Sulfide and Sulfate Solid Solubility in Lime, Magnesia, and Calcined Dolomite: Part I. CaS and CaSO₄ Solubility in CaO
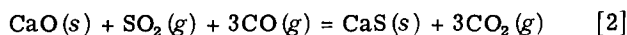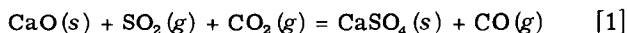
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In the present work the solid solubilities of CaS and CaSO$_4$ in burnt lime were investigated by equilibrating lime with CO-CO$_2$-SO$_2$ mixtures at temperatures from 950 to 1300°C. Also, the equilibrium constants for the formation of CaS and CaSO$_4$ were determined. At high oxygen activities, corresponding to a CO$_2$/CO ratio >100 in the gas, the sulfur dissolves in lime primarily as sulfate ions. At lower oxygen activities (CO$_2$/CO < 30), the sulfur goes into solution in lime essentially as sulfide ions. Over the temperature range investigated the limiting sulfide solubility is within 0.01 to 0.03 pct S, whereas the sulfate solubility is within 0.03 to 0.1 pct S, increasing with increasing temperature.

LIMESTONE invariably contains some sulfur, primarily in the form of pyrite; the average sulfur content is usually within the range 0.02 to 0.1 pct, but it can be as high as 0.3 pct. Since the specified maximum sulfur content of burnt lime used in oxygen steelmaking is about 0.03 pct, particular attention must be paid to the desulfurization during calcination of the limestone. Recently this subject was studied by Wriedt and Darken[1] and by Turkdogan and Rice.[2] From thermodynamic considerations and experimental investigations, the following conclusions were drawn.

The equilibrium sulfur pressure of pyrite is one atmosphere at 697°C. Therefore, during heating of the limestone to the calcination temperature, the pyrite dissociates to pyrrhotite and sulfur vapor which may react with CaCO$_3$ to form CaS, SO$_2$, and CO. Also, at the calcination front, that is the CaCO$_3$/CaO interface, S$_2$ may react with CO$_2$ to form SO$_2$ and CO. As SO$_2$ diffuses through the pores of the lime shell together with CO$_2$, some CaSO$_4$ may also form. For the conditions prevailing in calcination furnaces (shaft or rotary kiln) there are two key sulfur reactions to be considered.

$$CaO\,(s) + SO_2\,(g) + CO_2\,(g) = CaSO_4\,(s) + CO\,(g) \quad [1]$$

$$CaO\,(s) + SO_2\,(g) + 3CO\,(g) = CaS\,(s) + 3CO_2\,(g) \quad [2]$$

The respective equilibrium constants for these reactions are represented by

$$K_1 = \frac{p_{CO}}{p_{CO_2}} \frac{1}{p_{SO_2}} \quad [3]$$

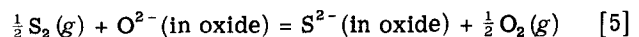$$K_2 = \left(\frac{p_{CO_2}}{p_{CO}}\right)^3 \frac{1}{p_{SO_2}} \quad [4]$$

The equilibrium SO$_2$ pressure for calcium sulfide in burnt lime increases with increasing p_{CO_2}/p_{CO} ratio. On the other hand, for calcium sulfate in burnt lime, the equilibrium SO$_2$ pressure increases with decreas-

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ing p_{CO_2}/p_{CO} ratio. From the compilation of available equilibrium data, Wriedt and Darken[1] derived the optimum gas compositions for effective desulfurization during the calcination of limestone. These were also verified experimentally by Turkdogan and Rice.[2] Also, it is evident from Reactions [1] and [2] that increasing total pressure would favor the sulfide and sulfate formation.
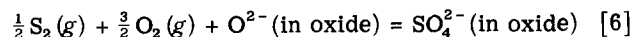
In addition to the dissociation of CaSO$_4$ or CaS during calcination, consideration should be given to the solid solution of sulfur in lime as sulfate and sulfide ions. According to the work of Kor and Richardson,[3] the solubility of CaS in lime is 0.003 pct S at 1500°C and 0.011 pct S at 1650°C. A literature survey revealed no previous work on the solubility of CaSO$_4$ in lime.

The chemistry of reactions between sulfur-bearing gases and slags is well known, as outlined for example by Fincham and Richardson,[4] and by Turkdogan and Darken;[5] there are, of course, many other similar published papers on this subject. Whether the solvent oxide is liquid or solid, the sulfide, sulfate, and pyrosulfate reactions are represented simply by
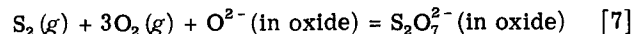
Sulfide:

$$\tfrac{1}{2} S_2\,(g) + O^{2-}\,(\text{in oxide}) = S^{2-}\,(\text{in oxide}) + \tfrac{1}{2} O_2\,(g) \quad [5]$$

Sulfate:

$$\tfrac{1}{2} S_2\,(g) + \tfrac{3}{2} O_2\,(g) + O^{2-}\,(\text{in oxide}) = SO_4^{2-}\,(\text{in oxide}) \quad [6]$$

Pyrosulfate:

$$S_2\,(g) + 3O_2\,(g) + O^{2-}\,(\text{in oxide}) = S_2O_7^{2-}\,(\text{in oxide}) \quad [7]$$

For a given activity in the gas, the lowest equilibrium sulfur concentration in the oxide is at an oxygen potential at which there is equal distribution of sulfide and sulfate ion concentrations in the oxide. At much higher oxygen activities the pyrosulfate ions may form.[5]

In the present work Reactions [5] and [6] in lime were investigated by equilibrating lime with CO, CO$_2$, and SO$_2$ gas mixtures up to saturation with CaS or CaSO$_4$.

EXPERIMENTAL

All the equilibrium measurements were made with calcined calcium carbonate (reagent grade) and dry

gas mixtures CO-CO_2-SO_2. The lime thus produced contained the following major impurities: 0.01 pct Ba, 0.04 pct Sr, 0.06 pct Na and < 0.01 pct K. The experimental results did not indicate any measurable interference of these trace impurities on the sulfide and sulfate solubilities in lime. Evidently these impurities are in solid solution in lime at the temperatures investigated, *i.e.*, at activities much below unity, hence no interference with the sulfur solubility measurements. About 1 g of calcium carbonate, contained in a platinum basket and suspended in the uniform-temperature zone of a vertical furnace, was first calcined at the desired experimental temperature in a CO-CO_2 mixture for about 1 h; this time was far in excess of that required for complete calcination. Then, a desired CO-CO_2-SO_2 mixture was flowed through the reaction tube at about 2 l (STP)/min for a period of 1 to 6 h, after which the sample was air-quenched by rapid removal from the furnace. The preliminary experiments indicated that the sulfur solution in lime in a given gas mixture reached equilibrium within about 1 to 2 h; that is, the sulfur solubility obtained did not change at reaction times longer than 2 h. Immediately after removal from the furnace, the sample was analyzed for total sulfur by the iodometric-combustion method.

The equilibrium measurements were made at temperatures from 950 to 1300°C with gas mixtures containing 0.1 to 60 pct SO_2 and CO_2/CO ratios from 3 to 200. The sulfur-solubility measurements were made up to the limit of saturation of lime with calcium sulfide or calcium sulfate, at which point there was a marked increase in the sulfur content of the sample. The formation of the sulfide or sulfate phase at a critical gas composition could be verified readily by a qualitative chemical test. The addition of a few drops of a cadmium acetate solution to the sample of sulfidized lime dissolved in water produced a dense yellow precipitate when lime was saturated with calcium sulfide. Saturation of the sample with calcium sulfate was verified by the barium chloride test.

