Study on the equilibrium between iron, sulphur and CO-CO_2 mixed gas.

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(Received Jan. 16, 1952)

I. Introduction

By the reaction between ferrous sulphide and $CO-CO_2$ mixed gas, it can be considered that SO_2 COS and CS_2 are produced. Besides them S_2 gas can also be considered to exist in the gas phase independent of $CO-CO_2$ mixed ratio. We have previously reported[1), 2)] some results of experiments in which the produced gas was conditioned to be only SO_2 or COS. Further, one of the authors has reported[3)] some results of the case where the produced gas is only CS_2 and also on the vapour pressure of S_2 gas both calculated from the already known thermodynamic data. Summarizing these results some calculations have been carried out on the equilibrium between ferrous sulphide and $CO-CO_2$ mixed gas. Furthermore some calculations were made on the equilibrium between sulphur in molten iron and $CO-CO_2$ mixed gas from the already known thermodynamic data and some data derived from our experiments.

II. Equilibrium between ferrous sulphide and CO-CO_2 mixed gas.

In case ferrous sulphide is in state of equilibrium with $CO-CO_2$ mixed gas, gaseous sulphides that can be considered to exist in the equilibrium gas phase are SO_2, COS, CS_2 and S_2. As for the case when only SO_2 or COS gas enters into the problem we have previously derived the relations, of which results have already reported[1), 2)], between p_{CO2} and p_{SO2} or p_{CO} and p_{COS} from the experimental data. CS_2 gas was proved to be negligibe according to the results of calculations carried out by one of the authors. S_2 gas which is produced by dissociation of ferrous sulphide and of which the partial pressure is constant at a given temperature independent of $CO-CO_2$ mixed ratio, was also proved to be negligible up to 1200°C by calculation. By calcuations carried out upon the relation between p_{CO} ($p_{CO}+p_{CO2}=1$) and p_{SO2} or p_{COS} over the temperature range of 600 to 1200°C, produced gases that should be taken into consideration according to $CO-CO_2$ mixed ratio are

listed qualitatively in Table 1. In this table were omitted gases, whose partial pressures were less than 1/100 of that of the main produced gas under the same conditions.

Table 1

Gases to be cousidered	Tem°C \ p_{OO}	0.99	0.9	0.7	0.5	0.3	0.1	0.01
	600	COS	COS	COS	COS	COS	COS	COS, SO_2
	800	COS	COS	COS	COS	COS	COS, SO_2	COS, SO_2
	1000	COS	COS	COS	COS	COS, SO_2	COS, SO_2	COS, SO_2
	1200	COS	COS	COS, SO_2	COS, SO_2	COS, SO_2	COS, SO_2	COS, SO_2

From the fact that 1 m³ of COS and SO_2 each contains 1430 g of sulphur we calculated the weight of sulphur in 1m³ of equilibrium gas from the partial pressure of the produced gas and obtained the relation between p_{CO} ($p_{CO} + p_{OO_2} = 1$) and $log\ S$ (g/m³) which is shown graphically in Fig. 1.

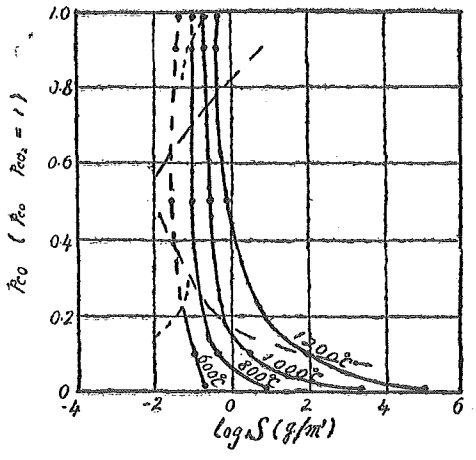

Fig. 1

As is clear from Table 1 the main gaseous sulphides that are produced by the reaction between ferrous sulphide and CO-CO_2 mixed gas are COS and SO_2. However, at a lower temperature COS plays a main role over almost the whole range of $CO-CO_2$ mixed ratio while at a higher temperature SO_2 increases with CO_2 enrichment at a very rapid rate as can be seen from Fig. 1, so SO_2 comes to play a greater role.

