

KINETICS AND MECHANISMS OF DEHYDRATION AND RECRYSTALLIZATION OF SERPENTINE—II, SPECTRUM OF ACTIVATION ENERGIES FOR RECRYSTALLIZATION*

by

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ABSTRACT

An order of magnitude calculation is made to determine the activation energies involved in the recrystallization of serpentine to forsterite. The so-called "activation energy spectrum" showing the proportion of material with different activation energies is estimated.

INTRODUCTION

It has been shown in the preceding paper that when powdered serpentines are heated in air at temperatures of about 570°C, the material is largely dehydroxylated and an X-ray amorphous phase is formed. This material recrystallizes to forsterite when heated at temperatures exceeding about 600°C but the maximum amount of forsterite is not developed until the temperature is raised to about 800°C. At each temperature of heat treatment above 600°C a certain amount of forsterite is formed in a relatively rapid reaction and this amount is scarcely increased when the time is extended from about 10 hr to 100 hr. With each increment of temperature a further rapid reaction takes place yielding additional forsterite which again remains of constant amount (or nearly constant) over long heating periods.

Similar thermal behavior had been observed in other solid state reactions and the general interpretation of such data is that the reaction involves a range or spectrum of activation energies. Perhaps the first investigation of this type was that of Vand (1943) who studied the annealing behavior of the electrical resistance of thin metallic films heated at successively higher temperatures. The annealing behavior of radiation-damaged solids has been shown to follow a similar time-temperature dependence (see for example the general discussion by Stone, 1961, and the summary by

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Primak and Bohmann, 1962). In the preceding paper, the term "chemically damaged solid" was used to describe the X-ray amorphous and largely dehydroxylated material formed from serpentine at about 570°C and from which forsterite crystallizes.

The general interpretation placed on the recrystallization-time-temperature curves is that the material can be considered as consisting of fractions each with its own activation energy for recrystallization. The fractions are considered to recrystallize independently of each other (which is probably an over-simplification) so that at any given temperature recrystallization of fractions up to a certain activation energy will take place rapidly, while fractions with higher activation energies will show relatively little reaction. With each increase of temperature, fractions with higher activation energies will recrystallize.

The purpose of the present paper is to bring forward additional experimental evidence and to give an order-of-magnitude calculation for the range of activation energies and fractions involved.

DEVELOPMENT OF FORSTERITE BY HEAT TREATMENTS AT SUCCESSIVELY HIGHER TEMPERATURES

If the model of a chemically damaged solid described previously is valid, then it should be possible to recrystallize more and more fractions of the

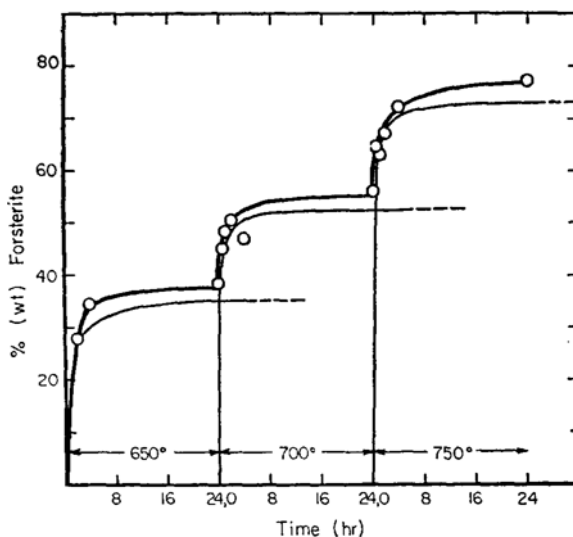


FIGURE 1.—Percentage of forsterite formed from dehydroxylated serpentine when heated for 20 hr at each of the temperatures 650, 700 and 750°C successively, compared with the percentages formed from samples heated directly from room temperature to these temperatures.

initial material by heating at a succession of temperatures, e.g. 650°C, 700°C, 750°C, and holding the material at each temperature sufficiently long to achieve equilibrium at that temperature. Moreover the final result achieved by these incremental temperature treatments should be the same as when the material is taken directly to the same final temperature.

