



Title	Equilibrium between FeS and mixed gas of H ₂ and H ₂ O
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Citation	Memoirs of the Faculty of Engineering, Hokkaido University, 9(1), 84-90
Issue Date	1952-03-31
Doc URL	http://hdl.handle.net/2115/37768
Type	bulletin (article)
File Information	9(1)_84-90.pdf



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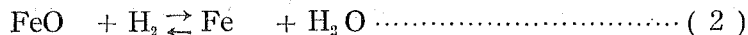
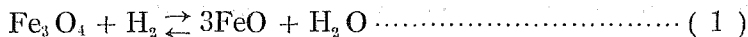
Equilibrium between FeS and Mixed Gas of H₂ and H₂ O.

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(Received Aug. 31, 1951)

Introduction

Reactions between FeS and mixed gas of H₂ and H₂O produce Fe, FeO or Fe₃O₄ and gaseous sulphides as the case of mixed gas of CO and CO₂, which has been previously reported by the author.¹⁾ As gaseous sulphides, in this case, H₂S, SO₂ and S₂ are considered to exist and the formation of SO₃ is negligible on account of the very low dissociation pressure of H₂O. Only one among Fe, FeO and Fe₃O₄ is stable according to the equilibrium relations shown as follows.



Although many observations are reported on these reactions the author uses the results obtained by Emmett and Schultz²⁾ for his calculations. As Emmett and Schultz did not show their results as a function of absolute temperature, the author calculated the equations as follows.

$$\log K_1 = \log p_{\text{H}_2\text{O}}/p_{\text{H}_2} = -3306.22/T + 3.455 \dots\dots\dots (3)$$

$$\log K_2 = \log p_{\text{H}_2\text{O}}/p_{\text{H}_2} = -854.28/T + 0.502 \dots\dots\dots (4)$$

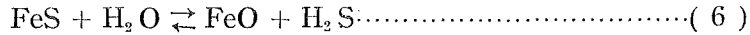
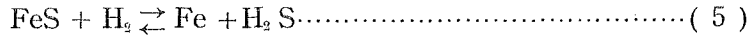
Using these equations the following table can be obtained.

Fe ₃ O ₄ + H ₂ ⇌ 3FeO + H ₂ O				
temp. °C	600	800	1000	1200
log p _{H₂O} /p _{H₂}	- 0.332	0.374	0.858	1.210
H ₂ , %	68.2	29.7	12.2	5.8
H ₂ O, %	31.8	70.3	87.8	94.2

FeO + H ₂ ⇌ Fe + H ₂ O				
temp. °C	600	800	1000	1200
log p _{H₂O} /p _{H₂}	- 0.477	- 0.294	- 0.169	- 0.078
H ₂ , %	75.0	66.3	59.6	54.5
H ₂ O, %	25.0	33.7	40.4	45.5

Formation of H₂S

On the formation of H₂S, three reactions are considered,



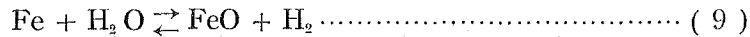
Reaction (5) is determined by the author as follows.³⁾

$$\log K_5 = \log p_{\text{H}_2\text{S}}/p_{\text{H}_2} = -3910.28/T + 0.887 \dots\dots\dots (8)$$

From this, log K₅ at 600°C, 800°C, 1000°C and 1200°C are calculated as follows:

temp. °C	600	800	1000	1200
log K ₅	-3.592	-2.757	-2.185	-1.768

When FeO is the stable product of the reaction, reaction (5) must be combined with



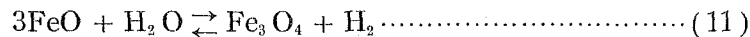
Therefore, from (8) and (4), the following equation is obtained.

$$\log K_6 = \log p_{\text{H}_2\text{S}}/p_{\text{H}_2} = -3056.0/T + 0.385 \dots\dots\dots (10)$$

By means of this equation, log K₆ can be calculated as follows.

