

Solubility of Iron Sulfides

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INFORMATION on the forms in which iron sulfides deposit from aqueous solutions, on how solubility changes with temperature and composition of the solution, and on the kinetics and mechanism for formation and dissolution (24), makes it possible to understand more fully the deposition of sulfides within ferrous metal process systems containing sulfide liquors, and to prescribe measures for abatement of troubles that may arise.

Using normal chemical concepts of ionic equilibrium and its shift with ionic concentrations and temperature, and the limited data available, predicted magnitudes and changes of concentration are calculated and compared with existing values. The amount of iron which can remain in solution with H₂S present is temperature-sensitive. In one large scale plant process to which these derived data were applied, the dual temperature process for heavy water production (3), this temperature sensitivity of solubility was in the required direction and magnitude to explain the behavior of troublesome depositions. Addition of predicted amounts of base to the entering water stream was a remedy.

NATURE OF SOLID PHASES

In flowing aqueous systems containing sulfides such as dissolved H₂S, in which water flows through ferrous metal apparatus and temperature changes are taking place, the character of the sulfide deposits varies. At low temperature (about 25° C.), troilite—FeS_{1.01}—is deposited; from about 40° to 150° C., pyrrhotite—FeS_{1.01-1.05}—from about 155° to over 210° C. marcasite—FeS₂. The high temperature deposits may often be dense marcasite, but more often are long, thin needles of marcasite with some sulfur (present as the result of some oxidation, probably accidental). This soft and bulky matrix has little physical strength, and is flammable. The pyrrhotite deposits are generally hard, dense, and crystalline. The crystals vary from microscopic to easily visible crystals 1 to 2 mm. in diameter.

While precipitation of iron sulfide by H₂S from a solution of ferrous ion at near room temperature has been considered as producing FeS, it is now apparent that this is not the case, at least at somewhat elevated temperatures. At higher temperatures, other forms of iron sulfide, richer in sulfur, are produced. The work of Anderson (2) on this and other nonstoichiometric compounds proves that, strictly speaking, FeS does not exist; only forms of compositions FeS_{1.01} to FeS_{1.2} and FeS₂ exist. Compositions approximating FeS_{1.01} crystallize as troilite; those near FeS_{1.2} crystallize as pyrrhotite, and are magnetic; those of FeS₂ crystallize as marcasite or pyrite. Of the latter two, marcasite is the more unstable up to 450° C., as judged by the 5.6 kcal. per mole difference in heats of formation at 20° C. [ΔH (pyrite) = 42.5 kcal. per mole; ΔH (marcasite) = 36.9 kcal. per mole, (20)]. That marcasite rather than pyrite forms below 450° C., despite the thermodynamic favoring of pyrite, must be due to the rate of deposition. If high, it will not permit time for the more stable pyrite to form.

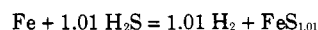
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SOLUBILITY OF IRON SULFIDES

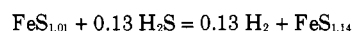
The amount of iron that can remain in aqueous solution with H₂S present is temperature-sensitive. The principal cause of the drop in solubility with increase of temperature from, say 40° to 120° C., is the change in magnitude of the constants for both the FeS solubility product and the secondary dissociation of H₂S. A second, smaller effect is probably introduced by the shift in equilibrium governing the troilite-pyrrhotite change. A still smaller effect is due to the drop in solubility of H₂S in water. In the higher temperature range, say 160° to 210° C., marcasite is the principal deposit. Here another factor enters: formation of the highly insoluble FeS₂.

The cardinal reactions resulting in formation of sulfide deposits are:

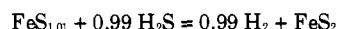
Troilite formation



Pyrrhotite formation



Marcasite or pyrites formation



In the following calculations for troilite, which is expressed chemically more accurately as FeS_{1.01} than as FeS, convention is followed with but small error by considering it as straight FeS in the equations. In the case of pyrrhotite, where the formula deviates more widely from integral units, the deviation from integral stoichiometry is taken into account.

The solubilities to be evaluated may be divided into: solubility of iron sulfides in water to which only acid or base is added—i.e., the only source of sulfide is the original iron sulfide; and solubility of iron sulfides in water to which other sulfide—e.g., H₂S, NaHS—and acid or base is added.

EQUATIONS FOR SOLUBILITY OF FeS IN SYSTEMS CONTAINING ADDED ACID OR BASE, BUT NO OTHER SULFIDE

Van Rysselberghe (28) has developed equations for the dependence of Fe⁻² concentration upon the acidity of aqueous solutions containing only the sulfide from the dissolved FeS

$$(\text{Fe}^{-2}) = K_s \left[1 + \frac{(\text{H}^+)}{K_2} + \frac{(\text{H}^+)^2}{K_1 K_2} \right] \quad (1)$$

where

- (Fe⁻²) = concentration iron ion, moles per liter
- (H⁺) = concentration hydrogen ion, moles per liter
- K₁ = first dissociation constant, H₂S
- K₂ = second dissociation constant, H₂S
- K_s = solubility product, FeS

Verhoogen (29, 30) with what now appears to be considerable overconfidence, attempted to apply the van't Hoff equation in evaluating the effect of temperature on the

solubility of FeS in such solutions over the rather wide temperature range of 25° to 400° C.

In systems containing other sulfide, plus acid or base, the equilibrium solubility of iron sulfide in water containing other added sulfide can readily be shown to follow closely the approximate equation

$$(H_2S) \cong \frac{(Fe^{+2})^3}{[(Fe^{+2})_0 - (Fe^{+2})]^2} \times \frac{4K_s}{K_1K_2} = \frac{(Fe^{+2})^3}{\left[\frac{K_s}{K_2} - (Fe^{+2})\right]^2} \times \frac{4K_s}{K_1K_2} \quad (2)$$

where

$$(Fe^{+2})_0 = K_s/K_2$$

In solutions containing added excess acid or base, Equation 3 holds

$$(H_2S) \cong \frac{\left[\frac{(A^-) - (B^+)}{2} - (Fe^{+2})\right]^2 (Fe^{+2})_0}{[(Fe^{+2})_0 - (Fe^{+2})]^2} \times (Fe^{+2}) \times \left(\frac{4}{K_1}\right) \quad (3)$$

where (H_2S) , (Fe^{+2}) , (A^-) , (B^+) are the molar concentrations of H_2S , ferrous ion, and added acid or added base, respectively, K_s is the solubility product of FeS, and K_1 and K_2 are the first and second ionization constants of H_2S . The approximation is a good one and holds where

$$[(A^-) - (B^+) - (Fe^{+2})]^2 \gg \left| \frac{1}{4} \left[-K_w + K_w \frac{(Fe^{+2})_0}{(Fe^{+2})} \right] \right| \quad (4)$$

K_w is the ionization constant for water.

The exact expression from which Equations 2 and 3 may be derived as approximations, is

$$2(Fe^{+2}) = -\left(\frac{K_1K_2}{K_s} (H_2S) (Fe^{+2})\right)^{1/2} + (A^-) - (B^+) + \frac{2K_s}{(Fe^{+2})} + \frac{K_1(H_2S) + K_w}{\left[\frac{K_1K_2}{K_s} (H_2S) (Fe^{+2})\right]^{1/2}} \quad (5)$$

or

$$(H_2S) = \frac{B^2 - 2AC - B(B^2 - 4AC)^{1/2}}{2A^2} \quad (6)$$

where

$$B^2 = \left[-(Fe^{+2}) + \frac{(A^-) - (B^+)}{2} + \frac{K_s}{(Fe^{+2})} \right]^2$$

$$AC = -\frac{K_w}{4} + \frac{K_wK_s}{4K_2} \times \frac{1}{(Fe^{+2})}$$

$$A^2 = \frac{K_1K_2(Fe^{+2})}{4K_s} - \frac{K_1}{2} + \frac{K_1K_s}{4K_2} \times \frac{1}{(Fe^{+2})}$$

$$C = \frac{-K_w}{2} \times \left[\frac{K_s}{K_1K_2(Fe^{+2})} \right]^{1/2}$$

It is derivable from the following equations by suitable combination:

Statement of ionic charge equivalence

$$2(Fe^{+2}) + (H^+) + (B^+) = 2(S^{-2}) + (HS^-) + (A^-) + (OH^-) \quad (7)$$

—i.e., the sum of the positive charges must equal the sum of the negative ones.

Solubility product of FeS

$$K_s = (Fe^{+2})(S^{-2}) \quad (8)$$

First and second ionization constants of H_2S

$$K_1 = \frac{(H^+)(HS^-)}{(H_2S)} \quad (9)$$

$$K_2 = \frac{(H^+)(S^{-2})}{(HS^-)} \quad (10)$$

The acidity of the solution will be defined by

$$(H^+) = \left[\frac{K_1K_2}{K_s} (H_2S)(Fe^{+2}) \right]^{1/2} \quad (11)$$

By using values for the constants shown in Table I and plotted in Figures 1 and 2, the curves for FeS solubility in water at various temperatures were computed and are shown in Figures 3 to 7 and Table II.

