

Studies on the Oxidation of Pyrite

(Part 2) Kinetics of the Oxidation of Pyrite

By

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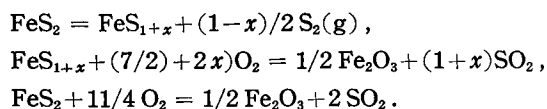
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Abstract

The kinetics of the oxidation of pyrite in the atmosphere of the mixed gas of O_2 , SO_2 and N_2 was studied. The results obtained were summarized as follows:

1. At $700^\circ\sim 900^\circ C$ where the thermal decomposition of pyrite proceeds quickly, the reaction occurs in two stages, the initial one is of the thermal decomposition of pyrite and the final one is of the oxidation of the thermal decomposition product, FeS_{1+x} . This phenomenon is more obvious at lower partial pressure of oxygen. The rate constant of the oxidation of FeS_{1+x} was found to be proportional to the partial pressure of oxygen, and the activation energy of this reaction was determined to be about 8.3 kcal.
2. At $550^\circ\sim 650^\circ C$, the thermal decomposition of pyrite proceeds slowly and, as a result, the following three reactions occur simultaneously,



For the mol fraction of x , y and z respectively for FeS_2 , FeS_{1+x} and Fe_2O_3 , the simultaneous differential equations were brought out and they were solved approximately.

We defined also the ratio of weight decrease w and it was shown as a function of time t by applying the solutions of the above equations. From the expression of this w , the rate constant of the direct oxidation of pyrite, k_3 , was obtained. This rate constant, k_3 , was also found to be proportional to the partial pressure of oxygen and its activation energy to be about 11.9 kcal.

3. The change of mol fraction x , y and z along the oxidation was computed. From

this computation, the amount of FeS_{1+x} formed as an intermediate product of the reaction was found to be dependent on the temperature of oxidation and the partial pressure of oxygen.

4. The calculated ratio of weight decrease w coincides considerably with the observed values at lower temperatures of the oxidation, but the coincidence is not good at higher temperatures.

Since the thermal decomposition proceeds very quickly at higher temperatures, the following assumptions on the reactions fit better than the simultaneous progress of the three reactions mentioned above;

a) at the initial stage, the thermal decomposition proceeds preferentially and FeS_{1+x} is formed, and

b) toward the end of the thermal decomposition, the oxidation of FeS_{1+x} commences, followed by the decomposition.

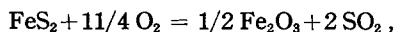
1. Introduction

Studies on the mechanism of oxidation of pyrite is important for the efficient production of sulphuric acid, for researches on the recovery of valuable metal components in the pyrite cinder and for smelting of sulphide minerals. In this report (Part 2), researches on the kinetics of the oxidation of pyrite between 550° and 900°C are described.

2. Premises on the atmosphere in the roasters

In the oxidizing roasting of pyrite with air, the partial pressure of oxygen gradually decreases and the partial pressure of sulphur dioxide increases along with the progress of the oxidation.

Assuming that the oxidation of pyrite can be expressed by



then, for 1 mol of FeS_2 ,

volume of O_2 combined with S is $22.4 \times 2 = 44.8$ (l) and

volume of O_2 combined with Fe is $22.4 \times 3/4 = 16.8$ (l).

Therefore,

the total volume of O_2 required for the oxidation is

$$22.4 \times 11/4 = 61.6 \text{ (l)}.$$

Now, assuming further that, when 1 mol of FeS_2 is oxidized with a (l) of air (where $a \geq 61.6/0.201$ (l)), a gas, whose concentration of oxygen is x (%) and that of sulphur dioxide is y (%), is generated, we have the following equations,

$$44.8/(a-16.8) = y/100$$

$$(0.208a-61.6)/(a-16.8) = x/100.$$

Hence,

$$931.8-58.1y = 44.8x. \tag{1}$$

In similar way, the following relations between x and y are derived;
for $\text{FeS}_2 + \text{O}_2 = \text{FeS} + \text{SO}_2$,

$$20.8-y = x, \tag{2}$$

for $\text{FeS}_2 + 8/3 \text{O}_2 = 1/3 \text{Fe}_3\text{O}_4 + 2 \text{SO}_2$,

$$931.8-35.7y = 22.4x \tag{3}$$

and for $\text{FeS} + 7/4 \text{O}_2 = 1/2 \text{Fe}_2\text{O}_3 + \text{SO}_2$,

$$465.9-35.7y = 22.4x. \tag{4}$$

Eqs. (1)~(4) are indicated by the straight lines in the O_2 - SO_2 - N_2 triangular diagram of Fig. 1. The observed composition of the gas in the multiple hearths furnaces¹⁾ when pyrite is roasted are also plotted in this figure. It is found that these observed values are biased and scattered in the lower part of the lines of Eqs.

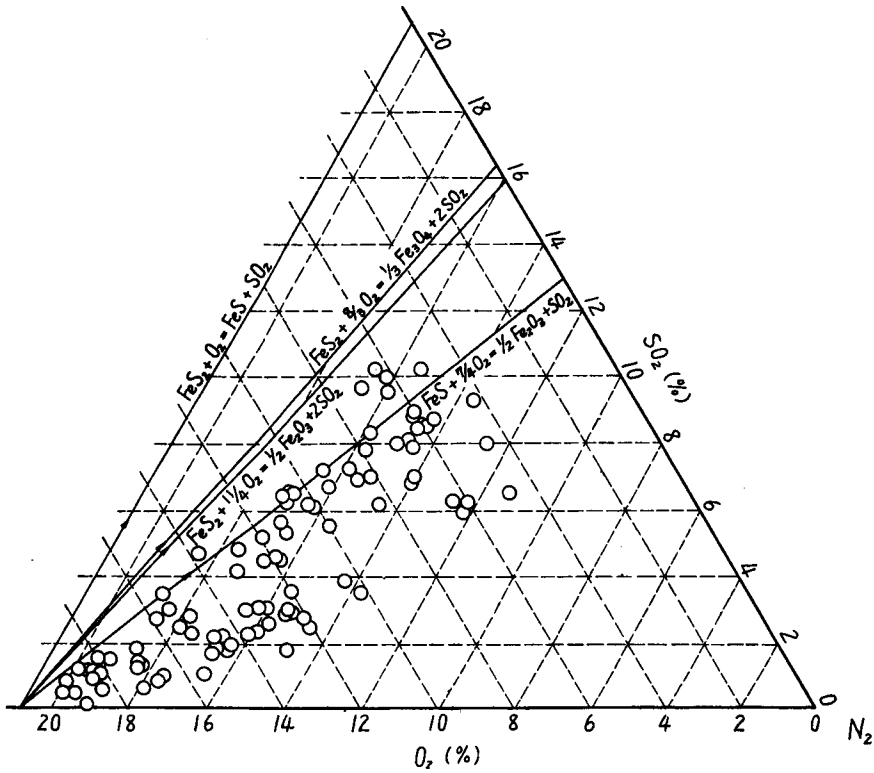


Fig. 1.

(1)~(4). This bias of the observed values is considered to be caused by (a) formation of SO_3 by the reaction of $\text{SO}_2 + 1/2 \text{O}_2 = \text{SO}_3$ in addition to the above reactions of the oxidation, (b) presence of H_2O due to the moisture of air and the ore²⁾, (c) difficulties in sampling of gas under negative pressure, and so forth.

When the gas in the roaster is assumed to be the mixture of O_2 , SO_2 and N_2 , the composition of the gas changes with the progress of the oxidation, from the composition of 20.8% O_2 and 79.2% N_2 (air) upwards along the lines in Fig. 1.

In the ordinary roaster of pyrite, the thermal decomposition of pyrite is considered to occur preferentially in the initial stage of roasting and the final product of the oxidation is assumed to be Fe_2O_3 . Therefore, in the roaster of counter-current type, such as the Herreshoff furnace in which air and the ore move in the inverse direction, it is supposed that the composition of the gas changes initially along the line of $\text{FeS} + 7/4 \text{O}_2 = 1/2 \text{Fe}_2\text{O}_3 + \text{SO}_2$ moving upwards from left to right, and at a certain point where the thermal decomposition of pyrite ceases, the composition leaves off the line and it moves along the line of $\text{FeS}_2 + 11/4 \text{O}_2 = 1/2 \text{Fe}_2\text{O}_3 + 2 \text{SO}_2$. Further, in the roasters of co-current type such as the flash-roasters in which air and the ore move in the same direction, the change of the composition of the gas is supposed to be followed by the line of $\text{FeS}_2 + \text{O}_2 = \text{FeS} + \text{SO}_2$ in the initial stage of the oxidation, to be followed by the line of $\text{FeS}_2 + 11/4 \text{O}_2 = 1/2 \text{Fe}_2\text{O}_3 + 2 \text{SO}_2$ in the final stage.

However, it is impossible to fix a point in Fig. 1, where the composition of gas transits from one line to the other because this point varies according to various roasting conditions. Moreover, by the oxidation in the roasters, Fe_3O_4 , FeSO_4 and others are formed besides Fe_2O_3 . Therefore, the circumstances vary somewhat from the above-mentioned considerations. In our study the composition of the gas was assumed to change along the line of $\text{FeS}_2 + 11/4 \text{O}_2 = 1/2 \text{Fe}_2\text{O}_3 + 2 \text{SO}_2$ for the most part. By this assumption, the following compositions of the gas shown in Table 1 were obtained by Eq. (1). In the studies hereafter, the oxidation of pyrite in the atmosphere of these compositions was investigated.

Table 1.

O_2 (%)	SO_2 (%)	N_2 (%)
20.8	0	79.2
15	4	81
10	8	82
5	12	83
3	14	83
1	15	84

3. The oxidation of pyrite at 700°~900°C

The thermal decomposition of pyrite proceeds rapidly above 700°C. At this temperature of 700°~900°C, the weight change of the sample by the oxidation was measured with the thermobalance of the previous report³⁾. The conditions of the measurements were as follows;

weight of sample; 400 mg,

particle size of the sample; 200~250 mesh,
 composition of gas mixture; mixed gas of O₂, SO₂ and N₂ whose composition
 was shown in Table 1.
 rate of flow of gas; 200 cc/min..

