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Solubility Constants and Free Enthalpies of Metal Sulphides, Part 6[1]:

A New Solubility Cell

By

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With 1 Figure

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A solubility cell which can be operated continuously over the temperature range 5–95 °C has been developed. The solubility of $Fe_{0.88}S$ (monoclinic pyrrhotite) in solutions

$$S_0 = ([H^+] = H\ m, [Na^+] = (1.00 - H)\ m, [ClO_4^-] = 1.00\ m)$$

at fixed partial pressures of H_2S has been investigated at 50.7 °C. The hydrogen ion concentration and the total concentration of iron(II) ion in equilibrium with the solid phase was determined by e.m.f. and analytical methods respectively. The data were consistent with

$$\log {}^*K_{pso} = \log \frac{[Fe^{2+}] p_{H_2S}}{[H^+]^2} = 3.80 \pm 0.10\ [50.7°C, 1\ m(Na)ClO_4]$$

according to the overall reaction

$$1.14\ Fe_{0.88}S_{(s)} + 2\ H^+_{(I=1m)} \rightleftarrows Fe^{2+}_{(I=1m)} + H_2S_{(g)} + 0.14\ S_{(s)}$$

1. Introduction

In order to obtain reliable solubility constants for metal sulphides, carbonates, hydroxides and oxides in aqueous media at elevated temperatures, a continuously operating solubility cell has been developed by modifying a cell described earlier[2]. Since solubility equilibria are sometimes established very slowly, evaporation and condensation rates have been kept as low as possible. Intimate contact between solid phase and solvent desirable for a high dissolution rate, was effected by percolation, thus avoiding excessive stirring which often results in supersaturated solutions. A constant gas atmosphere was maintained throughout the solubility measurements. Using the new cell, the solubility of monoclinic pyrrhotite, $Fe_{0.88}S$, was studied at 50.7 °C by an e.m.f. method, similar to that described previously[1]. Preliminary experiments have shown that this solid could not be equilibrated in aqueous solutions at room temperature within reasonable time intervals.

2. Experimental

2.1. *Procedure*

Solution $S_0([\mathrm{H}^+] = H\,m,\ [\mathrm{Na}^+] = (1.00 - H)\,m,\ [\mathrm{ClO_4}^-] = 1.00\,m)$ were equilibrated with solid $Fe_{0.88}S$ at varying partial pressures of H_2S. In the resulting solutions S the total concentrations of iron(II) ions were determined photometrically with o-phenanthroline[3]. The hydrogen ion concentration was followed using a galvanic cell

$$\mathrm{Ag, AgCl}\ \left|\begin{matrix}0.990\,m\ \mathrm{NaClO_4}\\ 0.010\,m\ \mathrm{NaCl}\end{matrix}\right. \vdots\ 1.000\,m\ \mathrm{NaClO_4}\ \Big|\ S_0 \text{ or } S\ \Big|\ \text{glass electrode}\quad [A]$$

At constant ionic strength the *Nernst* equation of cell $[A]$ may be written as

$$E = E_0 + \frac{R\,T \ln(10)}{F} \log[\mathrm{H}^+] + E_j \qquad (1)$$

A plot of $E - \frac{R\,T \ln(10)}{F} \log[\mathrm{H}^+]$ versus $[\mathrm{H}^+]$ at 50.7 °C and $I = 1.00\,m$ resulted in a straight line with slope -0.051 V/m. Thus the working equation was

$$E = E_0 + 0.06426 \log[\mathrm{H}^+] - 0.051\,[\mathrm{H}^+] \qquad (2)$$

The cell was calibrated frequently with solutions S_0.

Constant e.m.f. readings indicating equilibrium in solutions S were obtained within 48 hours.

2.2. *Materials*

Monoclinic pyrrhotite was prepared from reagent grade iron(III) oxide. The oxide was heated in a stream of CS_2 and CO_2 for 10 hours at 800 °C and then cooled to room temperature. According to *Adami* and *King*[4] this procedure should give stoichiometric hexagonal pyrrhotite. In this work, however always a mixture of metal deficient monoclinic and hexagonal phases respectively were obtained. The pure monoclinic phase was prepared by heating these mixtures for 15 hours at 280 °C in evacuated quartz tubes. Sulphur was determined by a standard iodometric technique[3] (% $S_{calc.} = 39.62$; found 39.44). The iron content was determined by the X-ray method of *Arnold*[5] (% $Fe_{calc.} = 60.38$; found 60.59). The X-ray pattern of the monoclinic phase agreed with ASTM 17-200. Hydrogen sulphide (99.85% H_2S) and a hydrogen sulphide/nitrogen mixture (9.8% H_2S) were taken from cylinders. All solutions were prepared according to the procedures described previously[6].