In a few experiments the equilibrium for sulfide or sulfate solubility was approached from the high-sulfur side by using lime samples previously sulfidized to about 3 pct S. The sulfur solubilities obtained (< 0.1 pct S) with these initially high-sulfur samples were in general accord with those obtained by using the sulfur-free lime samples.

With gas mixtures high in SO_2 and/or low in CO_2/CO ratio there was some sulfur deposition at the top of the furnace tube. However, there was no sulfur deposition in the lower part of the reaction tube, below the position of the sample. Since the sulfur deposition occurred only on the exhaust side of the gas stream, no difficulty was experienced in identifying the gas composition in the reaction zone from the ingoing gas composition.

Assuming that the gas equilibrium is maintained near the surface of the lime sample, the partial pressures of the gaseous species can be calculated from the available equilibrium data for all the pertinent gas reactions. For the ranges of temperatures and gas compositions employed in this work, the following are the predominant gaseous species in the equilibrated gas mixtures: CO_2, CO, COS, S_2, and SO_2; other species such as O_2, S, SO, SO_3, CS, and CS_2 are small enough

to be neglected in the calculations. With this simplification, the material balances for carbon (ΣC), sulfur (ΣS), and oxygen (ΣO) are represented by the following ratios for the ingoing gas mixture at $(p_{CO})_i + (p_{CO_2})_i + (p_{SO_2})_i = 1$ atmosphere.

$$\frac{\Sigma C}{\Sigma S} = \frac{1 - (p_{SO_2})_i}{(p_{SO_2})_i} = \frac{p_{CO_2} + p_{CO} + p_{COS}}{2p_{S_2} + p_{SO_2} + p_{COS}}$$

$$\frac{\Sigma C}{\Sigma O} = \frac{1 - (p_{SO_2})_i}{2 - (p_{CO})_i} = \frac{p_{CO_2} + p_{CO} + p_{COS}}{2p_{SO_2} + p_{COS} + 2p_{CO_2} + p_{CO}}$$

For the reaction $2CO + SO_2 = \frac{1}{2} S_2 + 2CO_2$,

$$K_S = \left(\frac{p_{CO_2}}{p_{CO}}\right)^2 \frac{(p_{S_2})^{1/2}}{p_{SO_2}}$$

For the reaction $3CO + SO_2 = COS + 2CO_2$,

$$K_C = \frac{(p_{CO_2})^2}{(p_{CO})^3} \frac{p_{COS}}{p_{SO_2}}$$

For the sum of all the predominant species,

$$p_{CO_2} + p_{CO} + p_{COS} + p_{S_2} + p_{SO_2} = 1$$

By simultaneous solution of these five equations, for known values of the equilibrium constants[6] K_S and K_C and known ingoing gas composition, the equilibrium partial pressures of the gaseous species were calculated through a computer program.

Examples are given in Fig. 1 showing the equilibrium ratio p_{CO_2}/p_{CO} at the indicated temperatures as a function of percent $(SO_2)_i$ in the ingoing gas. There is a pronounced increase in the equilibrium ratio p_{CO_2}/p_{CO} with increasing SO_2 content of the gas; this increase is much greater at lower temperatures. However, at low SO_2 contents with a CO_2/CO ratio in the ingoing mixture greater than 50, the equilibrium values p_{CO_2}/p_{CO} and p_{SO_2} are close to those in the ingoing mixture, particularly at higher temperatures. At low SO_2 contents, the equilibrium p_{SO_2} is markedly affected by the ratio $(CO_2/CO)_i$, particularly at lower temperatures. This is demonstrated in Fig. 2 for CO-CO_2-0.1 pct SO_2 mixtures.

RESULTS

Typical examples of experimental results for sulfate solubility in lime and the formation of calcium sulfate are shown in Figs. 3 and 4 for 1000 to 1300°C. The point of discontinuity on the solubility line gives the critical gas composition for calcium sulfate coexisting with lime. The slopes of the solubility lines increase with increasing p_{CO_2}/p_{CO} ratio in the gas phase as expected for the sulfate reaction [1].

At low p_{CO_2}/p_{CO} ratios the sulfur is in solution in lime primarily as sulfide ions. The results in Fig. 5 are typical examples of sulfide solubility and the formation of calcium sulfide in the presence of lime. The coordinates are for equilibrium gas compositions for the indicated ingoing gas mixtures. Near the point of discontinuity the solubility lines approach the theoretical slope—3:1 in this logarithmic plot for the sulfide reaction.

Table I. Experimental Results on Sulfide and Sulfate Solubility in Lime and Formation of CaS and $CaSO_4$ in $CO-CO_2-SO_2$ Mixtures at Atmospheric Pressure

$\dfrac{CO_2}{CO}_i$	$(SO_2)_i$, pct	S, wt pct	$\dfrac{P_{CO_2}}{P_{CO}}$	P_{SO_2} atm	K_1 atm^{-1}	$P_{SO_2}(P_{O_2})^{1/2}$, atm$^{3/2}$	K_2 atm^{-1}	$(P_{S_2}/P_{O_2})^{1/2}$
				950°C: $K_1' = 3.09 \times 10^7$; $K_2' = 8.91 \times 10^{10}$				
99	1.5	0.032	99	0.015	0.67	4.85×10^{-8}	–	–
				1000°C: $K_1' = 1.10 \times 10^7$; $K_2' = 1.15 \times 10^{10}$				
160	1.8	0.044	160	0.018	0.35	2.63×10^{-7}	–	–
99	3.2	0.040	99	0.032	0.32	2.88×10^{-7}	–	–
49	5.0	0.046	56	0.049	0.36	2.52×10^{-7}	–	–
32	2.7	0.027	36	0.026	–	–	1.79×10^6	6.44×10^3
24	1.3	0.025	27	0.012	–	–	1.64×10^6	7.02×10^3
18	0.3	0.017	18	0.0026	–	–	2.24×10^6	5.14×10^3
13	0.1	0.013	13	0.00075	–	–	2.93×10^6	3.93×10^3
				1050°C: $K_1' = 4.07 \times 10^6$; $K_2' = 2.51 \times 10^9$				
99	5.1	0.054	99	0.051	0.20	1.23×10^{-6}	–	–
18	1.0	0.022	18	0.0091	–	–	6.40×10^5	3.93×10^3
				1100°C: $K_1' = 1.62 \times 10^6$; $K_2' = 4.57 \times 10^8$				
155	7.4	0.069	155	0.074	0.087	7.08×10^{-6}	–	–
99	11.1	0.068	99	0.111	0.091	6.76×10^{-6}	–	–
49	19.7	0.069	55	0.196	0.093	6.60×10^{-6}	–	–
32	26.0	0.091	45	0.257	0.087	7.08×10^{-6}	–	–
24	30.0	0.105	41	0.295	0.083	7.41×10^{-6}	–	–
20	18,0	0.078	31	0.174	–	–	1.71×10^5	2.68×10^3
18	6.0	0.041	21	0.052	–	–	1.78×10^5	2.57×10^3
16	2.8	0.030	17	0.024	–	–	2.04×10^5	2.24×10^3
4.4	0.1	0.030	4.5	0.00054	–	–	1.69×10^5	2.70×10^3
				1180°C: $K_1' = 3.98 \times 10^5$; $K_2' = 5.10 \times 10^7$				
99	24.0	0.095	99	0.240	0.042	5.95×10^{-5}	–	–
				1200°C: $K_1' = 2.82 \times 10^5$; $K_2' = 2.63 \times 10^7$				
199	15.5	0.100	199	0.155	0.032	1.11×10^{-4}	–	–
99	29.5	0.102	99	0.295	0.034	1.04×10^{-4}	–	–
49	57.3	0.104	55	0.570	0.032	1.10×10^{-4}	–	–
24	57.0	0.115	37	0.567	0.047	0.75×10^{-4}	–	–
16	48.0	0.115	28	0.475	–	–	4.62×10^4	5.69×10^2
12	42.0	0.090	22	0.410	–	–	2.59×10^4	1.01×10^3
10	9.7	0.028	12	0.090	–	–	1.92×10^4	1.36×10^3
9	4.2	0.017	9.6	0.039	–	–	2.27×10^4	1.16×10^3
6	1.0	0.016	5.8	0.0097	–	–	2.01×10^4	1.31×10^3
				1300°C: $K_1' = 6.92 \times 10^4$; $K_2' = 2.40 \times 10^6$				
199	23.5	0.081	199	0.235	0.021	6.88×10^{-4}	–	–
99	47.5	0.089	99	0.475	0.021	6.88×10^{-4}	–	–
5	8.5	0.012	5.9	0.075	–	–	2.74×10^3	8.76×10^2
3	1.5	0.012	3.1	0.011	–	–	2.71×10^3	8.86×10^2

