The kinetics of the low→high transformation in albite
I. Amelia albite under dry conditions

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[Taken as read 23 March 1961]

Summary. The transformation was followed in Amelia albite powders by variation in $2\theta_{131}$–$2\theta_{1\bar{3}1}$ with time under isothermal conditions at various temperatures in the range 920°–1080° C. The activation energy of about 74 kcal mole^{-1} is rather larger than that obtained for the ordering process in synthetic $NaAlSi_3O_8$ under hydrothermal conditions.

FOLLOWING our study of the kinetics of the ordering process in synthetic triclinic $NaAlSi_3O_8$ (McConnell and McKie, 1960)[1] based on the experimental work of MacKenzie (1957), we began a series of kinetic investigations of disordering in heated natural albite, the first results of which are presented here. The disordering process in natural albite has not hitherto been the subject of detailed kinetic examination by X-ray powder techniques, but Tuttle and Bowen (1950) observed large differences in the rate of disordering of albite from different localities at 1050° C dry and MacKenzie (1957) recorded a few observations on the rate of variation of $2\theta_{131}$–$2\theta_{1\bar{3}1}$ in Amelia albite at 800° C, p_{H_2O} 14 000 lb/in.^{2} Schneider (1957) has made an interesting kinetic study, to which there will be further reference, of the disordering process in albite from Schmirntal, Tirol, by single crystal precession photography.

The material used in our experiments was coarsely crystallized albite from Amelia County, Virginia (specimen number 19626 in the Mineralogical Museum, University of Cambridge). After crushing to −150, +200 mesh and cleaning on the isodynamic separator, it was found[2] to contain 11·62 % Na_2O, 0·12 % K_2O, corresponding to $Ab_{98\cdot3}\,Or_{0\cdot7}$; calcium was not determined.

The specimen was heated in a small platinum container in a furnace with an element of Kanthal A.1 wire in a coiled coil, wound on a wide

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[1] This opportunity may be taken to correct two misprints in McConnell and McKie (1960): p. 446, l. 12; *for* log e *read* ln 10; p. 450, caption to fig. 6, l. 3: *for* dry *read* hydrothermal.

[2] Analyst: J. H. Scoon.

bore alumina tube. Within the latter was a small-bore tube in which the specimen and the recording thermocouple were placed, the annular space between the tubes being packed with alumina powder as shown in fig. 1. The controlling thermocouple element was placed close to the furnace-winding and operated in conjunction with an Ether Transitrol Controller. Independent checks on the temperature stability of the furnace indicated that it was possible to maintain the furnace at a temperature constant to within $\pm 1{\cdot}5°$ C over periods of the order of one month. The platinum–platinum-13 %-rhodium recording thermocouple was checked against the gold point at frequent intervals.

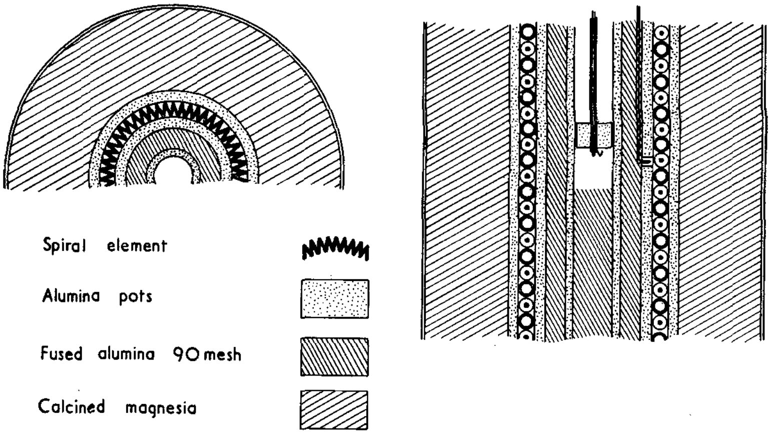

Fig. 1. Details of furnace construction.

At various known times the container was removed from the furnace, a portion adequate for a diffractometer mount removed, and the specimen returned to the furnace. Quenching to room temperature thus took place in air over a period of approximately one minute. After grinding finely and sedimenting on to a glass coverslip, each portion was taken four times over the range 2θ 32°–29° on a diffractometer using Cu-$K\alpha$ radiation and recording at three inches per degree of θ. The separation of the 131 and $1\bar{3}1$ peaks was measured at half-peak height with a vernier scale reading to 0·005 in.

The measurement of $2\theta_{131}-2\theta_{1\bar{3}1}$ limits the accuracy of the experiments. During the change the 131 peak maintains its shape, but the $1\bar{3}1$ peak, initially sharp and accurately measurable, becomes broad and of lower intensity as the change proceeds, sharpening again to some extent with close approach to the completely disordered state of high albite. The standard deviation of the mean of the four measurements of $2\theta_{131}$–$2\theta_{1\bar{3}1}$ for each experimental point varies from 0·01° to 0·08°.