The results of such an experiment are shown in Fig. 1, for serpentine powder previously described as "coarse powder". The material was heated for periods up to 20 hr successively at 650, 700 and 750°C. Other material was heated directly to 700°C and directly to 750°C. Samples were withdrawn from the furnace after various times and temperatures of heat treatment and the amount of forsterite was analysed at room temperature by X-ray diffraction intensity measurements using boehmite as the internal standard.

The results shown in Fig. 1 are clearly in conformity with the proposed model. The data shown in Fig. 2, for the crystallization of forsterite from the amorphous phase at 650°, 700°, 750° and 800°C, will be considered from the standpoint of this model.

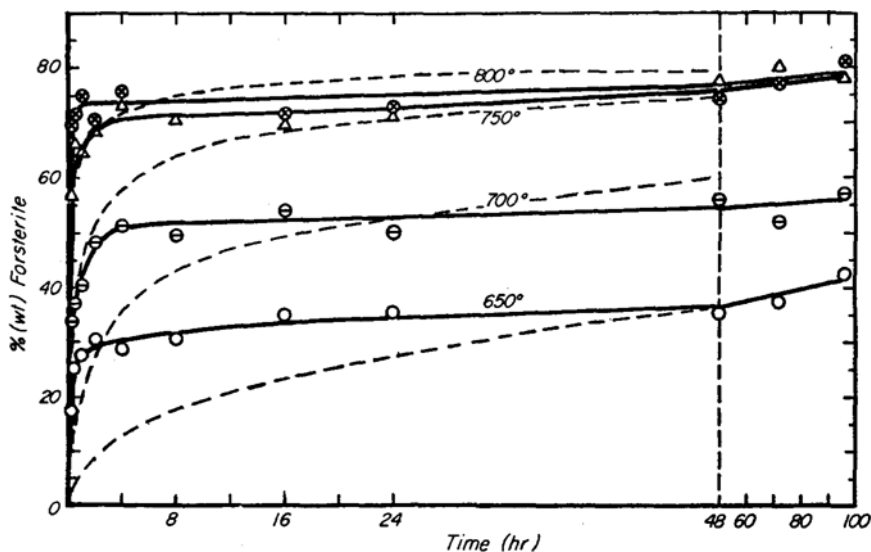


FIGURE 2.—Percentage of forsterite formed at various temperatures when heated for periods up to 100 hr. Full curves through experimentally determined values; dashed lines calculated from equation (6) and data in Table 1.

THEORETICAL BACKGROUND

Let the initial material be divided in fractions Q_i , with $\sum Q_i = 1$. Let the rate of reaction at time t of any fraction be proportional to the amount of unreacted material, Q_i :

$$-dQ_{ii}/dt = k_i Q_{ii} \quad (1)$$

or

$$Q_{ii} = Q_i \exp(-k_i t) \quad (2)$$

This assumption is obviously much too simple to account for curves of the type shown in Fig. 2, but for the present purpose a more complex analysis of these curves will not be attempted.

Let the product from component i at time t , P_{ii} , be proportional to the amount of reacted material;

$$\begin{aligned} P_{ii} &= \lambda (Q_i - Q_{ii}) \\ &= P_i (1 - \exp(-k_i t)) \end{aligned} \quad (3)$$

where P_i is the maximum product developed from Q_i .

Let the rate constant k_i be given by an Arrhenius type expression

$$k_i = A_i \exp(-E_i/RT), \quad (4)$$

then

$$P_{ii} = P_i [1 - \exp(-A_i e^{-E_i/RT} t)] \quad (5)$$

and the total product at time t is given by

$$P_t = \sum_i P_i [1 - \exp(-A_i e^{-E_i/RT} t)] \quad (6)$$

APPROXIMATE EVALUATION OF EXPERIMENTAL DATA

A straightforward analysis of the experimental data for P_t as a function of t for different temperatures T is not possible. By assuming that A_i is independent of i , one variable is removed, but a frontal attack is still not possible. The following order-of-magnitude analysis, however, serves to give a general idea of the quantities involved.

Figures 1 and 2 show that each 50°C increment of T from 650° to 800°C increases the yield of forsterite. Probably 600°C is the lowest temperature at which a measurable yield is obtained. Let Q_1 be the fraction of material which recrystallizes "quickly" at 600°C and let E_1 be the activation energy involved in the reaction, and let "quickly" be defined as 80 per cent of complete reaction in a period of 10 hr. This statement is broadly in accord with the data in Fig. 2. Let Q_2 be the additional material which reacts "quickly" in this sense at the next higher temperature, 650°C. Likewise define groups Q_3 , Q_4 and Q_5 which react at 700°, 750°, and 800°C respectively.