$$K_1 = \frac{P_{CO}}{P_{CO_2}} \frac{1}{P_{SO_2}} \quad \text{for sulfate equilibrium}$$

$$K_1' = \frac{P_{CO_2}}{P_{CO}} \frac{1}{(P_{O_2})^{1/2}} \quad \text{Therefore} \quad P_{SO_2}(P_{O_2})^{1/2} = \frac{1}{K_1 K_1'}$$

$$K_2 = \left(\frac{P_{CO_2}}{P_{CO}}\right)^3 \frac{1}{P_{SO_2}} \quad \text{for sulfide equilibrium}$$

$$K_2' = \left(\frac{P_{S_2}}{P_{O_2}}\right)^{1/2}\left(\frac{P_{CO_2}}{P_{CO}}\right)^3 \frac{1}{P_{SO_2}} \quad \text{Therefore} \quad \left(\frac{P_{S_2}}{P_{O_2}}\right)^{1/2} = \frac{K_2'}{K_2}$$

All the experimental results are summarized in Table I where pct S is the sulfur in solution in lime, as sulfide and sulfate ions in equilibrium with calcium sulfate or calcium sulfide. The equilibrium contants K_1 and K_2 are for sulfate and sulfide reactions as given by Eqs. [1] and [2]. Other derived values in Table I are discussed later.

The variation of the equilibrium SO_2 pressure over CaS or $CaSO_4$ and CaO with the oxygen activity, that is, the p_{CO_2}/p_{CO} ratio, is shown in Fig. 6, as determined from the results of the present work. The data points are close to straight lines drawn in this log-log plot with the theoretical slopes 3:1 and $-1:1$ for the sulfide and sulfate equilibrium, respectively. The points of intersection of the sulfide and sulfate lines are located on the univariant for co-existing CaO, CaS, and $CaSO_4$. At 1200°C and presumably higher, there is a marked curvature suggesting partial solubility of lime in CaS and $CaSO_4$.

As seen from the results in Table I, the equilibrium

gas compositions differ much from the composition of the ingoing gas mixture, particularly for CO_2/CO less than 50. The importance of gas equilibrium to accurate interpretation of the data is well demonstrated in Fig. 7 for 1100°C. The lines obtained in this log-log plot by
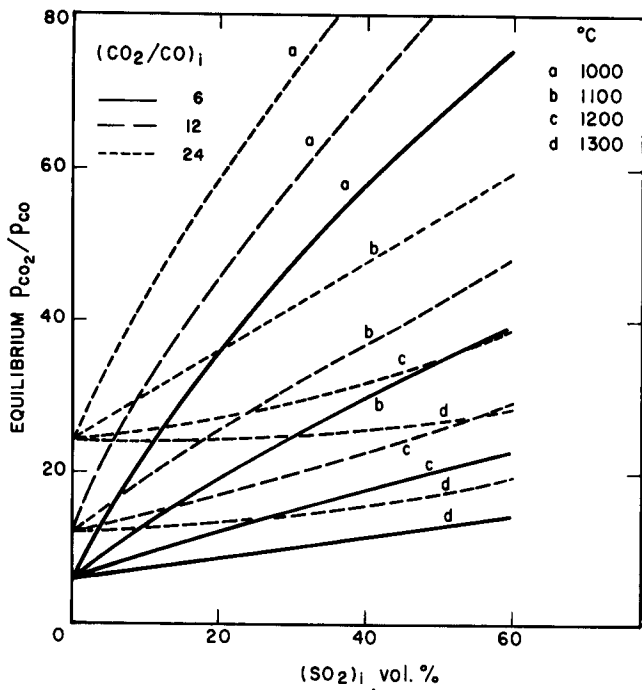

Fig. 1—Equilibrium ratios pCO_2/pCO at indicated temperatures as a function of pct $(SO_2)_i$ for indicated ratios $(CO_2/CO)_i$ in ingoing gas mixtures CO-CO_2-SO_2 at atmospheric pressure.
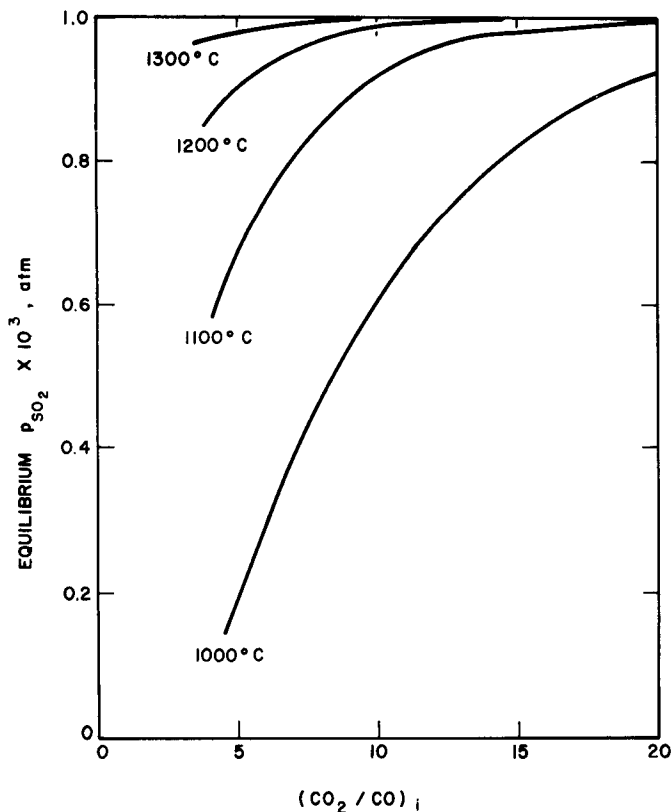