Results were shown in Fig. 2, 3 and 4. A knick point of the weight change curve was found in the oxidation at the low partial pressure of oxygen. This means that the reaction occurs in two stages, separately. That is, the rapid decrease of the weight in the initial stage of the reaction is due mainly to the thermal decomposition and the comparatively slow decrease that follows it is due to the oxidation of FeS_{1+x} which is a product of the thermal decomposition. This reaction of the oxidation of FeS_{1+x} is written by the following equation;

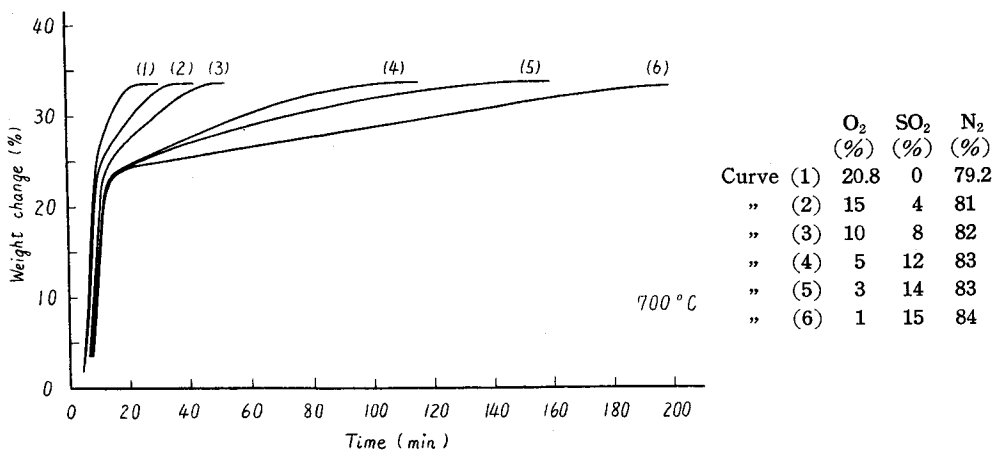
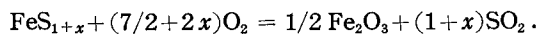


Fig. 2.

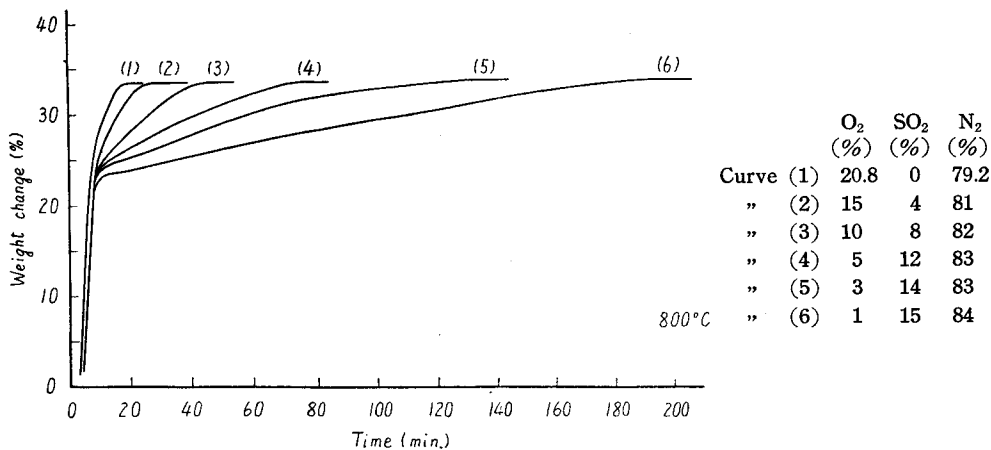


Fig. 3.

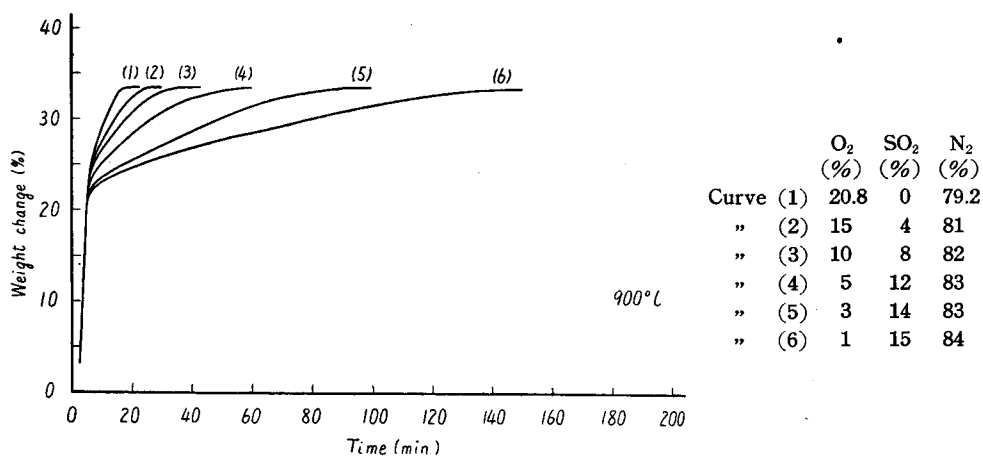


Fig. 4.

On the reaction of this kind, G.-M. Schwab⁴⁾ suggested the following equation of the reaction kinetics;

$$-dy/dt = k_2 y^{\frac{1}{2}}$$

where y is the mol fraction of FeS_{1+x} at time t , and k_2 is the rate constant of the reaction. Thence we obtain,

$$1 - y^{\frac{1}{2}} = k_2 t / 2$$

using the initial condition of $y=1$ at $t=0$.

A good linearity was obtained between $(1 - y^{\frac{1}{2}})$, which were computed from Figs. 2~4, and time t . The rate constants k_2 were obtained from the slope of these lines. The relation between the rate constant k_2 thus obtained and the partial pressure of oxygen in the atmosphere, p_{O_2} is shown in Fig. 5. As is clear from this figure, k_2 is found to be proportional to the partial pressure of oxygen. However, at a low partial

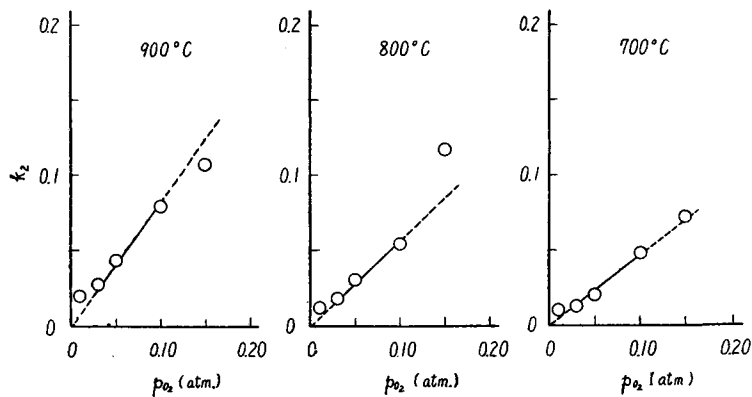
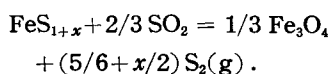


Fig. 5.

pressure of oxygen, especially at 0.01 atm. of oxygen, this proportionality does not exist, and the values of k_2 deviate somewhat from these lines. This is considered to be caused by the formation of Fe_3O_4 as an intermediate product by the following reaction,



This formation of Fe_3O_4 as an intermediate product will be discussed later in Part 3.

The logarithms of the rate constants k_2 were shown in Fig. 6, plotted against the reciprocals of the absolute temperature. Almost equal values of the slopes of these lines were obtained independently of the partial pressure of oxygen. An activation energy of 8.3 kcal

was obtained for the reaction by Ergun's method of computation⁵⁾, and this goes to show that this value is apparently attributable to the diffusion phenomenon.

4. The oxidation of pyrite at 550°~650°C

At the temperature of 550°C, 600°C and 650°C, the weight change of the sample due to the oxidation was measured with the thermobalance. The conditions of the measurements were same as in 3. The results obtained are shown in Fig. 7, 8 and 9. In the curves of weight change of these figures, the knicks as observed in the oxidation at higher temperature were not found.

Above 700°C, the thermal decomposition of pyrite proceeds very quickly and, consequently, the rate constants of the oxidation of FeS_{1+x} , k_2 , could be determined with considerable precision. On the other hand, at the temperature of between 550°C and 650°C where the direct sulphatization of pyrite can be neglected, the rate of the thermal decomposition becomes relatively small and, therefore, the direct oxidation of pyrite, which has remained undecomposed, occurs simultaneously with the thermal decomposition and the oxidation of FeS_{1+x} , which is the product of the thermal

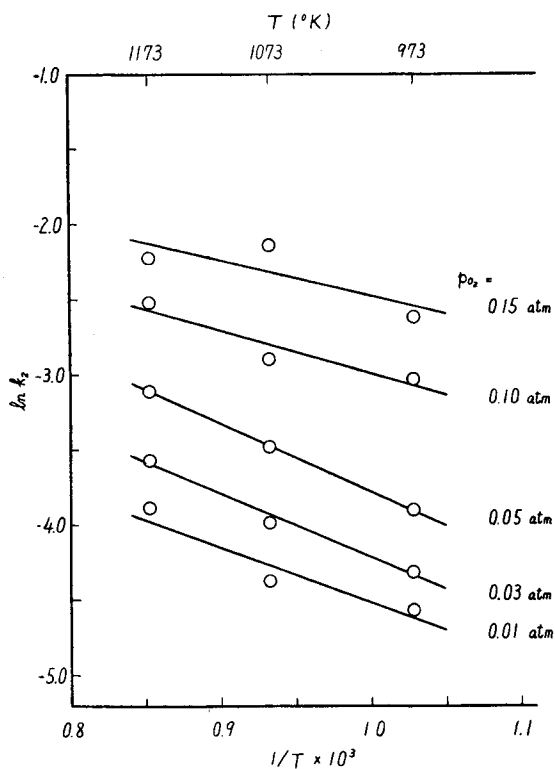


Fig. 6.

