The kinetics of the ordering process in triclinic $NaAlSi_3O_8$

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Summary. A kinetic analysis is presented of the data of MacKenzie (1957) on the hydrothermal treatment of $NaAlSi_3O_8$ under isobaric, isothermal conditions in the temperature range 450° C. to 1000° C.

The analysis indicates the existence of a smeared polymorphic transformation in the temperature range around 600° C. The activation energy for the transformation is about 60 kcal. mole^{-1} and has been equated with the process of self-diffusion involved in Al–Si ordering in the structure. Some dry-heating experiments and the influence of varying water vapour pressure are discussed.

It is our purpose to present a kinetic analysis of the experimental data of MacKenzie (1957) on the thermal transformation in triclinic $NaAlSi_3O_8$.[1] The advantages of studying MacKenzie's data on the transformation in triclinic $NaAlSi_3O_8$ in kinetic terms may be summarized briefly as follows. In studying equilibration rates in this way due allowance can be made for the temperature dependence of the rates and it is possible to demonstrate any singular changes or discontinuities in rate that are associated with change in equilibrium structural state as a function of temperature. Choice of an appropriate rate law permits one to extrapolate from incomplete equilibration data to the equilibrium state, but this is of secondary importance in an analysis of this type.

Kinetic data can only provide information about an accessible equilibrium state. The latter may be defined as an equilibrium state towards which a measurable rate of approach can be observed. Kinetic data taken by themselves do not define the status of an equilibrium state. A system may be defined as *quasi-equilibrated* if, under a given set of physico-chemical conditions, it does not move towards the true equilibrium state in any finite time. Such a state corresponds to a free energy minimum other than the lowest one appropriate to the imposed conditions, and results if the free energy of activation for passage to the true equilibrium state is prohibitively large.

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[1] It is considered advisable to restrict the use of the mineral name 'albite' to naturally occurring material since triclinic $NaAlSi_3O_8$ prepared in hydrothermal experiments may not be identical in every respect with natural albites.

Classification of polymorphic transformations. In order to facilitate later discussion of the character of the transformation in triclinic $NaAlSi_3O_8$, as defined by the kinetic data, it is necessary to comment here on some general aspects of polymorphic transformations. An important and practical classification of these is due to Ubbelohde, who emphasized, in an important review in 1957, that the thermodynamics of transformation in the solid cannot always be considered from the purely classical viewpoint, since co-operative effects in the solid must be considered.

Ubbelohde defined as *discontinuous* those transformations that show classical discontinuity in the measured specific heat and molar volume as functions of pressure and temperature. In practice such transformations usually involve major structural reorganization. *Continuous* transformations he defined as those that show no such discontinuity. Where continuity can be associated with the stable coexistence of two or more closely related structural modifications over a range of temperature, Ubbelohde has applied the term *smeared.* In the temperature range of a smeared transformation the free energy must include terms arising from the strain and internal surface energy associated with domain boundaries.

The domain texture produced under such conditions may render the true equilibrium state of the system inaccessible at lower temperatures because of the improbability of the necessary thermal fluctuations. In terms of the definition presented earlier such a system would be described as quasi-equilibrated at the lower temperature (cf. Bragg, 1940, for a discussion of similar effects in alloys).

Kinetic methods of detecting and studying polymorphic transformations. A number of techniques that utilize the theory of rate processes have been applied to the study of polymorphic transformations in solids. Examples include the use of electrical conductivity measurements by Landon and Ubbelohde (1957) and the use of isothermal diffusion coefficients by Johnson, Bristow, and Blau (1951). In such experiments, since the rate-controlling mechanism is one of diffusion, the temperature dependence of the rate processes may be described by the Arrhenius relationship $k = Ae^{-E_a/RT}$, where k is a suitably defined rate constant, E_a is the activation energy for the rate-controlling step in the diffusion process and is usually stated in calories/mole, T is the absolute temperature, R the gas constant, and A a term that includes the entropy of activation. In the temperature range of a thermal transformation A may change in value owing to the change in mechanism of the diffusion process. Outside such a temperature range A should be relatively independent of temperature.

The Arrhenius relationship may be applied to any rate process in which the rate-controlling step is one of diffusion. If a thermal transformation involves self-diffusion the application of this relationship to isothermal, isobaric equilibration rates from a defined initial structural state is valid. The diffusion potential, in this case, is defined by the free energy difference, ΔG, between the initial and equilibrium structural states at the temperature concerned and the character of the Arrhenius plot may be used to interpret the nature of the change in accessible equilibrium state as a function of temperature. If a structural transformation of appreciable magnitude occurs in the temperature range studied this will define, in general, a change in the A term of the Arrhenius relationship. An appropriate Arrhenius plot should demonstrate such a change; it may also provide direct evidence on the continuity and character of the transformation involved.

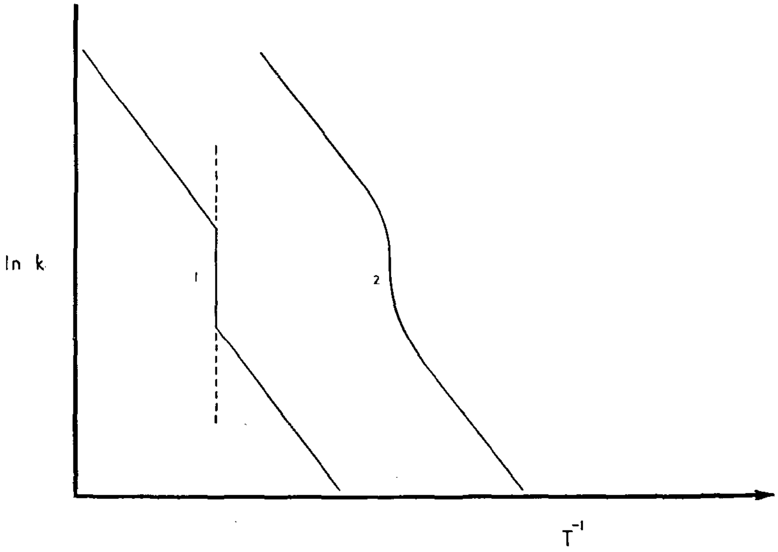

FIG. 1. Hypothetical Arrhenius plots of discontinuous (1) and continuous (2) transformations.