The disordering process in Amelia albite has been followed in these experiments by measurement of the parameter $\psi = 2\theta_{131}$–$2\theta_{1\bar{3}1}$, the same variable that was used to follow the ordering process in synthetic $NaAlSi_3O_8$ under hydrothermal conditions (MacKenzie, 1957; McConnell and McKie, 1960). The significance of ψ is discussed in the latter reference. The ordering process obeys, at least approximately, over its whole course a rate law of the form $-d\psi/dt = k(\psi - \psi_{\infty})^2$, where t is time in hours, ψ_{∞} is the limiting value of ψ as $t \to \infty$, and k is the rate constant. The disordering process, however, does not obey the analogous rate law $d\psi/dt = k'(\psi - \psi_{\infty})^2$, nor can it apparently be represented completely by any other simple rate equation. In the earlier stages of the process, however, ψ exhibits a linear variation with time corresponding to an initial rate law of the form $d\psi/dt = k$. In its later stages the process becomes slower than the initial rate law predicts and ψ appears to approach ψ_{∞} asymptotically. Because of the great length of the runs that would be necessary, the later stages have not been examined in sufficient detail to determine whether the limit ψ_{∞} is independent of temperature, but it may be noted that Schneider's (1957) single crystal work on Schmirntal albite indicated that ψ_{∞} was sensibly constant between 1050° C and 950° C.

The experimental data for Amelia albite are listed in table I and plotted for the earlier stages on fig. 2, where the standard deviation of the mean of the four measured values of ψ for each plotted point is shown. Data are given for isothermal runs at the temperatures 1080° C, 1038° C, 1000° C, 960° C, and 920° C. Repetition of the early parts of the runs at 1080° C and 1038° C has shown that the data are reproducible within the limits of accuracy of measurement of ψ.

The value of the rate constant in the initial rate law, $\psi - \psi_0 = kt$ in its integrated form, has been calculated from a regression of $\psi - \psi_0$ on t passing through the origin for each isothermal run. The results are given in table II, where each value of k is quoted with its standard error. The limit of applicability of the initial rate law was assessed by extending the regression to points of successively higher ψ until a marked increase in standard error was observed; the limit clearly decreases with decreasing temperature, but the manner of the temperature dependence of the limit is not clear.

The variation of rate with temperature can be interpreted in terms of the Arrhenius equation $\ln k = B - E/RT$, in which R is the gas constant, and B and E are independent of temperature to a first approximation. The data, plotted on fig. 3, show an excellent linear relationship between $\log k$ and T^{-1}. The standard error of $\log k$ lies in every case within the plotted circle of radius ±0·02. The activation energy E, which is a measure of the energy barrier involved in the disordering process, can be obtained from the data displayed on fig. 3 and is given by (slope) × R ln 10. A regression of $\log k$ on T^{-1} yields the value $E = 74{\cdot}3 \pm 1{\cdot}4$ kcal mole^{-1} for the activation energy and the value $B = 22{\cdot}95$ for the so-called probability factor over the range 1080° C to 920° C.

TABLE I. Values of $\psi = 2\theta_{131} - 2\theta_{1\bar{3}1}$ for Amelia albite heated isothermally for different lengths of time. Initial obliquity $\psi_0 = 1{\cdot}056 \pm 0{\cdot}010$. Final obliquity $\psi_\infty = 2{\cdot}000$

Run no.	Time (hours)	ψ	Run no.	Time (hours)	ψ
1080° C			1000° C		
0·1	2·0	1·105±0·033[1]	9·1	25·0	1·117±0·013
0·2	4·0	1·140±0·015	9·2	50·5	1·157±0·020
0·3	6·0	1·144±0·018	9·3	96·0	1·211±0·021
0·4	11·8	1·197±0·016	9·4	210·0	1·342±0·016
1·1	23·8	1·292±0·011	9·5	384·0	1·647±0·043
0·5	24·3	1·291±0·019	9·6	768·0	1·861±0·009
1·2	47·7	1·500±0·052			
1·3	92·9	1·840±0·024	960° C		
1·4	193·4	1·961±0·011	7·1	48·0	1·094±0·019
1·5	384·5	1·995±0·006	7·2	147·6	1·143±0·031
1·6	575·7	1·984±0·033	7·3	389·6	1·310±0·065
			7·4	1101·5	1·720±0·061
1038° C			920° C		
5·1	24·0	1·146±0·043	8·1	48·1	1·063±0·008
2·1	25·5	1·177±0·015	8·2	97·8	1·082±0·027
2·2	48·0	1·221±0·020	8·3	194·3	1·112±0·018
2·3	72·0	1·301±0·013	8·4	409·8	1·135±0·078
2·4	120·3	1·508±0·065	8·5	619·3	1·207±0·028
2·5	170·4	1·704±0·069	8·6	1219·5	1·567±0·034
2·6	240·1	1·824±0·064			
2·7	384·8	1·908±0·025			
2·8	600[2]	1·937±0·027			

[1] Standard deviation of the mean of four readings.