III. Equilibrium between sulphur in molten iron and CO-CO₂ mixed gas.

In the previous section the equilibrium between ferrous sulphide and $CO-CO_2$ mixed gas was considered. Next, we have investigated and carried out some calculations on the equilibrium between sulphur in molten iron and $CO-CO_2$ mixed gas. In such case SO_2, COS, CS_2 and S_2 can also be considered to be produced. About SO_2, CS_2 and S_2 one of the authors has previously carried out some calculations and reported[4] his results. As for COS, we carried out some calculations using the equation of the formation equilbrium of COS which was derived from the experimental data of reduction equilibrium of ferrous sulphide by CO gas which we have previously obtained[7]. The results of the calculatrous were as follows.

When we consider the equilibrium between molten iron and $CO-CO_2$ mixed gas, the iron oxide in molten iron that should be considered is only FeO. When CO/CO_2 ratio exceeds a certain value, the formation of free FeO does not occur, but with the enrichment of CO_2, molten iron becomes saturated with FeO and the formation of free FeO phase begins. In such case, at the equilibrium state whole content of Fe should be turned to FeO and consequently the expression $[S]$ (sulphur in molten iron) would be inappropriate, however, as far as molten iron exists, such expression should be allowed to show a tendency to equilibrium.

(i) Formation of COS

The following two reactions can be considered for the formation of COS.

$$[S] + CO \rightleftarrows COS \qquad (1)$$

$$[S] + CO_2 \rightleftarrows [O]_{Sat.} + COS \qquad (2)$$

The reaction (1) can be derived from the following two reactions.

$$[S] \rightleftarrows 1/2\, S_2 \qquad (3)$$

$$CO + 1/2\, S_2 \rightleftarrows COS \qquad (4)$$

Against reaction (3) the following equation is given by S. Matoba and T. Uno[5]

$$log\ K_3 = log\ p_{S_2}^{1/2}/[S] = -\ 9174.3/T + 2.704 \qquad (5)$$

Against reaction (4) we have computed[2] the equation

$$log\ K_4 = log\ p_{COS}/p_{CO} \cdot\ p_{S_2}^{1/2} = 6443.5/T - 5.418 \qquad (6)$$

From equations (5) and (6) we can derive the following equation against reaction (1)

$$log\ K_1 = log\ p_{COS}/p_{CO} \cdot [S] = -\ 2730.8/T - 2.173 \qquad (7)$$

Then, by combining this equation and the following equation which was given by Sanbongi[6] for $Fe-C-O$ system

$$CO_2 \rightleftarrows [O]_{Sat.}\ Sat\ in\ Fe + CO \qquad (8)$$

$$log\ K_8 = log\ p_{CO}/p_{CO_2} = -\ 4158.8/T + 3.24 \qquad (9)$$

we can derive the following equation for the reaction (2)

$$log\ K_2 = log\ p_{COS}/p_{CO_2} \cdot [S] = -\ 6889.6/T + 1.07 \qquad (10)$$

Reaction (1) is valid for the range where molten iron is not saturated with oxygen, while reaction (2) is for the range of saturated molten iron.

Equations (7) and (10) may be expressed as

$$log\ p_{COS} = log\ K_1 + log\ p_{CO} + log\ [S]$$

and

$$log\ p_{COS} = log\ K_2 + log\ p_{CO_2} + log\ [S]$$

respectively, so $log\ p_{COS}$ is functioned by $[S]$, p_{CO} or p_{CO_2}. Assuming $(p_{CO} + p_{CO_2})$ to be unity, the value of $log\ p_{COS}$ at a given $CO-CO_2$ mixed ratio and $[S]$ % can be computed as shown in Table 2.

