The Influence of Oxygen Pressure on the Reaction of Hydrogen Sulphide with Copper

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The influence of the oxygen pressure on the reaction of hydrogen sulphide with copper has been studied in the temperature range 25—164°C. The investigation demonstrates that the oxygen pressure has a large influence on the reaction rate and the growth forms of sulphide within large pressure intervals. The variation of the influence with the humidity, the temperature, and the hydrogen sulphide pressure has been studied.

1. INTRODUCTION

Several earlier investigations are available concerning the influence of oxygen on the sulphidation of copper and silver with hydrogen sulphide as the sulphidizing agent. These investigations mainly concern the problem of whether oxygen is a necessary component of the atmosphere for bringing about a sulphidation process with hydrogen sulphide at lower temperatures. Although a great deal of attention thus has been paid to the importance of oxygen, very little work has been done to investigate how the rate of sulphidation is affected by the oxygen pressure.

The present study is an attempt to investigate the influence of the oxygen pressure on the rate of the reaction between copper and an atmosphere containing oxygen and hydrogen sulphide.
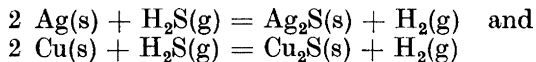
2. EARLIER INVESTIGATIONS

2.1. Atmosphere free from oxygen. At room temperature Merz and Weith,[1] Cabell,[2] Hahn,[3] and Lilienfeld and White [4] observed no reaction between silver and hydrogen sulphide. On the contrary, Schmel [5] observed a slow reaction. Merz and Weith [1] and Berthelot [6,7] found a slow reaction between copper and hydrogen sulphide.

At elevated temperatures both silver and copper react with hydrogen sulphide with the formation of hydrogen.[4,7] The kinetics of the reaction with

silver have been studied by Fjellström [8] and of the reaction with copper by Evans and Fearnehough [9] and by the present author.[10]

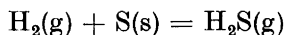The reactions in an atmosphere free from oxygen should be:

$$2 \text{ Ag(s)} + \text{H}_2\text{S(g)} = \text{Ag}_2\text{S(s)} + \text{H}_2\text{(g)} \quad \text{and}$$
$$2 \text{ Cu(s)} + \text{H}_2\text{S(g)} = \text{Cu}_2\text{S(s)} + \text{H}_2\text{(g)}$$

From the data shown in Table 1,[11] $\Delta G_{298}°$, the standard free energy change, of these reactions can be calculated to be -7.1 kJ/mole and -53.0 kJ/mole, respectively.

The free energy of the reactions at 25°C can be written as

$$\Delta G_{298} = \Delta G_{298}° + RT \ln \frac{p_{\text{H}_2\text{(g)}}}{p_{\text{H}_2\text{S(g)}}} \tag{1}$$

The equilibrium

$$\text{H}_2\text{(g)} + \text{S(s)} = \text{H}_2\text{S(g)}$$

has been studied by Pollitzer,[12] and the equilibrium ratio of the pressures of hydrogen and hydrogen sulphide has been determined in the temperature interval $40°-80°C$. Extrapolation of these data to 25°C gives at 25°C:

$$p_{\text{H}_2\text{(g)}}/p_{\text{H}_2\text{S(g)}} = 1.55 \times 10^{-6} \tag{2}$$

By combining eqns. (1) and (2), the free energies of the reactions of hydrogen sulphide with silver and copper in the absence of oxygen are found to be -40.0 kJ/mole and -85.9 kJ/mole, respectively.

These two reactions are thus thermodynamically possible even at room temperature. The reaction with silver, if it takes place at all, is, however, certainly very slow. Since the accuracy at least in some of the cases where this reaction has not been observed probably is too low to draw definite conclusions from the results, the question of whether a reaction between silver and hydrogen sulphide occurs at room temperature in the absence of oxygen is still open.