To illustrate this point schematic Arrhenius plots for a discontinuous and continuous transformation have been presented in fig. 1.

In attempting kinetic analysis of the isobaric, isothermal equilibration data presented by MacKenzie for the transformation in triclinic $NaAlSi_3O_8$ it is convenient, in the first instance, to use a relationship of the form $k = |\Delta G| A e^{-E_a/RT}$. The validity of this relationship can best be tested by studying the corresponding plot of ln k as a function of T^{-1} for the observed equilibration rates.

Experimental data.

In his main series of experiments MacKenzie (1957) was concerned with the behaviour under isothermal, isobaric conditions of a glass of composition $NaAlSi_3O_8$. The experiments cover the temperature range 450° C. to 1 000° C., and were mostly performed at p_{H_2O} 14 000 lb./in.^{2} He observed that crystallization to triclinic $NaAlSi_3O_8$ occurs rapidly and is followed by a slow change in unit cell dimensions. The post-crystallization changes in charges held for various times at known constant temperature and p_{H_2O} were followed by measurement after quenching of $2\theta_{131}-2\theta_{1\bar{3}1}$ on diffractometer traces taken with Cu-$K\alpha$ radiation. The variable $2\theta_{131}-2\theta_{1\bar{3}1}$ may be defined as obliquity and designated ψ. Obliquity-time data are given in full in table 3 (pp. 490–492) of MacKenzie (1957) and need not be reproduced here. Some further data were made available to us by Dr. W. S. MacKenzie, and are set down, with permission, in our table I.

Table I. Values of $\psi = 2\theta_{131}-2\theta_{1\bar{3}1}$ for $NaAlSi_3O_8$ crystallized for different lengths of time. (*We are indebted to Dr. W. S. MacKenzie for permitting us to include these unpublished additional data.*) In all runs p_{H_2O} was 14 000 lb./in.^{2}

Run no.	Time (hours)	ψ
525° C.		
336	71	1·826
351	71	1·816
350	232	1·789
335	327	1·774
550° C.		
287	24	1·833
288	24	1·835
87	24	1·895
550° C.		
88	24	1·900
357	71	1·832
338	71	1·814
315	140	1·772
356	232	1·799
314	258	1·722
337	327	1·816

MacKenzie also performed some subsidiary hydrothermal experiments and dry-heating experiments, which will be discussed later (p. 448). Only the data for the main series of experiments are involved in the sections immediately following.

The usefulness of the obliquity parameter ψ for following the change from the initially crystallized structure towards the equilibrium structure at any temperature and p_{H_2O} could not be evaluated *a priori*, since ψ has no clear quantitative relationship to structural state. The use, however, of rate constants derived from ψ is analogous to the use of electrical conductivity by Landon and Ubbelohde (1957) and of diffusion coefficients by Johnson, Bristow, and Blau (1951) in the study of thermal transformations in Na_3AlF_6 and sodium silicate glasses respectively.

KINETIC ANALYSIS OF MACKENZIE'S MAIN SERIES OF EXPERIMENTS.

The rate law. The rate of approach to equilibrium at any time is likely to be dependent in some simple manner on the amount of the departure of the system from equilibrium at that time. In terms of obliquity departure from equilibrium is measured by $\psi-\psi_\infty$, where ψ_∞ is the value towards which the obliquity tends at infinite time. Of simple rate laws based on $(\psi-\psi_\infty)^n$ it was found that the experimental data fitted best a law of the form

$$-d\psi/dt = k(\psi-\psi_\infty)^2. \tag{1}$$

The rate constant k is, to a first approximation, a function of temperature and p_{H_2O} only.

On integration and insertion of the limit $\psi \rightarrow \psi_0$ as $t \rightarrow 0$, the rate law becomes

$$kt = (\psi_0-\psi)/(\psi-\psi_\infty)(\psi_0-\psi_\infty). \tag{2}$$

The limiting obliquity ψ_0 is the extrapolated starting value of ψ, the value ψ would have had at zero time if the glassy charge had crystallized instantaneously instead of in half an hour or so. No physical meaning is attached to the value of ψ_0.

The integrated rate law is most conveniently represented in logarithmic form, as

$$\log(\psi_0-\psi)/(\psi-\psi_\infty) = \log t+\log k(\psi_0-\psi_\infty). \tag{3}$$

Fig. 2 shows a plot of $\log(\psi_0-\psi)/(\psi-\psi_\infty)$ against $\log t$ of the data for 700° C., p_{H_2O} 28 000 lb./in.^{2}

Evaluation of limits. The experimental data are such that accurate values of ψ_0 and ψ_∞ cannot usually be obtained by inspection. However, by rearranging the rate law in the form

$$\psi = \psi_0-k(\psi_0-\psi_\infty)(\psi-\psi_\infty)t, \tag{4}$$

estimating ψ_∞ by inspection, and plotting ψ against $(\psi-\psi_\infty)t$, an accurate value of ψ_0 can be obtained from the intercept on the ψ-axis. The value of ψ_∞ may then be refined by inserting the new value of ψ_0 in the rate equation written in the form

$$\psi = \psi_\infty + \{(\psi_0-\psi)/t\}.\{1/k(\psi_0-\psi_\infty)\}, \tag{5}$$

