

## On the Mechanism of the Continuous Transformation in Sodium Nitrate

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A model of the gradual transition in sodium nitrate at constant pressure is discussed on the basis of a consideration of intermolecular separations in the unit cell. A statistically possible O—O separation, which probably becomes accessible in the transition region, seems to have an important bearing on the mechanism of the transformation.

On heating at atmospheric pressure sodium nitrate changes gradually<sup>1-4</sup> from an ordered calcite-type, low-temperature structure<sup>5,6</sup> into a disordered high-temperature phase,<sup>7</sup> NaNO<sub>3</sub>-I. In the former case the oxygen atoms are situated in  $(x,x,0)$  etc. in space group  $R\bar{3}c$ , whereas the nitrate groups in the latter case are (mainly) distributed between two-fold disordered calcite- and aragonite-type positions (oxygen in  $(2x,x,z)$  etc. in space group  $R\bar{3}m$ , where  $c(R\bar{3}m) = c/2(R\bar{3}c)$ ). The arrangement of sodium ions is the same in both cases. Other types of orientation of the nitrate ions might possibly also be occupied in NaNO<sub>3</sub>-I, as suggested for other metal nitrates.<sup>8,9</sup> However, the relatively satisfactory agreement between observed and calculated data for NaNO<sub>3</sub>-I obtained without using these additional types of orientation indicates the fraction of molecules in the latter kind of orientation to be small in any case.

The transition is revealed on the  $C_p$  versus  $T$ -diagram as an "anomalous" part of the heat capacity, starting at temperatures below 200°C.<sup>1,3,4</sup> The heat capacity raises to a maximum at about  $t_c = 276^\circ\text{C}$  ("λ-point", "transition point"), from which it decreases rapidly to a normal value of further heating.

Since the transformation is continuous, a structural property of the low-temperature form should, in principle, be retained throughout the transition. Furthermore, properties specific of the high-temperature form only, should likewise become gradually accessible in the transformation region. Hence, the transition is most likely mainly of the positional (orientational) type, the "thermal" entropy being insignificant in this connection, in view of the previous discussion.

The increase in energy associated with increased disorder must be compensated for through the corresponding entropy increase, to which the contribu-

tion from the orientational disorder of the nitrate groups is probably most important. Table 1 shows values of the shortest, statistical intermolecular distances at various temperatures, calculated on the basis of the two types of orientation referred to above. The uncertainty in the data involving oxygen in calcite-type positions is due to a relatively small uncertainty in the corresponding unit cell dimensions and the NO bond length and may amount to a few thousands of an Ångström. The uncertainty in distances involving oxygen in aragonite-type positions, however, is considerably higher because of the uncertainty in the corresponding  $z$ -parameter of the oxygen atom, the position of which is determined with a relatively low precision at 290°C<sup>7</sup> and is unknown or purely hypothetical at lower temperatures. Reported Na – O contact distances for salts, involving polyatomic anions and six-coordinated sodium ions, show a considerable individual variation. The shortest separations in the salts are, however, frequently close to 2.40 Å, which is equal to the observed Na – O (calcite) separation (six-coordination) at room temperature and is close to the Na – O (aragonite) distance (three-coordination) observed at 290°C<sup>7</sup> in the present case. The Na – O (calcite) separation at 290 °C is 2.45 Å.<sup>7</sup> Considering these results together, a variation of the Na – O (aragonite) separation between 2.42 Å at 290°C and 2.38 Å at room temperature with an uncertainty of 0.03 Å seemed to be reasonably likely. The relative variation of this separation with temperature was taken equal to that observed for the Na – O (calcite) sep-

*Table 1.* Statistical intermolecular distances in sodium nitrate at various temperatures according to space group  $R\bar{3}m$ . True space group is  $R\bar{3}c$  at temperatures below  $t_c$ ;  $c(R\bar{3}c) = 2c(R\bar{3}m)$ . Intermolecular O – O distances between calcite-type positions are probably accurate to within a few thousands of an Ångström. Estimated deviations in distances, due to the uncertainty in the  $z$ -parameter of oxygen in the aragonite-type position, in parentheses. See text.  $d(\text{NO}) = 1.25$  Å (ass.). Unit cell data from Ref. 2. Distances in Ångström.