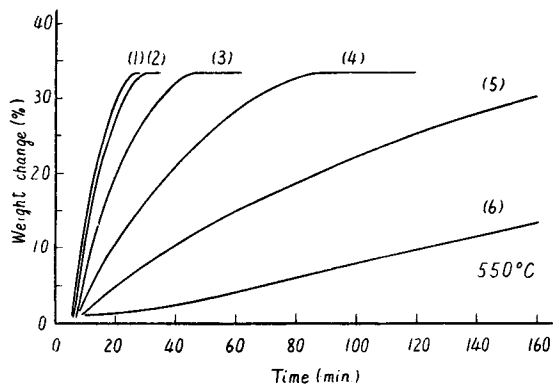


Fig. 7.

Curve	O ₂ (%)	SO ₂ (%)	N ₂ (%)
(1)	20.8	0	79.2
" (2)	15	4	81
" (3)	10	8	82
" (4)	5	12	83
" (5)	3	14	83
" (6)	1	15	84

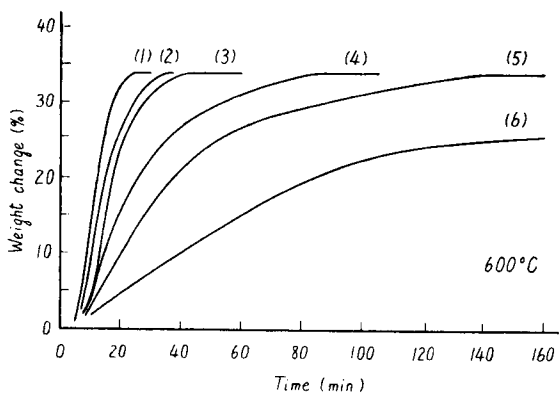


Fig. 8.

Curve	O ₂ (%)	SO ₂ (%)	N ₂ (%)
(1)	20.8	0	79.2
" (2)	15	4	81
" (3)	10	8	82
" (4)	5	12	83
" (5)	3	14	83
" (6)	1	15	84

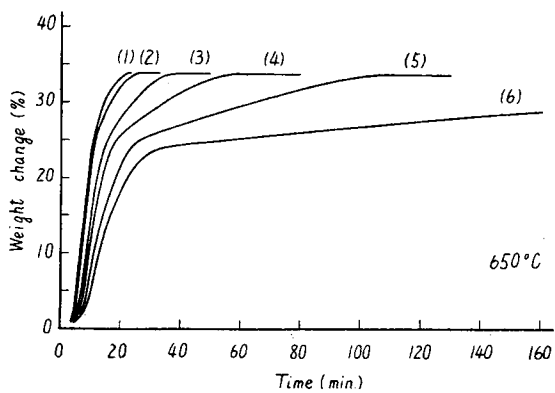
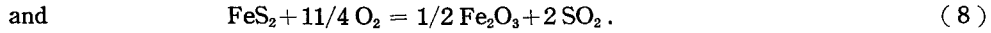
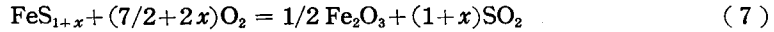


Fig. 9.

Curve	O ₂ (%)	SO ₂ (%)	N ₂ (%)
(1)	20.8	0	79.2
" (2)	15	4	81
" (3)	10	8	82
" (4)	5	12	83
" (5)	3	14	83
" (6)	1	15	84

decomposition. Eventually, the following three reactions occur simultaneously at this temperature range of 550°~650°C;



If we assume concerning these reactions that the thermal decomposition is followed by the equation of the first order reaction³⁾ and the oxidation of FeS_{1+x} and FeS₂ is followed by the empirical equation of Eq. (4) suggested by G.-M. Schwab, we then have the following simultaneous differential equations for the change of the mol fraction of FeS₂, FeS_{1+x} and 1/2 Fe₂O₃,

$$-\frac{dx}{dt} = k_1 x + k_3 x^{\frac{1}{2}} \quad (9)$$

$$\frac{dy}{dt} = k_1 x - k_2 y^{\frac{1}{2}} \quad (10)$$

$$\frac{dz}{dt} = k_2 y^{\frac{1}{2}} + k_3 x^{\frac{1}{2}} \quad (11)$$

where

- x : mol fraction of FeS₂ at time t ,
- y : " " of FeS_{1+x} at time t ,
- z : " " of 1/2 Fe₂O₃ at time t ,
- k_1 : the rate constant of the reaction (6),
- k_2 : " " " (7) and
- k_3 : " " " (8).

The following conditions exist with the mol fraction x , y and z ;

- (a) $x=1$ and $y, z=0$ at $t=0$, and $x, y=0$ and $z=1$ at $t \rightarrow \infty$,
- (b) from Eqs. (9), (10) and (11),
 $\frac{d}{dt}(x+y+z)=0$, thereafter, $x+y+z=\text{const.}=1$,
- (c) $x \geq 0$, $y \geq 0$ and $z \geq 0$.

These simultaneous differential equations can be solved approximately as follows.

At first, from Eq. (9), we obtain,

$$\frac{du}{dt} = -\frac{1}{2}(k_1 u + k_3)$$

where $x=u^2$. Hence

$$u = 1 - (1 + \mu) \left(1 - e^{-\frac{k_1 t}{2}}\right) = 1 - (1 + \mu) T^2$$

where

$$k_3/k_1 = \mu \quad \text{and} \quad 1 - e^{-\frac{k_1 t}{2}} = T^2.$$

Then we have,

$$x = u^2 = \{1 - (1 + \mu)T^2\}^2. \quad (12)$$

When $u = x^{\frac{1}{2}} = 0$ in Eq. (12),

$$T^2 = \frac{1}{1 + \mu},$$

or

$$t = -\frac{2}{k_1} \ln \frac{\mu}{1 + \mu} = t_0.$$

That is, when $t = t_0$, x becomes zero. Or, in other words,

$$\text{for } 0 < t < t_0 = -\frac{2}{k_1} \ln \frac{\mu}{1 + \mu}$$

$$x = \{1 - (1 + \mu)T^2\}^2. \quad (13)$$

Subsequently, from Eq. (10), we obtain,

$$2v \frac{dv}{dt} = k_1 x - k_2 v \quad (14)$$

where $y = v^2$.

On the other hand, since $\frac{dT}{dt} = \frac{k_1(1-T^2)}{4T}$ by the differentiation of $1 - e^{-\frac{k_1 t}{2}} = T^2$, we can write

$$\begin{aligned} 2v \frac{dv}{dt} &= 2v \frac{dv}{dT} \frac{dT}{dt} \\ &= \frac{k_1(1-T^2)}{2T} v \frac{dv}{dT}. \end{aligned}$$

Here, we express v as a power series of T as follows,

$$v = a_1 T + a_2 T^2 + a_3 T^3 + \dots$$

then

$$\begin{aligned} v \frac{dv}{dT} &= (a_1 T + a_2 T^2 + a_3 T^3 + \dots)(a_1 + 2a_2 T + 3a_3 T^2 + \dots) \\ &= \sum_{N=1,3,\dots} (N+1)(a_1 a_N + a_2 a_{N-1} + \dots + a_{\frac{N-1}{2}} a_{\frac{N+3}{2}} + \frac{1}{2} a_{\frac{N+1}{2}}^2) T^N \\ &\quad + \sum_{N=2,4,\dots} (N+1)(a_1 a_N + a_2 a_{N-1} + \dots + a_{\frac{N}{2}} a_{\frac{N}{2}+1}) T^N. \end{aligned}$$

Substituting Eq. (13) and above equations of v and $v \frac{dv}{dT}$ in Eq. (14), we obtain,

$$\begin{aligned} &\sum_{N=1,3,\dots} (N+1)(a_1 a_N + a_2 a_{N-1} + \dots + a_{\frac{N-1}{2}} a_{\frac{N+3}{2}} + \frac{1}{2} a_{\frac{N+1}{2}}^2) (T^{N-1} - T^{N+1}) \\ &+ \sum_{N=2,4,\dots} (N+1)(a_1 a_N + a_2 a_{N-1} + \dots + a_{\frac{N}{2}} a_{\frac{N}{2}+1}) (T^{N-1} - T^{N+1}) \\ &= 2\{1 - (1 + \mu)T^2\}^2 - 2v(a_1 T + a_2 T^2 + a_3 T^3 + \dots). \end{aligned}$$

where

$$k_2/k_1 = \nu$$

By rearranging the above equation, we have

$$\begin{aligned} & a_1^2(1-T^2)+4(a_1a_3+\frac{1}{2}a_2^2)(T^2-T^4)+6(a_1a_5+a_2a_4+\frac{1}{2}a_3^2)(T^4-T^6)+\dots \\ & +3a_1a_2(T-T^3)+5(a_1a_4+a_2a_3)(T^3-T^5)+7(a_1a_6+a_2a_5+a_3a_4)(T^5-T^7)+\dots \\ & = 2\{1-2(1+\mu)T^2+(1+\mu)^2T^4\}-2\nu(a_1T+a_2T^2+a_3T^3+\dots). \end{aligned}$$

The coefficients of the T^i terms of both sides of the equation are compared and $a_1, a_2, \dots a_5$ are obtained as follows;

$$\begin{aligned} a_1 &= \sqrt{2} \\ a_2 &= -\frac{2}{3}\nu \\ a_3 &= \frac{\sqrt{2}}{2}\left(\frac{\nu^2}{9}-\frac{1}{2}-\mu\right) \\ a_4 &= \frac{2}{15}\nu\left(\frac{\nu^2}{9}-\frac{7}{2}-\mu\right) \\ a_5 &= \frac{\sqrt{2}}{2}\left\{\frac{1}{12}\mu^2+\frac{1}{6}\mu\left(\frac{1}{15}\nu^2-\frac{3}{2}\right)-\frac{1}{16}+\frac{17}{180}\nu^2+\frac{1}{540}\nu^4\right\}. \end{aligned}$$

For $N \geq 6$, a_N are represented by the following general expression,

N : odd

$$\begin{aligned} a_N &= \frac{1}{(N+1)a_1}\left\{(N-1)(a_1a_{N-2}+a_2a_{N-3}+\dots+\frac{1}{2}a_{\frac{N-1}{2}}^2) \right. \\ & \quad \left. -(N+1)(a_2a_{N-1}+a_3a_{N-2}+\dots+\frac{1}{2}a_{\frac{N+1}{2}}^2)-2\nu a_{N-1}\right\} \end{aligned}$$