As may be seen by inspection of Equation 5 or 2 and 4, the limit of

$$(Fe^{+2}) = \frac{K_s}{K_2} = (Fe^{+2})_0 \text{ as } (H_2S) \rightarrow \infty.$$

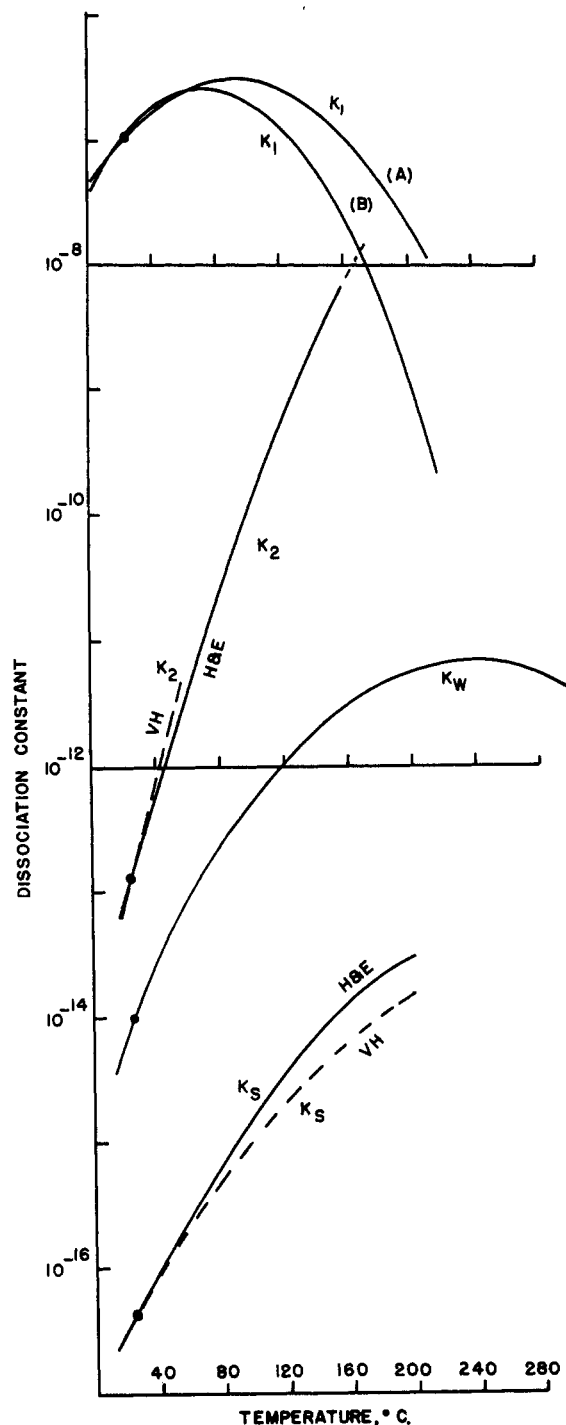
This parameter, $(Fe^{+2})_0$ is the maximum possible solubility of iron sulfide as FeS—i.e., not as other forms of FeS_x—at the conditions of temperature, etc., which govern the magnitudes of K_s and K_2 . It is a useful measure of over-all conditions for iron sulfide solubility.

The values were chosen on the basis of their apparent individual precision, and not primarily for their ultimate

Table I. Pertinent Constants Affecting FeS Solubility

Temp., ° C.	K_1	K_2	K_w	K_s	K_s^*	$(Fe^{+2})_0 = K_s/K_2 = (Fe^{+2})_{max.}$ Mole/Liter	$(Fe^{+2})_{max.}$ for FeS _{1.14} = $K_s/K_2 \times 0.526/K_g$}
25	1.02×10^{-7}	1.3×10^{-13}	1.008×10^{-14}	4.16×10^{-17}	2.80	3.20×10^{-4}	0.60×10^{-4}
40	1.55×10^{-7}	5.8×10^{-13}	2.92×10^{-14}	9.7×10^{-17}	3.02	1.67×10^{-4}	0.29×10^{-4}
80	2.88×10^{-7}	2.1×10^{-11}	23.4×10^{-14}	7.1×10^{-16}	3.43	3.39×10^{-5}	0.52×10^{-5}
90	3.0×10^{-7}	4.8×10^{-11}	3.6×10^{-13}	11.0×10^{-16}	3.50	2.30×10^{-5}	0.34×10^{-5}
120	2.55×10^{-7}	5.4×10^{-10}	1.02×10^{-12}	3.6×10^{-15}	3.63	6.7×10^{-6}	0.097×10^{-6}
138	...	2.8×10^{-9}	1.8×10^{-12}	7.0×10^{-15}	3.64	2.5×10^{-6}	0.035×10^{-6}
200	(0.22×10^{-7})	...	5.5×10^{-12}	(3×10^{-14})	(3.68)	...	...

* $K_s = (P_{H_2S}/P_{H_2S})^{0.14}$. See Equations 32 and 38.



←

Figure 1. Temperature dependence of certain dissociation constants important in iron sulfide solubility

Key: Points on curves are observed data, curves other than that for water (K_w) are calculated using thermodynamic methods. VH, calculated using the van't Hoff equation; H & E, calculated using the method of Harned and Embree. Curves for K_1 were calculated by the method of Harned and Embree, curve A using data of Tables I and VI, curve B using improved data of Table VI

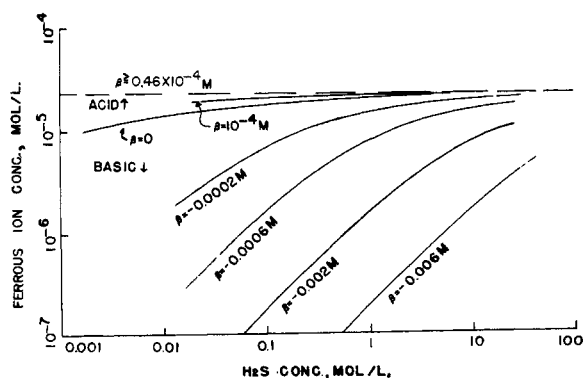


Figure 4. The calculated solubility of FeS in water containing H_2S and either acid or base at $90^\circ C$. $K_1 = 3.0 \times 10^{-7}$; $K_2 = 4.8 \times 10^{-11}$; $K_s = 11.0 \times 10^{-16}$; $K_w = 3.6 \times 10^{-15}$. See Figure 3 for explanation of β values

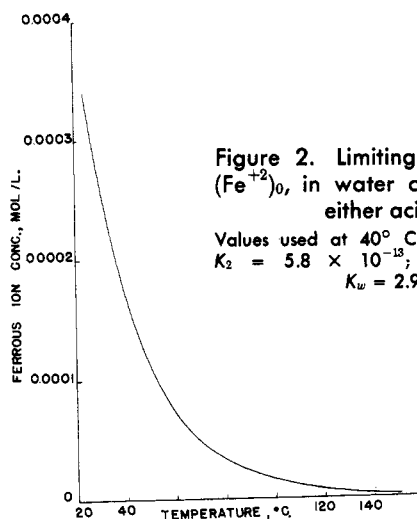


Figure 2. Limiting solubility of FeS, $(Fe^{+2})_0$, in water containing H_2S and either acid or base

Values used at $40^\circ C$: $K_1 = 1.55 \times 10^{-7}$; $K_2 = 5.8 \times 10^{-13}$; $K_s = 9.7 \times 10^{-17}$; $K_w = 2.92 \times 10^{-14}$

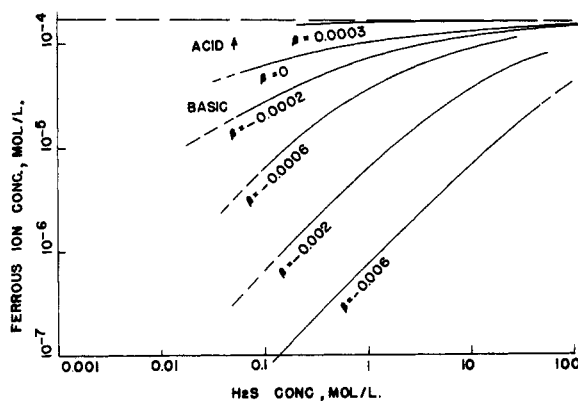


Figure 3. Calculated solubility of FeS in water containing H_2S and either acid or base at $40^\circ C$.