plotting ψ against $(\psi_0-\psi)/t$, and determining ψ_∞ from the intercept on

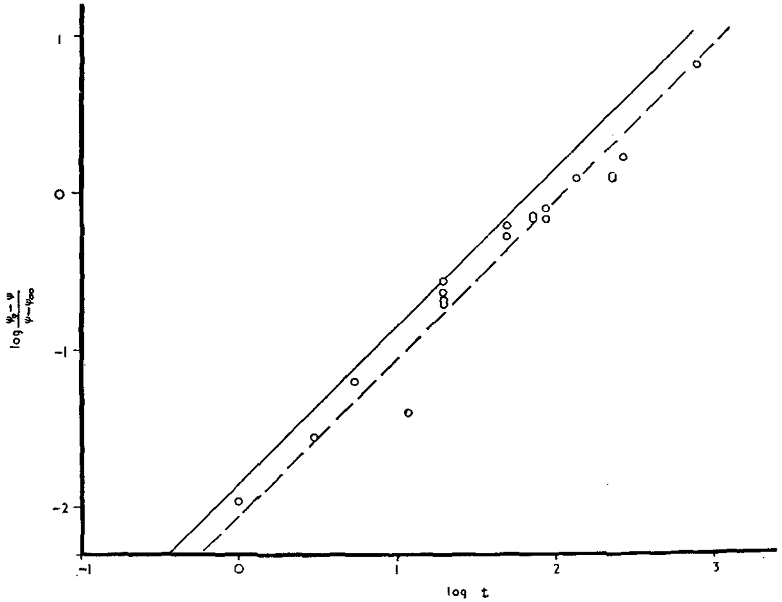

FIG. 2. Logarithmic plot of $(\psi_0-\psi)/(\psi-\psi_\infty) = k(\psi_0-\psi_\infty)t$ for 700° C., p_{H_2O} 28 000 lb./in.^{2} The solid line corresponds to k^*, and the broken line to $\bar{k}$.

the ψ-axis. Further refinement of ψ_0 can be achieved by replotting equation (4) using the improved value of ψ_∞ obtained from (5). Further refinement of ψ_∞ can then be achieved by replotting (5) using the improved value of ψ_0. The refinement procedure was repeated successively for ψ_0 and ψ_∞ until no further significant change occurred. Final values of ψ_0 and ψ_∞ are given in table II.

The value of ψ_∞ could not be estimated by inspection of the data for the lowest temperatures. For the first stage in the refinement, therefore, values were chosen consistent with the known variation of ψ_∞ with temperature at higher temperatures.

The limits ψ_0 and ψ_∞ are functions of temperature and of p_{H_2O}. Their dependence on p_{H_2O} will be considered in a later section (p. 446). The variation of ψ_∞ with temperature is shown in fig. 3, which differs from

TABLE II. Final estimates of the limiting obliquities ψ_0 and ψ_∞.

T (°C.)	p_{H_2O} (lb./in.^{2})	ψ_0	ψ_∞	T (°C.)	p_{H_2O} (lb./in.^{2})	ψ_0	ψ_∞
1 000	2 000	2·025	2·005	550	14 000	1·935	1·600
900	7 000	2·002	1·970	525	14 000	1·930	1·475
850	14 000	1·995	1·940	525	7 000	1·930	1·495
800	14 000	1·985	1·905	500	14 000	1·925	1·275
750	14 000	1·973	1·870	475	14 000	1·920	1·15
700	28 000	1·966	1·782	450	14 000	1·918	1·10
600	14 000	1·950	1·704				

the corresponding plot in MacKenzie (1957, p. 508) in being smoother due to the refinement of ψ_∞, and in extending to lower temperatures where an obvious turnover towards the obliquity of low albite is discernible. Fig. 3 thus represents the temperature dependence of structural state, as measured by obliquity, for triclinic $NaAlSi_3O_8$ equilibrated or quasi-equilibrated under MacKenzie's experimental conditions. Although it would probably be incorrect to interpret the structural states of soda-feldspars equilibrated under natural conditions quantitatively in terms of fig. 3, a semi-quantitative correspondence may be expected.

The obliquities of high albite (1·99) and of low albite (1·062) inserted on fig. 3 are those of Smith (1956), whose value for high albite differs from that (2·03) of Tuttle and Bowen (1950).

Determination of rate-constants. Rate-constants were calculated for each experimental point using equation (3) above. The scatter of the experimental points beneath the line of fastest rate, apparent in fig. 2, greatly exceeds the scatter attributable to error in the measurement of ψ ($\pm 0{\cdot}004$). The increased scatter must represent some real difference in the experimental conditions between individual experiments, and MacKenzie (1957, p. 499) considered in this connexion the influence of grain size. The most significant experimental points are those corresponding to the fastest rates; only the rate-constants, designated k^*, calculated from such points are used in subsequent sections. Values of $\log k^*$ are given in table III.

The rate-constants are pressure-dependent. Values of $\log k^*$ derived from experiments at various pressures, corrected to p_{H_2O} 14 000 lb./in.^{2} by the method of p. 446 where necessary, are also given in table III and plotted against $1/T$ in fig. 4.

An average rate-constant $\bar{k}$ has also been calculated, using equation (3), from all the experimental points under each set of physical conditions. Values of $\log \bar{k}$ with standard deviation and corrected to p_{H_2O} 14 000 lb./in.^{2} where necessary are given in the last column of table III, and plotted against $1/T$ in fig. 4.

