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GAS DIFFUSION DURING THE THERMAL ANALYSIS OF PYRITE

F. R. A. Jorgensen and *F. J. Moyle*

CSIRO DIVISION OF MINERAL CHEMISTRY,
P.O.BOX 124, PORT MELBOURNE, VIC. 3207, AUSTRALIA

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Maximum rates of weight loss were measured during thermal analysis experiments involving the oxidation of thin layers of pyrite particles (<37 to 212–300 μm screen size fractions) in oxygen-containing atmospheres (10–100%). The experimentally determined rates were compared with those calculated for several diffusion-based models. Good agreement was obtained with the model involving gas diffusion in the crucible.

Much attention has been devoted to analysing the results of thermal analysis in terms of the rate of the chemical reactions [1–6] and the heat transfer processes involved [7–9]. Comparatively little effort has been spent on analysing the other physical process of mass transfer. This is understandable as the early uses of thermal analysis were largely confined to studying thermal decompositions or phase changes where heat rather the mass transfer was the rate-determining process. However, when thermal analysis is used to study combustion reactions involving solids and gaseous reactants, mass transfer in the form of the diffusion of reactants and products in the crucible, can assume importance and, in some circumstances, can become the rate-determining factor.

In this paper, maximum rates of reaction were measured during thermal analysis experiments which involved the combustion of pyrite. The experimentally determined rates were compared with those predicted from various models involving consideration of the chemical reactions and gaseous diffusion.

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Experimental

Materials

Various size fractions were prepared by screening pyrite flotation concentrate from Mt Morgan in Queensland. This concentrate was relatively pure, containing only traces of copper and zinc. The major impurity was silica, the content of which (as represented by the acid-insoluble figure) varied from 0.4% in the <37 μm fraction to 1.4% in the 74–105 μm fraction. Microscopic examination of the individual grains in the various size fractions showed that they were relatively equiaxed in two dimensions and that the third dimension was approximately 1.4 times the other dimensions. When spread on the bottom of the crucible, they assumed a position with the long axis parallel to the base of the crucible. In screening, the ability of particles to pass a given aperture is determined by their two shorter dimensions. Thus the equivalent spherical diameter of average-sized particles in the 53–74 μm screen size fraction (the most commonly used in these experiments) was calculated to be 89 μm.

Equipment and method

Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TG) was carried out using a Rigaku "Thermoflex" analyser. The initial samples and final residues were weighed using a Perkin–Elmer microbalance. Pt–Pt 13% Rh thermocouples were used to measure the reference and sample temperatures. Small cylindrically shaped silica crucibles having an internal diameter of 4 mm and flowing atmospheres were used in most experiments. The maximum rate of weight loss from the crucibles was studied as a function of gas flowrate (0–205 $cm^3 min^{-1}$), mode of flow (i.e., up or down), heating rate (5–20° min^{-1}), sample mass (2–40 mg), particle size (<37 to 212–300 μm screen size fraction), crucible height (2.5, 5 and 7.5 mm nominal height) and oxygen concentration (10–100%) of the atmosphere. When the crucibles used in these experiments contained 5 mg of sample they had internal heights above the sample of 1.9, 4.3 and 6.9 mm respectively.

Results

A typical record of thermal analysis is shown in Fig. 1. Reaction, as shown by both the TG and DTA traces, became apparent above 430–450°. The main feature of the DTA trace was the large exothermic peak which occurred at temperatures between 500 and 550°. The TG curve was characterized by a period during which the rate of weight loss was both constant and at a maximum for the particular experiment. Although the period was short it accounted for much of the total reaction. Some of the TG traces showed a small arrest at the end of the period of maximum rate of weight loss. An example of this latter type of trace is shown elsewhere [10].

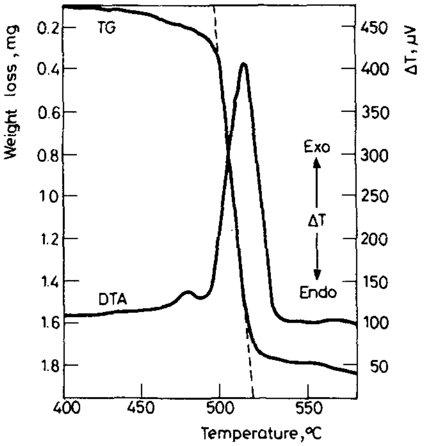

Fig. 1 Typical thermal analysis record of pyrite in air (sample wt. 5 mg, particle size 53–74 μm screen size fraction, heating rate 20°C min^{-1}, air flowrate 205 cm^3 min^{-1}, 2.5 mm nominal height silica crucible)

Effect of mode of flow, gas flowrate and heating rate

Preliminary investigations showed that the downflow mode had a number of disadvantages chief of which was that at high flowrates the gas tended to jet into the tops of the crucibles and upset the diffusion conditions. This mode also contributed to convection currents and turbulence. Subsequent work was therefore done in the upflow mode.