Fig. 2—Equilibrium SO_2 partial pressures at indicated temperatures as a function of ratio $(CO_2/CO)_i$ in ingoing gas mixtures CO-CO_2-0.1 pct SO_2 at atmospheric pressure.
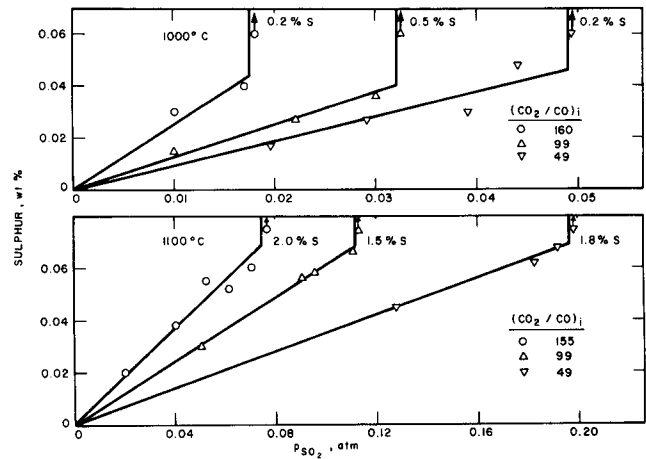
Fig. 3—Sulfate solubility in lime and formation of $CaSO_4$ in CO-CO_2-SO_2 mixtures at atmospheric pressure.

using the calculated gas compositions (from critical $(CO_2/CO)_i$ and pct $(SO_2)_i$ in the ingoing gas) have slopes in accord with the theory. On the other hand, the plot obtained by using $(CO_2/CO)_i$ and pct $(SO_2)_i$ for the sulfide and sulfate formation has no meaning in terms of reaction equilibrium, particularly for $(CO_2/CO)_i$ ratios below about 50.

DISCUSSION

The temperature dependence of the equilibrium constants K_1 and K_2, from the present work, is shown in Fig. 8.

For the sulfide equilibrium the temperature dependence of the equilibrium constant, for the temperature range 1000 to 1300°C, is represented by

$$\log K_2 = \frac{20,000}{T} - 9.270 \qquad [8]$$

Rosenqvist[7] determined the state of equilibrium for the reaction

$$CaO\,(s) + H_2S\,(g) = CaS\,(s) + H_2O\,(g) \qquad [9]$$
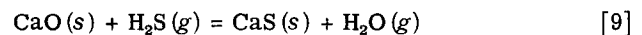
To compare the present results with those of Rosenqvist, Reactions [2] and [9] may be written in a more general form, thus

$$CaS\,(s) + \tfrac{1}{2}O_2\,(g) = CaO\,(s) + \tfrac{1}{2}S_2\,(g) \qquad [10]$$
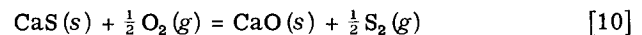
for which the equilibrium constant is given by the ratio $(p_{S_2}/p_{O_2})^{1/2}$. By combining the equilibrium constant $K_2 = (p_{CO_2}/p_{CO})^3/p_{SO_2}$ from Table I or p_{H_2O}/p_{H_2S} from Rosenqvist's measurements with the known equilibrium constants of the appropriate gas reactions,[6] these two sets of data are converted to $(p_{S_2}/p_{O_2})^{1/2}$ for Reaction [10]. The temperature dependence of the equilibrium constant $(p_{S_2}/p_{O_2})^{1/2}$ is shown in Fig. 9, in which two data points from the work of Kor and Richardson[3] are also included; the dotted line is that calculated from the compiled thermodynamic data.[6] The agreement between the results of different investigators is satisfactory. For the temperature range 750 to 1650°C the line in Fig. 9 may be represented by

$$\log\left(\frac{p_{S_2}}{p_{O_2}}\right)^{1/2} = \frac{4805}{T} - 0.133 \qquad [11]$$

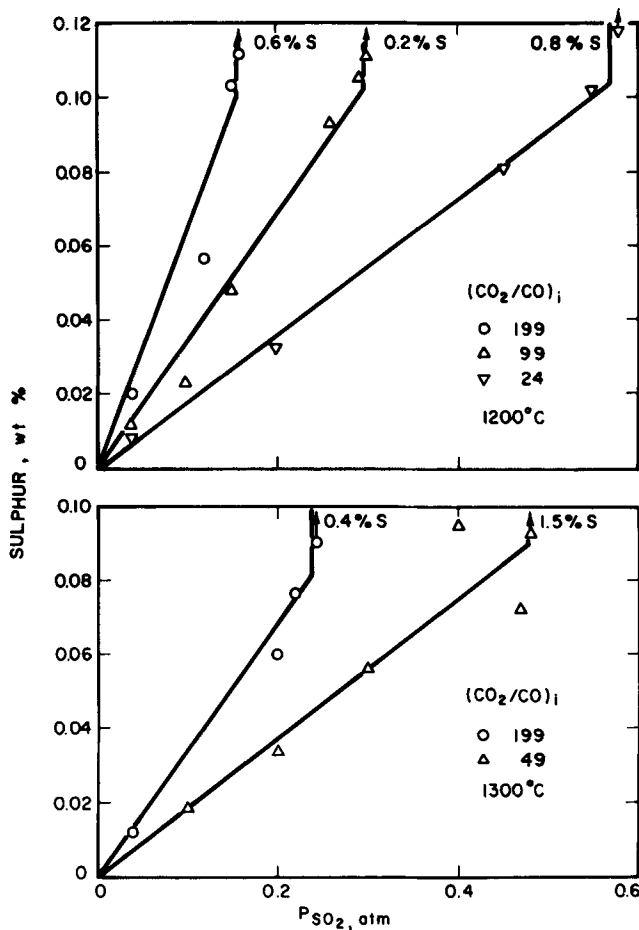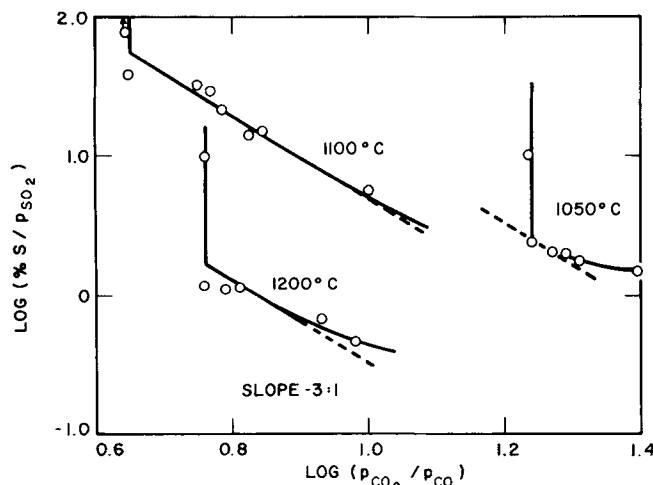Fig. 4—Sulfate solubility in lime and formation of $CaSO_4$ in CO-CO_2-SO_2 mixtures at atmospheric pressure.

Fig. 5—Sulfide solubility in lime and formation of CaS in CO-CO_2-SO_2 mixtures at atmospheric pressure.