For this model to account for the observed results, it is necessary for E_1, E_2, \dots , to be such that at 600°C, Q_1 reacts "quickly" but Q_2 scarcely at all; at 650°C, Q_1 and Q_2 must react quickly and Q_3 scarcely at all; and so on for each temperature.

To obtain this degree of "contrast" in the recrystallization behavior of the groups, the activation energies E_1, E_2, \dots , must be distributed appropriately. To obtain an order-of-magnitude estimate of the activation energy steps from one group to the next, consider that the rate constant k changes by an order of magnitude from one group to the next, i.e., consider

$$k_1/k_2 \approx 10$$

Then from equation (4), and taking A_i to be the same for all groups,

$$(E_2 - E_1)/RT \approx \ln 10.$$

With $T = 1000^\circ\text{K}$, $R = 2 \text{ cal/mol}/^\circ\text{C}$, one obtains

$$(E_2 - E_1) \approx 4.6 \text{ kcal/mol.}$$

This is no more than an order-of-magnitude estimate. If one takes $k_1/k_2 = 20$, then $(E_2 - E_1)$ is about 6.0 kcal/mol. It appears that an activation energy increment of about 5.0 kcal/mol is required between one group and the next to obtain the observed differences in recrystallized material with 50°C temperature increments.

A similar argument can be used to find the magnitude of the activation energies. The groups are defined according to their rates of reaction at temperature intervals of 50°C . Any particular group must react "quickly" in the sense already defined at a temperature T_2 but must react scarcely at all at a temperature $T_1 = T_2 - 50$. Taking the same order-of-magnitude ratio between the rates, and using equation (4), one can write

$$\frac{\exp(-E/RT_2)}{\exp(-E/RT_1)} \approx 10$$

or

$$\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \approx \ln 10 = 2.303.$$

Taking $T_2 - T_1 = 50^\circ$, $T_1 \approx T_2 = 1000^\circ\text{K}$, one calculates

$$E = 90 \text{ kcal/mol.}$$

TABLE 1.—ESTIMATED ACTIVATION ENERGY SPECTRUM FOR THE RECRYSTALLIZATION OF DEHYDROXYLATED SERPENTINE

Group	Temperature for "quick" reaction	Activation energy	Product from each group, P_i
1	600°C	80 kcal/mol	10%
2	650	85	30
3	700	90	25
4	750	95	12
5	800	100	4

Combining this value of E , with the estimated activation energy intervals, one can draw up a tentative tabulation of energies for the five groups under consideration. These are given in Table 1, together with estimated values of P_i , the percentage of forsterite ultimately formed from each reacting group. It is seen that $\Sigma P_i=81$ per cent which is the maximum amount of forsterite shown in Fig. 2.

Before equation (6) can be used, it is necessary to calculate A_i using the assumptions already set out. Taking $E=90$ kcal/mol, $T=700^\circ\text{C}=973^\circ\text{K}$, and assuming 80 per cent of full reaction in 10 hr, one obtains from equation (5), the value $A=9.3 \times 10^{14}$. This is not far removed from the value given by absolute rate theory, namely kT/h where k and h are respectively the Boltzmann and Planck constants, which for $T=1000^\circ\text{K}$ becomes 2.1×10^{13} . The nature of the present calculation does not justify any more detailed consideration of these frequency factors.

With $A=9.3 \times 10^{14}$, and the data set out in Table 1, the calculated curves shown by dashed lines in Fig. 2 are obtained.

DISCUSSION

It is emphasized that the present analysis is little more than an order-of-magnitude estimate of the "activation energy spectrum" for the recrystallization of dehydroxylated serpentine. The basis of the calculation, namely first-order kinetics, is obviously much too simple and cannot account for the sharp bends in the curves of Fig. 2. It appears that the activation energies spread over a range mainly from about 80 to 95 kcal/mol. For each 50°C increment of temperature an additional fraction of material with an activation energy about 5 kcal/mol higher is brought into a state where "rapid" reaction to forsterite becomes possible.

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