N : even

$$\begin{aligned} a_N &= \frac{1}{(N+1)a_1}\left\{(N-1)(a_1a_{N-2}+a_2a_{N-3}+\dots+a_{\frac{N-1}{2}}a_{\frac{N}{2}}) \right. \\ & \quad \left. -(N+1)(a_2a_{N-1}+a_3a_{N-2}+\dots+a_{\frac{N}{2}}a_{\frac{N+1}{2}})-2\nu a_{N-1}\right\}. \end{aligned}$$

Then using a_i , thus obtained, in $y^{\frac{1}{2}}=v=a_1T+a_2T^2+\dots$, we have,

$$\begin{aligned} y^{\frac{1}{2}} = v &= \sqrt{2}T - \frac{2}{3}\nu T^2 + \frac{\sqrt{2}}{2}\left(\frac{\nu^2}{9}-\frac{1}{2}-\mu\right)T^3 - \frac{2}{15}\nu\left(\mu+\frac{7}{2}-\frac{\nu^2}{9}\right)T^4 \\ & + \frac{\sqrt{2}}{2}\left\{\frac{1}{12}\mu^2+\frac{1}{6}\mu\left(\frac{1}{15}\nu^2-\frac{3}{2}\right)-\frac{1}{16}+\frac{17}{180}\nu^2+\frac{1}{540}\nu^4\right\}T^5 + \dots \end{aligned} \quad (15)$$

As shown above, at $t=t_0=-\frac{2}{k_1}\ln\frac{\mu}{1+\mu}$ where $x=0, T^2=1/(1+\mu)$. Therefore, from Eq. (15), $v(=v_0)$ and $y(=y_0)$ at $t=t_0$ are,

$$\begin{aligned} y_0^{\frac{1}{2}} = v_0 &= \left(\frac{2}{1+\mu}\right)^{\frac{1}{2}} - \frac{2}{3}\frac{\nu}{(1+\mu)} + \frac{\sqrt{2}}{2}\left(\frac{\nu^2}{9}-\frac{1}{2}-\mu\right)\frac{1}{(1+\mu)^{\frac{3}{2}}} - \frac{2}{15}\nu\left(\mu+\frac{7}{2}-\frac{\nu^2}{9}\right)\frac{1}{(1+\mu)^2} \\ & + \frac{\sqrt{2}}{2}\left\{\frac{1}{12}\mu^2+\frac{1}{6}\mu\left(\frac{1}{15}\nu^2-\frac{3}{2}\right)-\frac{1}{16}+\frac{17}{180}\nu^2+\frac{1}{540}\nu^4\right\}\frac{1}{(1+\mu)^{\frac{5}{2}}} + \dots \end{aligned}$$

As $x=0$, at $t=t_0$, from Eq. (10), we have,

$$\frac{dy}{dt} = k_2 y^{\frac{1}{2}}.$$

Hence,

$$v = y_0^{\frac{1}{2}} - \frac{k_2}{2}(t-t_0)$$

where $y=v^2$. From $y=0$ in the above equation, we obtain,

$$t-t_0 = \frac{2}{k_2} y_0^{\frac{1}{2}} = t_1.$$

Therefore at $t=t_0+t_1$, $y=0$.

In summary, for $0 < t < t_0$, Eq. (25) is fitted, and

$$\text{for } t_0 < t < t_0+t_1 = 2 \left(\frac{1}{k_2} y_0^{\frac{1}{2}} - \frac{1}{k_1} \ln \frac{\mu}{1+\mu} \right)$$

$$y^{\frac{1}{2}} = v = y_0^{\frac{1}{2}} - \frac{k_2}{2}(t-t_0) \quad (16)$$

These above-mentioned solutions of the simultaneous differential equations of Eq. (9) ~ (11) are summarized in Table 2.

Now, we define the ratio of weight decrease of the sample by the reactions, $w^{6)}$, as follows;

$$w = \frac{W_0 - W_t}{W_{\text{FeS}_2}} \quad (17)$$

where W_0 : initial weight of the sample

W_t : weight of the sample at time t

W_{FeS_2} : weight of FeS_2 component in the initial sample.

On the other hand, w is also represented as follows,

$$w = \frac{M_x - (xM_x + yM_y + zM_z)}{M_x} \quad (18)$$

where M_x : molecular weight of FeS_2

M_y : ,, ,, of FeS_{1+x}

M_z : ,, ,, of $1/2 \text{Fe}_2\text{O}_3$

and x , y and z are the mol fractions of FeS_2 , FeS_{1+x} and $1/2 \text{Fe}_2\text{O}_3$ at time t , respectively.

From Eq. (18), we have

$$w = ym_y + zm_z$$

where $m_y = 1 - M_y/M_x$, and $m_z = 1 - M_z/M_x$.

Table 2.

$t = 0$	$x = 1, y = 0, z = 0$
$0 < t < t_0$	$x = \{1 - (1 + \mu)T^2\}^2$ $y = \left[\sqrt{2} T - \frac{2}{3} \nu T^2 + \frac{\sqrt{2}}{2} \left(\frac{\nu^2}{9} - \frac{1}{2} - \mu \right) T^3 - \frac{2}{15} \nu \left(\mu + \frac{7}{2} - \frac{\nu^2}{9} \right) T^4 \right. \\ \left. + \frac{\sqrt{2}}{2} \left\{ \frac{1}{12} \mu^2 + \frac{1}{6} \mu \left(\frac{1}{15} \nu^2 - \frac{3}{2} \right) - \frac{1}{16} + \frac{17}{180} \nu^2 + \frac{1}{540} \nu^4 \right\} T^5 + \dots \right]^2$ $z = 1 - (x + y)$
$t = t_0$	$= -\frac{2}{k_1} \ln \frac{\mu}{1 + \mu}$ $x = 0$ $y = y_0 = \left[\left(\frac{2}{1 + \mu} \right)^{\frac{1}{2}} - \frac{2}{3} \frac{\nu}{(1 + \mu)} + \frac{\sqrt{2}}{2} \left(\frac{\nu^2}{9} - \frac{1}{2} - \mu \right) \frac{1}{(1 + \mu)^{3/2}} - \frac{2}{15} \nu \left(\mu + \frac{7}{2} - \frac{\nu^2}{9} \right) \frac{1}{(1 + \mu)^2} \right. \\ \left. + \frac{\sqrt{2}}{2} \left\{ \frac{1}{12} \mu^2 + \frac{1}{6} \mu \left(\frac{1}{15} \nu^2 - \frac{3}{2} \right) - \frac{1}{16} + \frac{17}{180} \nu^2 + \frac{1}{540} \nu^4 \right\} \frac{1}{(1 + \mu)^{5/2}} + \dots \right]^2$ $z = 1 - y_0$
$t_0 < t < t_0 + t_1$	$x = 0$ $y = \left\{ y_0^{\frac{1}{2}} - \frac{k_2}{2} (t - t_0) \right\}^2$ $z = 1 - y$
$t \geq t_0 + t_1$	$= 2 \left(\frac{y_0^{\frac{1}{2}}}{k_2} - \frac{1}{k_1} \ln \frac{\mu}{1 + \mu} \right)$ $x = 0, y = 0, z = 1$
where	$\mu = \frac{k_3}{k_1}, \quad \mu = \frac{k_2}{k_1} \quad \text{and} \quad T^2 = 1 - e^{-\frac{k_1 t}{2}}$

With the condition, $x + y + z = 1$, z is eliminated from the above expression as follows,

for $0 < t < t_0$

$$w = m_z(1 - x) + (m_y - m_x)y.$$

In this expression of w , Eqs. (13) and (15) are substituted, and we have

$$w = 2(m_y + m_z \mu) T^2 + \frac{4\sqrt{2}}{3} \nu (m_y - m_z) T^3 \\ + \left\{ m_y \left(\frac{2}{3} \nu^2 - 1 - 2\mu \right) - m_z \left(\mu^2 + \frac{2}{3} \nu^2 \right) \right\} T^4 \\ - \frac{2\sqrt{2}}{15} \nu (m_y - m_z) \left(\frac{\nu^2}{3} - \frac{9}{2} - 3\mu \right) T^5 + \dots \tag{19}$$

Because in Eq. (19), the terms of higher order can be neglected when t tends to become zero, w can then be approximated by the following expression,

$$w \doteq 2(m_y + m_z \mu) T^2. \quad (20)$$

The observed values of w computed from the results of the measurements are shown in Figs. 10~12, plotted against T^2 . The slope of the tangents of these curves drawn at the origin gives $2(m_y + m_z \mu)$ of Eq. (20). As m_y and m_z can be obtained from the molecular weight of FeS_2 , FeS_{1+x} and Fe_2O_3 , and μ is the ratio of k_3/k_1 of which k_1 is already known, we are able to compute k_3 , the rate constant of the reaction (8).

k_3 thus obtained, was plotted in Fig. 13, against the partial pressure of oxygen, p_{O_2} (atm.). From this figure, it was found that k_3 was nearly proportional to p_{O_2} , as in the case of k_2 in 3.

In Fig. 14, the logarithms of k_3 were plotted against the reciprocals of the absolute temperature. Calculating by Ergun's method, an activation energy of 11.9 kcal was obtained for the reaction (8). This value of the activation energy is attributable to the diffusion phenomenon.