K_1 , K_2 , K_s , K_w values same as in Figure 2. The concentration of added acid or base is indicated as β , where $+\beta = (A^-)$, and $-\beta = (B^+)$, the molar concentration of acid or base respectively

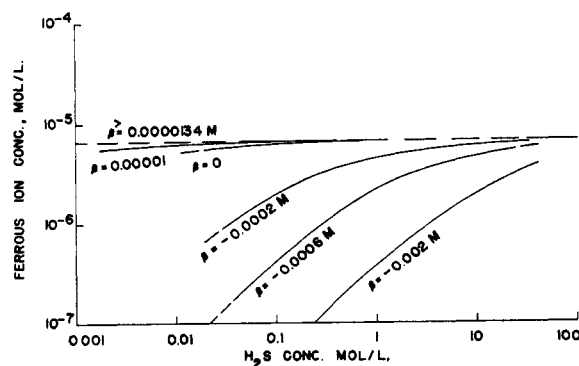


Figure 5. The calculated solubility of FeS in water containing H_2S and either acid or base at $120^\circ C$. $K_1 = 2.55 \times 10^{-7}$; $K_2 = 5.4 \times 10^{-10}$; $K_s = 3.63 \times 10^{-15}$; $K_w = 1.02 \times 10^{-12}$. See Figure 3 for explanation of β values

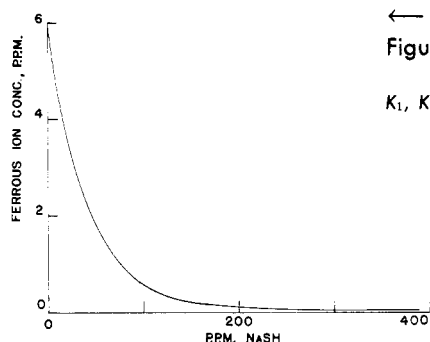


Figure 6. The effect of added base on the solubility of FeS at 140° C.

K_1 , K_2 , K_s , K_w values are same as in Figure 2

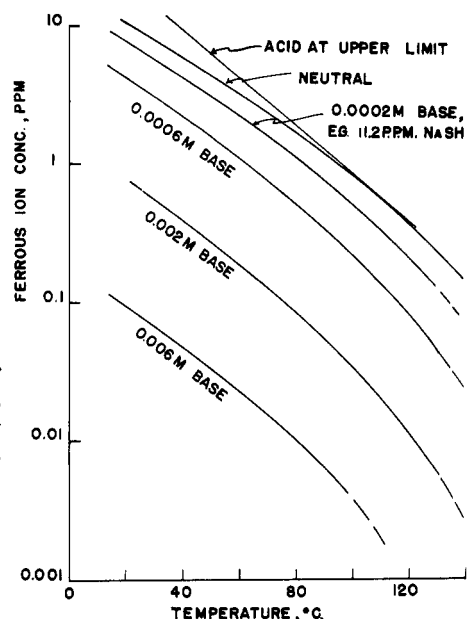


Figure 7. Temperature dependence of ferrous ion solubility in water saturated with H_2S at 250 p.s.i.g., to which the indicated amounts of excess acid or base have been added

effect on the absolute value of the iron solubility as later calculated. The absolute value of the iron solubilities calculated may be somewhat in error, but the relative changes shown are reasonably well indicated. To a rough approximation, for values of (Fe^{+2}) near $(Fe^{+2})_0 = K_s/K_2$, the iron solubility may be written

$$(Fe^{+2}) \cong \frac{K_s}{K_2} \left[1 - \frac{2K_s}{(K_2K_1)^{1/2}(H_2S)^{1/2}} \right] \quad (12)$$

which shows the iron solubility to vary directly as the ratio of K_s/K_2 . The upper limiting values of FeS solubilities at which solid FeS can still remain in equilibrium with the solution are shown in Figure 2.

Evaluation of Necessary Constants and Their Selection at 25° C. The following values for the several relevant constants have been selected from the literature and upon calculations of various published data:

$$\begin{aligned} K_1 &= 1.02 \times 10^{-7} & K_w &= 1.008 \times 10^{-14} \\ K_2 &= 1.3 \times 10^{-13} & K_s &= 4.16 \times 10^{-17} \end{aligned}$$

They are based on the following analyses.

K_1 , the First Dissociation Constant of H_2S . There have been numerous determinations of this constant (Table III).

The survey by Latimer, Kury, and Zielen (19), it is

judged, has yielded the most reliable value: $K_1 = 1.02 \times 10^{-7}$, at 25° C. This value was chosen for use in present work.

K_2 , the Second Dissociation Constant of H_2S . There have been a number of determinations of this constant:

K_2	Temp., ° C.	Reference
10^{-15}	25	(11)
2×10^{-15}	0	(12)
0.79×10^{-13}	20	(17)
3.63×10^{-13}	20	(18)
1.3×10^{-13}	25	(19)

The recent experimental and theoretical studies by Latimer and others appear to offer the most precise value of $K_2 = 1.3 \times 10^{-13}$, at 25° C.

K_w , the Dissociation Constant of Water. The dissociation constant of water has been rather well studied over a wide temperature range. The values selected from two comprehensive reviews are shown (Table IV).

Table II. Calculated Solubility of FeS at Selected Temperature Conditions

Temp., ° C.	(H ₂ S) at 250 p.s.i.g., M	(Fe ⁺²)		Concn. Acid or Base in Inlet Water, M	NaHS, P.P.M.
		P.p.m.	(Mole/l.) $\times 10^{-4}$		
40	1.1	9.5	1.70	(acid) $\geq 3.4 \times 10^{-4}$	...
		9.0	1.62	(acid) = 3×10^{-4}	...
		5.86	1.05	(acid) = (base) = 0	0
		4.19	0.75	(base) = 2×10^{-4}	11.2
		2.18	0.39	(base) = 6×10^{-4}	33.6
		0.38	0.068	(base) = 20×10^{-4}	112
		0.046	0.0083	(base) = 60×10^{-4}	336
90	0.595	1.28	0.230	(acid) $\geq 0.46 \times 10^{-4}$	...
		1.24	0.222	(acid) = 0.1×10^{-4}	...
		1.17	0.209	(acid) = (base) = 0	0
		0.76	0.136	(base) = 2×10^{-4}	11.2
		0.335	0.060	(base) = 6×10^{-4}	33.6
		0.053	0.0095	(base) = 20×10^{-4}	112
		0.0063	0.00113	(base) = 60×10^{-4}	336
120	0.482	0.374	0.067	(acid) $\geq 0.134 \times 10^{-4}$	...
		0.371	0.0665	(acid) = 0.10×10^{-4}	...
		0.363	0.065	(acid) = (base) = 0	0
		0.209	0.0375	(base) = 2×10^{-4}	11.2
		0.079	0.0142	(base) = 6×10^{-4}	33.6
		0.0109	0.00195	(base) = 20×10^{-4}	112

For this work, the values $K_w = 1.008 \times 10^{-14}$ at 25° C. and $K_w = 2.92 \times 10^{-14}$ at 40° C. were chosen. The value of K_w is not critically important, as the amounts of Fe^{+2} dissolved are generally much higher than the quantities of either ion produced by water dissociation—i.e., the term $B^2 \gg AC$ —hence the usefulness of the more easily handled approximate forms of the solubility equation, Equations 2 and 3.

Table III. Determination of K_1

$K_1 \times 10^8$	Temp., ° C.	Reference
12	18	(8)
9.1	18	(1)
5.7	18	(1, 8)
3 to 720	18	(12)
33.13	18	(8)
8.73	20	(18)
4.71	5	(31)
5.74	10	(31)
7.47	15	(31)
8.96	20	(31)
10.8	25	(31)
12.6	30	(31)
16.4	40	(31)
20.3	50	(31)
23.9	60	(31)
11.5	25	(11)
10.2	25	(19)

Table IV. Dissociation Constant for Water from 0° to 306° C.

Temp., ° C.	Log K_w (6)	$K_w \times 10^{14}$ (6)	Log K_w (11)	$K_w \times 10^{14}$ (11)
0	...	...	14.93	0.118
10	14.5346	0.292	14.72	0.190
18	...	...	14.23	0.58
20	14.1669	0.68	14.16	0.69
25	13.9965	1.008	13.99	1.005
30	13.8330	1.47	13.83	1.48
35	13.6801	2.09	...	...
40	13.5348	2.92	13.52	3.02
45	13.3960	4.02	...	...
50	13.2617	5.48	13.26	5.50
55	13.1369	7.29	...	...
60	13.0171	9.61	13.03	9.33
80	...	...	12.63	23.4
100	...	...	12.29	51.3
150	...	...	11.63	234
200	...	...	11.26	550
250	...	...	11.17	667 (max.)
300	...	...	11.40	398
306	...	...	11.46	347