°C	$(CO_2/CO)_i$	(pct $SO_2)_i$
1050	15–24	1.0
1100	4–10	0.1
1200	6–10	1.0

The top line in Fig. 8 is for the equilibrium constant K_1 for the co-existing phases CaO and $CaSO_4$. At 1195°C calcium sulfate undergoes a phase transformation.[8] The low-temperature β-$CaSO_4$ has a rhombic-dipyramidal structure with the following cell dimensions in Å:
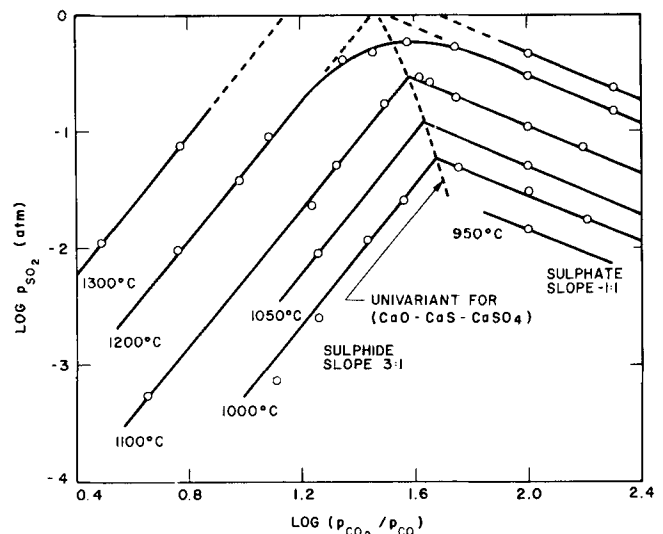
Fig. 6—Variation of equilibrium SO_2-pressure over CaS or $CaSO_4$ and CaO with oxygen activity $i.e.$, p_{CO_2}/p_{CO} ratio at indicated temperatures.
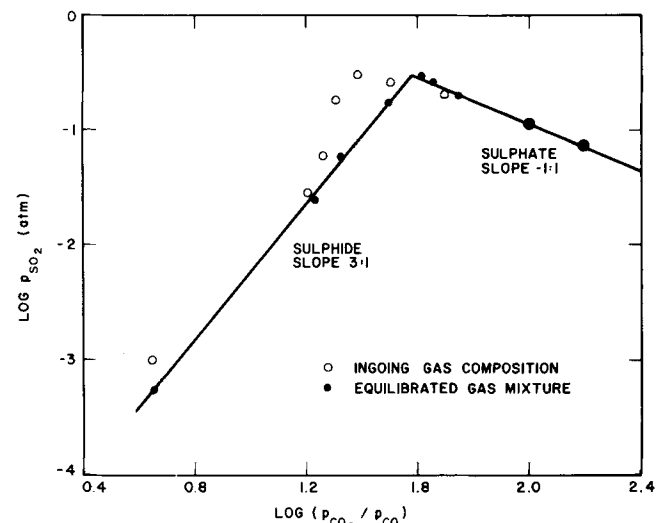
Fig. 7—SO_2 and CO_2/CO relation over CaS and $CaSO_4$ with CaO relative to ingoing and equilibrated gas compositions at 1100°C.

a = 6.22, b = 6.96, and c = 6.97. The high-temperature modification, α-$CaSO_4$, could not be quenched for structural studies. The heat of $\beta \rightarrow \alpha$ transformation is not known. The line for K_1 in Fig. 8 for the α-phase is based on the line for the β-phase by assuming a value of 2 kcal for the $\beta \rightarrow \alpha$ transformation; this is a reasonable approximation for solid-state phase transformation in carbonates, nitrates, sulfates, and so on. The value of K_1 at 1300°C is higher than would be expected from the extrapolation of the K_1 values obtained at lower temperatures; this is discussed later. The temperature dependence of K_1 may be represented by the following equations up to the lime-sulfate eutectic temperature 1365°C.[9]*

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*According to the measurements of Grieveson and Turkdogan (*Trans. TMS-AIME*, 1962, vol. 224, pp. 1086-95), the melting point of $CaSO_4$ is 1465°C. This is in good agreement with the value of 1462°C reported later by Rowe *et al.* (*J. inorg. nucl. Chem.*, 1965, vol. 27, p. 53).

Below 1195°C (β-phase): $\log K_1 = \dfrac{9617}{T} - 8.021$ [12]

From 1195 to 1365°C (α-phase): $\log K_1 = \dfrac{9180}{T} - 7.708$

[13]

The free energy of decomposition of calcium sulfate (α) has been determined by Dewing and Richardson[10] by a unique technique of differential thermal analysis in SO_2-O_2-N_2 mixtures at atmospheric pressure. The decomposition of $CaSO_4$ is represented by

$$CaSO_4\,(s) = CaO\,(s) + SO_2\,(g) + \tfrac{1}{2}O_2\,(g) \qquad [14]$$
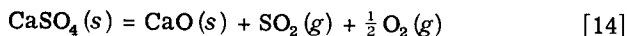
for which the equilibrium constant for unit activities of CaO and $CaSO_4$ is given by the product $p_{SO_2}\,(p_{O_2})^{1/2}$. The results of Dewing and Richardson and those derived from the present work are given in Fig. 10; the data from the present work were obtained by combining the experimental values of K_1 in Table I with the known equilibrium constants for the appropriate gas reactions.[6] These two sets of data from vastly different experiments are in very good agreement. The data point from the present work for 1300°C is lower than that of Dewing and Richardson; this is discussed later. The lines for α- and β-phases are drawn by again assuming 2 kcal for the heat of transformation, thus

Below 1195°C (β-phase):

$$\log p_{SO_2}(p_{O_2})^{1/2} = - \dfrac{24{,}120}{T} + 12.416 \qquad [15]$$

From 1195 to 1365°C (α-phase):

$$\log p_{SO_2}(p_{O_2})^{1/2} = - \dfrac{23{,}680}{T} + 12.111 \qquad [16]$$

The decomposition equilibrium for calcium sulfate was determined also by Zawadski[11] in the early 1930's by measuring the total equilibrium pressure of decom-

position. His values of $p_{SO_2}\,(p_{O_2})^{1/2}$, not given in Fig. 10, are 20 to 30 pct higher than those of Dewing and Richardson and of the present work.
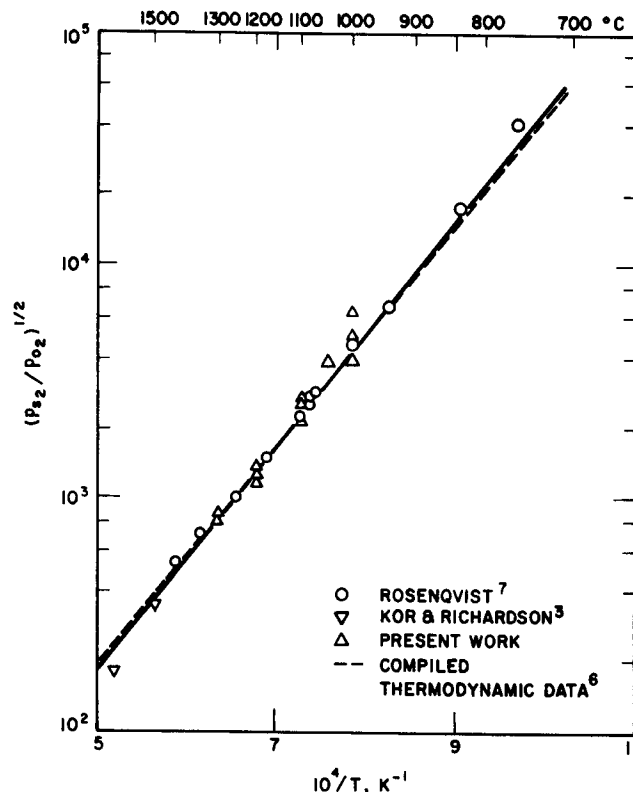