[2] Accurate only to ±50 hours.

It is necessary at this stage to consider the nature of the process responsible for the variation of ψ with time at elevated temperatures. Ferguson, Traill, and Taylor (1958) showed that low- and high-albite differed structurally essentially in the ordering of Al and Si atoms on tetrahedral sites and in the environment of the Na atom. Increase in ψ from ψ_0 to ψ_∞ can thus be regarded as a measure of the disordering of

Al, Si from the almost completely ordered state of low-albite to completely disordered high-albite; the environment of the sodium atom is closely related to, and probably determined by, the state of ordering on tetrahedral sites. The activation energies observed are, as might be expected, rather lower than the Si–O bond energy of 88·2 kcal mole^{-1} (Pauling, 1960, p. 85), since in passing from one tetrahedral site to another during the disordering process Si and Al atoms are never entirely freed from bonding to neighbouring oxygen atoms.

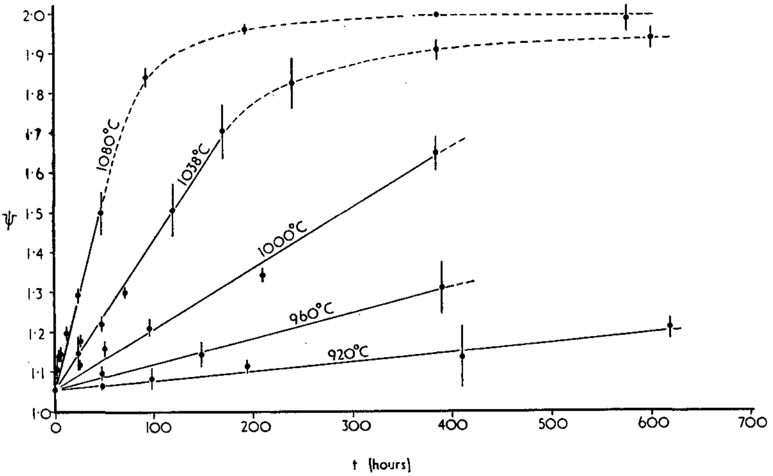

FIG. 2. Plot of ψ against t for isothermal dry heating of Amelia albite from the data of table I. The rate curves are drawn solid in the region where the initial rate law applies.

TABLE II. Variation of initial rate constant k with temperature in Amelia albite heated dry

T (° C)	k (degrees hours^{-1})	Limit of initial rate law: highest included	Limit of initial rate law: lowest excluded
1080	0·0097 ±0·0003	1·500	1·840
1038	0·00375 ±0·00005	1·704	1·824
1000	0·00151 ±0·00002	1·647	1·861
960	0·000646 ±0·000012	1·310	1·720
920	0·000232 ±0·000009	1·207	1·567

It is appropriate now to consider some comparable data. Schneider's (1957) detailed single crystal study of the kinetics of the disordering process in Schmirntal albite produced an account of the variation of γ^*

with time at 950, 1000, and 1050° C. The parameter ψ is related to the reciprocal lattice parameters by the equation

$$\psi = 4 \sin^{-1}\{\Phi\ (c^*\cos\alpha^* + a^* \cos\gamma^*)\},$$

where $\Phi = 3\lambda b^*/(d^*_{131}+d^*_{1\bar{3}1}).\cos\tfrac{1}{2}(\theta_{131}+\theta_{1\bar{3}1})$. The quantities Φ, $c^*\cos\alpha^*$, and a^* vary by 0·45 %, 7·0 %, and 0·27 % between low- and high-albite, while $\cos\gamma^*$ varies through zero by a factor of more than 9; $c^*\cos\alpha^* + a^*\cos\gamma^*$ varies by a factor of 1·7. Values of γ^* can thus be converted to ψ using linear interpolations for Φ, $c^*\cos\alpha^*$ and a^* without introduction of serious error. Using the values of ψ obtained in this manner the rate constant k for the initial rate law can be calculated from a regression of $\psi - \psi_0$ on t passing through the origin. The initial rate law extends to higher values of ψ for Schmirntal than for Amelia albite; the decrease in rate as ψ_∞ is approached is correspondingly more sudden for Schmirntal albite. The calculated rate constants, 0·0049±0·0001 at 1050° C, 0·00086±0·00002 at 1000° C, and 0·000247±0·000009 at 950° C, are plotted in logarithmic form against T^{-1} on fig. 3. Analysis of the temperature dependence of rate constant in terms of the Arrhenius equation by a regression of log k on T^{-1} leads to the evaluation of the constants : activation energy $E = 96\pm11$ kcal mole^{-1} and $B = 31{\cdot}13$. The relatively large standard error of the activation energy would appear to be attributable not to the method of derivation of ψ from the measured reciprocal lattice parameters, but rather to the lower accuracy of single crystal data compared with powder data; Schneider's experimental points do not lie on less smooth curves when expressed in terms of ψ than when γ^* is plotted.