Table V. Available Data on FeS Solubility

Temp., ° C.	K	Reference	Conditions
25	2,800	(5)	Follows precipitation in strong acid
25	8,300	(5)	Follows precipitation NaOAc buffered solution
25	4,000	(5)	Follows partial solution of FeS in acetic acid
16	4,780	(27)	pH 3.30, precipitated from FeSO_4 , H_2S , plus trace of NaOH (after 1 hour)
17	5,250	(27)	pH 3.40, precipitated as above, but after 12 hours
14	1,200	(27)	pH 3.54, as above, but after 48 hours
15	1,970	(27)	pH 3.15, precipitated from FeSO_4 , H_2S , plus trace of H_2SO_4 (after 14 hours)
14	1,420	(27)	pH 3.05, as above, but after 18 hours
25	9,000	(15, 16)	Fresh
25	12,000	(16)	Aged 20 hours
25	9,000	(16)	Aged 70 hours
25	2,200	(16)	Aged 7 days
25	100	(16)	Aged 30 days
25	4,000	(16)	Drastically aged (30 days)
90	228	(16)	Aged 20 hours
90	60	(16)	Aged 70 hours

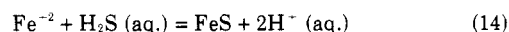
For present purposes, the following values for $K = [(\text{Fe}^{+2})(\text{H}_2\text{S})/(\text{H}^+)^2]$ were selected, as is justified later: 1300 at 14° C., 1380 at

K_1 , Solubility Product of FeS. The solubility of FeS has been the subject of much investigation by both direct and indirect experiment. Direct determinations, though difficult, have given K_1 values generally larger than those found by indirect means based on thermodynamic reasoning. The reasons for this are probably related to particle sizes and short equilibration times used by the various experimenters, and to the considerable effect of atomic hydrogen on the activity of free iron and iron sulfides.

Direct Determinations. It has been found convenient in practice to use the relations

$$K = \frac{(\text{Fe}^{+2})(\text{H}_2\text{S})}{(\text{H}^+)^2} = \frac{K_1}{K_1 K_2} \quad (13)$$

(to describe the equilibrium in the reaction)



(governing the solubility of iron sulfide)

The available data are summarized in Table V.

Indirect Determination. By using the known free energies of formation of the ionization reaction, it should be possible to calculate the solubility of FeS. The absolute value of the constant found is highly sensitive to the precision of the ΔF values, as differences between large numbers are used. Kapustinsky (13) calculated newer values for the free energy of formation of sulfide ion. Treadwell and Gubeli (27) calculated

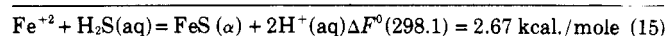
$$K = 95 = \frac{(\text{Fe}^{-2})(\text{H}_2\text{S})}{(\text{H}^+)^2} \text{ at } 25^\circ \text{ C.}$$

Using our selected values of K_1 and K_2 , this indicates a value of

$$K_1 = 1.3 \times 10^{-18}$$

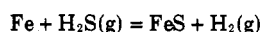
In view of the importance of a rather precise understanding of the sulfide deposition process, it seems worthwhile to dig into the background of the thermodynamics used in arriving at the solubility of FeS. There are two lines of attack.

Method I



25° C., and 60 at 90° C. Using $K_1 = 1.02 \times 10^{-7}$ and $K_2 = 1.3 \times 10^{-13}$, $K_1 = 10^{-17}$ for 25° C. was obtained.

Treadwell and Gubeli (27) give $\Delta F^0 = -18,490 + 1.62 \times 4.573 \times T$ for



ΔF^0 for the ionization of iron is based on the normal electrode potential as 0.44 volts (4, 25). Patrick (23) has recently shown that for H_2 -free iron this is closer to 0.409. However, the older value of 0.44 volt for "hydrogenated iron" is used, inasmuch as this will give results more consistent with the type used industrially which is actually used in the presence of H_2 . Similarly, the ΔF^0 for hydrogenated iron is used for later calculations. To be more consistent, ΔF^0 's should be used for Fe of exactly the same hydrogen content, but these data are not yet available.

For the equilibrium in reaction 15, as usually written,

$$K = \frac{(\text{Fe}^{+2})(\text{H}_2\text{S})}{(\text{H}^+)^2}$$

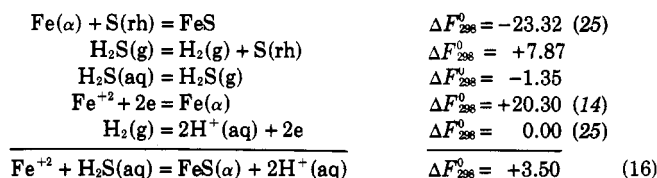
and $\Delta F_{298}^0 = RT \ln K = -2670$ cal. per mole whence,

$$K_{25^\circ} = 91 = \frac{K_1}{K_1 K_2}$$

Using the selected K_1 and K_2 values gives

$$K_1 = K_{25} \times K_1 K_2 = 91 \times 1.01 \times 10^{-7} \times 1.3 \times 10^{-13} = 1.2 \times 10^{-16}$$

Method II.



$$\Delta F_{298}^0 = RT \ln K = 3500 \text{ cal./mole}$$

$$\log K = \frac{3500 \times 0.4343}{1.986 \times 298.16} = 2.566$$

Using the selected K_1 and K_2 values gives

$$K_1 = K \times K_1 \times K_2 = 370 \times 1.02 \times 10^{-7} \times 1.3 \times 10^{-13} = 4.9 \times 10^{-16}$$

The values of the solubility product of FeS, K_1 , are summarized in Table VI.

The selection of K and K_2 has been from a simple average of the seven best values:

$$\begin{aligned} 25^\circ \text{C.}, K &= 1380 \\ 14^\circ \text{C.}, K &= 1300 \\ 90^\circ \text{C.}, K &= 60 \\ 25^\circ \text{C.}, K_1 &= 2 \times 10^{-17} (+2; -1 \times 10^{-17} \text{ est. precision}) \\ 90^\circ \text{C. using } K_1 &= 3.0 \times 10^{-7} \\ K_2 &= 4.8 \times 10^{-11} \\ K_1 &= 8.7 \times 10^{-16} \end{aligned}$$

The general agreement of the values, although not perfect, whether determined by direct experimental or indirect experimental means plus thermodynamic reasoning, is to be considered encouraging.

Using our own experimental data of $(\text{Fe}^{+2})_{\text{obsd}} \cong 6.02$ p.p.m. at $40^\circ \text{C.} = 1.11 \times 10^{-4} M$. Since $(\text{Fe}^{+2})_0 = (K_1/K_2) = \text{ca. } 1.5 \times (\text{Fe}^{+2})_{\text{obsd}}$ at $1.1M \text{ H}_2\text{S}$ (see Equation 12) and K_2 at $40^\circ \text{C.} = 5.8 \times 10^{-13}$, the value for K_1 (40°C.) = $1.5 \times 1.11 \times 10^{-4} \times 5.8 \times 10^{-13} = 9.7 \times 10^{-17}$.

Assuming a coefficient of thermal change of 2.33 in going from 25° to 40°C. as calculated from the Harned and Embree equations (9) using $\Delta H^0 = +9.5$ kcal., we arrive at a K_1 value at 25°C. of 4.16×10^{-17} , using our data. This is satisfactorily close to the value of $2(+2, -1) \times 10^{-17}$ obtained from literature values. The value 9.7×10^{-17} at 40°C. and 4.16×10^{-17} at 25°C. will accordingly be used in these calculations.

Calculation of Constants for Elevated Temperature. Using the values arrived at previously for 25°C. and applying more or less appropriate factors based on thermodynamic approximations where necessary, the calculations proceeded as follows:

K_1 at Elevated Temperatures. For estimating values of K_1 at somewhat higher temperatures, the modified equations of Harned and Embree (7, 9, 10) may be used. They found $\log K/K_m = -p(t - t_m)^2$ and

$$\Delta H^0 = -2.3(p/2)RT^2(t - t_m)$$

to hold for a large number of acids and bases where

K_m = dissociation constant maximum
 t = temperature, $^\circ \text{C.}$
 t_m = temperature at K_m
 p = constant, generally about 5×10^{-6} degree $^{-2}$
 T = absolute temperature

It is more convenient for computational purposes (and perhaps more precise) to use the integrated form of the van't Hoff equation in the derivation, giving

$$\log K'/K = \frac{\Delta H^0}{2.303 R} (1/T - 1/T') \quad (17)$$

Table VI. Known Values of Solubility Product of FeS

Temp., $^\circ \text{C.}$	$K = \frac{(\text{Fe}^{+2})(\text{H}_2\text{S})}{(\text{H}^+)^2}$	K_1 (assuming $K_1 = 1.02 \times 10^{-7}$ $K_2 = 1.3 \times 10^{-13}$ at 25°C.)	Reference	Method
	$= \frac{K_1}{K_1 K_2}$			
14	1300	...	(27)	Direct chemical
25	2800	3.7×10^{-17}	(5)	Direct chemical
25	(8300)	...	(5)	Direct chemical (with acetate ion present)
25	(4000)	...	(5)	Direct chemical (with acetate ion present)
25	100	1.3×10^{-18}	(16)	Direct chemical
25	2200	2.9×10^{-17}	(16)	Direct chemical
25	4000	5.3×10^{-17}	(16)	Direct chemical
25	...	3.8×10^{-20}	(13)	Thermodynamic
25	95	1.3×10^{-18}	(27)	Thermodynamic
25	91	1.2×10^{-18}	Method I	Thermodynamic
25	370	4.9×10^{-18}	Method II	Thermodynamic
25 (av.)	1380 (av.)	2×10^{-17} (av.)	Av. of all	Except Kapustinski value (13)
90	60	...	(16)	Direct chemical

$$\Delta H^0 = -4.606 \times p \times RTT' \left(\frac{t+t'}{2} - t_m \right) \quad (18)$$

$$t_m = t + \frac{\Delta H^0}{2.303 \times p \times RT \times T_m} \quad (19)$$

and

$$\log K'/K = -p(t' - t)(t' + t - 2t_m) \quad (20)$$

The data of Wright and Maass (31) fit the equation

$$\log (K/K_m) = -10^{-4}(t - t_m)^2 \quad (21)$$

$$(p = 10^{-4} \text{ rather than } 5 \times 10^{-5})$$

rather well over the range 5° to 60° C., with $t_m = 93.5^\circ$ C. and $K_m = 3.35 \times 10^{-7}$. Using this method of calculation, values in Table VII were calculated.