temp. °C	600	800	1000	1200
log K ₆	-3.116	-2.463	-2.016	-1.690

Under the condition where Fe₃O₄ is produced, reaction (7) must be considered, and this is obtained by combining reaction (6) with the reaction



Calculating from (3) and (10),

$$\log K_7 = \log p_{\text{H}_2} \cdot p_{\text{H}_2\text{S}}^3 / p_{\text{H}_2\text{O}}^4 = -5661.80/T - 2.300 \dots\dots\dots (12)$$

By this equation log K₇ can be calculated as follows:

temp. °C	600	800	1000	1200
log K ₇	-9.003	-7.763	-6.905	-6.280

From the above calculations, the following three equations can be introduced.

$$\log p_{\text{H}_2\text{S}} = \log K_5 + \log p_{\text{H}_2} \dots\dots\dots (13)$$

$$\log p_{\text{H}_2\text{S}} = \log K_6 + \log p_{\text{H}_2\text{O}} \dots\dots\dots (14)$$

$$3\log p_{\text{H}_2\text{S}} = \log K_7 - \log p_{\text{H}_2} + 4\log p_{\text{H}_2\text{O}} \dots\dots\dots (15)$$

Therefore, log p_{H₂S} is shown as a function of p_{H₂} and p_{H₂O}. At a given temperature the following table can be calculated for log p_{H₂S}.

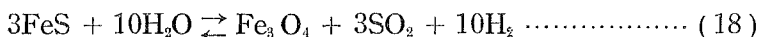
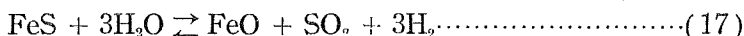
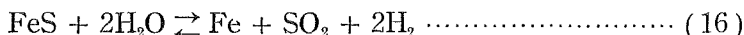
log p_{H_2S}

H ₂ %	99	95	90	80	70	50	30	20	10	5	1
H ₂ O %	1	5	10	20	30	50	70	80	90	95	99
600°C	-3.596	-3.614	-3.638	-3.689	-3.639	-3.302	-3.003	-2.897	-2.721	-2.597	-2.340
800°C	-2.761	-2.779	-2.803	-2.854	-2.912	-2.764	-2.618	-2.454	-2.286	-2.154	-1.897
1000°C	-2.189	-2.207	-2.231	-2.282	-2.340	-2.317	-2.171	-2.113	-2.030	-1.898	-1.641
1200°C	-1.772	-1.790	-1.814	-1.865	-1.923	-1.991	-1.845	-1.787	-1.736	-1.689	-1.432

This relation is shown in Fig. 1.

Formation of SO₂

In the case of SO₂ formation, the following three equations can be considered :



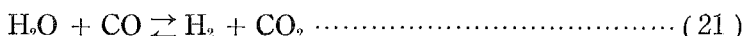
The author determined the equilibrium constant of the reaction⁴⁾



as

$$\log K_{19} = \log p_{\text{SO}_2}^3 \cdot p_{\text{CO}}^{10} / p_{\text{CO}_2}^{10} = -52669.7/T + 22.438 \dots (20)$$

The equilibrium constant of the reaction



has been precisely determined by many authorities and Maurer and Bischof⁵⁾ gave the following equation :

$$\log K_{21} = \log p_{\text{CO}_2} p_{\text{H}_2} / p_{\text{H}_2\text{O}} \cdot p_{\text{CO}} = 2203.4/T + 5.1588 \times 10^{-5} T + 2.5426 \times 10^{-7} T^2 - 7.4617 \times 10^{-11} T^3 - 2.3 \dots\dots\dots (22)$$

Calculating log K_{21} between 600°~1200°C, the author gave a simple equation for this reaction as follows.

$$\log K_{21} = 1775.87/T - 1.634 \dots\dots\dots (23)$$

This equation agrees well with equation (22) in this temperature range.