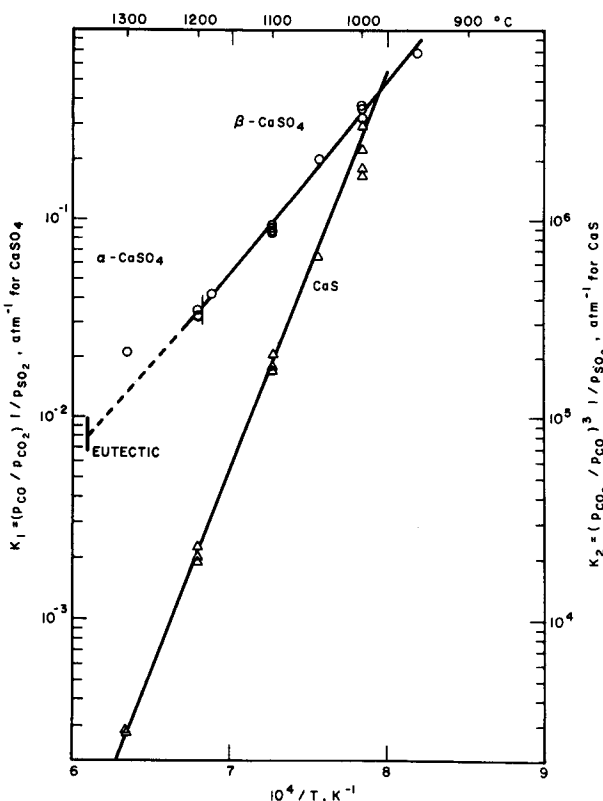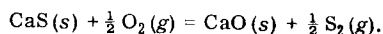Fig. 9—Temperature dependence of the equilibrium constant for reaction

$$CaS\,(s) + \tfrac{1}{2}O_2\,(g) = CaO\,(s) + \tfrac{1}{2}S_2\,(g).$$

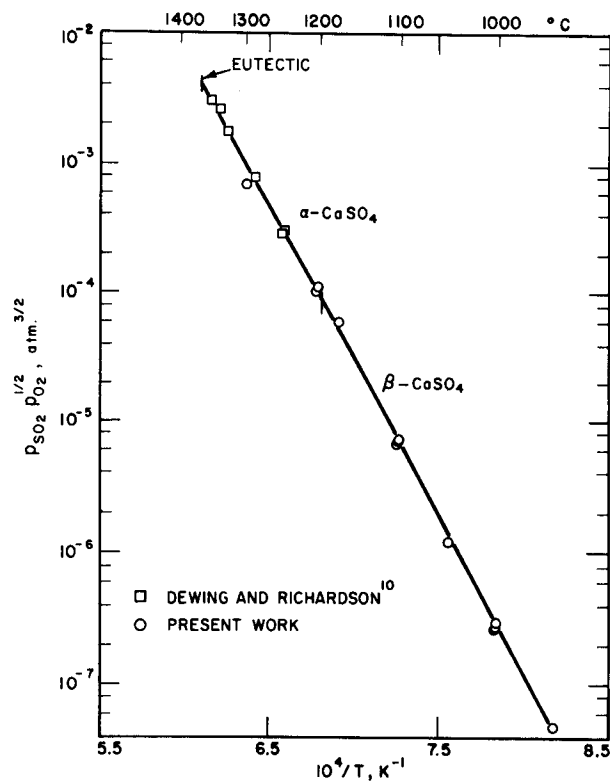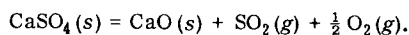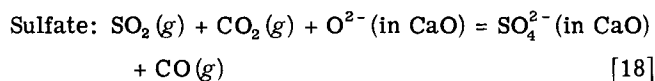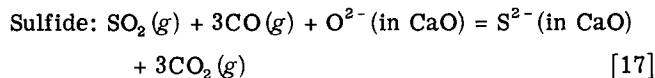Fig. 8—Temperature dependence of equilibrium constants K_1 and K_2.

Fig. 10—Temperature dependence of the equilibrium constant for reaction

$$CaSO_4\,(s) = CaO\,(s) + SO_2\,(g) + \tfrac{1}{2}O_2\,(g).$$

In accord with Eqs. [5] and [6], the sulfide and sulfate reactions investigated may be represented by the following reactions involving CO, CO_2, and SO_2.

Sulfide: $SO_2(g) + 3CO(g) + O^{2-}$ (in CaO) $= S^{2-}$ (in CaO)

$$+ 3CO_2(g) \qquad [17]$$

Sulfate: $SO_2(g) + CO_2(g) + O^{2-}$ (in CaO) $= SO_4^{2-}$ (in CaO)

$$+ CO(g) \qquad [18]$$

It is seen that at sufficiently low oxygen activities, at which the sulfide reaction predominates, the sulfur content of lime (in solid solution as sulfide ions) is inversely proportional to the ratio $(p_{CO_2}/p_{CO})^3$ for a given equilibrium p_{SO_2} in the gas. At high oxygen activities where the sulfate reaction predominates, the sulfur content of lime (in solid solution as sulfate ions) is directly proportional to the ratio p_{CO_2}/p_{CO}, for a given equilibrium p_{SO_2} in the gas.

In a log-log plot in Fig. 11, the slopes of the sulfur solubility lines are shown as a function of p_{CO_2}/p_{CO} for several temperatures. The curves approach the limiting slopes of -3 and 1 for the sulfide and sulfate solubilities at low and high oxygen activities, respectively. Within the intermediate range of oxygen activities, the sulfur is in solution in lime as sulfide and sulfate ions.

The total sulfur in solution in lime saturated with CaS or $CaSO_4$ is shown in Fig. 12 for 1000, 1100, and 1200°C as a function of the ratio of sulfate activity to sulfide activity, $(a_S)_1/(a_S)_2$, where

$$(a_S)_1 = K_1 p_{SO_2}(p_{CO_2}/p_{CO})$$

$$(a_S)_2 = K_2 p_{SO_2}(p_{CO}/p_{CO_2})^3$$

From the limiting sulfide and sulfate solubilities the total sulfur in the intermediate mixed region calculated for ideal solution of these ions in lime is shown by the dotted curve. It appears that, within the limits of experimental error, it is reasonable to say that the concentrations of sulfide and sulfate ions in lime are nearly proportional to their respective activities. The maximum sulfur solubility in lime is, of course, at the univarient equilibrium where CaO, CaS, and $CaSO_4$ coexist.
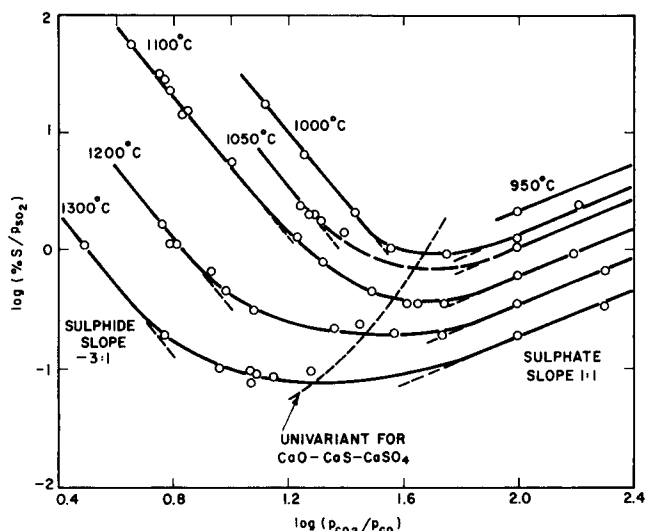

Fig. 11—Sulfide-sulfate solubility in lime.