The difference in activation energy in the Schmirntal and Amelia cases is so great that it is likely to be real, and not merely introduced by differences in the method of following the change in the two cases. It can, moreover, scarcely be related to difference in bulk composition; the Amelia specimen is $Ab_{98\cdot3}$ and Schmirntal is $Ab_{99\cdot9}$. A more likely hypothesis is that the differing kinetics are due to detailed differences in the nature of the ordered state. Ferguson, Traill, and Taylor (1958) suggested that the sodium atom was distributed over two distinct adjacent sites in low-albite. It would seem likely that a domain structure, as yet unobserved, exists in low-albite such that there is a particular distribution of sodium atoms between the two sites in each domain. The nature of the domain structure and the kinetically critical matter of the stability of domain boundaries have probably been determined by the nature and concentration of impurities introduced during crystallization and by the subsequent thermal history of the specimen. Although no quantitative interpretation of the difference in activation energy for the disordering process in Amelia and Schmirntal albites can be offered at present, it would seem that a qualitative explanation on these lines is very probable. Further kinetic studies of the disordering phenomena in albites from other localities may cast some light on this problem.

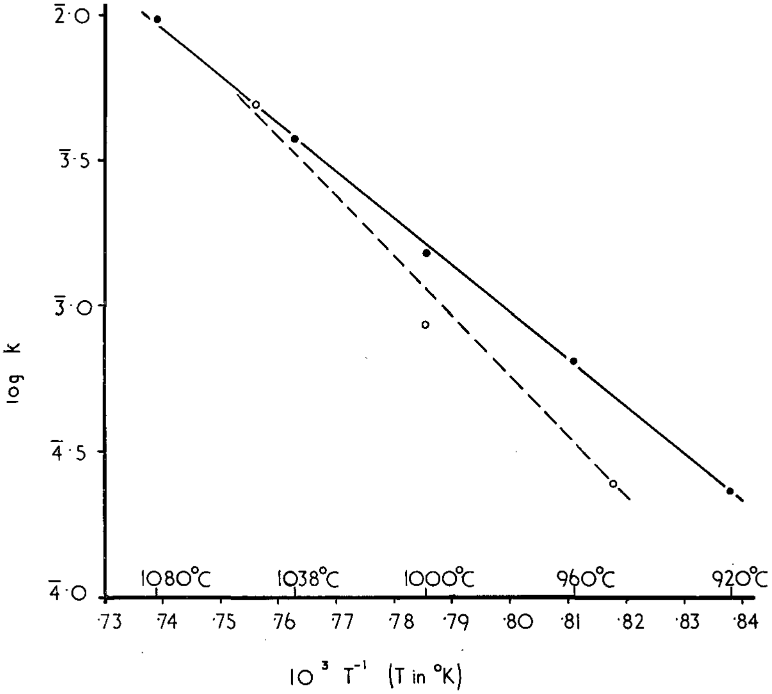

FIG. 3. Plot of logarithmic rate constant against reciprocal absolute temperature. Solid circles: Amelia albite, derived from the data of table I. Open circles: Schmirntal albite, from the single crystal data of Schneider (1957) for which rate constants are given in table II. The Arrhenius equation is represented by a solid line for Amelia and by a broken line for Schmirntal.

In a previous paper we showed that MacKenzie's (1957) hydrothermal experiments on synthetic $NaAlSi_3O_8$ led to activation energies of 61·6 ± 0·2 kcal $mole^{-1}$ between 900 and 700° C and 55·9 ± 0·2 kcal $mole^{-1}$ between 550 and 450° C for the ordering process. No direct comparison can be made with the present results for the disordering process in Amelia albite under dry conditions. On the one hand, a higher activation energy is expected for any process under dry conditions than under hydrothermal conditions. Similar activation energies would be expected for ordering and disordering processes provided they have, as they may well have, analogous mechanisms; the activation energy is then the height of the same energy barrier between equilibrium states of similar energy in a reversible process approached from opposite directions. The main difference in the kinetics of ordering and disordering processes is likely to be in the value of the constant B of the Arrhenius equation. B is a measure of the probability of the transition state transforming in a favourable manner for the progress of the change; B should thus be smaller for an ordering process. B cannot however be compared where one set of experiments is in the dry and the other under hydrothermal conditions.

An investigation of the disordering process in Amelia albite under hydrothermal conditions is in progress and both dry and hydrothermal kinetic studies of albite from other localities are in hand.

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