From (19) and (23), for the reaction (18)

$$\log K_{18} = \log p_{\text{SO}_2}^3 \cdot p_{\text{H}_2}^{10} / p_{\text{H}_2\text{O}}^{10} = -34911.0/T + 6.098 \dots (24)$$

is introduced and log K_{18} can be calculated as follows :

temp. °C	600	800	1000	1200
log K_{18}	-33.892	-26.438	-21.328	-17.603

Equilibrium constant for the reaction (17) can be calculated from (24), and (3) as follows :

$$\log K_{17} = \log p_{\text{SO}_2} \cdot p_{\text{H}_2}^3 / p_{\text{H}_2\text{O}}^3 = -12739.07/T + 3.184 \dots (25)$$

temp. °C	600	800	1000	1200
log K ₁₇	-11.408	-8.688	-6.823	-5.464

Equilibrium constant for the reaction (16) can be calculated from (25) and (4) as follows:

$$\log K_{16} = \log p_{\text{SO}_2} \cdot p_{\text{H}_2}^2 / p_{\text{H}_2\text{O}}^2 = -13593.35/T + 3.686 \dots (26)$$

temp. °C	600	800	1000	1200
log K ₁₆	-11.884	-8.983	-6.992	-5.542

From these results the following equations can be obtained:

$$\log p_{\text{SO}_2} = \log K_{16} - 2 (\log p_{\text{H}_2} - p_{\text{H}_2\text{O}}) \dots (27)$$

$$\log p_{\text{SO}_2} = \log K_{17} - 3 (\log p_{\text{H}_2} - p_{\text{H}_2\text{O}}) \dots (28)$$

$$3 \log p_{\text{S}_2} = \log K_{18} - 10 (\log p_{\text{H}_2} - p_{\text{H}_2\text{O}}) \dots (29)$$

Then if the temperature was constant $\log p_{\text{SO}_2}$ becomes the function of $\log p_{\text{H}_2} - \log p_{\text{H}_2\text{O}}$, that is $p_{\text{H}_2}/p_{\text{H}_2\text{O}}$. Fig. 2 represents the relation between $\log p_{\text{SO}_2}$ and $\log p_{\text{H}_2}/p_{\text{H}_2\text{O}}$.

When $p_{\text{H}_2} + p_{\text{H}_2\text{O}} = 1$, $\log p_{\text{SO}_2}$ is calculated as follows:

log p _{SO₂}											
H ₂ , %	99	95	90	80	70	50	30	20	10	5	1
H ₂ O, %	1	5	10	20	30	50	70	80	90	95	99
600°C	-15.875	-14.442	-13.792	-13.088	-12.512	-11.297	-10.070	-9.290	-8.116	-7.034	-6.645
800°C	-12.974	-11.541	-10.891	-10.187	-9.719	-8.688	-7.584	-6.806	-5.632	-4.550	-2.161
1000°C	-10.983	-9.550	-8.900	-8.196	-7.728	-6.823	-5.719	-5.017	-3.928	-2.846	-0.457
1200°C	-9.533	-8.110	-7.550	-6.746	-6.278	-5.404	-4.360	-3.658	-2.283	-1.605	0.784

From these results Fig. 3 is obtained.

Dissociation Pressure of S₂

S₂ vapour produced by the dissociation of FeS has nothing to do with the gas composition.

Therefore from the equation described before,³⁾

$$\log p_{\text{S}_2} = -16916.4/T + 6.64 \dots (31)$$

$\log p_{\text{S}_2}$ at 600°C, 800°C, 1000°C, 1200°C are calculated as follows.

temp. °C	600	800	1000	1200
log p _{S₂}	-12.74	-9.13	-6.65	-4.84

Sulphur content in Gas atmosphere

From the above calculations, at given H_2 % in H_2-H_2O mixture, gaseous sulphide which shows greatest partial pressure is tabulated as follows. Besides this gas, some gaseous sulphides whose partial pressure is greater than 1/100 of the greatest are also described here.

