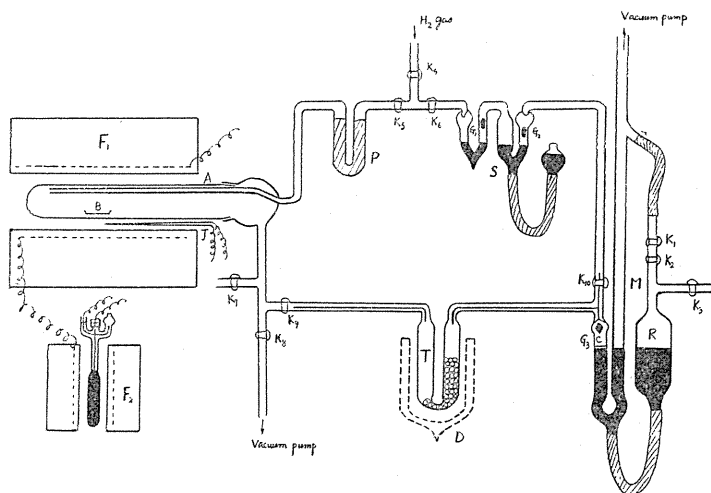


FIG. 1. Experimental arrangement.

### 3) Experimental Procedure

Considering, beforehand, the mutual relation among the sulphur content of pyrrhotite to be estimated, the equilibrium composition of gaseous mixture expected and the volume of the gaseous space in the apparatus, the amounts of the sample weighed in the boat *B* was selected to be 2.5, 2, 1.5 g. etc. so that the sulphur content of the solid phase, when the equilibrium state was attained, might be within the limits of its solubility in pyrrhotite. The boat *B* containing the sample was placed at a position nearly in the middle of the reaction tube *A* and then the whole system was evacuated to remove the absorbed substances which might be present within the apparatus. When high vacuum was attained, keeping mercury level of manometer at the constant position *C*, the purified hydrogen gas was admitted into the reaction system through the cock *K*<sub>1</sub>. The experimental temperature was 440°C. It required the time from 24hr to 30hr to attain to the equilibrium state, but the experiment was lasted from 36hr to 48hr to make sure of it.

When the equilibrium state was attained, the cocks *K*<sub>9</sub>, *K*<sub>10</sub> were closed and the total pressure in the trap *T* was observed under the condition of the constant temperature and volume and then the trap *T* was cooled with liquid oxygen contained in the Dewar's vessel *D* and the trap was evacuated through the cock *K*<sub>8</sub>.

After high vacuum was obtained, the cock *K*<sub>9</sub> was closed and the vessel *D* was removed and solid hydrogen sulphide in the trap *T* was vapourized and its partial pressure was measured.

Sulphur content of pyrrhotite was determined by the following analytical method: 0.5 g. of the sample was brought into solution with HNO<sub>3</sub> and KClO<sub>3</sub>, and repeatedly evaporated to dryness after addition of HCl. Precipitating ferric hydroxide from the solution, sulphur was estimated as BaSO<sub>4</sub>.

### 4) Experimental Results

Results of the measurement were shown in Table 1. In Fig. 2,  $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$  was plotted against sulphur content in pyrrhotite. Owing to imperfect deoxidation of pyrrhotite, the values of No. 4 and 6 were extraordinarily higher than those of the other cases; these pyrrhotite were those prepared by reaction of pure hydrogen sulphide on ferric oxide. (It is possible to suppose that their values are high owing to the presence of SO<sub>2</sub> formed by reaction with trace of oxides as suggested by Rosenquist.<sup>2)</sup>) From the relation in the figure, it may be said that Raoult's law does not hold for sulphur in pyrrhotite.

TABLE 1. Experimental Results

No. of Exp.	P <sub>total</sub> (mm)	P <sub>H<sub>2</sub></sub> (mm)	P <sub>H<sub>2</sub>S</sub> (mm)	P <sub>H<sub>2</sub>S</sub> /P <sub>H<sub>2</sub></sub>	Sulphur Contents of Pyrrhotite FeS <sub>1+x</sub> : 1 + x
1	724.0	670.0	54.0	0.081	1.076
2	703.0	504.5	198.5	0.393	1.123
3	738.2	434.3	303.9	0.700	1.144
4	676.7	282.8	393.9	1.392	1.083
5	722.0	257.6	464.4	1.803	1.189
6	712.1	248.6	463.5	1.864	1.135

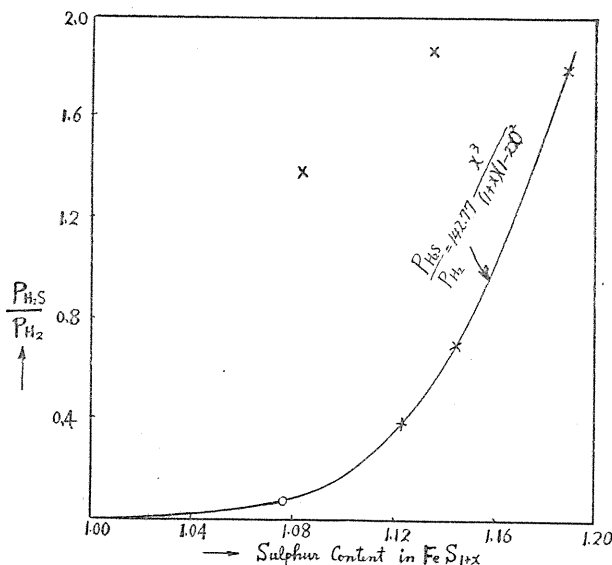
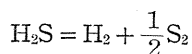


FIG. 2. Relation between ratio  $P_{H_2S}/P_{H_2}$  and sulphur content of pyrrhotite  $FeS_{1+x}$ .  
 × : Sample 1. — Prepared by reaction of hydrogen sulphide on ferric oxide.  
 ○ : Sample 2. — Prepared by reaction of hydrogen sulphide on metallic iron.