Temperature (°C)	23	100	150	200	225	250	275	290
$\text{O}_C(x, x, 0) - \text{Na}(2/3, 1/3, -1/6)$	2.400	2.409	2.416	2.423	2.429	2.435	2.446	2.450
$\text{O}_A(2x, x, z) - \text{Na}(2/3, 1/3, -1/6)$	2.380 (0.030)	2.386 (0.030)	2.393 (0.030)	2.398 (0.030)	2.403 (0.030)	2.409 (0.030)	2.418 (0.030)	2.420 (0.030)
$\text{O}_A(2x, x, z) - \text{O}_A(2/3 - 2x, 1/3 - x, 1/3 - z)$	2.271 (0.062)	2.309 (0.062)	2.331 (0.062)	2.360 (0.061)	2.378 (0.061)	2.406 (0.060)	2.449 (0.059)	2.462 (0.059)
$\text{O}_A(2x, x, z) - \text{O}_A(1 - x, x, z)$	2.906 (0.000)	2.910 (0.000)	2.913 (0.000)	2.916 (0.000)	2.918 (0.000)	2.919 (0.000)	2.920 (0.000)	2.922 (0.000)
$\text{O}_A(2x, x, z) - \text{O}_C(1 - x, 0, 0)$	2.823 (0.004)	2.827 (0.004)	2.830 (0.004)	2.832 (0.004)	2.833 (0.004)	2.834 (0.004)	2.835 (0.004)	2.837 (0.004)
$\text{O}_C(x, x, 0) - \text{O}_A(2/3 - 2x, 1/3 - x, 1/3 - z)$	2.660 (0.040)	2.692 (0.040)	2.711 (0.040)	2.735 (0.040)	2.751 (0.040)	2.775 (0.040)	2.811 (0.040)	2.822 (0.040)
$\text{O}_C(x, x, 0) - \text{O}_C(1 - x, 1 - x, 0)$	2.571	2.575	2.578	2.581	2.583	2.584	2.585	2.587
$\text{O}_C(x, x, 0) - \text{O}_C(2/3 - x, 1/3, 1/3)$	2.905	2.931	2.948	2.969	2.984	3.005	3.037	3.046

aration. The values of interatomic distances involving oxygen in aragonite-type orientations were determined on this basis. However, the choice of basis is not critical for the general conclusion drawn in the following discussion.

Three of the listed O—O separations in Table 1 are significantly below 2.8 Å, twice the reported van der Waals radius of oxygen, at the lower temperatures. The assumption that these are inaccessible at equilibrium, corresponds to arranging the lattice in either the ordered calcite-type structure, or the ordered aragonite-type structure, or as a mixture of almost ordered domains (layers) of these structures. This statement is based on the following observation: If a nitrate group is placed in an aragonite-type orientation, the three nearest neighbour anions, towards which the NO bonds of the former are pointing in the projection along the hexagonal *c*-axis, must occupy the same type of aragonite orientation. Further inspection shows then that a pyramidal arrangement of nitrate groups in ordered aragonite-type positions will arise, having the axis along the hexagonal *c*-axis. A nitrate group outside this pyramid may occupy either an aragonite- or a calcite-type position. One of the two possible aragonite-type orientations, identical with the previous one, would give rise to a pyramidal arrangement of nitrate ions similar to that described above, the other to a pyramid of ordered nitrate groups, the axis of which pointing in the opposite direction of the former. On the other hand, if a nitrate ion is placed in a calcite-type position, the three next neighbour nitrate groups, towards which the NO bonds of the former are pointing, may either be in the same kind of calcite-type orientation or in either of the two aragonite-type orientations. It follows that the nitrate groups in a pure calcite-type structure must occupy ordered positions in planes perpendicular to the hexagonal *c*-axis.

