

279. Amphiboles. Part II.¹ The Kinetics of the Oxidation of Crocidolite.

By W. E. ADDISON, G. H. NEAL, and J. H. SHARP.

The rate of oxidation of crocidolite at different pressures and temperatures is shown to depend upon whether the surface is clean or covered by a layer of water formed during oxidation; the activation energies are 21 and 33 kcal./mole, respectively. The surface water is tenaciously held and completely inhibits oxidation if either the temperature or the oxygen pressure is sufficiently low.

It was shown in the preceding paper that the oxidation of crocidolite can be represented by the reaction, $4\text{Fe}^{2+} + 4\text{OH}^- + \text{O}_2 \longrightarrow 4\text{Fe}^{3+} + 4\text{O}^{2-} + 2\text{H}_2\text{O}$, accompanied by a side-reaction, $4\text{Fe}^{2+} + \text{O}_2 \longrightarrow 4\text{Fe}^{3+} + 2\text{O}^{2-}$. The present paper is concerned with a kinetic study of this oxidation.

EXPERIMENTAL AND RESULTS

The system used is that described in Part I.¹ During kinetic experiments the cold trap was filled with solid carbon dioxide or liquid nitrogen, to freeze out water formed during oxidation; a change in the volume of oxygen in the system then measures the extent of oxidation, which is here expressed in c.c. of oxygen (corrected to N.T.P.) taken up per gram of crocidolite. The pressure of gas in the system could be maintained constant within ± 2 mm. by manual adjustment of the levelling device. Since the rate of oxidation proved to be almost independent of pressure, such minor fluctuations are unimportant.

The material used was that described in Part I as R.S.13, and each sample was outgassed overnight at 10^{-6} mm., at the highest temperature to be used in its oxidation.

The oxidation of crocidolite has been followed at constant pressure (range, 5—45 cm.) and constant temperature (range 350—480°). Typical plots of the rate of oxidation are shown in Fig. 1. With a carbon dioxide trap the rate is constant for a considerable period (Fig. 1B, 440°, 6.6 cm.); with a liquid nitrogen trap (Fig. 1A, 442°, 15.8 cm.), however, the initial rate falls slightly during the first hour and thereafter remains constant. In both cases the linear plot continues until approximately half of the available ferrous iron has been oxidised, provided that the pressure of oxygen is sufficiently great. Under those conditions when the rate decreases with time, a linear plot of rate against the square root of time is obtained.

The rates of oxidation of different samples of the same material under the same experimental conditions were found to vary. Whereas other workers² have found that the rates of oxidation of different samples are proportional to surface area, no such dependency has been found in the present work. Therefore, variations in temperature and pressure had to be studied without a change of sample.

Effect of Pressure.—This was investigated by starting an oxidation at a relatively high pressure (~ 45 cm. with a carbon dioxide trap, or ~ 15 cm. with a liquid nitrogen trap) and allowing the pressure of oxygen to decrease as reaction proceeded. The rate of oxidation was found to decrease slightly with pressure, typically from 0.32 to 0.26 c.c. g.⁻¹ hr.⁻¹, corresponding to a pressure change from 15.6 to 1.0 cm.; this rate is not proportional to $p^{1/n}$ where n has any sensible value.

In these oxidation runs at varying pressure, reaction always stopped completely, although a significant pressure of oxygen remained in the gas phase. Some values of these critical pressures are given in Table 1 along with the volume of oxygen which had been taken up.

TABLE 1.

O ₂ taken up (c.c./g. of crocidolite)	3.29	2.59	0.75	0.16	0.05
Critical pressure (cm.)	10.68	6.64	1.68	0.38	0.14

It can be seen that the critical pressure is to some extent related to the extent of oxidation and it may be related also to temperature and rate of oxidation. The highest value at which

¹ Part I, preceding paper.

² E.g., Anderson, Roberts, and Harper, *J.*, 1955, 3946.

reaction has been observed to stop is 10.68 cm., although no attempt has been made to attain an upper limit. When reaction has stopped and the sample has been pumped out for several hours, reaction can be restarted at the pressure at which it had previously stopped.

In those runs in which reaction was followed to completion at pressures above 30 cm. as described in Part I,¹ it was verified that reaction had not stopped because of the attainment of a critical pressure, since a further increase in the oxygen pressure, or outgassing of the sample followed by the admission of further oxygen, did not promote further reaction.