Statistical Calculations

It may be considered that pyrrhotite has the same crystal structure of NiAs type as FeS but it contains a excess amount of sulphur on account of the structure consisting of vacant lattice position. Therefore, Takeuchi's method<sup>1)</sup> to calculate the equilibrium constant of reduction of Wüstite by hydrogen can be also applied similarly to this case of pyrrhotite.

The equation for the reaction in the gaseous phase may be written as follows :



When the equilibrium was attained

$$\lambda_{H_2}[\lambda_{S_2}]^{1/2} = \lambda_{H_2S}$$

then

$$[\lambda_{S_2}]^{1/2} = \frac{n_{H_2S}}{n_{H_2}} \frac{f_{H_2} e^{-X_{H_2}/kT}}{f_{H_2S} e^{-X_{H_2S}/kT}} \tag{1}$$

where  $\lambda$  : absolute activity,  $n$  : number of molecule,  
 $f$  : partition function,  $X$  : excess energy.

Supposing that  $N$  is number of iron atom,  $N_0$  is number of holes,  $\zeta$  is energy required for formation of one hole,  $\xi$  is exchange energy of electron,  $K(T)$  is partition function of FeS couple, then the partition function of solid phase  $\Gamma_s$  is represented as follows ;

$$\Gamma_s = [K(T)]^{N_1+N_0} \frac{(N_1+N_0)!}{N_1!N_0!} e^{-N_0\zeta/kT} \frac{N_1!}{(2N_0)!(N_1-2N_0)!} e^{-2N_0\xi/kT}$$

For free energy of solid phase, we have

$$F_s = -KT \ln \Gamma_s \quad (2)$$

and for free energy of gaseous phase

$$F_g = -KT \ln \frac{1}{n_{S_2}!} (f_{S_2} e^{-x_{S_2}/kT})^{n_{S_2}} \quad (3)$$

By means of Stirling's formula, the equilibrium condition becomes, from (2) and (3), as follows;

$$[\lambda_{S_2}]^{1/2} = \left[ \frac{n_{S_2}}{f_{S_2} e^{-x_{S_2}/kT}} \right]^{1/2} = \frac{4}{K(T)} \frac{(N_0)^3}{(N_I + N_0)(N_I - 2N_0)^2} e^{(2\zeta + \xi)/kT} \quad (4)$$

Now then, put  $\frac{N_0}{N_I} = x$ ,

$$\frac{4}{K(T)} e^{(2\zeta + \xi)/kT} \frac{f_{H_2S}}{f_{H_2}} \frac{e^{-x_{H_2S}/kT}}{e^{-x_{H_2}/kT}} = \alpha(T),$$

from (1) and (4)

$$\frac{n_{H_2S}}{n_{H_2}} = \frac{x^3}{(1+x)(1-2x)^2} \alpha(T),$$

since

$$P_{H_2S} V = n_{H_2S} kT, \quad P_{H_2} V = n_{H_2} kT,$$

then

$$\frac{P_{H_2S}}{P_{H_2}} = \frac{x^3}{(1+x)(1-2x)^2} 2 \alpha(T),$$

where  $\alpha(T)$  is an unknown function which must be evaluated from one value of a experimental couple of  $P_{H_2S}/P_{H_2}$  and  $x$ .

From the experimental data  $P_{H_2S}/P_{H_2} = 0.081$  and  $x = 0.076$ ,  $\alpha(T)$  can be calculated to be 142.77. Substituting this value in the above equation, we obtain

$$\frac{P_{H_2S}}{P_{H_2}} = 142.77 \frac{x^3}{(1+x)(1-2x)^2}.$$

In Fig. 2, the curve expressed by this equation was shown in comparison with the observed values. It may be said that the activity of sulphur in pyrrhotite can be calculated by the statistical method from one value of experimental measurement;  $P_{H_2S}/P_{H_2}$  is the value being in proportionate to activity in pyrrhotite.

### Summary

- 1) This study was made of the equilibrium conditions in the reaction between hydrogen gas and various solutions of sulphur in pyrrhotite at 440° C.
- 2) The experimental results show that activity coefficient of sulphur in pyrrhotite is considerably deviated from unity at 440° C.
- 3) The equilibrium relation obtained by the statistical calculation is in good agreement with the experimental one.

### Reference

- 1) S. Takeuchi and K. Igaki: Nippon Kinzoku Gakkai 14 (1950), 23.
- 2) T. Rosenquist: J. Iron Steel Inst. 176 (1954), 37.