A structural model constructed on this basis corresponds to a very limited disorder on a thermodynamic scale and is in this respect in accordance with the observed ordered room temperature structure. Positional disorder of the sodium ions, additional orientational disorder of the nitrate groups as referred to previously or disorder originating in more conventional types of lattice defects are apparently also rather limited, since these sources were not found to contribute appreciably to the gross structure of the high-temperature phase.<sup>7</sup>

In looking for a cause of the gradual transition in sodium nitrate, these sources may therefore be disregarded as a first approximation and are consequently ignored in the following discussion unless further noted. It appears from Table 1 that two of the three O—O separations in question are well below the limit of 2.8 Å at all experimental temperatures and are therefore hardly accessible at any temperature. The third distance, between oxygen atoms in the two different types of position, respectively, shows a considerable temperature dependence and approaches gradually the limit of van der Waals contact at temperatures not far from that of the onset of the transition as revealed by the *C<sub>p</sub>*-measurements. Correspondingly, the probability of occurrence of the O—O separation and hence the disorder of the system should increase with temperature from practically zero at lower temperatures to significant values in the transition region as indicated from both sources of information. However, accurate assignment of the point of transitional onset from consideration of intermolecular distances relative to an assumed inter-

molecular contact separation is uncertain for various reasons. Firstly, a considerable uncertainty is inherent in the basic data, including the assumed limits of the intermolecular contact separation, normally given as an *average* value to within two figures. Secondly, there is a certain arbitrariness associated with interpreting observed, statistical intermolecular separations as actual separations at equilibrium because of effects of statistical overlap of atomic positions. This means for instance that the *actual* O–O separations of the type in question may be a little longer than the corresponding statistical values listed in Table 1. However, the following representation of the state of disorder is in agreement with the previous observations.

As the temperature increases from low temperatures, some of the nitrate groups turn from ordered calcite-type positions (Fig. 1, a) into either of the aragonite-type orientations (Fig. 1, b), the fraction of such molecules increasing

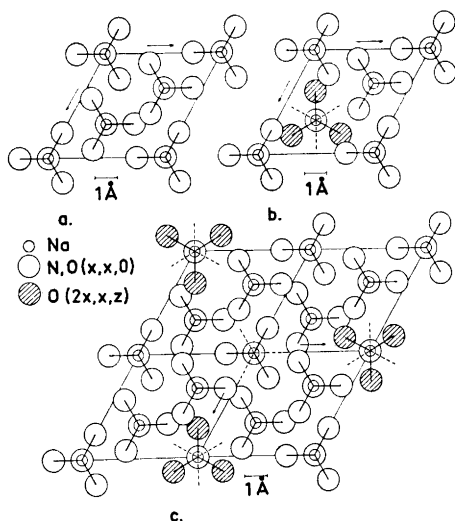


Fig. 1. a. The ordered calcite-type structure of sodium nitrate at low temperatures as viewed along the hexagonal  $c$ -axis. The sodium ions are situated equally distant from two and two nitrate groups separated a distance  $c$  along the hexagonal axis. b. The structure incorporating an element of aragonite-type disorder occurring at somewhat higher temperatures. c. A possible configuration of nitrate groups making both calcite-type orientations simultaneously accessible to the central nitrate group.

steadily with temperature. The accessibility of the alternative calcite-type orientations, however, requires certain configurations of nitrate groups in aragonite-type positions, to occur in a plane perpendicular to the hexagonal  $c$ -axis (disregarding the possibility of arranging the molecules in the two types of calcite-positions separately in ordered domains, since this gives rise to a very small disorder as noted above). The simplest arrangement of this kind consists of three nitrate ions in aragonite-type orientations arranged trigonally about a central nitrate group (next neighbours) at a distance equal to the hexagonal  $a$ -axis apart. The central nitrate group may then occupy either of the two calcite-type orientations according to the present restriction (Fig. 1, c) (apart from the aragonite-type orientations). The conditional probability implies that there be more nitrate groups in the two aragonite-type positions together than in the single, *alternative* calcite-type orientation alone. The complexity of the disorder increases with temperature as the fraction of molecules

in the latter type of position becomes more significant. The fractions of molecules in the two calcite-type orientations should finally become equal ("complete disorder"). This corresponds to complete extinction of reflections for which  $l=2n+1$  (hexagonal indexing in  $R\bar{5}c$ ), which is reported for  $\text{NaNO}_3\text{-I}$  at  $290^\circ\text{C}$ . The possibility for a nitrate group to reorient between calcite-type positions is expected to increase with temperature since the fraction of nitrate groups in aragonite-type orientations increases, while the possibility of reorientation between aragonite-type orientations should decrease.