H_2 , %	99	95	90	80	70	50	30	20	10	5	1
H_2O , %	1	5	10	20	30	50	70	80	90	95	99
600°C	$\log p_{H_2S}$ -3.596	$\log p_{H_2S}$ -3.614	$\log p_{H_2S}$ -3.638	$\log p_{H_2S}$ -3.689	$\log p_{H_2S}$ -3.639	$\log p_{H_2S}$ -3.302	$\log p_{H_2S}$ -3.003	$\log p_{H_2S}$ -2.897	$\log p_{H_2S}$ -2.729	$\log p_{H_2S}$ -2.597	$\log p_{H_2S}$ -2.304
800°C	$\log p_{H_2S}$ -2.761	$\log p_{H_2S}$ -2.779	$\log p_{H_2S}$ -2.803	$\log p_{H_2S}$ -2.854	$\log p_{H_2S}$ -2.912	$\log p_{H_2S}$ -2.764	$\log p_{H_2S}$ -2.618	$\log p_{H_2S}$ -2.454	$\log p_{H_2S}$ -2.286	$\log p_{H_2S}$ -2.154	$\log p_{H_2S}$ -1.897 $\log p_{SO_2}$ -2.161
1000°C	$\log p_{H_2S}$ -2.189	$\log p_{H_2S}$ -2.207	$\log p_{H_2S}$ -2.231	$\log p_{H_2S}$ -2.282	$\log p_{H_2S}$ -2.340	$\log p_{H_2S}$ -2.317	$\log p_{H_2S}$ -2.171	$\log p_{H_2S}$ -2.113	$\log p_{H_2S}$ -2.030 $\log p_{SO_2}$ -3.928	$\log p_{H_2S}$ -1.898 $\log p_{SO_2}$ -2.846	$\log p_{H_2S}$ -1.641 $\log p_{SO_2}$ -0.457
1200°C	$\log p_{H_2S}$ -1.772	$\log p_{H_2S}$ -1.790	$\log p_{H_2S}$ -1.814	$\log p_{H_2S}$ -1.865	$\log p_{H_2S}$ -1.923	$\log p_{H_2S}$ -1.991	$\log p_{H_2S}$ -1.845	$\log p_{H_2S}$ -1.787 $\log p_{SO_2}$ -3.658	$\log p_{H_2S}$ -1.736 $\log p_{SO_2}$ -2.283	$\log p_{H_2S}$ -1.689 $\log p_{SO_2}$ -1.605	$\log p_{H_2S}$ -1.432 $\log p_{SO_2}$ 0.784

Only the gases described in this table have important influence upon sulphur content in the mixed gas of H_2 and H_2O , and the other gases can be neglected.

Now, as both H_2S and SO_2 contain 1430g S per $1 m^3$, from above table S grams contained in $1 m^3$ at equilibrium state are calculated as follows:

H_2 , %	99	95	90	80	70	50	30	20	10	5	1
H_2O , %	1	5	10	20	30	50	70	80	90	95	99
600°C S g/m ³ $\log S$	0.3625 -0.4407	0.3478 -0.4586	0.3290 -0.4827	0.2926 -0.5337	0.3283 -0.4837	0.7134 -0.1467	1.4201 0.1523	1.8132 0.2585	2.6684 0.4263	3.6165 0.5583	6.5365 0.8154
800°C S g/m ³ $\log S$	2.4796 0.3944	2.3787 0.3762	2.2508 0.3523	2.002 0.3015	1.7518 0.2435	2.4625 0.3914	3.4463 0.5373	5.0279 0.7014	7.4017 0.8693	10.0315 1.0014	27.0023 1.4314
1000°C S g/m ³ $\log S$	9.2535 0.9663	8.8788 0.9484	8.4013 0.9244	7.4703 0.8733	6.5369 0.8153	6.8912 0.8383	9.6454 0.9891	11.0239 1.0483	13.5149 1.1308	20.1277 1.3032	531.893 2.7258
1200°C S g/m ³ $\log S$	24.1670 1.3832	23.1946 1.3654	21.9505 1.3414	19.5195 1.2905	17.0742 1.2323	14.6003 1.1644	20.4347 1.3104	23.6662 1.3741	33.7223 1.5279	64.7647 1.8113	8748.71 3.9419

This relation is shown in Fig. 4.