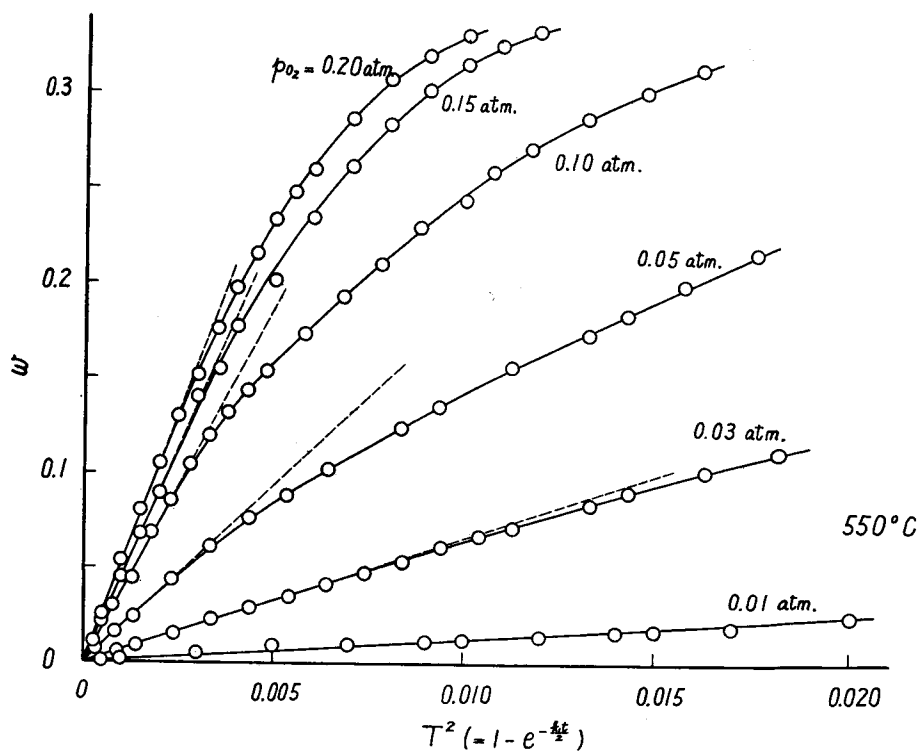


Fig. 10.

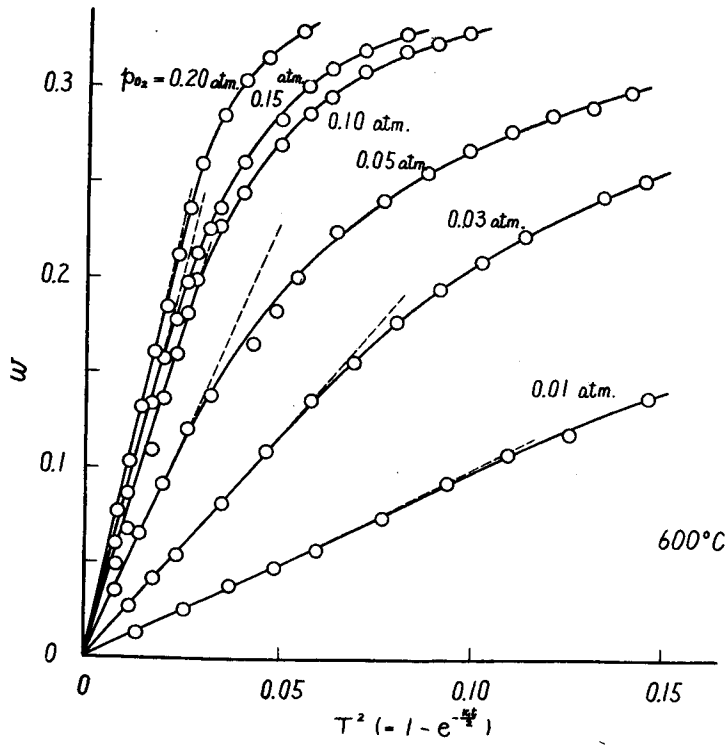


Fig. 11.

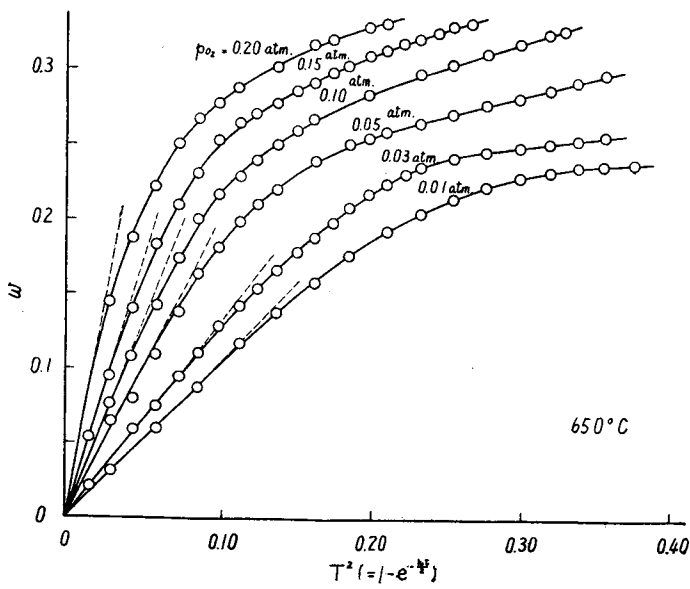


Fig. 12.

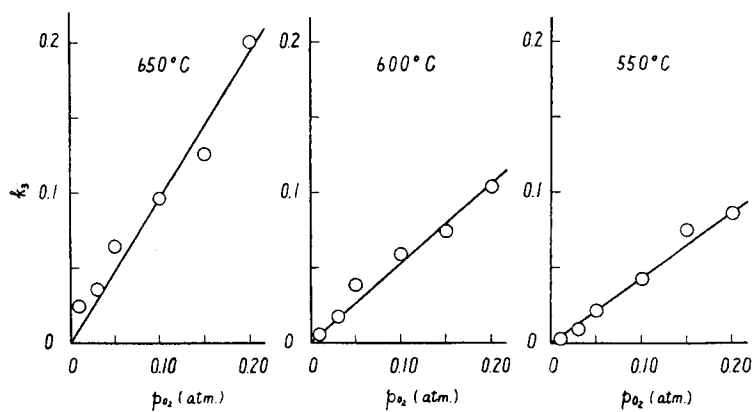


Fig. 13.

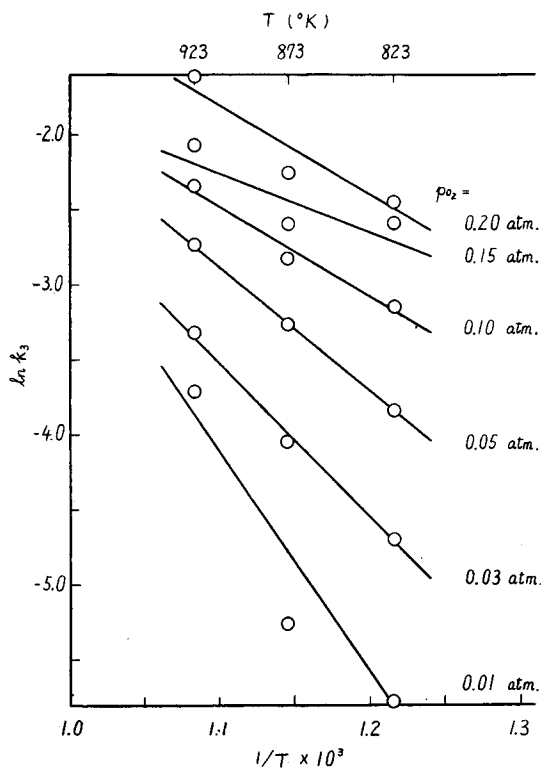


Fig. 14.

5. Change of the mol fraction of FeS_2 , FeS_{1+x} and Fe_2O_3 by the oxidation

Previously, the rate constant k_1 of the thermal decomposition of pyrite was determined in Part 1³). Now, the rate constants of the oxidation of FeS_{1+x} and FeS_2 , k_2 and k_3 respectively, were obtained in the preceding sections. The logarithms of these rate constants were summarized in Fig. 15 against the reciprocals of the absolute

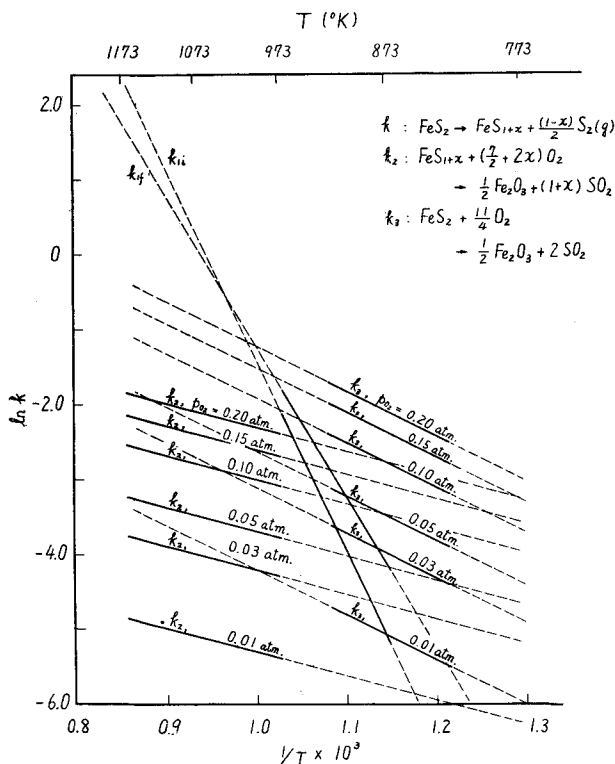


Fig. 15.

temperature. In this figure, the thick lines represent the values at the temperature where the measurements were made, and they are prolonged toward both sides with thin broken lines. Further, for the lines of k_2 and k_3 , the common value of the slopes calculated with Ergun's method were adopted, and their intercepts were obtained on the assumption of the proportionality of the rate constants to the partial pressure of oxygen.

On the presumptions that the reactions in the atmosphere of the mixed gas of O_2 , SO_2 and N_2 at $600^\circ \sim 800^\circ\text{C}$ proceed according to the reactions (6), (7) and (8), and that the values determined in Fig. 15 can be used as the rate constants of these

reactions, the change of the mol fraction of FeS_2 , FeS_{1+x} and Fe_2O_3 can be computed with the equations of Table 2. Of the solution of Table 2, y and z were approximate solutions, therefore, in the computation of y , the terms below T^7 were employed and those of higher order were omitted. The results obtained are shown in Fig. 16, 17, 18 and 19.