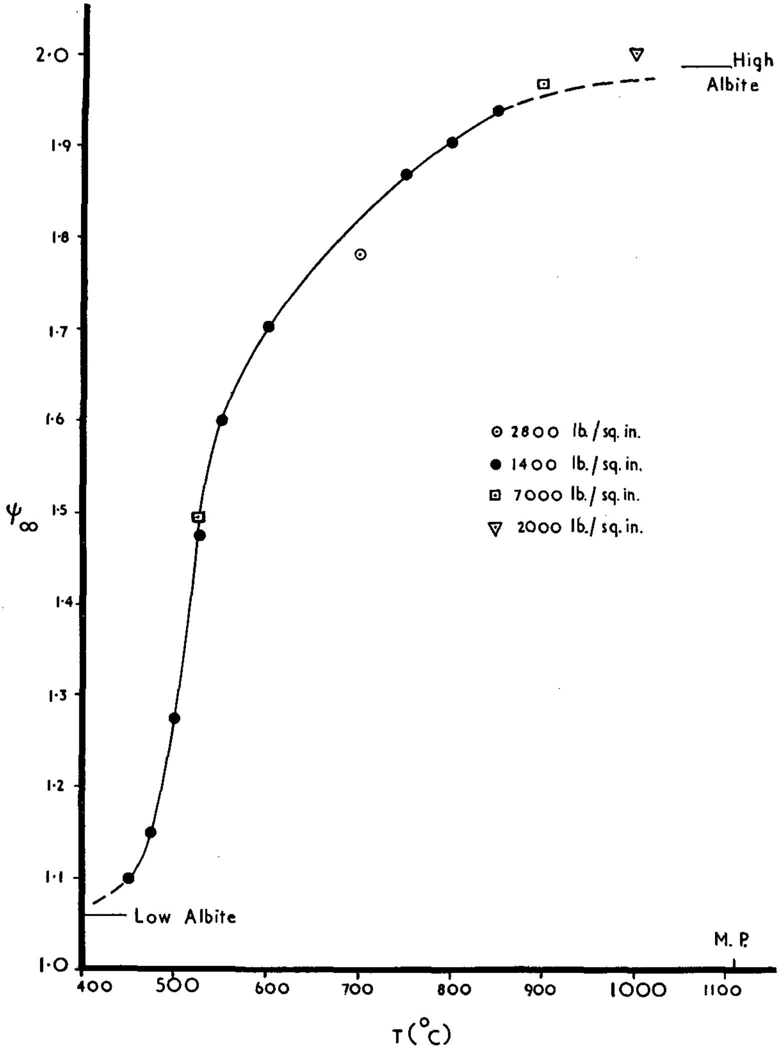

FIG. 3. The temperature-dependence of ψ_∞.

VARIATION OF RATE-CONSTANT WITH TEMPERATURE.

In fig. 4 the rate-constant for the fastest rate observed at each experimental temperature is plotted in the form log k^* against T_∞^{-1}. Between

TABLE III. The fastest rate-constants, k^*, together with the fastest (k^*) and average ($\bar{k}$) constants corrected to $p_{\mathrm{H_2O}} = 14\,000$ lb./in.²

T (°C.)	$10^4 . T^{-1}$ (K^{-1})	$p_{\mathrm{H_2O}}$ (lb./in.²)	log k^*	log $\bar{k}^*$ at 14 000 lb./in.²	log $\bar{k}$ at 14 000 lb./in.²
1 000	7·86	2 000	0·66	1·08	0·75 ± 0·51
900	8·53	7 000	0·78	0·93	0·46 ± 0·32
850	8·90	14 000	0·79	0·79	0·01 ± 0·60
800	9·32	14 000	0·03	0·03	$\bar{1}$·43 ± 0·49
750	9·78	14 000	$\bar{1}$·32	$\bar{1}$·32	$\bar{1}$·09 ± 0·18
700	10·28	28 000	$\bar{2}$·88	$\bar{2}$·73	$\bar{2}$·52 ± 0·17
600	11·46	14 000	$\bar{2}$·67	$\bar{2}$·67	$\bar{2}$·38 ± 0·18
550	12·15	14 000	$\bar{2}$·73	$\bar{2}$·73	$\bar{2}$·27 ± 0·27
525	12·53	14 000	$\bar{2}$·45	$\bar{2}$·45	$\bar{2}$·03 ± 0·45
525	12·53	7 000	$\bar{2}$·28	$\bar{2}$·43	$\bar{2}$·24 ± 0·20
500	12·94	14 000	$\bar{3}$·81	$\bar{3}$·81	$\bar{3}$·51 ± 0·18
475	13·37	14 000	$\bar{3}$·08	$\bar{3}$·08	$\bar{3}$·02 ± 0·05
450	13·83	14 000	$\bar{4}$·89	$\bar{4}$·89	$\bar{4}$·63 ± 0·28

900° C. and 700° C. log k^* decreases linearly with increasing T_∞^{-1}. A good linear relationship likewise holds between 550° C. and 450° C. The two lines differ little in slope, but the low-temperature line has a much larger intercept on the log k^*-axis. No error can be put on the values of log k^* because they represent *limiting* rates. The existence of straight-line relationships is in itself justification for paying special attention to such limiting fastest rates.

A marked break occurs in the plot in the region between 700° C. and 550° C., and must indicate the presence of a thermal transformation of some considerable magnitude in this temperature range. Rate of change of obliquity is greatly increased on passing down through the transformation; points lying on the low-temperature line correspond to rates about 500 times faster than would be indicated by the extension of the high-temperature line below the transformation temperature. Evidence that the transformation is smeared is provided by the situation of the experimental point for 600° C. between the two lines. The temperature limits of the smeared transformation cannot be evaluated from the available data, but may be regarded as lying in the range 575° C. to 625° C.

The mean rate constant $\bar{k}$, also shown on fig. 4, plots systematically below k^*, shows a marked break between 700° C. and 550° C., and is appaerntly subject to rather more pronounced smear.

The experimental point for 1 000° C. is aberrant. Inaccuracy inherent in the smallness of $(\psi_0-\psi)$ and $(\psi-\psi_\infty)$ over the whole time-range at 1 000° C., proximity to the melting-point (1 118° C.), and possible