The temperature dependence of the limiting solubility of CaS and $CaSO_4$ is shown in Fig. 13, together with values obtained by Kor and Richardson[3] for CaS at 1500 and 1650°C. According to the present work, the limiting CaS solubility in lime reaches a maximum of
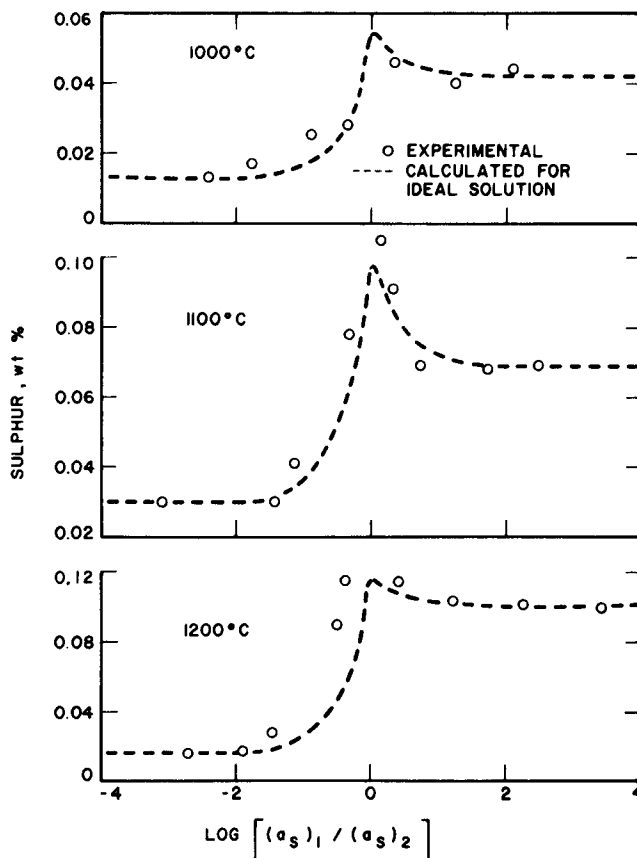

Fig. 12—Sulfide and sulfate solubility in lime as a function of the ratio (activity sulfate/activity sulfide).
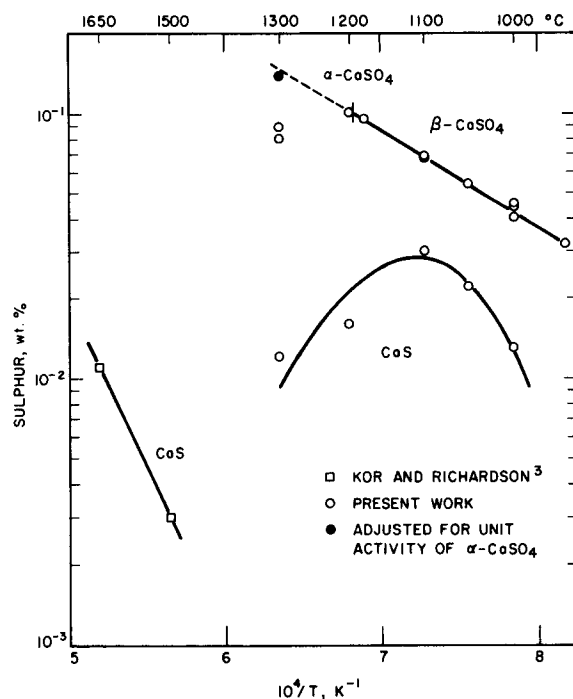

Fig. 13—Temperature dependence of $CaSO_4$ and CaS solubility in lime.

0.03 pct at about 1100°C. The nonlinearity of the log (pct S) vs $1/T$ plot may be an indication of a strong temperature effect on the defect structure of lime relative to vacant sites where sulfide ions are accommodated. It is difficult at present to account for the apparent disparity between the CaS-solubility data of Kor and Richardson at high temperatures and those of the present work at lower temperatures.

The temperature dependence of the limiting sulfate solubility in equilibrium with β-CaSO$_4$ is represented well by a straight line in Fig. 13. By assuming 2 kcal for the $\beta \rightarrow \alpha$ phase transformation, the solubility line is drawn for the α-phase. The filled data point for 1300°C is the experimental solubility adjusted to unit activity of α-CaSO$_4$ as discussed below.

As pointed out earlier (Fig. 8), the equilibrium constant K_1 for the formation of α-CaSO$_4$ is a factor of 1.6 higher than that estimated by extrapolation of the K_1 values from lower temperatures. By inference, this observation would suggest a marked solubility of CaO in α-CaSO$_4$ such that the activity of α-CaSO$_4$ is lowered to 0.63. Pursuing this line of argument, the limiting sulfate solubility, 0.089 pct S, determined experimentally for 1300°C would be that for lime-saturated CaSO$_4$ at 0.63 activity. The solubility adjusted to the unit activity of α-CaSO$_4$ would be 0.14 pct S, which is the value shown by a filled circle in Fig. 13. Also, a marked curvature on the 1200°C isotherm in Fig. 6 in the mixed sulfide-sulfate region suggests some mutual solid solution between CaS and CaSO$_4$.

Samples of CaO-CaSO$_4$ mixtures quenched to room temperature from 1300°C were examined by X-ray. The diffraction pattern of CaSO$_4$ was that of the β-phase. That is, the high-temperature α-phase could not be retained by quenching;* therefore, the suggested

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*Also Rowe *et al.*[8] were not able to quench the α-phase.

CaO solubility in α-CaSO$_4$ could not be verified. A suitable high-temperature X-ray technique should be employed to evaluate the extent of CaO solubility in α-CaSO$_4$.

In contrast with the foregoing tentative deductions, the experimental results of Dewing and Richardson[10] (Fig. 10) do not suggest much CaO solubility in α-CaSO$_4$ at 1300°C or higher. In the experimental work of Dewing and Richardson, in which the DTA technique was employed, the reaction time was short. Perhaps for this reason there was little or no solution of CaO in α-CaSO$_4$, hence their data may correspond closely to that for the unit activity of the α-phase.

The sulfate reaction (Eq. [6] or [18]) may be represented also by

$$SO_2(g) + \tfrac{1}{2}O_2(g) + O^{2-}(\text{in oxide}) = SO_4^{2-}(\text{in oxide})$$

[19]
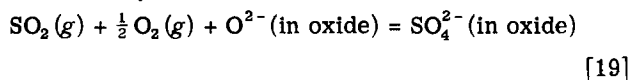
for which the equilibrium relation is given by

$$k_1 = \frac{\text{pct S}}{p_{SO_2}(p_{O_2})^{1/2}}$$

[20]

The values of k_1 are obtained from the limiting sulfate solubilities in lime. The temperature dependence of k_1 is shown in Fig. 14, where one data point is included from the work of Turkdogan and Darken[5] for a lime-saturated CaO-CaSO$_4$ melt. In the previous work with calcium ferrite melts[5] it was found that the enthalpy

change accompanying Reaction [19] decreases (more negative) with decreasing iron oxide content. For the melt containing about 70 mole pct CaO and 30 mole pct iron oxides, the enthalpy change was estimated to be about -105 kcal. Depending on the interpretation of the previous data,[5] this enthalpy value could be as high as -95 kcal. From the slope of the line in Fig. 14 for solid lime, the enthalpy change for Reaction [19] is found to be -96.1 kcal, which is close to that for the lime-rich calcium ferrite melts mentioned above.