2.2. Atmosphere containing oxygen. The presence of oxygen makes the reactions between the metals and hydrogen sulphide at low temperatures proceed much faster.

The reaction with silver has been studied by Hahn [3] and Lilienfeld and White [4] with special attention paid to the influence of water vapour. An earlier investigation [13] has demonstrated that a slow reaction takes place with both copper and silver even in a dry atmosphere.

Kinetic studies of the reaction of silver with hydrogen sulphide containing oxygen have been performed by Tammann and Köster[14] by observations of the interference colours, by Reinhold and Seidel,[15] Drott,[16,17] and Fjellström.[8] The reaction with copper has also been studied by Tammann and Köster [14] and by the present author.[10,13]

The method used by Tammann and Köster in determining the thickness of the sulphide film has some limitations, as has been pointed out by Evans.[18] Several investigations [8,10,13,16,17] have demonstrated, that the film does not grow as a plane layer, which is a pre-requisite condition by using this method. Further, Tammann and Köster in their expressions for the reaction rates

neglect the strong influence on the reaction rates exerted by variations in the partial pressures of the reacting gases.

The influence of the oxygen pressure on the reaction rate has been studied by Drott [17] and Fjellström [8] for the reaction with silver and by the present author [10] for the reaction with copper. The relations between reaction rate and oxygen pressure presented in the investigation last mentioned have, however, been shown to give a too simplified representation of the pressure dependance, as the investigation was performed only at three different oxygen pressures and in several types of reaction vessels.

Table 1. [11]

Substance	Enthalpy of formation $-\Delta H_{298}$ kcal/mole	Standard entropy S_{298} cal/deg, mole
$H_2S(g)$	4.815	49.15
$H_2(g)$	—	31.211
$Ag(s)$	—	10.206
$Ag_2S(s)$	7.6	34.8
$Cu(s)$	—	7.96
$Cu_2S(s)$	19.000	28.9

3. PLANNING OF THE INVESTIGATION

The only systematic and extensive investigation of the influence of the oxygen pressure on a sulphidation process is that performed by Fjellström [8] concerning the reaction with silver. This investigation was performed at rather high temperatures, where the reaction of hydrogen sulphide with silver is rather different from that with copper. It is therefore of interest to investigate how the oxygen pressure influences the reaction with copper, and at the same time extend the temperature interval down to room temperature.

Table 2. Experimental conditions.

Relative humidity	Temperature °C	p_{H_2S} atm.
0.00 0.52 1.00	25	0.02
0.00	25 57 93 117 164	0.02
0.00	117	0.005 0.02 0.10

Earlier investigations [10,13] have demonstrated that the reaction rate is affected by the temperature, the humidity of the atmosphere and the hydrogen sulphide pressure. The present investigation has therefore been divided into three parts. Within each of these, two of the three variables were held constant, and the variation of the reaction rate with the oxygen pressure was studied at a number of constant values of the third variable. The reaction conditions are put together in Table 2.

4. EXPERIMENTAL METHODS

The performance of the experiments has been described earlier.[10] The quartz helical balance has been used at the higher temperatures and glass bulbs at the lower temperatures. The amount of sulphur has in the latter case been determined electrometrically and gravimetrically. Since the surface of the reaction products varies with the reaction conditions and the reaction rate, the surfaces have been studied in an electron microscope by means of carbon replicas.