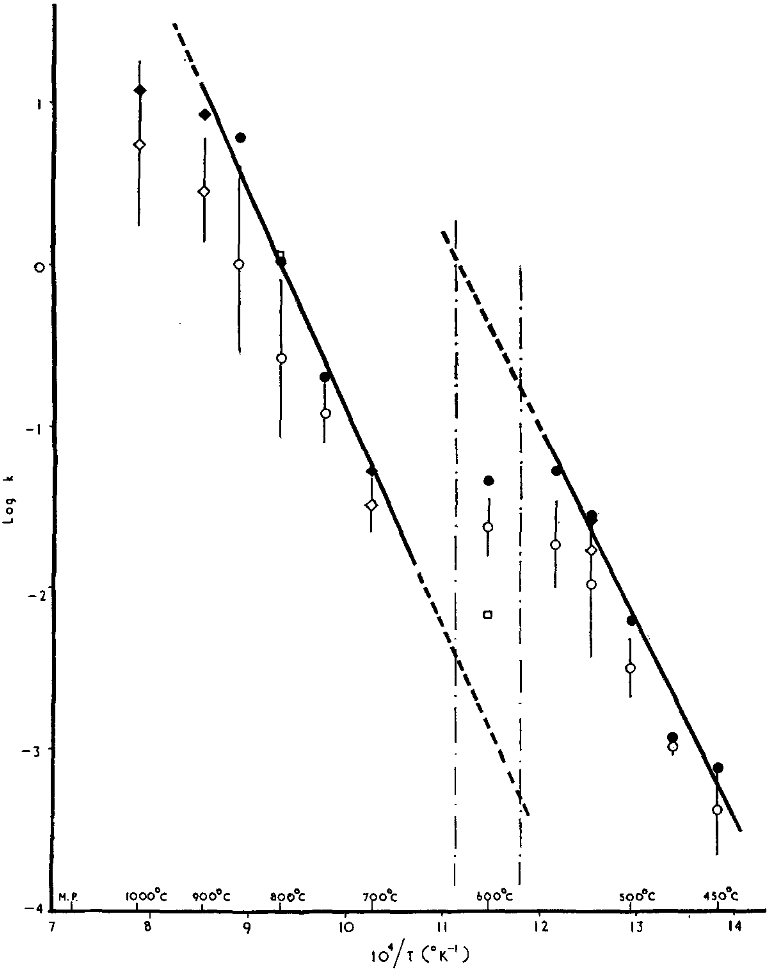

FIG. 4. Plot of log k against T^{-1}. ● refers to maximum rate constants (k^*), and ϕ to average rate constants ($\bar{k}$) at $p_{\mathrm{H_2O}}$ 14 000 lb./in.^{2} in the main series. ◆ refers to maximum rate constants, and ◊ to average rate constants corrected to $p_{\mathrm{H_2O}}$ 14 000 lb./in.^{2} from other pressures. □ refers to the reheating experiments 1 and 2 of table V.

involvement in the analbite → monalbite inversion may explain its departure from the high-temperature line.

Activation energies. The linear sections of the plot of log k^* against T^{-1} can be interpreted in terms of the Arrhenius equation

$$\ln k = B - E/RT \tag{6}$$

in which R is the gas constant, and B and E are independent of temperature to a first approximation. The validity of the application of the Arrhenius equation to the rate of a solid-state reaction followed by measurements of a physical variable lies in the excellence of the fit of the data to the equation in the temperature ranges 900° C. to 700° C. and 550° C. to 450° C. Analogous use of the Arrhenius equation in the study of a solid state transformation has been made by McKie (1959) in the study of the low → high inversion in yoderite.

The activation energy E, which is a measure of the height of the energy barrier involved in the process responsible for the variation of obliquity, can be obtained from the slope of the linear portions of the graph of fig. 4, and is given by (slope) $\times R \log e$. Above the transformation, between 900° C. and 700° C., $E = 61{\cdot}6 \pm 0{\cdot}2$ kcal. mole^{-1}. Below the transformation, between 550° C. and 450° C., $E = 55{\cdot}9 \pm 0{\cdot}2$ kcal. mole^{-1}. The values[1] of E have been calculated from a regression of $\log k$ on T^{-1}, and the limits quoted are standard deviations.

VARIATION OF RATE WITH PRESSURE.

The effect of varying p_{H_2O} may be to alter the limiting obliquity ψ_∞ and to alter the rate constant itself. Although the data are rather scanty some attempt has been made to evaluate both of these effects.

Values of ψ_∞ for runs at two pressures at 525° C. are listed in table II. The value of ψ_∞ for p_{H_2O} 28 000 lb./in.^{2} at 700° C. is also given in table II, and may be compared with the value ψ_∞ 1·825 for 14 000 lb./in.^{2} read from the smooth curve of fig. 3 at the same temperature. These are the only two items of experimental data relating ψ_∞ to p_{H_2O}. A simple, reasonable assumption would seem to be that the fractional change in ψ_∞ is proportional to the fractional change in p_{H_2O}, the coefficient of proportionality being determined by the two experimental points. The value of ψ_∞ at a pressure p is then given by

$$\psi_\infty(p) = \psi_\infty(p_s)\{1 - 0{\cdot}024(p - p_s)/p_s\}, \tag{7}$$

where p_s is 14 000 lb./in.^{2} This relationship leads to values of ψ_∞ at 900° C. and 1 000° C. for p_{H_2O} 14 000 lb./in.^{2} that would lie fairly well on the smooth curve of fig. 3.

The variation of rate constant with p_{H_2O} can be considered in terms of an expression of the form $k = k_p \cdot p^n_{H_2O}$, where k_p is a rate constant inde-

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[1] Though conventionally referred to as kcal. per mole, the units would be more exactly described as kcal. per formula-weight; there can be no true mole of a tectosilicate.

pendent of p_{H_2O}; k_p is also independent of total pressure since in all MacKenzie's experiments total pressure is equal to p_{H_2O}. Significant values of n will be zero, or some simple fraction, or some small integer. The expression is most conveniently considered in the form

$$\log k = \log k_p + n \log p_{H_2O}. \tag{8}$$

Values of $\log k$ are plotted against $\log p_{H_2O}$ for all the relevant data in fig. 5.