Effect of Temperature.—A sample was outgassed at the highest temperature to be used, then cooled to the lowest temperature, and oxidation was followed at that temperature for the

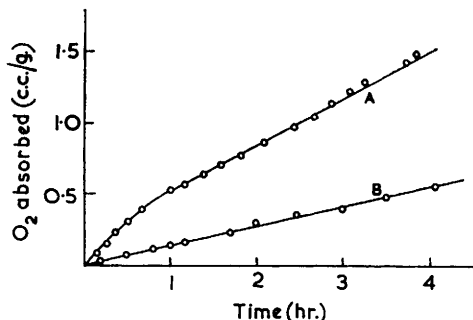


FIG. 1. Typical plots of the rate of oxidation of crocidolite.

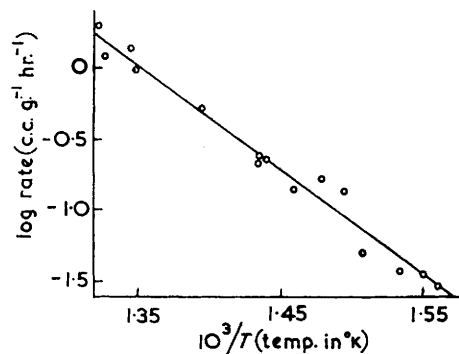


FIG. 2. Activation energy plot for the oxidation of crocidolite, with a carbon dioxide trap in the system.

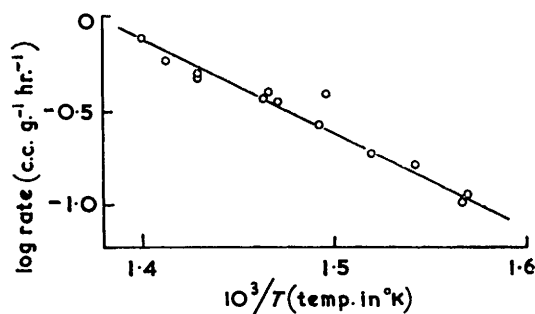


FIG. 3. Activation energy plot for the oxidation of crocidolite with a liquid-nitrogen trap in the system.

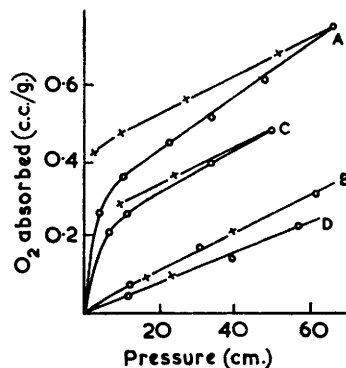


FIG. 4. Sorption of oxygen by crocidolite at 0°. O denotes sorption, X denotes desorption.

least time necessary to determine the rate accurately. Further oxidations were then followed at successively higher temperatures, one of two alternative procedures being used. Either the sample was outgassed for some time after the first rate had been determined, and oxygen was re-admitted at a higher temperature; or the temperature was raised without the sample's being outgassed, and the period during which the temperature was being raised was neglected from a kinetic standpoint. With a carbon dioxide trap the two procedures gave the same result, but with a nitrogen trap the former yielded an initial curved portion of the rate plot at each oxidation temperature. As many as five temperatures could be studied with the one sample.

When the logarithm of the rate is plotted against the reciprocal of temperature, a straight line is obtained from which an activation energy is calculated. Table 2 gives the activation energies found, for various runs, from the linear portions of the plots. Columns 5 and 10 of

Table 2 show a factor of 4 between extremes in rate for samples of the same material. In Fig. 2 are plotted the data of runs 1—3, where conditions are similar, the experimental points of run 2 being scaled by a factor of 0.18/0.10 and those of run 3 by 0.18/0.13 in order that the

TABLE 2.

Run	Trap	O ₂ press. (cm.)	E (kcal./ mole)	Rate of oxidn. at 402.5° (c.c. g. ⁻¹ hr. ⁻¹)	Run	Trap	O ₂ press. (cm.)	E (kcal./ mole)	Rate of oxidn. at 402.5° (c.c. g. ⁻¹ hr. ⁻¹)
1	CO ₂	28.9	30	0.18	4	CO ₂	6.9	32	0.04
2	CO ₂	36.3	33	0.10	5	N ₂	12.2	34	0.05
3	CO ₂	31.9	32	0.13					

three runs can be plotted on the same scale. The activation energy thus evaluated is 33 kcal./mole.