From these results, important gaseous sulphide produced by the reactions between FeS , H_2 and H_2O is seen to be H_2S . But at high H_2O content or at high temperature, SO_2 plays also an important role.

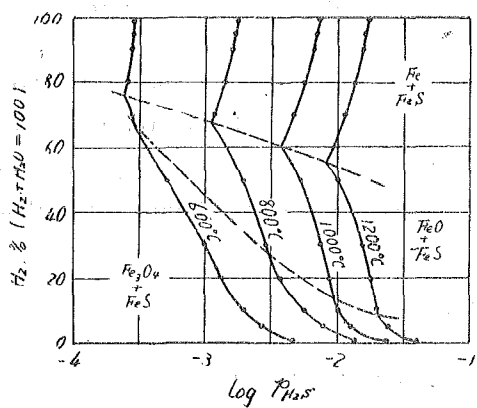


Fig. 1

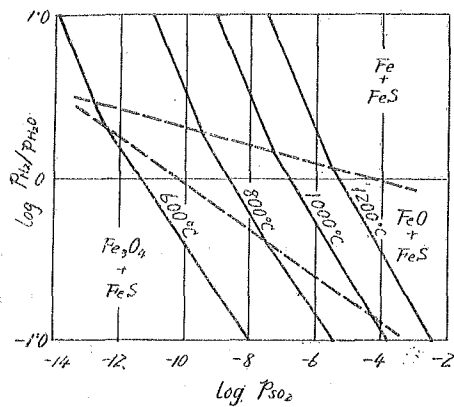


Fig. 2

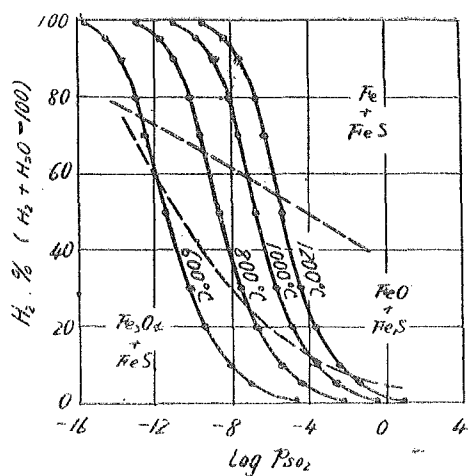


Fig. 3

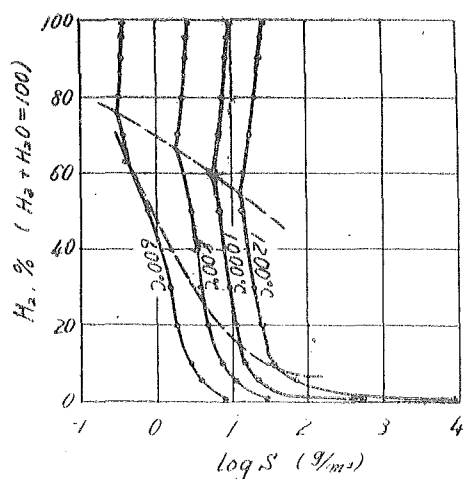


Fig. 4

Conclusion

From the calculations on the partial pressures of H_2S , SO_2 and S_2 as gaseous sulphides produced by the reactions between FeS , H_2 and H_2O , the author calculated the sulphur content in gas atmosphere at equilibrium state.

By this calculation, H_2S and SO_2 are the important gases at the equilibrium state of the reactions between FeS , H_2 and H_2O . This is similar to the formation of COS and SO_2 in the reactions between FeS , CO and CO_2 . But as H_2S is more stable than COS , mixed gas of H_2 and H_2O is preferable for desulphurization than that of CO and CO_2 at the reducing side.

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