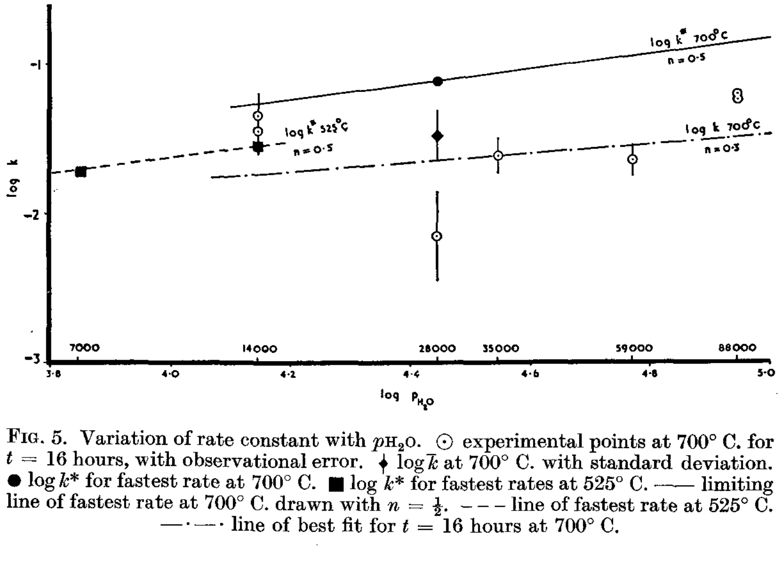

FIG. 5. Variation of rate constant with p_{H_2O}. ⊙ experimental points at 700° C. for $t = 16$ hours, with observational error. ⧫ $\log \bar{k}$ at 700° C. with standard deviation. ● $\log k^*$ for fastest rate at 700° C. ■ $\log k^*$ for fastest rates at 525° C. —— limiting line of fastest rate at 700° C. drawn with $n = \frac{1}{2}$. - - - line of fastest rate at 525° C. —·—· line of best fit for $t = 16$ hours at 700° C.

MacKenzie (1957, p. 488) performed a special series of experiments at 700° C. to investigate the effect of p_{H_2O}. Values of ψ_∞ calculated by use of equation (7), and of $\log k$ calculated by use of equation (3) are listed for each of these experimental points in table IV, and $\log k$ is plotted in fig. 5. The values of $\log k$ are given with observational error. A difficulty in interpreting these results is that very short times were used and consequently the observational error is large. Whatever hypothesis is used to describe the variation the points at 7 000 lb./in.^{2} appear to be aberrant; they are in any case subject to particularly large observational error. The points at 28 000 lb./in.^{2} yield values of $\log k$ lying outside the standard deviation of $\log \bar{k}$ for the same temperature and pressure (table III). The regression line of $\log k$ on $\log p_{H_2O}$ fitted to the experimental points between 14 000 and 88 000 lb./in.^{2} has n=0·3 with

TABLE IV. Variation of k with p_{H_2O}.

700° C., t = 16 hours, $\psi_0 = 1{\cdot}966$

p_{H_2O} (lb./in.^{2})	ψ_∞	$\log k$ (for each experiment)
7 000	1·847	$\bar{2}{\cdot}92 \pm 0{\cdot}20$, $\bar{2}{\cdot}62 \pm 0{\cdot}42$
14 000	1·825	$\bar{2}{\cdot}55 \pm 0{\cdot}16$, $\bar{2}{\cdot}65 \pm 0{\cdot}15$
28 000	1·782	$\bar{3}{\cdot}84 \pm 0{\cdot}30$ (twice)
35 000	1·759	$\bar{2}{\cdot}38 \pm 0{\cdot}12$ (twice)
59 000	1·684	$\bar{2}{\cdot}35 \pm 0{\cdot}10$ (twice)
88 000	1·593	$\bar{2}{\cdot}79 \pm 0{\cdot}02$, $\bar{2}{\cdot}76 \pm 0{\cdot}02$

700° C.—fastest rate

p_{H_2O} 28 000 lb./in.^{2} $\log k^*$ $\bar{2}{\cdot}88$

525° C.—fastest rate

p_{H_2O} 7 000 lb./in.^{2} $\log k^*$ $\bar{2}{\cdot}28$

p_{H_2O} 14 000 lb./in.^{2} $\log k^*$ $\bar{2}{\cdot}45$

a standard deviation $\pm 0{\cdot}3$, and does not distinguish between the simple cases of $n = 0$ and $n = \frac{1}{2}$. In spite of their scatter the points do, however, all lie beneath the line with $n = \frac{1}{2}$ through $\log k^*$ for the fastest rate at 28 000 lb./in.^{2}

More reliable data on the variation of rate constant with p_{H_2O} is provided by the fastest rates for the two series of experiments (given in table III) at 525° C. The comparison of fastest rates is likely to be more accurate than the comparison of $\log k$ for individual experiments; ψ_∞ has, moreover, been obtained by considering each series in terms of equations (4) and (5). The relationship they exhibit (fig. 5) is consistent only with a value of $n = \frac{1}{2}$.

All the evidence is consistent with, and that for 525° C. points directly to, a relationship between rate constant and p_{H_2O} of the form

$$k = k_p \cdot \sqrt{p_{H_2O}}.$$

KINETIC ANALYSIS OF MACKENZIE'S OTHER EXPERIMENTS.

After concluding the description of his main series of experiments, MacKenzie (1957, pp. 500–505) described some other experiments, the kinetics of which may be considered in the light of our treatment of the main series. Only one experiment was performed for each set of physical conditions, and therefore we cannot evaluate $\log k^*$, but must be satisfied with the lower accuracy of a comparison of $\log k$ calculated by means of equation (3) for each experimental point. In these experiments the limiting obliquity ψ_0 ceases to be a fictional obliquity extrapolated to zero time, but is the actual obliquity of the crystalline starting material at the beginning of the experiment. MacKenzie's data and the values of $\log k$ calculated therefrom are summarized in table V.

Subsequent hydrothermal treatment of synthetic transitional triclinic $NaAlSi_3O_8$. Synthetic material from runs at 600° C. and 800° C. was reheated at 800° C. and 600° C., respectively, the same p_{H_2O}, 14 000

TABLE V. Data on heat treatment of synthetic and natural $NaAlSi_3O_8$.