The energy needed in changing the orientation of a nitrate group from the ordered calcite-type orientation to an aragonite-type position is expected to decrease with temperature in the transition region. This is in agreement with the corresponding increase in unit cell dimensions<sup>2</sup> and consequently in the O—O separations *etc.*, reducing the strong repulsion *etc.*, between closely spaced oxygen atoms. Furthermore, it follows from the previous discussion that the energy needed in the same orientational change is on the average less in an already disordered matrix than in the completely ordered one, and should therefore decrease with temperature. Correspondingly, the rate of change in disorder should increase with temperature till a maximum is reached at or near  $t_c$ , which would be the temperature of complete disorder if effects of thermal energy and entropy actually were zero. Since such effects are most likely small at elevated temperatures, the actual temperature of complete disorder should be rather close to  $t_c$ .

A more quantitative treatment of the model could be of interest, using the condition of thermodynamic equilibrium. However, evaluation of the general expression relating the orientational entropy to the fraction of molecules in the various sets of equilibrium position is difficult, and the choice of proper values for the fixed parameters in the energy terms considerably arbitrary. Comparison with results of analyses of X-ray diffraction and thermal data obtained at various temperatures in the transformation region would be of importance. The present treatment is, however, restricted to a prediction of the relative amount of calcite-type character of the structure in a state of complete disorder as defined above and assumed for  $\text{NaNO}_3\text{-I}$  at  $290^\circ\text{C}$ .

The condition of thermodynamic equilibrium in the system at a given temperature may be written as follows

$$\frac{\partial G}{\partial x_1} = \frac{\partial H}{\partial x_1} - T \frac{\partial S}{\partial x_1} = 0$$

where  $G$ ,  $H$ , and  $S$  are Gibbs energy, the enthalpy, and the entropy of the system, respectively.  $x_1$  is the fraction of nitrate groups in the aragonite-type orientation.

It appears from the previous discussion that

$$\frac{\partial H}{\partial x_1} \geq 0, \text{ so that } \frac{\partial S}{\partial x_1} = \frac{1}{T} \frac{\partial H}{\partial x_1} \geq 0$$

The equality sign refers to the limit where the enthalpy difference between the two kinds of position approaches zero, *i.e.* in practice at elevated tempera-

tures. The inequality corresponds to regions to the left of the maximum in the  $S$  versus  $x_1$ -diagram.

Using the approximation  $S = S_t + S_c$ , where  $S_c$  = thermal entropy and  $S_t$  = configurational (orientational) entropy, one obtains on differentiation and substitution into the previous equation

$$\frac{\partial S_t}{\partial x_1} + \frac{\partial S_c}{\partial x_1} = \frac{1}{T} \frac{\partial H}{\partial x_1} \geq 0$$

$\partial S_t / \partial x_1$  is relatively small and approaches zero at higher temperatures.  $S_c$  may be written in terms of previously defined quantities as follows

$$S_c = R \sum_{i=1}^2 x_i \ln \frac{g_i}{x_i} + k \ln (1 - P)$$

where  $P$  is given by eqn. 2, Ref. 7.  $k$  is Boltzmann's constant.

Combining the latter two relationships leads to the following approximation, putting  $\partial S_t / \partial x_1 = 0$

$$\frac{\partial S_c}{\partial x_1} = R \ln \frac{g_1 x_2}{g_2 x_1} - \frac{1}{1 - P} \frac{\partial P}{\partial x_1} = \frac{1}{T} \frac{\partial H}{\partial x_1} \geq 0$$

In the present case  $g_1 = g_2 (= 2)$ , so that  $\ln \frac{g_1 x_2}{g_2 x_1} = 0$ , when  $x_1 = x_2 (= 0.5)$ .

Inspection of eqn. 2 (Fig. 3), Ref. 7, in connection with the forbidden O - O separations in Table 1, indicates that the  $P$ -function is nearly symmetrical with respect to interchanging indices representing the two types of nitrate orientation. This gives the approximation

$$\partial P / \partial x_1 = 0 \text{ for } x_1 = x_2 (= 0.5)$$

so that in the present case

$$x_1 \leq 0.5$$

with  $x_1 = 0.5$  as the limiting value, which is consistent with a previous estimate of  $x_1$  equal to 0.55, obtained in an analysis of X-ray diffraction data referred to 290°C.<sup>7</sup> This suggests that the enthalpy difference between the two types of orientation is small at the experimental temperature.

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