5. RESULTS

5.1. The influence of oxygen pressure at different humidities. In these experiments copper was sulphidized at 25°C in a gaseous mixture, where the partial pressure of hydrogen sulphide was 0.02 atm. The pressure of oxygen varied, and nitrogen was added to a total pressure of 0.50 or 1.00 atm. The relative humidity in the reaction vessels was held constant by the presence of water, magnesium nitrate hexahydrate or anhydrous magnesium perchlorate, which gave relative humidities of 1.00, 0.52, and 0.00 respectively.
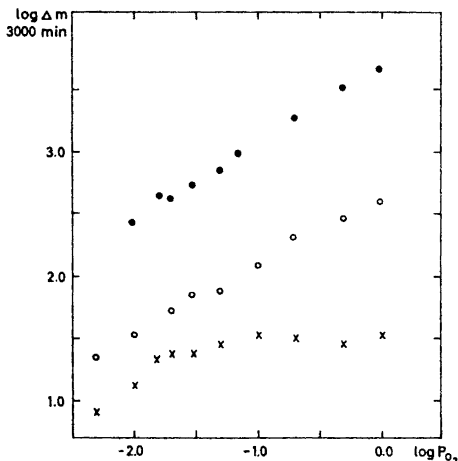

Fig. 1. The logarithm of the weight increase after 3000 min reaction at a hydrogen sulphide pressure of 0.02 atm. as a function of the logarithm of the oxygen pressure. Temperature +25°C. Crosses: relative humidity 0.00; open circles: 0.52; filled circles: 1.00.
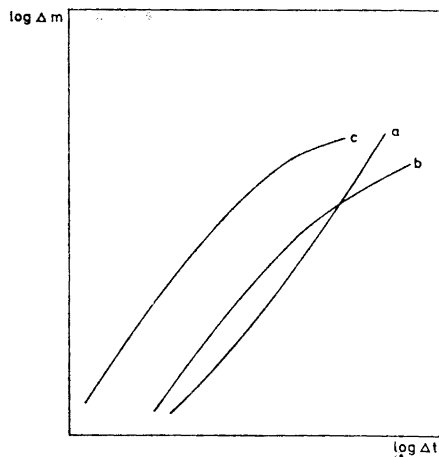
Fig. 2. Different types of kinetic curves in dry atmosphere at higher temperature.

At each oxygen pressure a rather small number (1—7) of specimens was sulphidized. The appearance of the kinetic curves obtained was broadly speaking independent of the oxygen pressure, but varied with the humidity in the way described earlier.[13]

From the kinetic curves or from single measurements the weight increase after a reaction period of 3000 min was obtained. The logarithm of this weight increase at different oxygen pressures was set off as a function of the logarithm of the oxygen pressure (Fig. 1).

From this figure it is evident that at the relative humidities of 1.00 and 0.52 the reaction rate is approximately proportional to $p_{O_2}^{0.5}$. This is in rather good agreement with earlier observations at 2°C and a relative humidity of 1.00.[10]

In the dry atmosphere the concentration of sulphur increases with the oxygen pressure up to an oxygen pressure of approximately 0.02 atm. When the oxygen pressure is further increased, the reaction rate remains constant.

5.2. Influence of the oxygen pressure at different temperatures. The influence of the oxygen pressure on the reaction rate and the growth forms in a dry atmosphere was, besides at 25°C, also investigated at 57°C with glass bulbs as reaction vessels and at 93°, 117°, and 164°C in the quartz helical balance. The pressure of hydrogen sulphide was in all these experiments 0.02 atm.

At the lower oxygen pressures and higher temperatures kinetic curves with a constant or slightly increasing gradient in a log-log diagram were obtained (curve *a*, Fig. 2). The gradient is as a rule larger than 1. In this pressure range (interval *a*) an increase of the oxygen pressure brings about a shorter incubation period for the fast reaction step, which causes an increase of the reaction rate. The sulphide, which in all cases consists of Cu_2S, mainly forms whiskers (Fig. 3), which cover an increasing part of the surface when the oxygen pressure is raised within the interval.
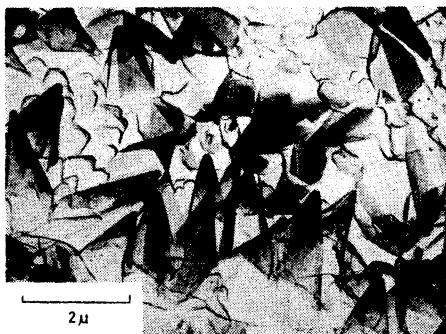

Fig. 3. Whiskers.