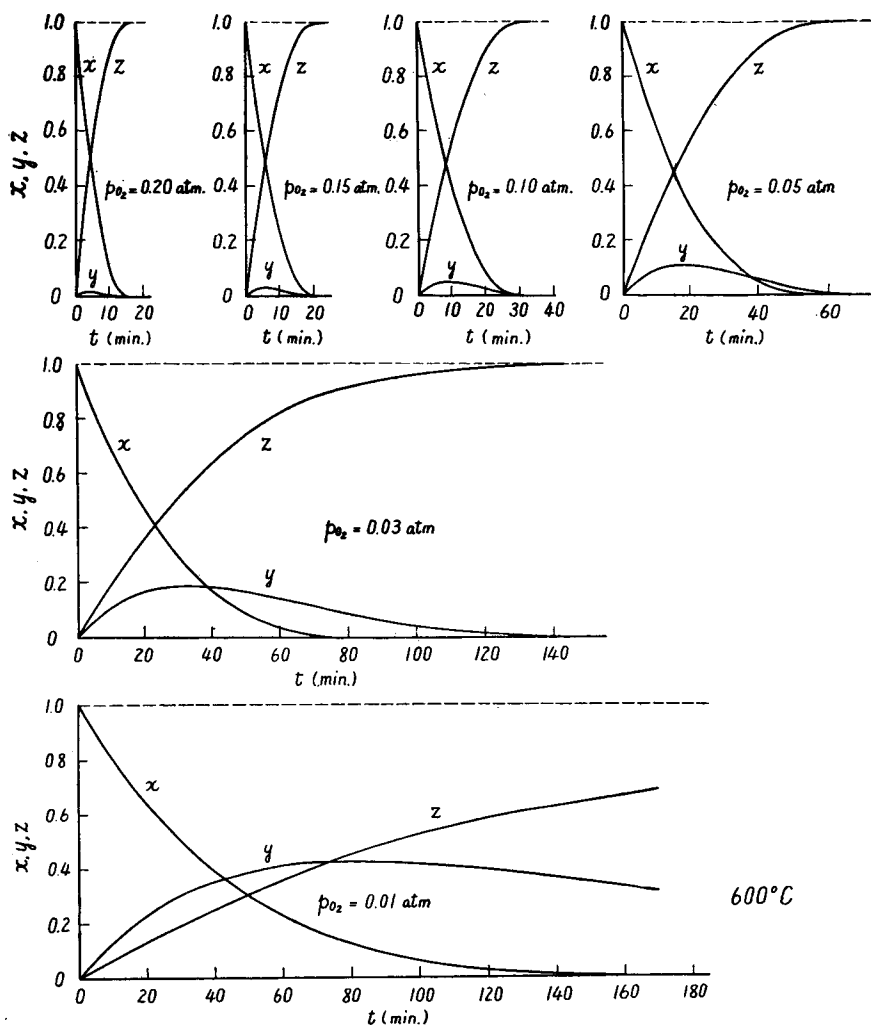


Fig. 16.

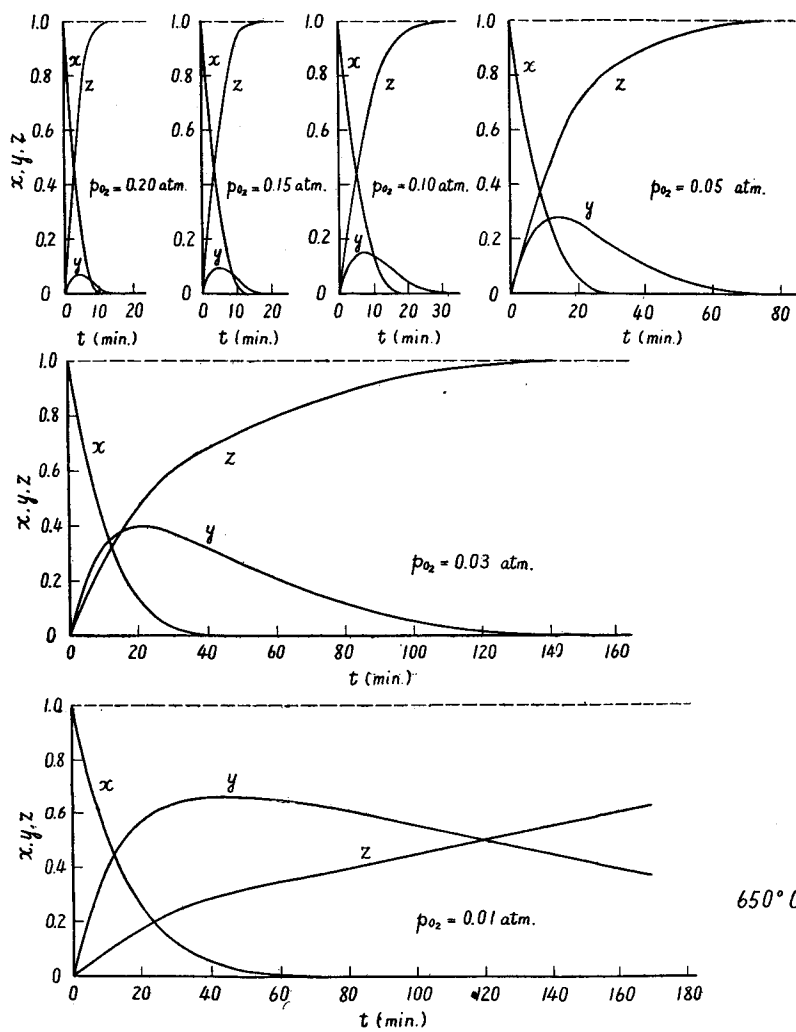


Fig. 17.

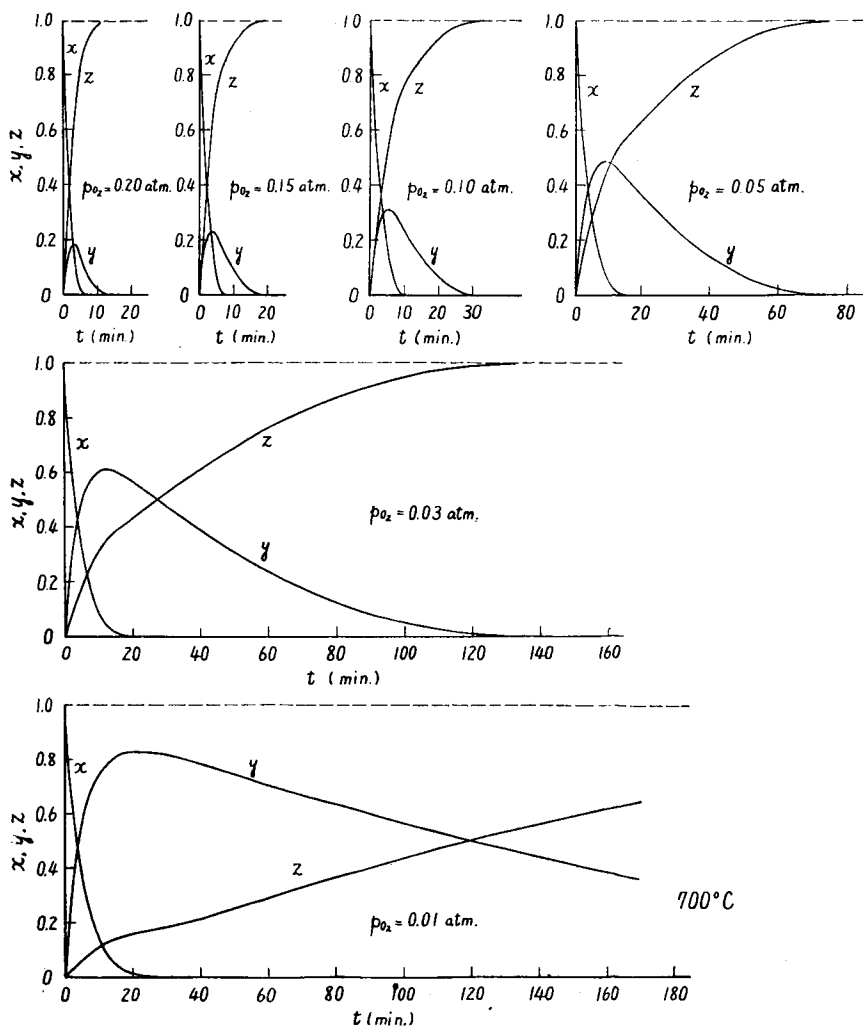


Fig. 18.

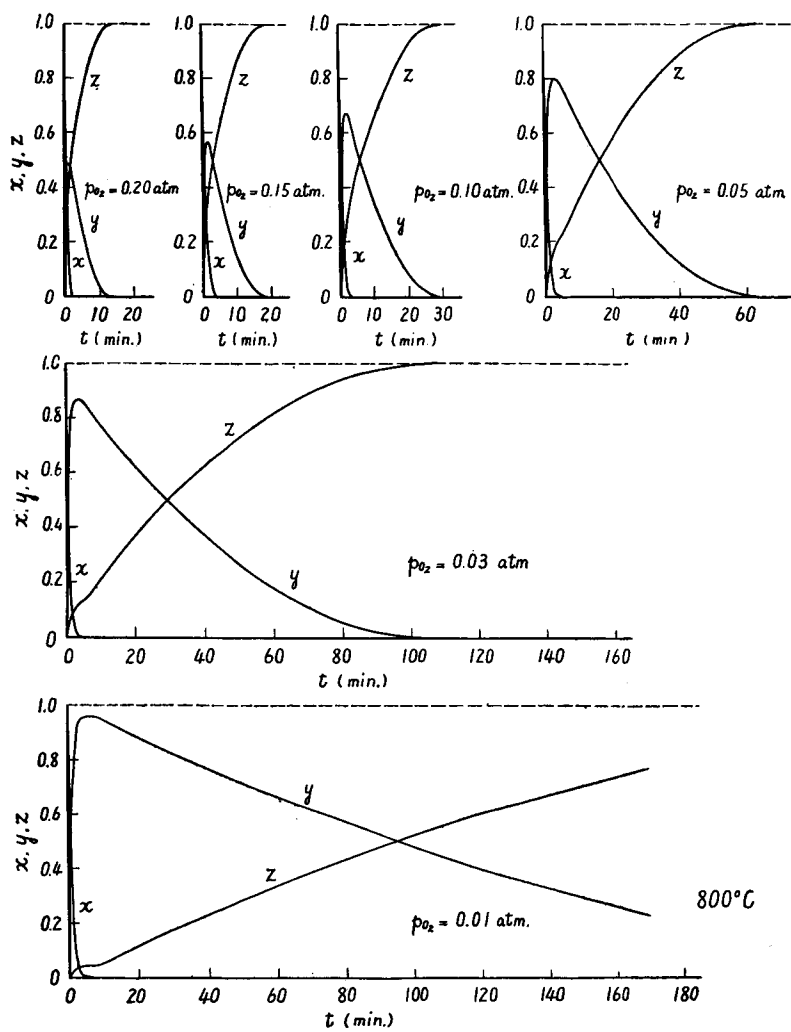


Fig. 19.