Table VII. Calculated First Dissociation Constants for H₂S

Temp., ° C.	K_1
25	1.02×10^{-7}
40	1.55×10^{-7}
80	2.88×10^{-7}
90	3.0×10^{-7}
120	2.55×10^{-7}
200	(0.221×10^{-7})

Revised Values for First Dissociation Constant of H₂S. Where the effect of temperature on K_1 was discussed above, it was said that the data of Wright and Maass fit rather well the equation:

$$\log (K/K_m) = -10^{-4}(t - t_m)^2 \text{ with } t_m = 93.5^\circ \text{ C.}$$

and

$$K_m = 3.35 \times 10^{-7}$$

Later analysis showed that a somewhat better fit is to be had from the equation

$$\log (K/K_m) = -1.5 \times 10^{-4}(t - t_m)^2 \text{ with } t_m = 75.9^\circ \text{ C.}$$

and

$$K_m = 2.57 \times 10^{-7}$$

The newer equation gives a result only slightly different from the old at lower temperatures and the newer values calculated from it do not materially change the solubility values calculated at lower temperatures. The new values do, however, afford a better estimate of the probable value of K_1 in the range of 200° C., which will be useful in other work.

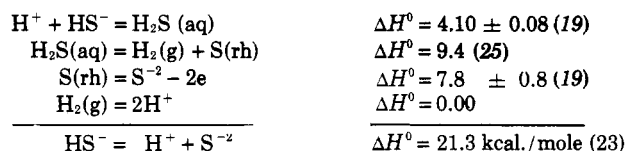
Temp., ° C.	Old Values	New Values
25	1.07×10^{-7}	1.02×10^{-7}
40	1.55×10^{-7}	1.70×10^{-7}
90	3.0×10^{-7}	2.3×10^{-7}
120	2.55×10^{-7}	1.32×10^{-7}
200	2.2×10^{-8}	1.27×10^{-9}

This fit with the Harned and Embree equation removes some of the embarrassment noted by Wright and Maass (31) and Kelly (14) in calculating temperature changes in K_1 .

K_2 at Elevated Temperatures. The integrated form of the van't Hoff equation (assuming ΔH^0 constant in the interval) is

$$\ln \frac{K_{2(T_2)}}{K_{2(T_1)}} \cong \frac{\Delta H^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (22)$$

The values of ΔH^0 for K_2 may be found from the following relations



$$\ln \frac{K_{2(T_2)}}{K_{2(T_1)}} = \frac{21.3}{1.986} \times 10^3 \left[\frac{1}{298.16} - \frac{1}{313.16} \right]$$

$$K_{2(40)}/K_{2(25)} = e^{1.724} = 5.61$$

$$K_{2(40^\circ \text{ C.})} = 1.3 \times 10^{-13} \times 5.61 = 7.3 \times 10^{-13}$$

For estimating dissociation constants over somewhat wider ranges than the above van't Hoff equation permits, the method of Harned and Embree (9) is useful. By using these latter equations, and the value of $\Delta H = 21.3$ kcal. for the second step of H₂S ionization, we find $t_m = 453^\circ$ C.

The values of K_2 calculated on this basis are shown in Table VIII.

Table VIII. Calculated Second Dissociation Constants for H₂S

Temp., ° C.	K_2 , Calcd. from Harned and Embree Equations
25	1.3×10^{-13}
40	5.8×10^{-13}
80	2.1×10^{-11}
90	4.8×10^{-11}
120	5.4×10^{-10}

K_1 for FeS. The values of K_1 at elevated temperatures were evaluated by three means:

The experimental determination of Kolthoff of $K = K_2/K_1K_2$ at 90° C. (Table V or VI).

Use of van't Hoff approximation.

Use of Harned and Embree relations.

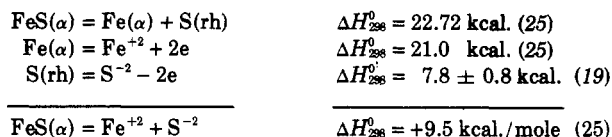
Concordant results were obtained.

Kolthoff and Griffith (16) obtained data at 90° C. from which $K = K_2/K_1K_2 = 60$ is obtained. Using the values $K_1 = 3.0 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$ found above, one may obtain $K_1 = 8.7 \times 10^{-16}$ at 90° C.

The van't Hoff equation gives the change in K_1 for very limited temperature ranges (5° to 10° C.) in ionic solutions:

$$\ln K_1'/K_1 = \frac{\Delta H^0}{R} (1/T - 1/T') \quad (24)$$

ΔH^0 is evaluated as follows:



The calculations of K_1 at various temperatures using $\Delta H^0 = 9.5$ kcal. per mole and the van't Hoff equation are shown in Table IX.

The Harned and Embree equations, while developed and tested using only acid and base constants, seem applicable to the solubility product of insoluble salts, inasmuch as the salts may be considered the product of interaction of the cation as a base and the anion as an acid.

Table IX. Calculations of K_s for Elevated Temperatures

Temp., ° C.	From Kolthoff's Experiments and Present K_1 , K_2 Values	From Harned and Embree Equations	By van't Hoff, Equations
25	4.16×10^{-17}	4.16×10^{-17}	4.16×10^{-17}
40	...	9.7×10^{-17}	8.9×10^{-17}
80	...	7.1×10^{-16}	...
90	13.2×10^{-16}	11.0×10^{-16}	7.4×10^{-16}
120	...	3.63×10^{-15}	2.1×10^{-15}
(200)	...	(3×10^{-14})	1.5×10^{-14}

Using the Harned and Embree equations as for K_1 and K_2 , and the value of $\Delta H^0 = 9.5$ kcal./mole,

$$t_m = t + \frac{\Delta H^0}{2.303 \times p RT T_m} = 277^\circ \text{C.}$$

Hence from $\log K'_s/K_s = -p(t' - t)(t' + t - 2t_m)$ where p was assumed as 5×10^{-5} as before, the values of K_s at various temperatures were calculated (Table IX).

Inasmuch as the Harned and Embree values appear somewhat more consistent with the experimental ones, they are used for further calculations.

On theoretical grounds, $K_2 \leq K_1/4$. However, inspection of Figure 1 shows the extrapolated values of K_1 and K_2 to have an apparent crossover near 200°C . This will not be found to be real. Rather, the p coefficient of curvature of the Harned and Embree equation for K_2 is probably much larger than 5×10^{-5} , perhaps nearer 5×10^{-4} , causing the K_2 values to remain within the envelope of the K_1 values, as they doubtless will. Until more precise experimental data are available, the coefficient 5×10^{-5} of Harned and Embree will be employed.

CALCULATION OF SOLUBILITY CURVES

Change in FeS Solubility Limit with Temperatures. The maximum solubility of FeS as FeS at any temperature in a water- H_2S plus acid or base medium is

$$(\text{Fe}^{+2})_0 = K_s/K_2 \quad (26)$$

That for $\text{FeS}_{1.14}$ is

$$(\text{Fe}^{+2})_0 = \frac{K_s}{K_2} \times \frac{(P_{\text{H}_2}/P_{\text{H}_2\text{S}})^{0.14}}{K_g} \quad (\text{See Equation 48}) \quad (27)$$

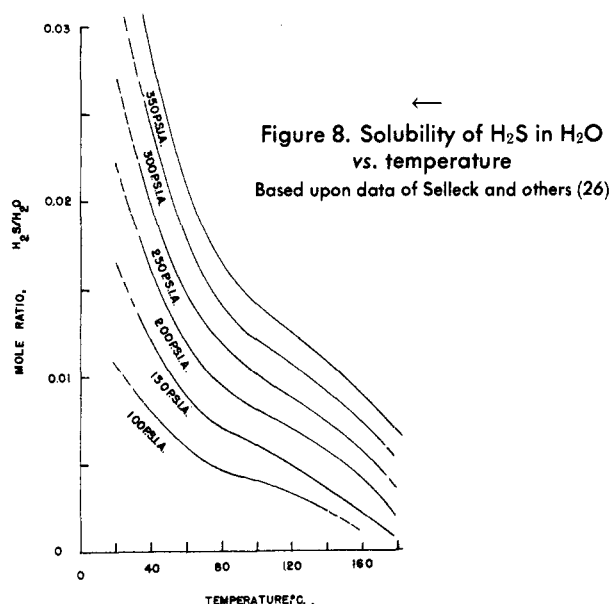


Figure 8. Solubility of H_2S in H_2O vs. temperature
Based upon data of Selleck and others (26)

Using the values for K_s , K_2 , and K_g for various temperatures as found earlier, the maximum solubilities of FeS and $\text{FeS}_{1.14}$ at various temperatures are shown in Table I and Figure 2.