When the oxygen pressure is further increased, another type of reaction is, however, observed. Here the kinetic curves in a log-log diagram have a gradient which from the beginning of the reaction is fairly constant and then decreases (curve *b*, Fig. 2). The sulphide forms columnar crystals such as have been observed earlier [10,13,19] (Fig. 4). At the onset of the decrease in the gradient,

these crystals have grown together to a broadly speaking continuous layer (Fig. 5). At the lowest oxygen pressures of this pressure range (interval *b*), as at very low and very high pressures in interval *a*, both areas covered by whiskers and areas covered by columnar crystals are observed.
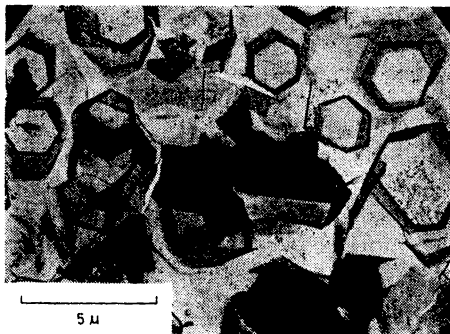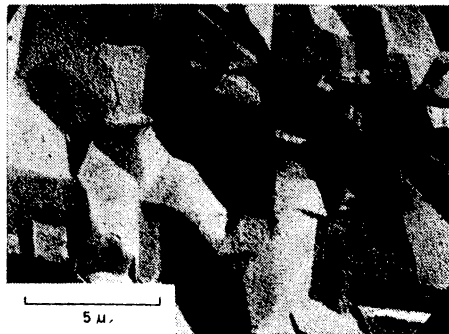

Fig. 4. Separate columnar crystals.   *Fig. 5.* Columnar crystals which have grown together.

When the oxygen pressure is still further increased the incubation period of the fast reaction step decreases, which brings about an increase of the reaction rate (compare the curves *b* and *c* in Fig. 2). The columnar crystals become completely dominating. At last an oxygen pressure is reached, where the incubation time does not become shorter with increased oxygen pressure. This brings about a pressure interval (interval *c*) where the reaction rate is broadly speaking independent of the oxygen pressure.

In Fig. 6 are shown some of the kinetic curves obtained at a temperature of 93°C. Among these curves, the curves I and II can be brought to interval *a*, the curve III to interval *b* and the curves IV and V to interval *c*.
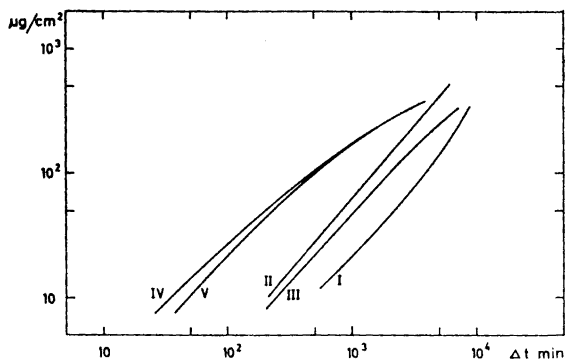

Fig. 6. Kinetic curves at a temperature of 93°C and a hydrogen sulphide pressure of 0.02 atm. The oxygen pressures I: 0.0025 atm., II: 0.005 atm., III: 0.02 atm., IV: 0.05 atm., V: 0.10 atm.