When a nitrogen trap was used and the first of the experimental procedures given above was adopted, the rate of oxidation at zero time was determined by drawing a tangent to the curve of the rate plot. Data from three runs are shown in Fig. 3 and the activation energy thus obtained is 21 kcal./mole, which is significantly different from that obtained from Fig. 2.

Oxidation has been followed kinetically at temperatures as low as 350°, where the rate is very slow. D.T.A. experiments³ detect the beginning of the exotherm only at 410°. It has been shown that oxidation can occur, however, even at 0° when physical sorption of oxygen also occurs (see Fig. 4). An oxygen isotherm, A, was measured on crocidolite previously outgassed at 450° and found to be irreversible. The crocidolite was outgassed at liquid-air temperature, at which it had been shown that oxygen could be completely removed but any water formed as a product of oxidation would not be desorbed; a further isotherm (B) was measured at 0° where sorption was less than in the earlier experiment and reversible. This sequence was repeated on the same sample after outgassing again at 450°, with the same result (curves C and D). The irreversibility is attributed to chemical reaction, and the reversibility to purely physical sorption due to the inability of the oxygen to penetrate the water layer at that temperature and effect oxidation.

DISCUSSION

It is in accord with the mechanism of a surface reaction, as postulated in Part I,¹ that oxidation at constant pressure should proceed at a constant rate since ferrous and hydroxyl ions on the surface are being renewed constantly as reaction proceeds. Only when all the ferrous iron in some ribbons is completely oxidised does the effective concentration of that ion, and hence the rate of oxidation, decrease. It is also in accord that reaction proceeds only at ends of ribbons of cations, *i.e.*, at ends or discontinuities of fibres, and hence the effective surface for the reaction is not the total surface measured by B.E.T. methods, but rather the effective area of fibre ends, which cannot readily be measured experimentally.

The existence of critical pressures below which oxidation does not proceed can be attributed to the presence of a film of adsorbed water on the surface of the crocidolite which is not removed by a cold trap so long as there is oxygen in the gas phase. When the critical pressure is reached the oxygen is no longer able to diffuse through the water layer, and reaction stops. The slight decrease in the rate of oxidation with pressure is also accounted for by the presence of this water film, since the rate of diffusion of oxygen through the film will be proportional to its pressure. When a sample has been outgassed after the attainment of a critical pressure, further oxidation can proceed as the water has been removed.

The vapour pressure of water is considerably greater at -78° than at -196°, and in consequence desorption of freshly formed water from the surface of the crocidolite should be easier when there is a liquid-nitrogen trap in the system; so oxidation must then proceed further before a complete layer of water is formed on the surface. It is suggested

³ Vermaas, *Trans. Geol. Soc. South Africa*, 1953, **55**, 199; Cilliers, Freeman, Hodgson, and Taylor, *Econ. Geol.*, 1961, **56**, 1421.

that, whereas the linear portions of the rate plots correspond to oxidation in the presence of a complete coverage of the active sites by a water layer, the curved portions obtained at the onset of reaction when a nitrogen trap is used correspond to reaction that is retarded as the layer is being formed. It has been found that when two samples are oxidised at the same temperature, that which oxidises the more rapidly reaches a constant rate faster although the volume of oxygen taken up in the two cases is approximately the same. When a carbon dioxide trap is used desorption of water from the surface is slower and the curved part of the rate plot corresponding to the completion of the water layer is so short that on only one occasion was evidence of it detected.

In accordance with the presence of this water layer, the lower activation energy of 21 kcal./mole corresponds to the oxidation of a fresh surface since it is a rate extrapolated to zero time when there can be no water present. The difference between the two activation energies is then related to the energy required to enable oxygen to penetrate through a monolayer of water. The lower activation energy represents the energy associated with the migration of electrons and protons through the bulk of the solid to produce ferrous and hydroxyl ions on the surface.

Conclusions.—The oxidation of crocidolite is a surface reaction which can occur even at 0°. The water formed on oxidation is very tightly held on the surface and prevents more than superficial oxidation at low temperatures. It also prevents oxidation at higher temperatures if the pressure of oxygen falls below a definite limiting value. The activation energy of the oxidation is 33 kcal./mole when the active sites of the surface are covered by a layer of water, and 21 kcal./mole when the surface is free from water.

THE UNIVERSITY, NOTTINGHAM.

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