Table 2

p_{CO}		0.99	0.9	0.8	0.7	0.5	0.3	0.2	0.1	0.01
p_{CO_2}		0.01	0.1	0.2	0.3	0.5	0.7	0.8	0.9	0.99
Temp °C	[S] %	$\log p_{COS}$								
1500	1.0	−4.25	−4.29	−4.05	−3.88	−3.66	−3.51	−3.45	−3.40	−3.36
	0.1	−5.25	−5.29	−5.05	−4.88	−4.66	−4.51	−4.45	−4.40	−4.36
	0.01	−6.25	−6.29	−6.05	−5.88	−5.66	−5.51	−5.45	−5.40	−5.36
1600	1.0	−4.17	−4.15	−3.85	−3.67	−3.45	−3.30	−3.24	−3.19	−3.15
	0.1	−5.17	−5.15	−4.85	−4.67	−4.45	−4.30	−4.24	−4.19	−4.15
	0.01	−6.17	−6.15	−5.85	−5.67	−5.45	−5.30	−5.24	−5.19	−5.15
1700	1.0	−4.10	−3.96	−3.66	−3.48	−3.26	−3.11	−3.06	−3.01	−2.96
	0.1	−5.10	−4.96	−4.66	−4.48	−4.26	−4.11	−4.06	−4.01	−3.96
	0.01	−6.10	−5.96	−5.66	−5.48	−5.26	−5.11	−5.06	−5.01	−4.96

The relations in Table 2 are shown graphically for each temperature in Figs. 2 to 4. These values are somewhat higher than those that one of the authors has computed from the equation which Lewis and Lacey[7] had given for the formation of *COS*.