Fig. 7. Fundamental diagram showing the reaction rate as a function of the logarithm of the oxygen pressure. Crosses: whiskers; circles: columnar growth; triangles: both whisker and columnar growth. The pressure intervals *a*, *b*, and *c* are marked.
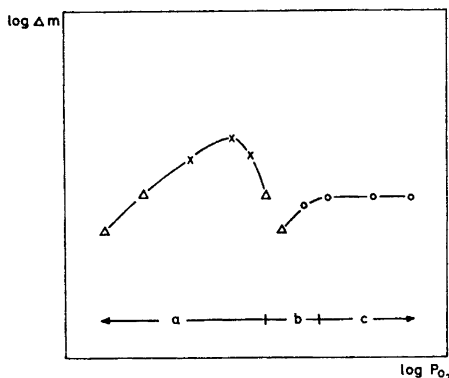
If the logarithm of the weight increase after a certain reaction period is set off as a function of the logarithm of the oxygen pressure, a diagram essentially as shown in Fig. 7 is obtained at a given temperature. In this diagram the pressure intervals *a*, *b*, and *c* and the characteristic growth forms within each interval are marked. The curve branches corresponding to interval *a* and the two other intervals are not comparable along the ordinate axis, as their relative heights depend on the reaction period chosen.

In Fig. 8 is shown the dependence of the reaction rate on the oxygen pressure at a number of temperatures and at a hydrogen sulphide pressure of 0.02 atm.
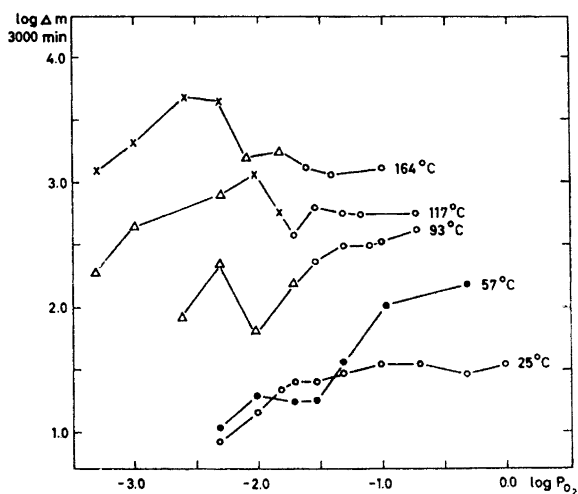

Fig. 8. The logarithm of the weight increase after 3000 min reaction at a hydrogen sulphide pressure of 0.02 atm. and at different temperatures as a function of the logarithm of the oxygen pressure. Crosses: whiskers; circles: columnar growth; triangles: both whisker and columnar growth.

From Fig. 8 it is evident that interval a becomes less marked at lower temperatures and cannot be observed at 25°C. At the lowest temperatures whiskers are formed very occasionally. The extent of interval b decreases when the temperature is raised and this interval has completely disappeared at 164°C.

5.3. Influence of the oxygen pressure at different hydrogen sulphide pressures. To investigate the variation of the influence of the oxygen pressure with the hydrogen sulphide pressures, experiments were performed at 117°C with hydrogen sulphide pressure of 0.005, 0.02, and 0.10 atm. and with different oxygen pressures. From the kinetic curves thus obtained the logarithm of the weight increase after a reaction period of 3000 min was obtained, and set off in a diagram as a function of the logarithm of the oxygen pressure (Fig. 9). From this diagram it appears that the ranges of the different oxygen pressure intervals are dependent on the hydrogen sulphide pressure.
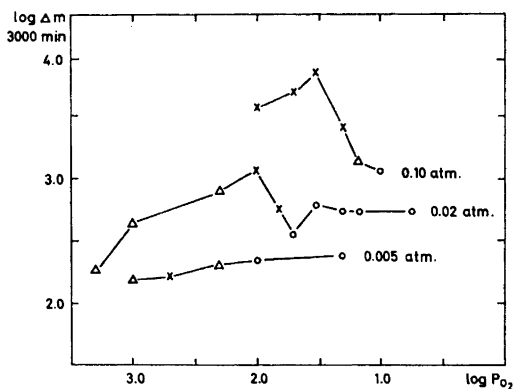

Fig. 9. The logarithm of the weight increase after 3000 min reaction at three different hydrogen sulphide pressures as a function of the logarithm of the oxygen pressure. Temperature + 117°C. Crosses: whiskers; circles: columnar growth; triangles: both whisker and columnar growth.