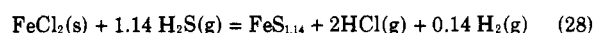
Calculated FeS Solubility at Selected Conditions. Using the equations developed above, Equations 2 to 12, and constants arrived at earlier, the course of the FeS solubilities was calculated for FeS in water at several temperatures containing various practicable concentrations of acid, or base, and H_2S . The general curves shown in Figure 3, 4, and 5 describe the effects of H_2S and acid or base at 40° , 90° , and 120°C .

The effect of added base on the solubility of FeS in H_2O saturated with H_2S at 250 p.s.i.g. is shown in Figure 6. This is of particular interest in applications covering the use of caustic addition to combat deposition. The effect of acid or base at various temperatures in water saturated with H_2S at 250 p.s.i.g. is shown in Figure 7.

Solubility of H_2S in Water at Elevated Pressures and Temperatures. The data of Selleck, Carmichael, and Sage (26) have been replotted into more conveniently usable form (Figures 8 and 9). These data were used for this article.

Effect of Higher Sulfide Forms on Concentration of Dissolved Iron. While it has been common to consider the precipitation of iron sulfide by H_2S from solutions of ferrous ion at near room temperatures as producing FeS, it is apparent that this is not the case at somewhat elevated temperatures. At the higher temperatures, other forms of iron sulfide, richer in sulfur, are produced.

Solubility of Pyrrhotite. For arriving at values of the solubility of the iron sulfide precipitated at or near room temperatures—i.e., up to about 40°C .—the previous calculations are probably valid. However, extension of these equations beyond 120°C . is not valid, because the formation of pyrrhotite, marcasite, or pyrite governs the manner of removal of iron from solution; and this takes place under different rules. Fortunately, data necessary for the calculation of the behavior of pyrrhotite precipitation are available in the literature, based primarily on the work of Lukes, Prutton, and Turnbull (21), who studied the following equilibrium:



finding

$$\log_{10} K_p = (-4320/T) + 6.71 \quad (29)$$

$$K_p = P_{\text{HCl}}^2 \times P_{\text{H}_2}^{0.14} / P_{\text{H}_2\text{S}}^{1.14} \text{ over the range } 340^\circ \text{ to } 460^\circ \text{C.} \quad (30)$$

$$\Delta F_{298.16^\circ \text{K.}}^0 = 10,610 \text{ cal./mole} = -RT \ln K_p \quad (31)$$

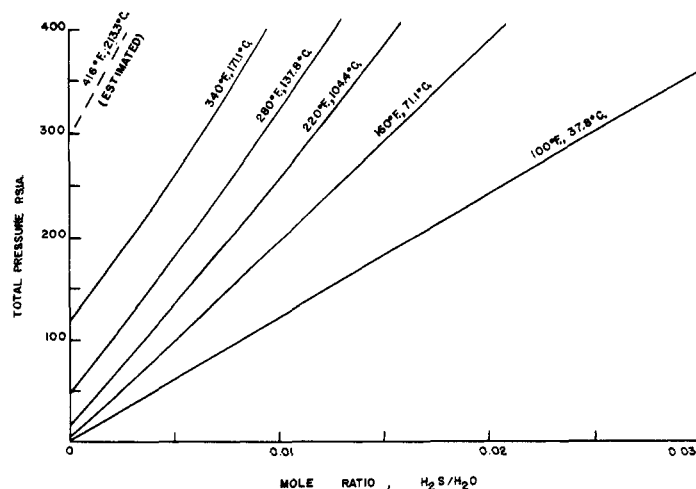
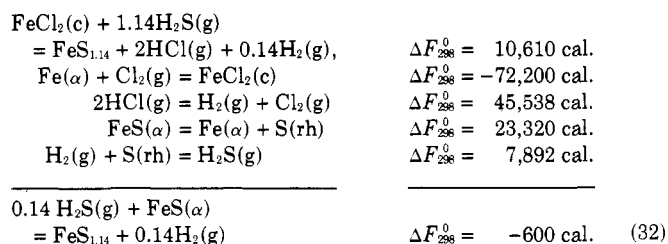


Figure 9. Solubility of H_2S in H_2O vs. pressure
Based upon data of Selleck and others (26)

The above reaction may be combined with others for which the free energies are known (25) to give the needed information.



The temperature coefficient of the reaction may be ascertained from the following equations:



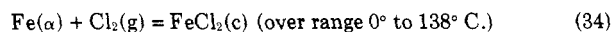
$$\log_{10} K_p = -4320/T + 6.71 \quad (21)$$

$$K_p = P_{\text{HCl}}^2 \times P_{\text{H}_2}^{0.14} / P_{\text{H}_2\text{S}}^{1.14} \quad (\text{measured over the range } 340^\circ \text{ to } 460^\circ \text{ C.})$$

$$\Delta F^0 = -RT \ln K_p = -2.303 RT (-4320/T + 6.71)$$

$$= -0.0307 T + 19.76 \text{ kcal. } (T \text{ in } ^\circ \text{K.})$$

$$\Delta F_{298,16}^0 = 10.61 \text{ kcal./mole}$$



$$\Delta F^0 \cong 72.2 + 2.92 \times 10^{-2} (T - 298) \\ = -80.9 + 0.0292 T \quad (22, 25)$$

$$\Delta F_{298,16}^0 = -72.2 \text{ kcal./mole } (25)$$



$$\Delta F^0 \cong +45.54 + 0.45 \times 10^{-2} (T - 298) \\ = 44.20 + 0.0045 T \\ (\text{over range } 0^\circ \text{ to } 1000^\circ \text{ C.}) (22, 25).$$

$$\Delta F_{298,16}^0 = 45.54 \text{ kcal. } (25)$$



$$\Delta F^0 = +22.20 - 0.01308 T \log T + 13.19 \times 10^{-6} T^2 \\ + 0.03219 T \quad (T \text{ in } ^\circ \text{K.}) \quad [\text{Kelley equation } (14) \\ \text{modified to fit NBS } (25) \text{ } 25^\circ \text{ C. point}].$$

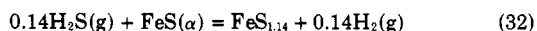
$$\Delta F_{298,16}^0 = 23.32 \text{ kcal./mole}$$



$$\Delta F^0 = -3.752 + 7.02 \times 10^{-3} T \log T \\ + 1.86 \times 10^{-6} T^2 - 31.82 \times 10^{-3} T$$

$$\Delta F_{298,16}^0 = -7.892 \text{ kcal./mole}$$

By adding Equations 33 to 37, Table X was constructed. It enables calculation of the free energies at any temperature from 0° to 138° C. for the reaction



with the equation

$$\Delta F_{\text{total}}^0 = 1.51 - 0.00606 T \log T + 15.06 \times 10^{-6} T^2 + 0.0034 T \quad (38)$$

$$K_g = (P_{\text{H}_2}/P_{\text{H}_2\text{S}})^{0.14} \quad (39)$$

The probable absolute precision of the ΔF values is $\pm 1 \text{ kcal.}$; the probable relative precision of the change in ΔF from one temperature to the other is much greater, probably $\pm 0.1 \text{ kcal. per mole}$ or better.