At flowrates above 100 cm^3 min^{-1} the maximum rate of weight loss became independent of further increases. To ensure adequate supply of oxygen all subsequent experiments were carried out using a flowrate of 205 cm^3 min^{-1}.

Similarly investigation of the effect of heating rate showed that at slow heating rates (e.g., 5 deg/min^{-1}) a considerable proportion of the total reaction occurred before maximum rates of weight loss were attained. Measurements showed that when the heating rate exceeded 10 deg min^{-1}, the period of the maximum rate of reaction represented more than 80% of the total and was little affected by further increases in heating rate. In order to make accurate rate measurements, we chose to maximize this period of the total reaction. Our experiments were therefore performed at a heating rate of 20 deg min^{-1} which was the maximum recommended for our equipment.

Effect of sample size

Samples ranging from 2 to 40 mg were employed in these tests, the results of which are shown in Fig. 2. Visual observation showed that about 5 mg of sample was necessary to give reasonably complete coverage of the base of the crucible. The increasing rate of weight loss up to this point was probably due to increasing coverage of the base of the crucible whereas above this point the increasing rate probably resulted from the diminishing free space above the sample. As will be discussed later, there is the possibility that at more than single layer coverage there is the risk of mixed reactions; accordingly, sample size in subsequent experiments was limited to 5 mg.

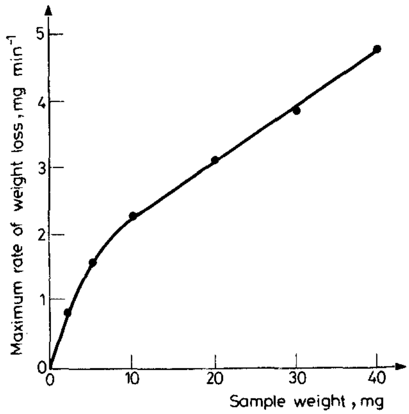

Fig. 2 The effect of sample weight on maximum rate of weight loss during the oxidation of pyrite in air (53–74 μm screen size fraction, heating rate 20°C min^{-1}, air flowrate 205 cm^3 min^{-1}, 2.5 mm nominal height silica crucible)

Effect of particle size and oxygen concentration

The effect of these variables on the maximum rate of weight loss is shown in Fig. 3. Oxygen concentration can be seen to have a large effect on the maximum rate of weight loss whereas the effect of particle size was only small. In the latter case the apparent slight decrease with increasing particle size may reflect the increasing silica contents in the larger size fractions. The oxidation of pyrite is highly exothermic and the sample temperature exceeded the programmed temperature during the period of maximum reaction rate. In the 100% atmosphere, this was most pronounced.

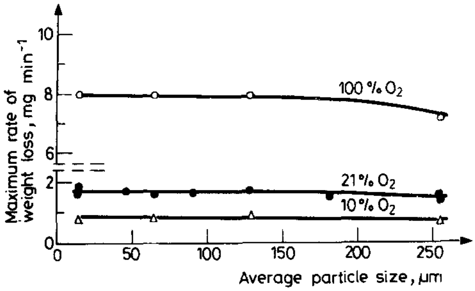

Fig. 3 The effect of oxygen concentration of the atmosphere and average particle size of pyrite on the maximum rate of weight loss. △ 10%, ● 21%, ○ 100% O_2. (Sample wt. 5 mg, heating rate 20°C min^{-1}, gas flowrate 205 cm^3 min^{-1}, 2.5 mm nominal height silica crucible)

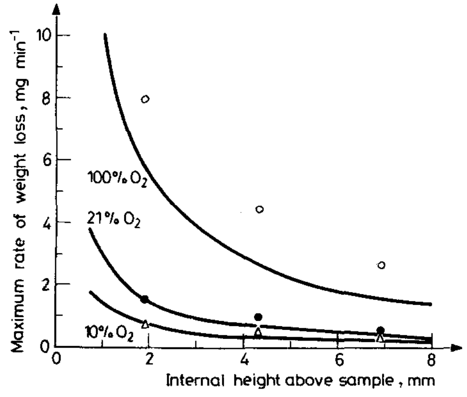

Fig. 4 The effect of crucile height and oxygen concentration of the atmosphere on the maximum rate of weight loss of pyrite. △ 10%, ● 21%, ○ 100% O_2. Calculated values shown by solid lines. (Sample wt. 5 mg, heating rate 20°C min^{-1}, gas flowrate 205 cm^3 min^{-1}, 53–74 µm screen size fraction)