2.3. *Apparatus*

The solubility cell, as drawn in Fig. 1, consists of a reaction compartment (1) separated from the measuring compartment (2) and the filtrate compartment (3) by sintered glass frits (*a*). The solid compound is reacted in (1) with ca. 80 ml of solution S_0 which percolates through (*a*) into the filtrate compartment (3) where hydrogen sulphide is bubbled through the solution. Gradually the level of the solution in (3) increases until the end of the solvent-recycling tube (*c*) is reached. Then the gas stream pushes a few ml of the solution into (1), thus closing the cyclic process. In order to avoid evaporation the H_2O partial pressures of the incoming and leaving gas are kept low and essentially equal by leading it through two similar condensers. The electrodes, the thermometer and the condenser for the leaving H_2S are mounted through the four ground joints of the cover (4). Both the reference electrode and the solubility cell are thermostatted by a water jacket (5). The e.m.f. was measured with a digital pH-meter (Beckman, type 4500).

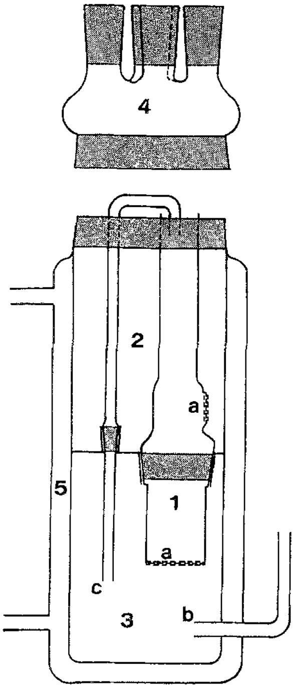

Fig. 1. Solubility cell: *1* reaction compartment, *2* measuring compartment, *3* filtrate compartment, *4* cover, *5* water jacket, *a* glass frits, *b* gas inlet, *c* solvent recycling tube

3. Results and Discussion

To ensure that true equilibrium was established H and p_{H_2S} were varied over a range of 10^{-1} to 10^{-3} m and 0.9 to 0.09 atm respectively.

The pertinent data are summarized in Table 1. The errors quoted are standard deviations.

Table 1. *Solubility of* $Fe_{0.88}S$ *at 50.7 °C and* $I = 1.00$ *m* $(Na)ClO_4$

$10^3 H$	$10^3 (H - [H^+])/2$	$10^3 [Fe^{2+}]_{tot}$	p_{H_2S}	$-\log [H^+]$	$\log {}^*K_{pso}$
	mole/kg H_2O		atm		
100.7	49.01	49.52	0.816	2.567	3.74_1
100.7	49.03	50.65	0.823	2.573	3.76_7
30.0	14.27	14.72	0.827	2.833	3.75_0
30.0	14.32	14.40	0.812	2.863	3.79_5
30.0	14.33	14.86	0.840	2.870	3.83_6
10.0	4.60	4.90	0.832	3.101	3.81_3
10.0	4.63	4.65	0.824	3.129	3.84_2
3.0	1.30	1.32	0.825	3.390	3.81_7
3.0	1.30	1.20	0.837	3.392	3.78_5
1.0	0.39	0.44	0.824	3.656	3.87_1
1.0	0.35	0.43	0.826	3.524	3.59_8
1.0	0.35	0.44	0.817	3.525	3.60_6
1.0	0.38	0.44	0.816	3.628	3.81_1
100.7	49.90	54.60	0.0813	3.043	3.73_3
30.0	14.81	15.09	0.0826	3.429	3.95_5
10.0	4.89	4.38	0.0810	3.670	3.89_0
3.0	1.45	1.24	0.0814	3.979	3.96_2

Plots of $\log ([Fe^{2+}]_{tot} \cdot p_{H_2S})$ versus pH were linear giving a slope of -1.93 ± 0.06. This is in reasonable accordance with the overall reaction (3)

$$1.14\, Fe_{0.88}S_{(s)} + 2\, H^+_{(I=1m)} \rightleftarrows Fe^{2+}_{(I=1m)} + H_2S_{(g)} + 0.14\, S_{(s)} \qquad (3)$$

The average value for the solubility constant is

$$\log {}^*K_{pso} = 3.80 \pm 0.10\ [50.7\ °C,\ I = 1\ m\,(Na)ClO_4].$$

The values of column 2 and 3 in Table 1 are in fair agreement, consequently indicating the absence of iron species other than Fe^{2+}. It should be emphasized, however, that solubility data are comparatively insensitive to the formation of weak complexes[7] e.g. $Fe(SH)^+$. These species should therefore be investigated separately in homogeneous solutions.

No direct comparison of our results and previous data is possible. Using the results of *Pohl*[8], and the *Davies* approximation[9] of the *Debye—Hückel* equation, we calculated for the respective solubility constant at ionic strength zero

$$\log {}^{T*}K_{pso} = 3.71 \quad (25\ °\mathrm{C},\ I = 0).$$

According to the results of *Berner*[10] this value shows that monoclinic pyrrhotite has about the same thermodynamic stability as greigite Fe_3S_4. Further work on the solubilities of synthetic and natural iron sulphides is now under progress.

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