At a hydrogen sulphide pressure of 0.005 atm., interval b cannot be observed and the pressure dependence within interval a is small. At a hydrogen sulphide pressure of 0.10 atm. experiments could not be performed at a higher oxygen pressure than 0.10 atm., and consequently the intervals b and c cannot be observed. The formation of columnar crystals at the oxygen pressure of 0.10 atm. indicates, however, that a transition to interval b or c starts near to this point.

In Fig. 10 the same weight increase as in Fig. 9 has been plotted as a function of the logarithm of the ratio p_{O_2}/p_{H_2S}. This diagram shows that the ranges of the different intervals are determined by this ratio. A transition from interval a to interval b or c occurs when the partial pressures of hydrogen sulphide and oxygen are about equal, while the maximum rate within interval a is achieved at a somewhat smaller ratio.
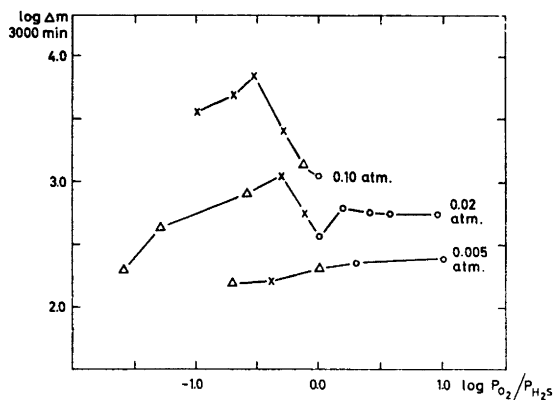
Fig. 10. The logarithm of the weight increase after 3000 min reaction at three different hydrogen sulphide pressures as a function of the logarithm of the pressure ratio p_{O_2}/p_{H_2S}. Temperature $+117°C$. Crosses: whiskers; circles: columnar growth; triangles; both whisker and columnar growth.

6. DISCUSSION

6.1. General remarks. Generally speaking, the reaction between copper and hydrogen sulphide becomes faster if oxygen is present. The oxygen probably converts the hydrogen sulphide to a more reactive sulphur compound, and this product subsequently reacts with the copper.[4],[10] The oxidation of the hydrogen sulphide may occur in an adsorbed state on the surface of the specimen.

Kinetic curves and apparent activation energies [10] make it probable that the rather fast reaction step is caused by nucleation and crystal growth. It is evident, that this step is affected by the oxygen pressure. Probably the effect is indirect in such a way that the amount of reactive sulphur formed by oxidation of hydrogen sulphide directly influences the reaction.

How the oxygen pressure in detail will affect this process may depend on several factors. Among these the following can be considered.

a. The rate of formation of the reactive sulphur compound by the reaction between hydrogen sulphide and oxygen. If this reaction occurs in the gaseous state, the rate ought to increase with increasing partial pressures of both the gases. If the reaction takes place in an adsorbed state, the rate ought to in the main increase with increasing pressure of the gaseous component present in deficit on the surface. An increased pressure of the other component certainly brings about a faster reaction step, but will on account of competition decrease the supply of the first gas.

b. The latter conditions mentioned above are also valid for the reaction step between gas and metal, if the reaction of the gaseous components occurs in the gaseous state. Here the excess gas will compete with the reactive sulphur.

c. The strong dependence of the reaction rate on the gas pressures [10] indicates that a reaction step on the phase interface or in the gas determines the total rate of the reaction. This will therefore be affected by the morphology of the interface. If the interface between the gas and the solid body is uneven, this may give rise to differences in transport possibilities, adsorption conditions and consumption of gas at different points on the surface. This means that the concentration of reactive sulphur becomes uneven, which brings about different chemical potentials to different points. These potential differences may change with the oxygen pressure, at which the growth of the sulphide crystals and the underlying layer becomes dependent on the oxygen pressure.