	Initial crystallization			Subsequent heat treatment				
	T (°C.)	p_{H_2O} (lb./in.^{2})	ψ_0	T (°C.)	p_{H_2O} (lb./in.^{2})	t (hours)	ψ	$\log \lvert k \rvert$
1.	600	14 000	1·844	800	14 000	92	1·897	0·07
2.	800	14 000	1·930	600	14 000	162	1·885	$\bar{3}\cdot84$
3.	850	14 000	1·951	1 080	dry	168	1·988	$\bar{2}\cdot81$
4.	850	14 000	1·951	1 080	dry	504	2·008	$\bar{2}\cdot81$
5.	800	14 000	1·921	1 080	dry	168	1·964	$\bar{2}\cdot54$
6.	800	14 000	1·921	1 080	dry	504	1·985	$\bar{2}\cdot41$
7.	750	14 000	1·890	1 080	dry	168	1·963	$\bar{2}\cdot66$
8.	750	14 000	1·890	1 080	dry	504	1·962	$\bar{2}\cdot18$
9.	600	14 000	1·805	1 080	dry	168	1·911	$\bar{2}\cdot37$
10.	600	14 000	1·805	1 080	dry	504	1·925	$\bar{2}\cdot01$
11.	Natural Amelia albite		1·060	800	14 000	90	1·848	$\bar{1}\cdot27$
12.			1·060	800	14 000	311	1·844	$\bar{2}\cdot69$

Experiments 1 and 2 are described on p. 504, 3–10 on p. 501, and 11 and 12 on p. 502 of MacKenzie (1957). The rate-constant is written $\log |k|$ because both k and $\psi_0 - \psi_\infty$ are negative, except in experiment 1, since obliquity is increasing with time instead of decreasing as in the main series of experiments.

lb./in.^{2}, being applied during preparation and subsequent heat treatment. The rate-constants for the subsequent heating are plotted in fig. 4, and it can be seen that they are not markedly divergent from the rate-constants for the main series of experiments at the same temperature and p_{H_2O}. They do not yield any kinetic evidence of the non-isothermal history of the material, and merely correspond to equilibration under the conditions of reheating. It is significant that the rate-constant for increasing obliquity at 800° C. should correspond so closely to that for decreasing obliquity in the main series experiment at the same temperature.

Dry heating of synthetic transitional triclinic $NaAlSi_3O_8$. Synthetic material prepared isothermally at various temperatures in the range 600° C. to 800° C. was heated dry at 1 080° C. at atmospheric pressure. The obliquity increased in each case towards the value expected for ψ_∞ at 1 080° C., which will approach ψ 2·03 of high albite. Rate constants have been calculated for each experimental point, assuming a value of 2·030 for ψ_∞, and are plotted against temperature of preparation in fig. 6. It is observed that in general, the higher the temperature of preparation of the synthetic material, the higher is the rate constant for equilibration under dry conditions at high temperature. The amount of the departure of the synthetic $NaAlSi_3O_8$ from the equilibrium obliquity appropriate to its temperature of preparation appears to have no systematic effect on the rate constant for dry reheating.

The observed rates ($\bar{2}\cdot0 \leqslant \log k \leqslant \bar{2}\cdot8$) are 200 to 2 000 times slower than the rate of equilibration ($\log k \simeq 1{\cdot}2$) inferred from fig. 4 and equation (8) for 1 080° C., p_{H_2O} 14·7 lb./in.^{2} Two factors may be responsible for the slowness observed: firstly, the absence of water; and secondly, the starting material was crystalline and partly equilibrated under hydrothermal conditions, whereas in the main series of experiments the starting material was a glass, which crystallized and equilibrated at the same temperature and p_{H_2O}. The results discussed in the previous section make it clear, however, that it is absence of water that is primarily responsible for the slowness of dry equilibration.

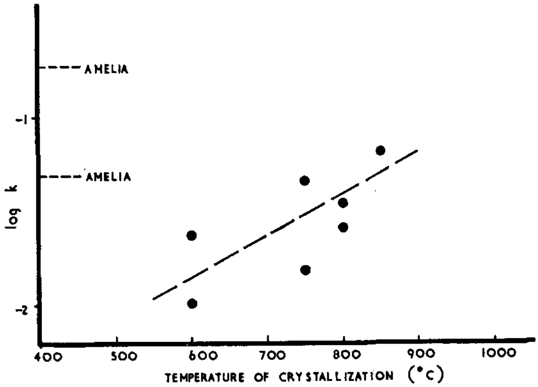

FIG. 6. Graph of rate constant against temperature of crystallization for dry heating at 1 080° C. of synthetic transitional triclinic $NaAlSi_3O_8$. Broken lines represent rate constants for dry heating of Amelia albite.

Hydrothermal treatment of Amelia albite. MacKenzie's two experiments show an increase in obliquity towards the value of ψ_∞ 1·905 corresponding to the experimental conditions, 800° C., p_{H_2O} 14 000 lb./in.^{2} The rate constants are smaller: 0·2 and 0·05 times k^* for the fastest equilibration of synthetic triclinic $NaAlSi_3O_8$ under like conditions. The slowness of hydrothermal equilibration may be due in part to neither experiment happening to display the fastest rate, and in part to the presumably very low equilibration temperature of the natural pegmatitic material.

DISCUSSION.

Comparison of 'wet' and 'dry' equilibration rates. MacKenzie has noted (1957, p. 505) that synthetic transitional $NaAlSi_3O_8$ heated in the dry at 700° C. and 14 000 lb./in.^{2} did not show any measurable change in obliquity after 140 hours' treatment. He has also indicated that no changes can be produced, in laboratory time, in either low-temperature albites or synthetic albites, except near the melting-point, unless water vapour is present.