Effect of height of crucible

Results obtained for three different heights of crucible are shown in Fig. 4. Also shown are the maximum rates of weight loss (solid lines) which were calculated as described in the next section for the three oxygen concentrations used in these experiments. Crucible height, particularly at the higher concentrations of oxygen can be seen to have a pronounced effect on the maximum rate of weight loss.

Discussion

During the period of maximum weight loss, the constancy of the rate of reaction indicates that the reaction was not limited by diffusion through the growing product layer around each particle. The small effect of particle size also supports this contention. Rather, the indications are that the reaction was limited by diffusion either in the crucible or through the stagnant sheath surrounding each particle. In order to explore and differentiate between these possibilities, measured maximum rates of weight loss were compared with those calculated for both situations.

The rate of weight loss is determined by the flux of oxygen and the overall chemical reaction taking place. In an earlier study [10], we showed that hematite (α-Fe_2O_3) was the solid end product of the reaction. Small amounts of pyrrhotite ($Fe_{1-x}S$), sulphate and possibly magnetite (Fe_3O_4) formed as thin layers of intermediate reaction product but in amounts which were small in comparison with the amount of ferric oxide. For the purposes of calculating the mass transfer, the reaction for small sample weights may therefore be represented by

$$2FeS_2 + 11/2O_2 \rightarrow Fe_2O_3 + 4SO_2 \tag{1}$$

or

$$2FeS_2 + 15/2O_2 \rightarrow Fe_2O_3 + 4SO_3 \tag{2}$$

depending upon whether SO_2 or SO_3 is assumed as the main gaseous product of the reaction.

Equilibria in the sulphur-oxygen system at 800 K, which were calculated using JANAF [11] data and assuming air as the source of oxygen, are shown in Fig. 5. Under limiting oxygen diffusion conditions the concentration of oxygen at the particle surface (or base of the crucible) would approach zero and Fig. 5 indicates that SO_2 would be the primary gaseous product of the reaction. However, in diffusing away the SO_2 would encounter increasing concentrations of oxygen and SO_3 would become the predominant gaseous sulphur-containing species. This would occur quite close to the particle surface (or base of the crucible) and, under

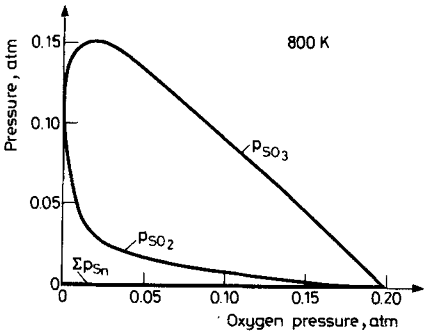

Fig. 5 Gaseous equilibria in the sulfur-oxygen system at 800 K for a total pressure of 0.2 atm

equilibrium conditions, one would expect the rate of mass transfer to be determined by the diffusion of oxygen against a counterflow of SO_3. Similar conclusions apply for other oxygen concentrations.

Table 1 The calculated effect of oxygen concentration on the maximum rates of weight loss, mg min^{-1} (1.9 mm internal depth of crucible)

Oxygen concentration (%)	10	21	100
Rate of wt. loss (reaction (1)*	0.76	1.54	5.88
Rate of wt. loss (reaction (2)*	0.56	1.14	4.38

* See text.

Although equilibrium considerations indicate the presence of substantial amounts of SO_3, the attainment of gaseous equilibrium at these temperatures is slow. This is evidenced by the use of catalysts in sulphuric acid manufacture and it is probable in our experiments that most of the SO_2 remained unconverted. To cover this possibility, mass transfer calculations were made for both cases, i.e., for reactions according to Eqs (1) and (2).

When large sample weights are used (i.e., multiple layers), it is possible that the overall reaction could occur in two successive stages, i.e.,

$$FeS_2 + O_2 \rightarrow FeS + SO_2 \tag{3}$$

followed by

$$2FeS + 7/2O_2 \rightarrow Fe_2O_3 + 2SO_2 \tag{4}$$

In this situation, the rate of reaction may change with time depending on the relative extent of reactions (3) and (4). To avoid this complication, most of the experiments were conducted using 5 mg of sample which was sufficient to ensure coverage of the base of the crucible.