If the equilibrium constant is, K_g (Equation 39), the well known relation

$$\Delta F^0 = -RT \ln K_g$$

$$\Delta F_{298}^0 = -0.61 \text{ kcal./mole}$$

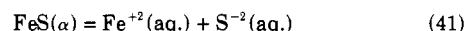
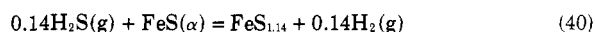
gives

$$K_g (298^\circ \text{ K.}) = 2.80$$

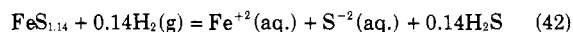
$$\Delta F_{300}^0 = 1.03 \text{ kcal./mole}$$

$$K_g (400^\circ \text{ K.}) = 5.71$$

The above equations with the constants indicated in Table X can be used to find the solubility product of pyrrhotite:



Subtracting gives



with

$$\Delta F_p = -RT \ln K_p = -RT \ln K_s + RT \ln K_g \quad (43)$$

and

$$K_p = K_s / K_g$$

Since

$$K_s = (\text{Fe}^{+2})(\text{S}^{-2}) \quad (44)$$

and

$$K_g = (P_{\text{H}_2}/P_{\text{H}_2\text{S}})^{0.14} \quad (39)$$

then

$$K_p = K_s / K_g = (\text{Fe}^{+2})(\text{S}^{-2}) \times (P_{\text{H}_2\text{S}}/P_{\text{H}_2})^{0.14} \quad (45)$$

Hence for pyrrhotite, $\text{FeS}_{1.14}$,

$$(\text{Fe}^{+2})(\text{S}^{-2}) = K_s \frac{(P_{\text{H}_2}/P_{\text{H}_2\text{S}})^{0.14}}{K_g} \quad (46)$$

instead of

$$(\text{Fe}^{+2})(\text{S}^{-2}) = K_s \quad (8)$$

as for FeS (troilite).

As a consequence of this simple relationship between pyrrhotite and troilite equilibria, the variation of iron concentration with acidity or H_2S concentration may be found from Equations 2 to 12 by merely replacing K_s by

$$(K_s/K_g)(P_{\text{H}_2}/P_{\text{H}_2\text{S}})^{0.14} \quad (47)$$

throughout. For example, the limiting solubility of Fe^{-2} , $(\text{Fe}^{-2})_0$, for FeS together with $\text{FeS}_{1.14}$ in equilibrium with H_2S , acid and water may be expressed by

$$(\text{Fe}^{-2})_0 = \frac{K_s}{K_2} \times \frac{(P_{\text{H}_2}/P_{\text{H}_2\text{S}})^{0.14}}{K_g} \quad (48)$$

It is interesting to examine the magnitude of the effect of this "pyrrhotite" factor:

$$\frac{(P_{\text{H}_2}/P_{\text{H}_2\text{S}})^{0.14}}{K_g}$$

on the solubility of iron in the aqueous phase where, for example,

Table X. Free Energies vs. Temperature for Pyrrhotite Precipitation

ΔF^0	Constant	Term in $T \log T$	Term in T^2	T	ΔF^0_{298} , Kcal.	K_s
ΔF^0_1	19.76	...	...	-0.0307	10.61	...
ΔF^0_2	-80.9	...	...	+0.0292	-72.20	...
ΔF^0_3	44.20	...	...	+0.0045	45.54	...
ΔF^0_4	22.20	-0.01308	$+13.19 \times 10^{-6}$	+0.0322	+23.32	...
ΔF^0_5	-3.752	+0.00702	1.865×10^{-6}	-0.03182	-7.89	...
ΔF^0_{net}	1.51	-0.00606	$+15.06 \times 10^{-6}$	+0.0034	-0.62	...
At 298° K.	1.51	-4.471	+1.339	+1.012	-0.61	2.80
At 400° K.	1.51	-6.31	+2.41	+1.36	-1.03	...
At 40° C.	1.51	-4.735	1.475	1.064	-0.686	3.015
At 80° C.	1.51	-5.450	1.877	1.200	-0.863	3.425
At 90° C.	1.51	-5.631	1.985	1.234	-0.902	3.50
At 120° C.	1.51	-6.178	2.326	1.336	-1.006	3.63

$$P_{H_2}/P_{H_2S} \cong 0.01$$

$$\text{At } 25^\circ \text{ C.: } K_s = 2.80, \quad (P_{H_2}/P_{H_2S})^{0.14} = 0.526$$

$$\text{At } 127^\circ \text{ C.: } K_s = 5.71, \quad (P_{H_2}/P_{H_2S})^{0.14} = 0.526$$

Hence the maximum solubility of Fe^{+2} and approximately the actual solubility in neutral water will be

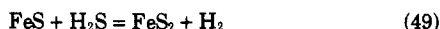
$$(\text{Fe}^{+2})_0 \text{ at } 25^\circ \text{ C.} = \left(\frac{K_s}{K_2} \right)_{298^\circ \text{ K.}} \times 0.188$$

$$(\text{Fe}^{+2})_0 \text{ at } 127^\circ \text{ C.} = \left(\frac{K_s}{K_2} \right)_{400^\circ \text{ K.}} \times 0.092$$

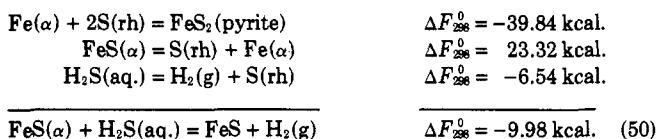
This means that aside from other effects of H_2S solubility changes or effects of temperature on K_s and K_2 , the solubility of iron is cut 50% by heat in the range studied, and this merely by the shift in equilibrium for pyrrhotite formation.

The Solubility of Pyrite. The solubility of pyrite is considerably less than that of FeS in mixtures of H_2O and added H_2S —i.e., the form FeS_2 is energetically preferred. This may be seen from the following considerations:

The reaction



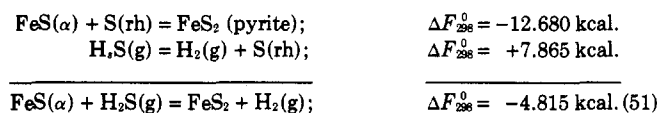
will normally proceed far to the right. The thermodynamics are as follows:



using the values of Rossini and coworkers (25).

This shows the conversion of FeS to pyrite by H_2S to be favored by a rather large amount of free energy, about 10 kcal.

The variation of this with temperature cannot be easily ascertained from International Critical Tables (25); however, the older data of Kelley (14) may be used to give a fair idea of the effects to be expected:

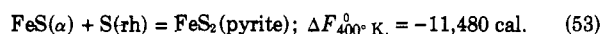


Rossini and others (25) give -16.32 instead of -12.68 kcal. for the first reaction.

The equilibrium constant (assuming these values) at 298° K. (25° C.) is:

$$K_y = \frac{P_{H_2}}{P_{H_2S}} = e^{-\frac{\Delta F^0}{RT}} = 3.4 \times 10^3 \quad (52)$$

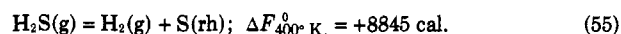
The value of K_y at elevated temperatures may be obtained from the equations given by Kelley (14) for:



$$-\Delta F^0 = 16,080 + 11.72 T \log T - 15.9 \times 10^{-3} T^2 - 35.64 T \quad (54)$$

(T in degrees absolute, ΔF in calories)

and for



$$-\Delta F^0 = -3725 + 7.02 T \log T + 1.865 \times 10^{-3} T^2 - 31.82 T$$

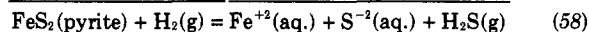
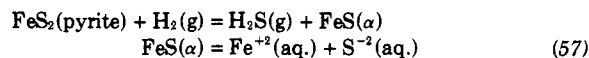
At 400° K. (127° C.), $\text{FeS}(\alpha) + \text{H}_2\text{S}(\text{g}) = \text{FeS}_2(\text{pyrite}) + \text{H}_2(\text{g})$;

$$\Delta F^0_{400} = -2.635 \text{ kcal.} \quad (56)$$

hence at 400° K., the equilibrium constant is:

$$K_y = \frac{P_{H_2}}{P_{H_2S}} = e^{-\frac{\Delta F^0}{RT}} = 27.5$$

The variation of Fe^{+2} concentration can be found by combining these relations with those for FeS .



$$\Delta F_y = -RT \ln K_B = -RT \ln K_s + RT \ln K_y \quad (59)$$

Therefore

$$K_B = K_s / K_y$$

Since

$$K_s = (\text{Fe}^{+2})(\text{S}^{-2}) \text{ and } K_y = \frac{P_{H_2}}{P_{H_2S}}$$

then

$$K_B = K_s / K_y = (\text{Fe}^{+2})(\text{S}^{-2}) \frac{P_{H_2}}{P_{H_2S}}$$

Hence for pyrite

$$(\text{Fe}^{+2})(\text{S}^{-2}) = \frac{K_s}{K_y} \times (P_{H_2}/P_{H_2S}) \quad (60)$$

instead of

$$(\text{Fe}^{+2})(\text{S}^{-2}) = K_s$$

as for FeS (troilite).