It is convenient to discuss separately the possible effects of hydrostatic pressure and water-vapour pressure. In general the hydrostatic pressure dependence of solid diffusion processes is likely to be small. Some change in rate in a solid-state reaction may be produced if the stability of the equilibrium phase or phase assemblage is favoured by increased hydrostatic pressure, but in the absence of this effect increase in pressure may in practice decrease the rate of diffusion in much the same way as increase in pressure increases the viscosity of liquids (Glasstone, Laidler, and Eyring, 1941, p. 541). These considerations suggest that the hydrostatic pressure dependence of equilibration rates in the case of triclinic $NaAlSi_3O_8$ is likely to be small.

The observed change in equilibration rates under dry and hydrothermal conditions must necessarily be associated with the direct participation of water or its dissociation products in the mechanism of the transformation process. Such participation necessarily defines a change in the free energy of activation for the transformation process.

The dependence of equilibration rates on water vapour pressure. Analysis of the p_{H_2O}-dependence of the rate of transformation has been given in a previous section. The analysis, particularly in the case of experiments at 525° C., indicates that the rates depend on the square root of the total water-vapour pressure. Such relationship would be consistent with the direct participation of H^+ in the transformation process since the activity of H^+ in the vapour phase bears a corresponding relationship to the total water-vapour pressure.

The hydrogen-ion concentration in the vapour phase can only be relevant in the transformation mechanism if the solid is capable of ion exchange with the vapour phase. The necessary ion-exchange process may be considered a type of hydrolytic equilibrium; the exchange process being comparable with the hydrolysis of $AlSi_3O_8^-$ in the vapour.

Equilibrium between the vapour and the solid may be written:

$$\begin{array}{lll} Na^+\quad OH^- & H^+ & \\ & & AlSi_3O_8^- \\ H_3O^+ & Na^+ & \\ \text{VAPOUR} & \text{SOLID} & \end{array}$$

If the equilibrium constant for the ion-exchange process and the dissociation constant for water are not materially affected by the change in pressure involved, the proton concentration in the solid will be proportional to the square root of the total water vapour pressure.

The activation energy for the process of transformation in triclinic $NaAlSi_3O_8$, as already noted, is of the order of 60 kcal./mole. In the absence of more data on the precise mechanism of the transformation process it would be incorrect to identify this energy with any specific mechanism, but it may be equated, in a general way, with a rate-controlling diffusion mechanism involving Al–Si ordering in the structure. The data of Pauling (1940, p. 53) indicate that the Si–O bond energy is of the order of 90 kcal./mole. The activation energy for the removal of Si from an SiO_4 tetrahedron must be of approximately equal magnitude. Data on the diffusion of sodium in compounds of similar type indicate a much lower activation energy, of the order of 20 kcal./mole.

The rapidity of the ordering process in triclinic $NaAlSi_3O_8$ under hydrothermal conditions must be related to the provision of a suitable mechanism for the ordering process.

Structural aspects of the transformation. Ferguson, Traill, and Taylor (1958) have given detailed accounts of the structures of both high- and low-albite. In high-albite the structural data indicate that Al and Si have an apparently random distribution over available tetrahedral sites and that the sodium atom in the averaged cell appears to occupy an ellipsoidal volume which may represent a time or space average over different positions. The authors suggested the possibility of two distinct sites for the sodium atom. From a study of the tetrahedral bond-lengths in low-albite Ferguson and others suggested that the major part of the Al was present on one of the four symmetrically distinct tetrahedral sites and that the 'average' volume occupied by the sodium atom was much smaller.

The structural data and the present kinetic analysis present independent and compatible evidence on the role of Al–Si ordering in the high–low albite transformation. The role of Al–Si ordering should not, however, be emphasized to the exclusion of other possible aspects of the transformation. Clearly the role of the sodium atom is also of considerable importance.

The kinetic analysis provides important evidence on the degree of continuity of the ordering process in triclinic $NaAlSi_3O_8$ as a function of temperature. Slow change in the obliquity in the temperature ranges above 650° C. may define a change in the degree of Al–Si order in this temperature range. In the region of 600° C. a rapid change in the degree of order of Al and Si is implied. This change possibly comes close to being discontinuous and may, at present, be conveniently described as a smeared transformation. Below 500° C. there appears to be further change in obliquity defining further change in the degree of Al–Si order.

Petrological considerations. The immediate petrological applications of this study are limited, but clearly the occurrence of low-albite in rocks implies either crystallization below the transformation temperature or the inversion of high-albite by slow cooling under hydrothermal conditions through the critical temperature range about 600° C. where the rates of transformation are fast. The structural state of low-albite may be expected to be influenced in detail by differing physical conditions of crystallization and cooling rate; such differences in adjustment towards the low-temperature equilibrium state are implicit in the different dry-heating behaviour of low-albite from various localities, even though detailed structural analyses of materials of varying origin are lacking. The rarity of high-albite in nature ($Ab \geqslant 95$) is to be ascribed perhaps in part to the high rate of transformation to the low-temperature modification around 600° C.

It would be of some interest to follow the transformation at 600° C. away from the albite composition and to examine its participation in peristeritic exsolution, its bearing on the general problem of the intermediate plagioclases, its influence on the alkali–feldspar solvus and in the wider field of the silica–nepheline–kalsilite system.

General conclusions. The existence of a smeared transformation in triclinic $NaAlSi_3O_8$ has been recognized by examination of the temperature variation of rate of transformation, and it would therefore seem appropriate to stress the usefulness of a kinetic approach to certain feldspar problems and to polymorphic transformations in general. The study of the rate of approach to equilibrium provides information on the mechanism of the process that cannot be derived from the mere observation of equilibrium. Moreover, if the mechanism of reaction or inversion is known, extrapolation to experimentally unattainable conditions may be attempted and some explanation offered for natural cases of non-equilibrium. In general the interrelations of feldspar phases in a rock should be considered on a time–temperature basis, rather than on the assumption of complete equilibration down to some minimum temperature below which no change occurred. But in interpreting natural processes in terms of experimental hydrothermal data it must also be borne in mind that variation of catalyst may exert a profound influence on the mechanism by which a reaction or polymorphic inversion takes place. Such considerations may even determine the accessibility of the true equilibrium state.

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