6.2. *Discussion of the results.* In an atmosphere with relative humidity considerably larger than zero, probably some kind of condensation occurs, which brings about a faster reaction. The relation between the relative humidity and the reaction rate has been studied earlier.[13] The condensed water makes it, however, more difficult for the gases to reach the surface of the specimen, and, besides the circumstances mentioned under a and b above, the rate may also be affected by the transport of the gases through the liquid film. As the transport of oxygen or reactive sulphur through this film probably is a rather slow process, an increase in the oxygen pressure brings about a faster transport and a faster reaction if the other conditions remain unaltered. This is in accordance with Fig. 1.

In a dry atmosphere when columnar crystals are formed (pressure intervals b and c) the enlargement of the surface is moderate (Figs. 4 and 5). The reaction rate from the beginning increases when the oxygen pressure is raised, which is in accordance with any of the alternatives in the preceding section. The increase is larger than in a wet atmosphere, as the oxygen or the reactive sulphur here more easily gets into contact with the specimen surface. With further increase in the oxygen pressure, later on a state is reached where a raised oxygen pressure does not cause any considerable change in the reaction rate. The limit of this range is raised if the pressure of the hydrogen sulphide increases, and is lowered if the temperature is raised.

The independance of the reaction rate on the oxygen pressure can have several explanations. Some of them are:

a. The concentration of oxygen is large enough to consume all the hydrogen sulphide available.

b. The concentration of reactive sulphur is so large, that it does not limit the process.

c. The competition between oxygen and reactive sulphur or hydrogen sulphide stifles the reaction.

At a higher temperature the amount of oxygen already at the upper limit of interval a is evidently sufficient to make the reaction independent of the oxygen pressure according to one of the alternatives above.

Within the intervals b and c there is a nucleation and crystal growth in three dimensions. When a continuous layer of columnar crystals has been formed (Fig. 5), growth occurs only perpendicularly to the surface, and the reaction rate decreases. A similar effect, although more pronounced, has been observed by Fjellström [8] for the reaction with silver. With these rather

thick layers, diffusion of metal through the layer might be rate determining.

The boundary between the intervals b and c is displaced towards a lower oxygen pressure when the temperature is raised. In the investigation of the reaction with silver Fjellström [8] could observe only these two intervals. In that case the boundary seems to be independent of the temperature.

In those cases where whiskers are formed (broadly speaking interval a), a considerable enlargement of the surface occurs. The formation of whiskers will only occur if the pressure ratio of oxygen and hydrogen sulphide is less than about 1, and this limit seems to be largely independent of the temperature.

The formation of whiskers may be explained in the following way. The small supply of oxygen brings about an impoverishment of reactive sulphur on the surface between the nuclei first formed. In some places a concentration gradient will be formed, and whiskers will grow according to the mechanism earlier discussed.[19,20] The whiskers will thus always grow outwards into a gas where the supply of both the gaseous components is relatively large, compared with the conditions close to the underlying layer, where on the contrary an impoverishment takes place.

The reaction rate therefore becomes constant or even increasing,[21] and becomes larger at higher oxygen pressures. A continuous, fairly even layer will never be formed, and a decrease of the reaction rate corresponding to the later stages at higher pressure ratios is not observed.

From the observations made it is to be expected that most of those reactions at moderate temperatures between metals and hydrogen sulphide, where the rate determining step is some reaction at the phase interface will have a rate dependent on the oxygen pressure. This ought to be especially valid in the sulphidation of metals which react slowly with hydrogen sulphide. In these cases the reaction can be expected to speed up as a consequence of the formation of a more reactive sulphur compound. How the influence of the oxygen pressure will manifest itself in each separate case, is expected to depend on the properties of the solid phases formed at the reaction.

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