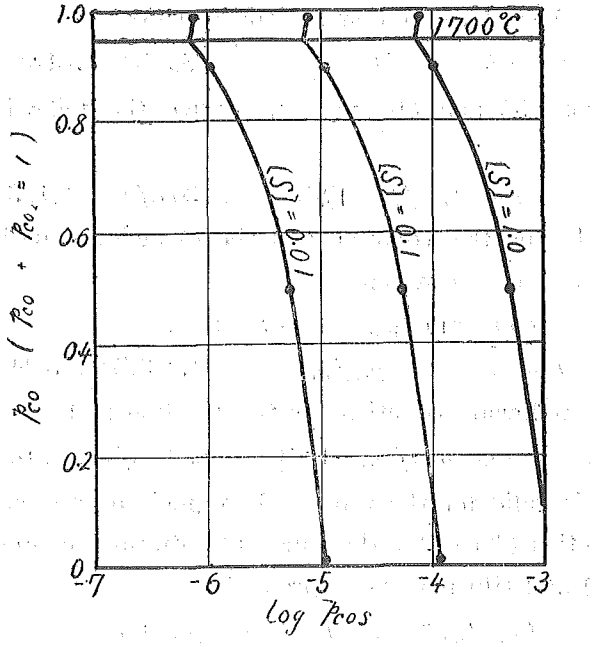

Fig. 2

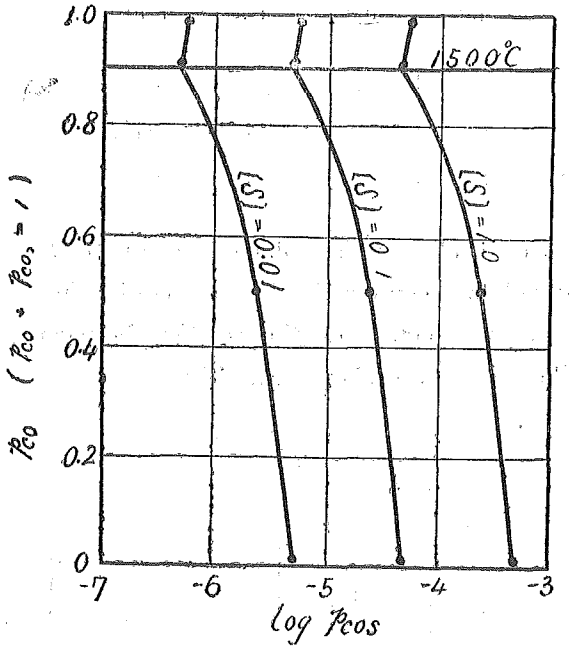

Fig.3

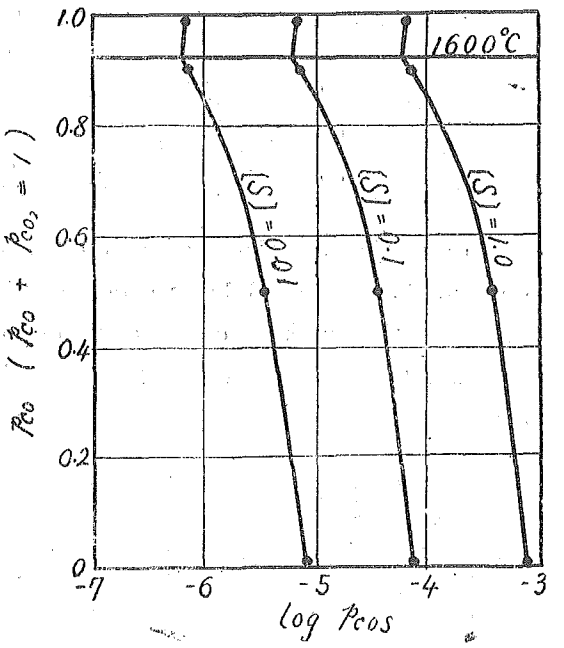

Fig. 4

(ii) Sulphur content in the equilibrium gas phase.

Here, we are going to consider the content of sulphur that can exist in the equilibrium gas phase when $CO-CO_2$ mixed gas is in equilibrium state with sulphur in molten iron. As for SO_2, CS_2 and S_2 gas we used the previously reported[4] data and for COS the above described ones.

The details of calculation will not be given here. Gaseous sulphides in the equilibrium gas phase that should be considered according to [S] % and $CO-CO_2$ mixed ratio at 1500, 1600 and 1700°C are listed qualitatively in Table 3. In this table are omitted gases whose partial pressures were less than 1/100 of that of the main produced gas under same conditions.

Table 3

	P_{CO} / [S]%	0.99	0.9	0.7	0.5	0.3	0.1	0.01
	1500°C							
Gases to be considered	1.0	COS, S_2	COS, S_2, SO_2	COS, S_2, SO_2	COS, SO_2	SO_2	SO_2	SO_2
	0.1	COS, S_2	COS, S_2, SO_2	COS, SO_2	COS, SO_2	SO_2	SO_2	SO_2
	0.01	COS	COS, SO_2	COS, SO_2	COS, SO_2	SO_2	SO_2	SO_2
	1600°C							
Gases to be considered	1.0	COS, S_2	COS, S_2, SO_2	COS, S_2, SO_2	SO_2	SO_2	SO_2	SO_2
	0.1	COS, S_2	COS, S_2, SO_2	COS, SO_2	SO_2	SO_2	SO_2	SO_2
	0.01	COS, S_2	COS, S_2, SO_2	COS, SO_2	SO_2	SO_2	SO_2	SO_2

Gases to be considered	[S]% \ P_{CO}	0.99	0.9	0.7	0.5	0.3	0.1	0.01
		1700°C						
	1.0	COS, S_2, SO_2	COS, S_2, SO_2	COS, S_2, SO_2	SO_2	SO_2	SO_2	SO_2
	0.1	COS, S_2, SO_2	COS, S_2, SO_2	COS, SO_2	SO_2	SO_2	SO_2	SO_2
	0.01	COS, S_2, SO_2	COS, S_2, SO_2	COS, SO_2	SO_2	SO_2	SO_2	SO_2

From the fact that 1 m³ of *COS* and SO_2 each contains 1430 g and 1 m³ of S_2 contains 2860 g of sulphur we derived the sulphur content in 1 m³ of equilibrium gas from the partial pressure of produced gas and computed the relation between p_{CO} ($p_{CO} + p_{CO_2} = 1$) and $log\ S$ (g/m³). The results are shown graphically in Figs. 5 to 7.