From these results of computation, it was shown that at a fixed partial pressure of oxygen, the amount of FeS_{1+x} formed was larger when the temperature was higher and that, at a fixed temperature, it was also larger when the partial pressure of oxygen is lower. The maximum values of the computed mol fraction of FeS_{1+x} formed in the oxidation, y_{\max} , are shown in Fig. 20.

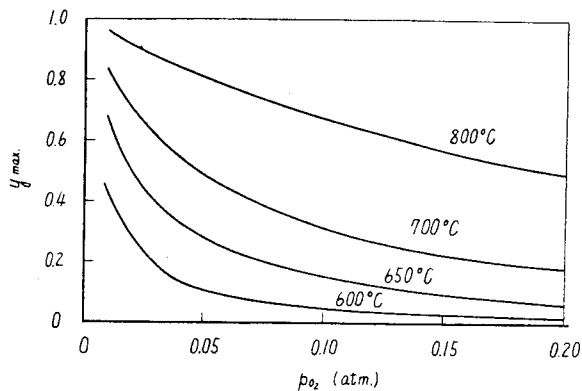


Fig. 20.

6. The ratio of weight decrease w

The ratio of weight decrease by the reactions of oxidation is shown as a function of t in Eq. (19). Among the constants in this equation, k_1 , k_2 , k_3 could be determined from the results of Fig. 15, and M_x , M_y , M_z from the molecular weight of the reaction components.

Or, in another way, w can be computed from the equation,

$$w = m_z(1-x) + (m_y - m_z)y$$

using the results of computation of x and y in the previous section.

In these two ways of determination, M_x and M_z can be obtained immediately from the chemical formula of FeS_2 and Fe_2O_3 . However, the molecular weight, M_y , of FeS_{1+x} varies after the coefficient $(1+x)$ of the formula. Since it was conceivable from the results of Part 1³⁾ that the composition of FeS_{1+x} formed in the intermediate stage of the oxidation is near the upper limit of solubility of sulphur in FeS_{1+x} , the formula of $\text{FeS}_{1.14}$ was used in the computation of the molecular weight.

The calculated values, $w_{\text{calc.}}$, and the observed values, $w_{\text{obs.}}$, which were measured with the thermobalance are shown in Fig. 21, 22, 23 and 24. The coincidence of both values was found fairly good in the case of 600°C and 650°C, but at higher temperatures, for example of 700°C or 800°C, they do not coincide well. At such a temperature as 800°C, the thermal decomposition proceeds so quickly that the reaction may

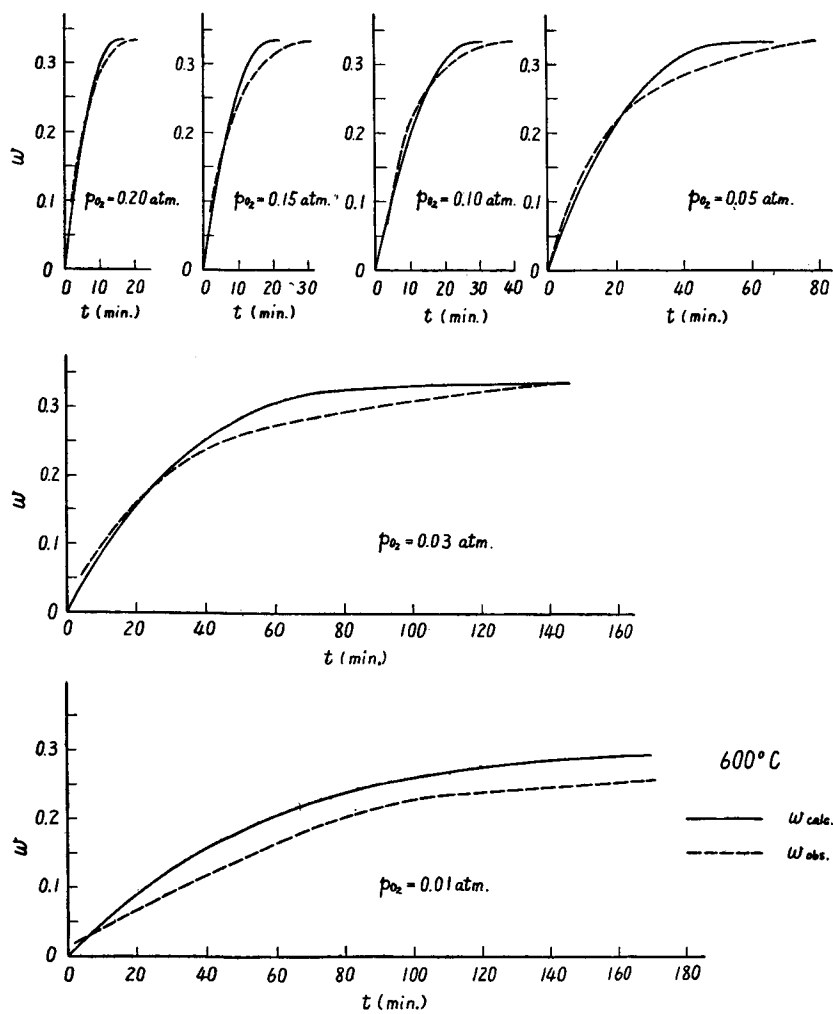


Fig. 21.

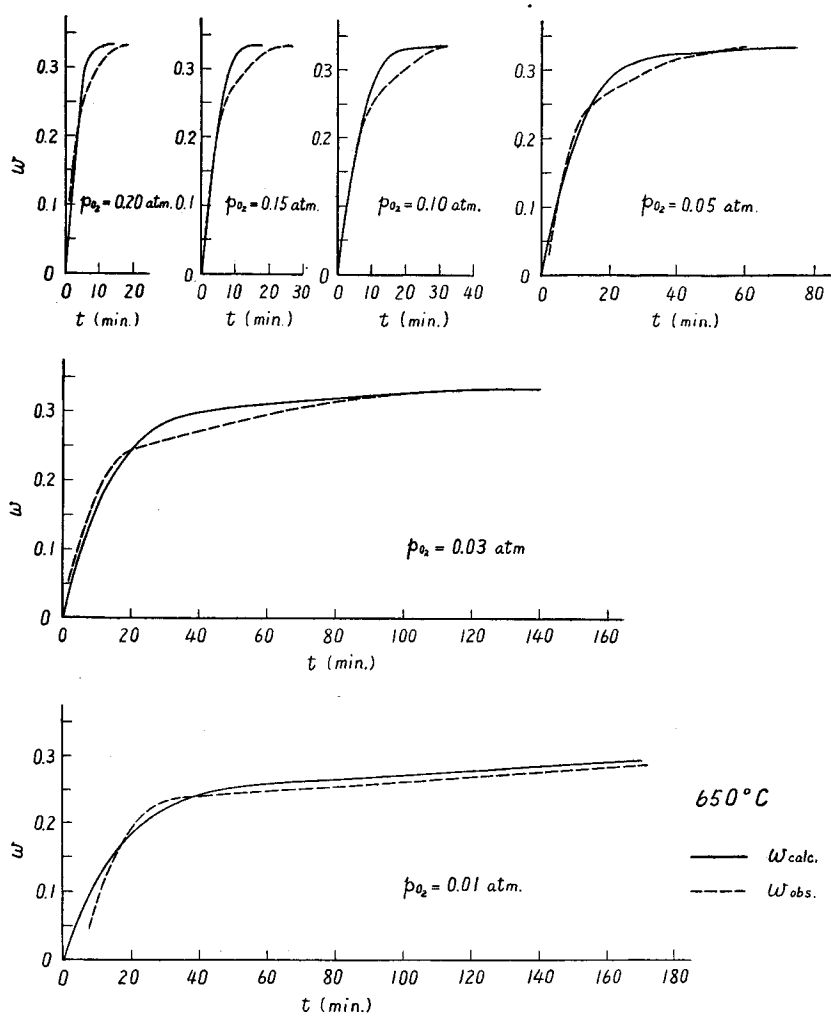


Fig. 22.

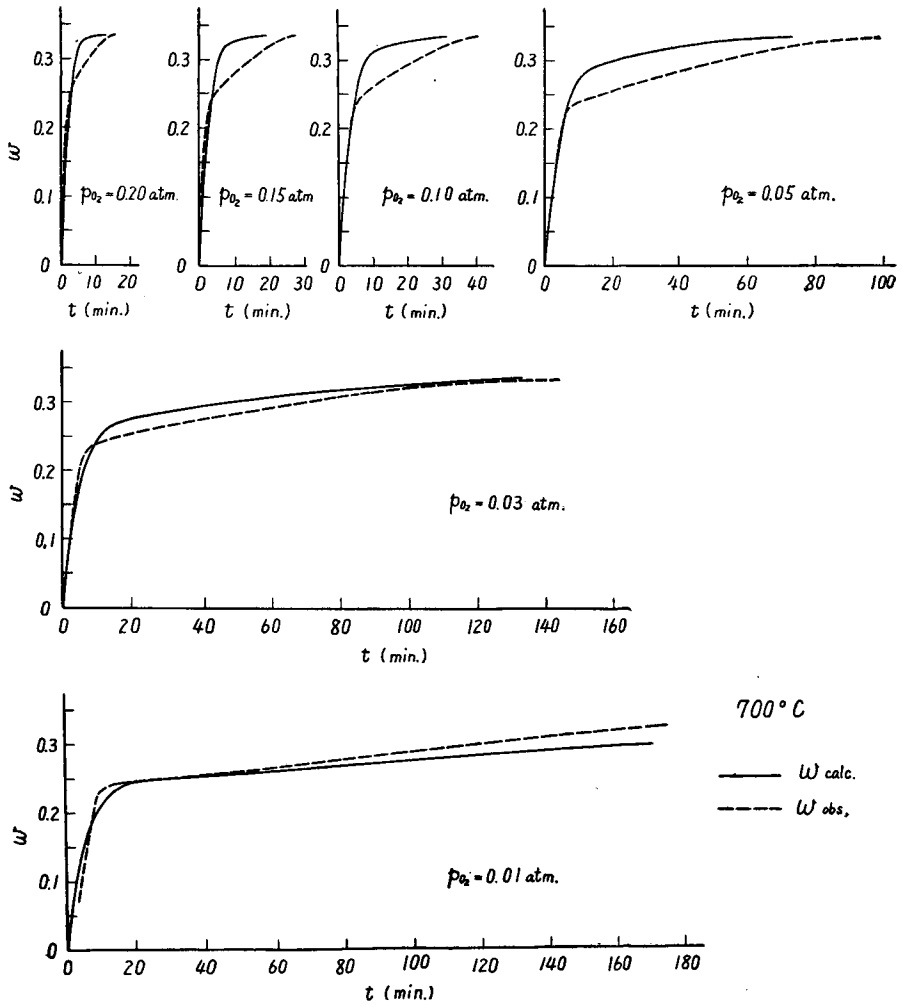


Fig. 23.