Diffusion to a single particle

According to equations (1) and (2), oxygen would have to diffuse to the particle against a counterflow of SO_2 or SO_3. Nitrogen, if present, would remain essentially stagnant. The molar fluxes of product and reactant gases are not equal and there is a net flow of gas (i.e., Stefan flow) to the particle surface. The resultant flux of oxygen is determined by both its diffusional flux and the Stefan flow. Mulcahy and Smith [12] studied the kinetics of combustion of pulverized fuel and developed equations to allow calculation of the flux of oxygen to the particle surface. When Stefan flow considerations are involved these authors give

$$N_{Ox} = \frac{DP[\ln(1-\partial f_v)]}{\partial RTr} \tag{5}$$

where N_{0x} is the molar flux of oxygen to the particle surface
D the diffusion coefficient of oxygen
P the total pressure
R the gas constant
T the absolute temperature
f_v the mole fraction of oxygen in the bulk gas phase
r the particle radius
∂ a dimensionless parameter used to account for the effects of the Stefan flow.

Using this equation we have calculated the molar fluxes of oxygen and the attendant rates of weight loss in air for reactions (1) and (2) for 5 mg of sample. In performing these calculations, we assumed an equivalent spherical diameter of 89 μm (see materials Section), a temperature of 530°, and made use of the diffusion coefficients calculated as described in Appendix 1 and listed in Table 2. Our calculated rates of weight loss for reactions (1) and (2) are 397 and 171 mg min^{-1} respectively. Comparison of these calculated rates of weight loss with those determined experimentally in Figs 2–5 show the former to be several orders of magnitude larger. It seems unlikely therefore that the rate of reaction was limited by the diffusion of oxygen through the stagnant sheath surrounding individual particles. This conclusion is also supported by the experimental observation that the maximum rates of weight loss are relatively independent of particle size.

Table 2 Values of binary diffusion coefficients ($cm^2\ s^{-1}$)

	273 K	793 K
N_2—O_2	0.181*	0.913***
SO_2—N_2	0.104**	0.564***
O_2—SO_2	—	0.575***
SO_3—N_2	—	0.523***
O_2—SO_3	—	0.507***

* Perry Chilton [14]

** Reid & Sherwood [15].

*** Estimated (see Appendix 1)

Diffusion in the crucible

For the purposes of calculating the oxygen flux in the crucible, we have used an equation that was originally developed by Asaki and colleagues [13] to study the oxidation of ferrous sulphide melts in tubes. When SO_2 is the diffusing species, this has the form

$$X^+_{0x} = \left\{ X^*_{0x} - \frac{1}{1-\frac{1}{k}} + \frac{X^*_{Nit}}{1-\frac{1}{k}\frac{(1-r_1)}{(r_2-r_1)}} \right\} \cdot \exp\left\{ BN_{0x}r_1\left(1-\frac{1}{k}\right)\right\} + \\ + \frac{1}{1-\frac{1}{k}} - \left\{ \frac{X^*_{Nit}}{1-\frac{1}{k}\frac{(1-r_1)}{(r_2-r_1)}} \right\} \cdot \exp ABN_{0x} \tag{6}$$

where X_{0x}, X_{Nit} refer to mole fractions of oxygen and nitrogen, * and $^+$ indicate the top and bottom of the crucible, N_{0x} is the molar flux of oxygen, and k the ratio of the flux of O_2 to that of SO_2. A, r_1, r_2 and B have the following significance where D is the binary diffusion coefficient for the pairs of gases shown and C is the total molar concentration of the gases

$$A = \frac{D_{(SO_2-N_2)}}{D_{(N_2-O_2)}} - \frac{1}{k}, \qquad r_1 = \frac{D_{(SO_2-N_2)}}{D_{(O_2-SO_2)}}$$

$$r_2 = \frac{D_{(SO_2-N_2)}}{D_{(N_2-O_2)}}, \qquad B = \frac{1}{CD_{(SO_2-N_2)}}$$

A similar expression may be written for the case where SO_3 is the diffusing species. Under limiting oxygen diffusion conditions X^+_{0x} approaches zero and the flux of oxygen may be estimated from Eq. (6) or its SO_3 counterpart.