In an exactly analogous treatment given the pyrrhotite solubility relations, the variation of iron concentration in

equilibrium with pyrite is given by merely replacing K_1 in Equations 2 to 12 by

$$\frac{K_1}{K_y} \times \frac{P_{H_2}}{P_{H_2S}}$$

For example, the limiting equilibrium solubility of Fe^{+2} , $(Fe^{+2})_0$ for FeS present with FeS_2 is

$$(Fe^{+2})_0 = \frac{K_1}{K_2} \text{ for just FeS}$$

but is

$$(Fe^{+2})_0 = \frac{K_1}{K_2} \times \frac{1}{K_y} \frac{P_{H_2}}{P_{H_2S}} \text{ for (FeS + FeS}_2\text{)} \quad (61)$$

Let us look, for example, at the magnitude of the effect of this "pyrite" factor—i.e., $1/K_y P_{H_2}/P_{H_2S}$ —on the amount of Fe^{+2} in solution in equilibrium at conditions where:

$$P_{H_2}/P_{H_2S} \cong 0.01$$

At 25° C., $K_y = 3.4 \times 10^3$; at 127° C., $K_y = 27.5$

Hence the limiting solubility of Fe^{+2} in plain water will be

$$(Fe^{+2})_0 \text{ at } 25^\circ \text{ C.} \cong (K_1/K_2)_{25} \times \frac{0.01}{3.4 \times 10^3} = 3 \times 10^{-6} (K_1/K_2)_{25}$$

$$(Fe^{+2})_0 \text{ at } 127^\circ \text{ C.} \cong (K_1/K_2)_{25} \times \frac{0.01}{27.5} = 3.6 \times 10^{-4} (K_1/K_2)_{400}$$

This means that aside from other effects of temperature on K_2 and K_1 , the equilibrium solubility of the mixed sulfides is cut manyfold by the conversion of FeS to pyrite—i.e., ferrous ion is much more tightly bound as FeS_2 than as FeS.

For comparison purposes, the (limiting) concentrations of dissolved iron in equilibrium with various iron sulfides are shown in Table XI.

There is the further conclusion to be drawn that since the limiting Fe^{+2} solubility for FeS_2 is so very low, the concentration of acid required to prevent its precipitation

$$[(Fe^{+2})_0 = (H^+)_{lim.}]$$

is also very low, even at high H_2S concentrations.

APPLICATIONS

Unexpectedly heavy and peculiarly localized deposits of sulfides were interfering with a large scale dual temperature process for producing heavy water (3), which used ferrous metal equipment to hold the required aqueous hydrogen sulfide liquors. The heavy deposits appeared on both mild steel and stainless steel components and only in the hot sections of the process stream. It appeared that sulfide deposition in gross amounts on stainless steel equipment is necessarily the result of deposition from the process stream, for stainless steel is only slightly attacked by H_2S - H_2O

solutions and acquires only a thin sulfide coating from chemical attack. The presence of appreciable amounts of ferrous ion in the process streams in addition to the normal iron content of entering process water indicated continuous corrosion of mild steel components of the equipment.

The heavy water process concerned operates at about 250 p.s.i. pressure, and at temperatures from about 25° to 210° C. For economic reasons, mild steel was used in much of the construction. That it can be used successfully depends on the formation of an adherent protective coating of iron sulfide, formed rapidly during initial exposure except where erosion is caused by high liquid velocities or spray impingement. At such locations, the more resistant stainless steel must be used. It remained to identify and properly subdue the cause of deposition.

There are three principle mechanisms of surface fouling:

Crystallization from supersaturated solutions, as in the formation of scale from bicarbonate hardness in water.

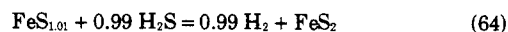
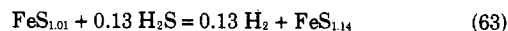
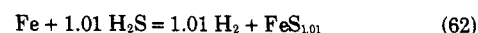
Deflocculation of suspended colloids, as in the deposition of iron hydroxides from certain river waters in the absence of chlorine.

Surface catalysis of reactions to form insoluble precipitates from ingredients waiting to react in the liquid medium, as in the formation of manganese dioxide fouling from manganous-bearing water to which chlorine or oxygen is added.

Of these three deposition mechanisms, crystallization from supersaturated solution is indicated for the sulfide process concerned. This is evidenced by the macrocrystalline nature of the deposits, by the complete ability of solubility relations to account for the site of deposition and (coupled with the flow rate) to account for the amounts of deposits observed, and by the almost complete repression of depositions by the addition of base in the amounts prescribed by the solubility hypothesis.

In this process, water entering and leaving the system contains little iron (about 0.5 p.p.m.). The process streams, however, transitorily contain 1 to 6 p.p.m. because of the dissolution of iron sulfide corrosion products from the walls. The concentrations match closely those predicted by the preceding calculations. In all units where deposition is marked or observed, the temperature of the H_2S -saturated water is rising. This increase in temperature decreases sulfide solubility, causes evolution of H_2S , and increases pH. The deposits which interfere with operations are therefore mainly the results of leaching off the iron sulfides from the corroded iron surfaces by the cold process streams, followed by redeposition of the dissolved sulfide as the liquid is heated.

The principal reactions affecting deposition are



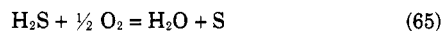
The presence of metallic iron at the walls retards the formation of higher sulfides. This permits troilite ($FeS_{1.01}$),

Table XI. Concentrations of Ferrous Iron in Equilibrium with Various Iron Sulfides

Solid Phase	Expression for $(Fe^{+2})_0$	Temp., ° C.	K_1	K_2	K_g	K_y	$\frac{P_{H_2}}{P_{H_2S}}$	$(Fe^{+2})_0$
FeS	K_1/K_2	25	4.16×10^{-17}	1.3×10^{-13}	...	...	0.01	3.20×10^{-4}
		127	4.7×10^{-15}	9×10^{-10}	...	...	0.01	5.2×10^{-6}
FeS- $FeS_{1.14}$	$\frac{K_1}{K_2} \times \left(\frac{P_{H_2}}{P_{H_2S}}\right)^{0.14} \times \frac{1}{K_g}$	25	4.16×10^{-17}	1.3×10^{-13}	2.80	...	0.01	6.0×10^{-5}
		127	4.7×10^{-15}	9×10^{-10}	3.63	...	0.01	7.6×10^{-7}
FeS- FeS_2	$\frac{K_1}{K_2} \times \left(\frac{P_{H_2}}{P_{H_2S}}\right) \times \frac{1}{K_g}$	25	4.16×10^{-17}	1.3×10^{-13}	...	...	0.01	10^{-9}
		127	4.7×10^{-15}	9×10^{-10}	...	$\sim 3.4 \times 10^3$ ~ 27.5	0.01	2×10^{-9}

for example, to exist at conditions that otherwise would promote formation of higher sulfides. The same is true for pyrrhotite ($\text{FeS}_{1.14}$). Marcasite, then, is found only where the rate of formation from FeS and H_2S in a solid phase reaction overrides the rate of reduction by the metal walls. Pyrite, which requires slower rates of formation than marcasite, would be formed only rarely.

In addition to iron sulfides, small quantities of sulfur are occasionally found, especially in the marcasite deposits, probably formed by the accidental admission of oxygen, which causes the reaction:



The presence of such free sulfur doubtless aids the formation of higher iron sulfides.

Pursuant to the above calculations and reasoning, a calculated amount of sodium hydrosulfide was added to the feed water of the plant process stream. A rapid and stable reduction of the iron content of the process streams was observed at all points. The troublesome deposits thereafter formed only very slowly, confirming the analysis.

ACKNOWLEDGMENT

The writer expresses appreciation for data supplied by O. Carboni, J.F. Proctor, A.L. Marston, M.L. Richards, and B.S. Johnson, Jr., all of E.I. du Pont de Nemours & Co.

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CORRECTION

In the article, "Prediction of Boiling Points of Liquid Mixtures," by Isamu Nagata [*J. CHEM. ENG. DATA* **6**, 1961], the following changes should be made:

On page 586, Equation 1 should read

$$\frac{y_i}{y_j} = \frac{x_i}{x_j} \left(\frac{x_i + x_j a_{ij}}{x_j b_{ij} + x_i c_{ij}} \right)$$

On page 587, Equation 24 should read

$$b_{12} \cdot b_{23} \dots b_{ij} \dots b_{n1} = 1$$

On page 588, the data source for *n*-heptane under cyclohexane should be (29, 36); for toluene (28, 36).

On page 589, the first words in the fourth line of the sixth paragraph should be methanol-ethanol.

On page 590, the third paragraph from the bottom (second column) should read: Hence $T_{12} = 361.9$.

On page 591, in Table III, the T_3 value for toluene should be 383.8.

CORRECTION

In the article, "New Generalized Equation for Gas Diffusion Coefficient," by Ning Hsing Chen and Donald F. Othmer [*J. CHEM. ENG. DATA* **7**, 37 (1962)], the following changes should be made:

On page 38, the third line from the bottom (second column) and on page 40 (Equation 19) 0.3666 should be 2.326.

On page 39 (Table II, No. 22, column 6) 0.0733 should be 0.0773.

On page 41, fifth line from the bottom (second column), the name should be Ning Hsing Chen.