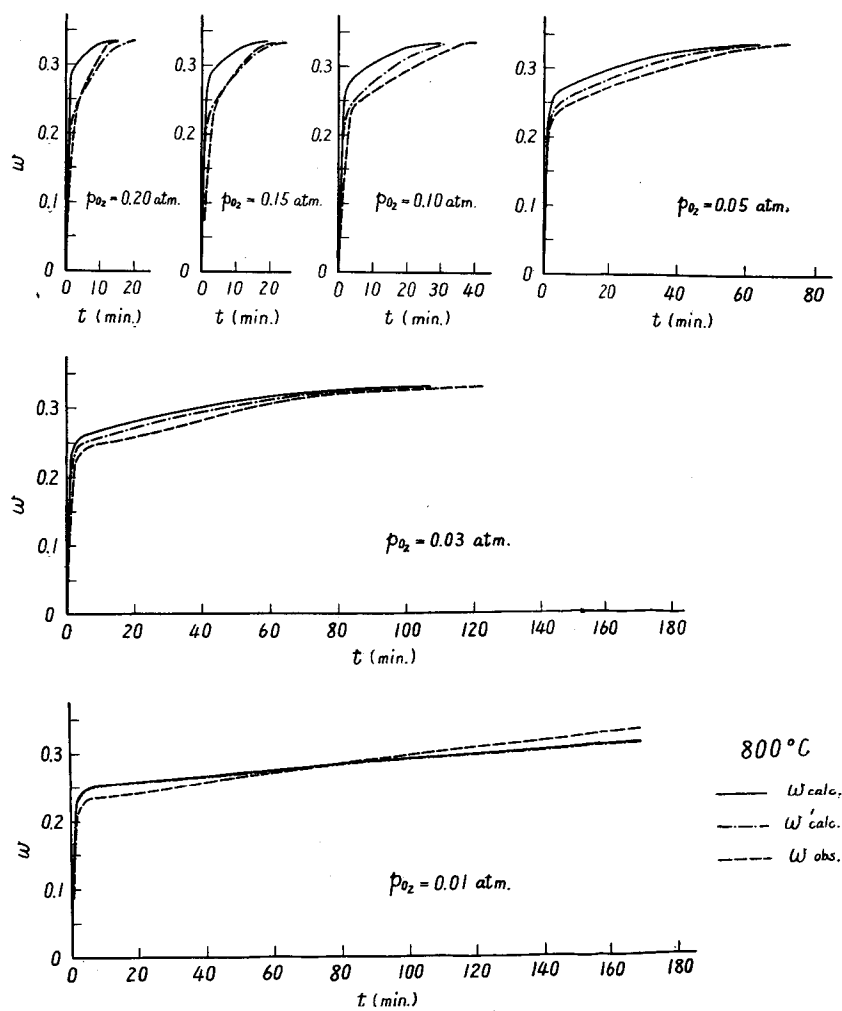


Fig. 24.

be considered to occur in the following two separate stages rather than in the simultaneous progress of the reactions of (6), (7) and (8);

a) in the initial stage, the thermal decomposition proceeds very quickly and FeS_{1+x} is formed, and

b) toward the end of the thermal decomposition, the oxidation of FeS_{1+x} commences, followed by the decomposition.

After this assumption, we have the following differential equations in place of the Eqs. (9)~(11).

a) for $0 < t < t_0$

$$x+y=1, z=0, \text{ and } x; 1 \rightarrow 0.01, y; 0 \rightarrow 0.99$$

$$-\frac{dx}{dt} = k_1 x, \quad \frac{dy}{dt} = k_1 x \quad (21)$$

b) for $t_0 < t < t_0 + t_1$

$$x=0, y+z=1, \text{ and } y; 0.99 \rightarrow 0, z; 0 \rightarrow 1$$

$$-\frac{dy}{dt} = k_2 y^{\frac{1}{2}}, \quad \frac{dz}{dt} = k_2 y^{\frac{1}{2}}. \quad (22)$$

In these equations, the initial stage of the reaction was assumed to be the stage of decrement of the mol fraction of FeS_2 from 1 to 0.01.

From Eqs. (21) and (22), we obtain,

$$t=0,$$

$$x = 1, \quad y = 0, \quad z = 0$$

$$0 < t < t_0$$

$$x = e^{-k_1 t}, \quad y = 1 - e^{-k_1 t}, \quad z = 0$$

$$t = t_0 = -\ln \frac{0.01}{k_1}$$

$$x = 0.01, \quad y = 0.99, \quad z = 0$$

$$t_0 < t < t_0 + t_1$$

$$x = 0, \quad y = \left\{ 1 - \frac{k_2}{2}(t - t_0) \right\}^2, \quad z = 1 - y$$

$$t = t_0 + t_1$$

$$x = 0, \quad y = 0, \quad z = 1$$

$$t_0 + t_1 < t$$

$$x = 0, \quad y = 0, \quad z = 1.$$

w was computed with this solution, and $w'_{\text{calc.}}$, thus obtained was also plotted in Fig. 24 with the dot-dash line. They coincide better with the observed values, $w_{\text{obs.}}$, than the calculated values, $w_{\text{calc.}}$, of w from the Eqs. (9)~(11).

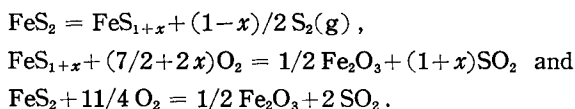
7. Summary

Studies were carried out on the kinetics of the oxidation of pyrite in the atmosphere of the mixed gas of O₂, SO₂ and N₂. The results obtained were summarized as follows.

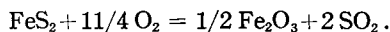
1. At 700°~900°C where the thermal decomposition of pyrite proceeds quickly, a knick point was observed in the curve of weight change by the oxidation measured with the thermobalance. This knick point was more obvious at lower partial pressure of oxygen. The reaction occurred separately in two stages, and the initial stage was the thermal decomposition of pyrite and the final stage was the oxidation of the thermal decomposition product, FeS_{1+x}.

With the empirical equation of the reaction kinetics suggested by G.-M. Schwab, the rate constant of the oxidation of FeS_{1+x}, was calculated. This rate constant, k_2 , was found to be proportional to the partial pressure of oxygen. The activation energy of this reaction was almost constant independent of the partial pressure of oxygen, and it was determined to be about 8.3 kcal.

2. At 550°~650°C, the thermal decomposition of pyrite proceeds slowly and, as a result, the following three reactions are considered to proceed simultaneously;



Of these three reactions, it is assumed that the thermal decomposition of pyrite is followed by the equation of first order reaction, and the oxidation of FeS_{1+x} and FeS₂ is followed by the empirical equation suggested by G.-M. Schwab. On these assumptions, we formulated the simultaneous differential equations on the mol fraction of FeS₂, FeS_{1+x} and Fe₂O₃ and obtained the approximate solutions, in which the mol fractions, x , y and z were shown as a function of time t . Further, with the relations between these mol fractions and the ratio of weight decrease, w was also shown as a function of time t . From the slope of the tangents drawn at the origin in the diagram of observed w vs. $T^2(=1 - e^{-\frac{k_3 t}{z}})$, the rate constant k_3 of the following reaction was obtained;



This rate constant, k_3 , was also found to be proportional to the partial pressure of oxygen. An activation energy of about 11.9 kcal was obtained for this reaction.

3. The rate constant of the thermal decomposition of pyrite, k_1 , the rate constant of the oxidation of FeS_{1+x}, k_2 and the rate constant of the oxidation of FeS₂, k_3 were substituted in the solutions of the above-mentioned simultaneous differential

equations, and the change of the mol fraction of FeS_2 , FeS_{1+x} and Fe_2O_3 along the oxidation was calculated. The results of computation showed that the amount of FeS_{1+x} formed at the intermediate stage of the oxidation became larger at higher temperatures when the partial pressure of oxygen was fixed, and that it became larger at lower partial pressures of oxygen when the temperature was fixed.

4. The ratio of weight decrease w was shown as a function of time t , and it was compared with the observed values measured with the thermobalance. At the temperature of 600°C and 650°C , both values coincided considerably, but at higher temperatures, their coincidence was not good.

At such a high temperature as 800°C , the following assumptions fit in better with the results of the measurements than the simultaneous progress of the above-mentioned three reactions;

- a) in the initial stage of the reaction, the thermal decomposition proceeds very quickly and FeS_{1+x} is formed, and
- b) toward the end of the thermal decomposition, the oxidation of FeS_{1+x} commences, followed by the decomposition.

References

- 1) These observed values were cited from the roasting tests in the multiple hearths furnaces. (K. Nishihara and Y. Kondo, Mem. of Faculty of Eng., Kyoto Univ., **14**, 145, (1952).)
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- 5) S. Ergun, Ind. and Eng. Chem., **48**, 2063, (1956).
- 6) K. Niwa et al, J. Japan Inst. of Metals, **18**, 1, (1954).