Fluxes of oxygen and corresponding rates of weight loss were calculated for reactions (1) and (2). The calculations were prepared to show the effects of the concentration of oxygen in the atmosphere and height of crucible. Calculated values showing the effect of the former variable are shown in Table 1 and may be directly compared with the experimentally determined values shown in Fig. 3. The calculated values (SO_2 case) were less than the experimentally determined rates of weight loss, the ratio between calculated and experimental values ranging from 0.84 in 10% O_2 atmosphere to 0.74 in 100% O_2. It can also be seen that the calculated rates of weight loss, assuming the presence of SO_3, were about 25% lower than in the presence of SO_2 and that the agreement with the experimental values was not as good. Figure 4 shows the effect of height of crucible at various concentrations of oxygen. In this case, the calculated values (SO_2 case) are shown by the solid lines. Again it can be seen that the calculated values were less than those measured and that in all cases the ratio was better than 0.50, the agreement being better for the shorter crucibles. Once again, the calculated values for SO_3 (not shown) were about 70% of the corresponding SO_2 values.

In all instances, the calculated values were below the experimentally determined rates of weight loss. Undoubtedly some of this disparity was due to overtemperatures but it is thought that the whole of the discrepancy can not be attributed to this cause (see Appendix 1). Rather it is more likely due to errors in the estimation of the diffusion flux. Considering the many assumptions involved, it is considered that there is good agreement between the calculated and measured rates of weight loss and that this agreement justifies our claim that the maximum rates in our experiments were limited by diffusion in the crucibles.

Conclusions

Mass transfer, during thermal analysis experiments involving the combustion of pyrite, was analysed in terms of several diffusion-based models. The experimentally determined maximum rates of weight loss were shown to be in good agreement with values calculated for a model, assumming diffusional limitations in the crucible. This model also accounted for the effects of oxygen concentration of the atmosphere and height of crucible.

Although thermodynamic analyses predicted that the sulphur in the gas phase would be oxidized to SO_3, better agreement was obtained when the kinetic calculations were based on the presence of SO_2. This may indicate kinetic limitations on the attainment of gaseous equilibrium in the crucible. The calculated rates of weight loss were always lower than those measured but were always more than 50% and in most cases 70–80% of the measured rates. The differences between the calculated and measured rates were thought to be due to a combination of overtemperatures and errors associated with the estimation of the diffusion flux.

This work has shown that when thermal analysis is used to study combustion reactions the rate of reaction can be limited by diffusion in the crucible. This applies even when very shallow crucibles and small weights of sample are employed. The likelihood of this limitation should be borne in mind when considering thermal analysis for the study of combustion reactions.

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Appendix 1

Evaluation of Diffusion Coefficients

To calculate the flux of oxygen, it was necessary to know the binary diffusion coefficients for N_2—O_2, SO_2—N_2, O_2—SO_2, SO_3—N_2 and O_2—SO_3. Data on diffusion coefficients at elevated temperatures are generally not available and must either be estimated from data obtained at lower temperatures or predicted from theoretical correlations based upon the molecular theory of gases. In this work a version of Hirschfelder, Bird and Spotz equation [13] was used to either estimate or extend the data shown in Table 2.

The flux is dependent on the concentration of oxygen in the gas phase and the diffusion coefficient. Since the former varies as T^{-1} and the latter as $T^{3/2}$, the overall flux is dependent on $T^{1/2}$. The flux would not therefore be expected to be very sensitive to changes in temperature (e.g., at 550°C a temperature rise of 30°C would change the calculated diffusion flux by less than 2%).

Zusammenfassung — Maximale Geschwindigkeiten des bei der Oxydation von in dünnen Schichten aufgebrachten Pyritteilchen (<37 bis 212–300 μm Teilchengröße) in 10–100% Sauerstoff enthaltenden Atmosphären auftretenden Gewichtsverlustes wurden im Verlaufe von thermoanalytischen Experimenten gemessen. Die erhaltenen Werte werden mit denen für einige, die Diffusion berücksichtigenden Modelle berechneten verglichen. Gute Übereinstimmung wurde bei dem die Gasdiffusion im Tiegel berücksichtigenden Modell erhalten.

Резюме — Измерены максимальные скорости потери веса при термическом анализе процесса окисления тонких слоев частиц пирита с размером от 37 до 212–300 μм в атмосфере с содержанием кислорода от 10 до 100%. Экспериментально найденные скорости были сопоставлены с вычисленными на основе некоторых диффузионных моделей. Хорошее совпадение было получено для модели, включающей диффузию газа в тигель.