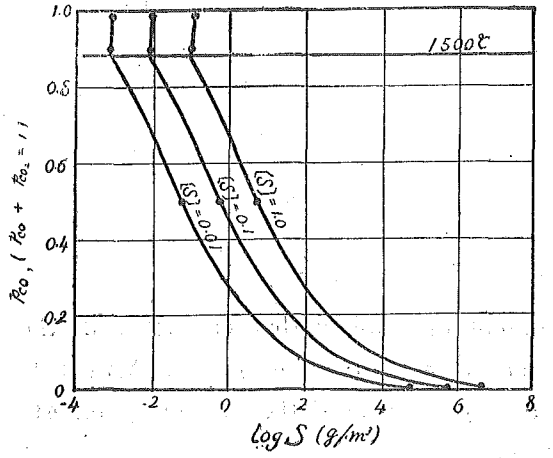

Fig. 5

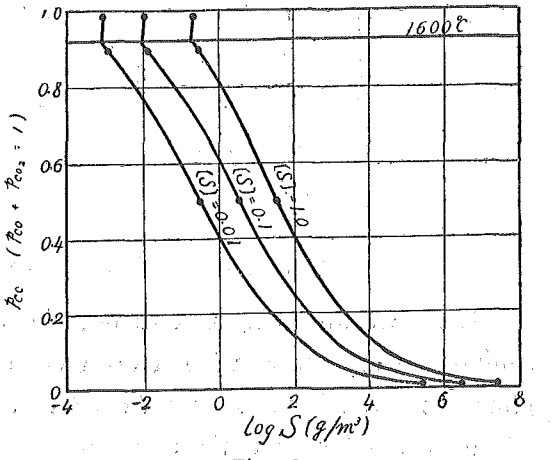

Fig. 6

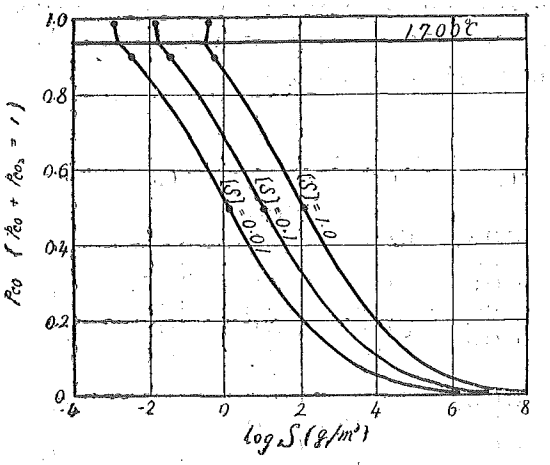

Fig. 7

It is clear from these tables and figures that SO_2 plays a main role over almost the whole range of $CO-CO_2$ mixed ratio while COS should be considered only when CO exceeds 50 %. Further, at higher temperature S_2 can not be ignored at higher [S] %. From Fig3. 5 to 7 it will be seen that under strong oxidizing atmosphere a considerable amount of sulphur can exist in the gas phase while under reducing atmosphere only a small amount of sulphur can exits.

IV. Conclusions

When ferrous sulphide is in a state of equilibrium with $CO-CO_2$ mixed gas, assumming SO_2, COS, CS_2, and S_2 to exist in the gas phase and calculating their partial pressure, we have obtained the main gaseous sulphide at different CO/CO_2 mixed ratios and further computed the amount of sulphur that can exist in the gas phase at the equilibrium state. From these results it became clear that COS plays a main role even at rather high CO_2 % range, however, at extreme high CO_2 % range SO_2 supersedes COS. Further we carried out some calculations on sulphur in molten iron in which case the partial pressure of gaseous sulphide in gas phase is affected by sulphur content in molten iron. In this case COS and SO_2 also become the main gaseous sulphides. SO_2 has become the main gas already from high CO% range and COS comes into the problem only over the range where CO exceeds 50 %, and also at higher temperature S_2 gas can not be ignored at higher [S] %.

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