Although calcium oxide has a stoichiometric composition with presumably little defect in the crystal structure, it is capable of taking into solution some sulfide and sulfate ions. In ionic crystals the radius of S^{2-} is 1.84Å, whereas the radius of S^{6+} in SO$_4^{2-}$ is 0.29Å.[12] This difference in ionic size may account for the sulfate solubility being greater than the sulfide solubility. Since the crystal radius of S^{6+} is smaller than that of Ca^{2+} (0.99Å), solution of SO$_4^{2-}$ in CaO is expected to decrease its lattice parameter; with the solution of S^{2-} ions in lime, a lattice expansion is anticipated. With the limited information available at present, it is premature to speculate on the defect structure of lime and on the atomistic model of a solution of sulfide and sulfate ions in lime.

As pointed out earlier, Reactions [1] and [2] are the key reactions in the desulfurization of lime during calcination. Using the available equilibrium data, Wriedt and Darken[1] evaluated the optimum gas composition for effective desulfurization during the calcination of limestone. They showed that at oxygen activities in the gas corresponding to p_{CO_2}/p_{CO} ratios in the range 30 to 60 the calcium sulfide or sulfate may decompose readily at calcination temperatures. In fact, in our previous investigation[2] it was found that lime could
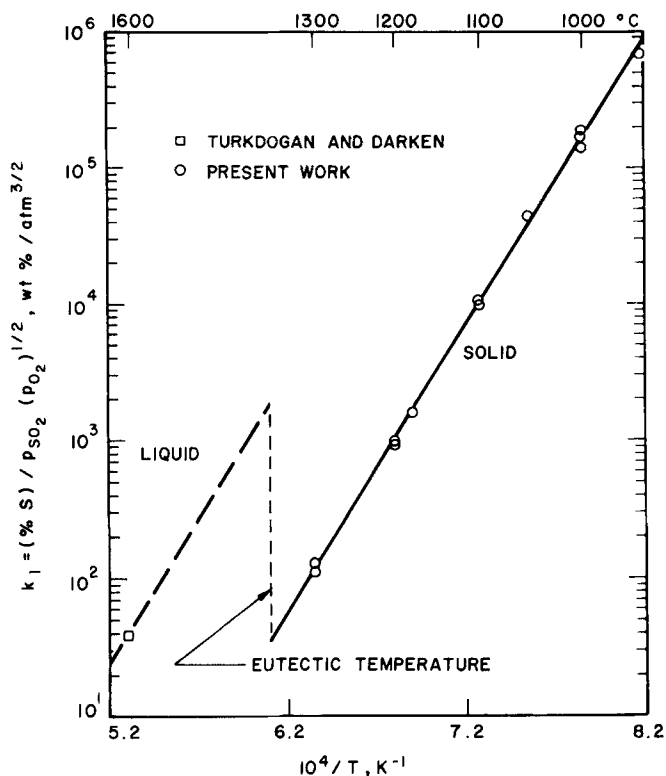

Fig. 14—Temperature dependence of equilibrium constant k_1 for sulfate solution in solid and liquid CaO-CaSO$_4$ solutions.

be desulfurized rapidly during calcination in CO_2 containing 1 to 10 pct CO.

However, because of noticeable sulfur solubility in lime, the optimum gas composition for effective desulfurization becomes more critical. This is demonstrated in Fig. 15, which shows the sulfur content of lime as a function of oxygen activity at 1200°C with 0.02, 0.1, and 0.5 pct SO_2 in the gas (these are equilibrium gas compositions). In the rotary-kiln calcination the fuel is usually fully combusted with 0.1 to 0.5 pct excess oxygen, corresponding to a p_{CO_2}/p_{CO} ratio of about 10^4 at 1200°C. In the shaft furnace, however, the p_{CO_2}/p_{CO} ratio is about 10.

We see from the equilibrium relation in Fig. 15 that, even at low SO_2 contents (< 0.1 pct) in the gas, there may be little or no desulfurization of lime if the p_{CO_2}/p_{CO} is much above 1000 or much below 50. The gas composition for effective desulfurization is seen to be more critical for the rotary-kiln calcination; under these conditions most of the sulfur is in solution in lime as sulfate ions. Fig. 15 also shows that by adjusting the p_{CO_2}/p_{CO} ratio in the furnace atmosphere within the range 100 to 300, low residual sulfur in lime could be obtained even when there is as much as 0.5 pct SO_2 in the furnace gas.

CONCLUSIONS

Sulfur dissolves in lime as sulfide or sulfate ions, depending on the oxygen potential. The temperature dependence of the sulfide solubility is complex; the limiting sulfide solubility in lime in equilibrium with CaS reaches a maximum of 0.03 pct at about 1100°C. The limiting $CaSO_4$ solubility in lime increases from 0.032 pct S at 950°C to 0.1 pct S at 1200°C. At 1300°C the sulfate solubility decreases to about 0.085 pct.

From the values of the equilibrium constant, $p_{SO_2}(p_{O_2})^{1/2}$, for the formation of $CaSO_4$ and the sulfate solubility in lime at 1300°C, it is deduced that there might be appreciable CaO solubility in α-$CaSO_4$ at temperatures from 1300 to the eutectic temperature 1365°C.

At intermediate oxygen activities the sulfur dissolves in lime as sulfide and sulfate ions. The results indicate that the ideal-solution law can be assumed for S^{2-} and SO_4^{2-} in lime. The maximum solubility is at the univariant equilibrium, where CaO, CaS, and
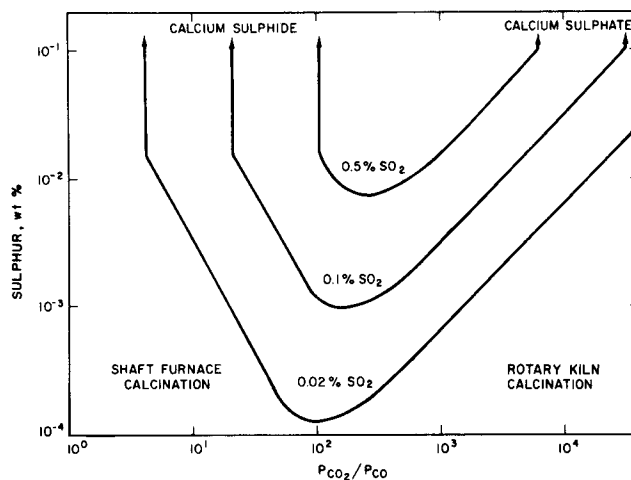

Fig. 15—Sulfide and sulfate solubility in lime at 1200°C as a function of gas composition in relation to average gas composition in shaft furnace and rotary kiln calcination.

$CaSO_4$ co-exist, at which the total sulfur in solution is that given by the sum of the limiting S^{2-} and SO_4^{2-} solubilities.

The equilibrium constants for the CaS and $CaSO_4$ formation, $(p_{S_2}/p_{O_2})^{1/2}$ and $p_{SO_2}(p_{O_2})^{1/2}$, respectively, are in close agreement with those determined by other investigators who used vastly different experimental techniques.

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