[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

GRADUAL TRANSITION IN SODIUM NITRATE. I. PHYSICO-CHEMICAL CRITERIA OF THE TRANSITION

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Until a few years ago the only transitions recognized in pure crystalline solids were of the polymorphic kind, that is, inversions from one crystalline modification of a substance to another. Inversions of this type are characterized by a more or less great change in the crystal lattice, and each modification has well-defined physical properties which alter by discontinuous steps, theoretically at a point at which two neighboring modifications can be considered to be in equilibrium. From the standpoint of thermodynamics these inversions are analogous to melting in the sense that we can express all the quantities involved by means of a Clapeyron equation and, particularly, there is an equilibrium value of the (latent) heat of transition and of the (latent) volume change at the inversion point which is a function of the temperature and pressure. The salient characteristic of the polymorphic inversions is the phenomenon of hysteresis; the transformations are prompt in some cases, but often they are so sluggish that geologic times have failed to effect the conversion from the unstable to the stable modification in certain minerals. A consequence of this retardation in the inversion is that there is a (hysteresis) band of temperature and pressure values within which two modifications can coexist with little or no tendency to transform.

Some substances exhibit apparent transitions which are abnormal when contrasted with the true polymorphic changes. The specific heat curves, for example, increase gradually over a long interval below the transition point; instead of a discontinuous change at this point, the specific heat merely reaches gradually a high value, and then gradually but more rapidly sinks to a normal value. Other criteria have not yet been sufficiently investigated in most cases, but it is fairly certain from the measurements that have been made that there is very little change in the crystal lattice, and that the volume alters gradually rather than discontinuously on changing the temperature.

The examples hitherto described all occur at temperatures below 0°. The first was ammonium chloride, studied by Simon,[1] who later investigated other ammonium salts. These investigations showed that the heat capacity curves pass through well-defined maxima in the neighborhood of −30 to −50°, the different anions in combination with the NH_4^+ altering

[1] F. Simon, *Ann. Physik*, **68**, 241 (1922); Simon and Simson, *Naturwiss.*, **38**, 880 (1926); Simon, Simson and Ruhemann, *Z. physik. Chem.*, **129**, 339 (1927); Simon and Bergmann, *ibid.*, **8B**, 255 (1930).

the temperature of the peak of the curve only a few degrees. Structurally there is apparently no change, and the expansion curves are gradual, but with abnormal contours in the neighborhood of the transition temperatures (when defined as the temperatures of the peak of the specific heat curves). On the basis of these results it has been suggested that the phenomenon is due to intramolecular rearrangement of the ammonium ions. Other examples are found in the specific heat curves for a number of condensed gases,[2] for which unfortunately other criteria are lacking. Hendricks[3] on the other hand has noted that crystal structure studies on the primary alkyl ammonium halides at room temperature lead to the postulate of a collinear carbon chain, whereas at liquid air temperatures the staggered chain is the more probable. This is in accord with a suggested explanation based on the quantum mechanics, offered by Pauling,[4] who postulates a transition from oscillatory to rotatory motion within the lattice of a crystal. Smits[5] has studied the thermodynamic aspects of the problem, and arrives at a series of pseudo-binary diagrams, without definite suggestions as to the nature of the pseudo-components.

It should be emphasized that the experimental evidence presented in the literature is lacking in one important aspect, namely, that of the reproducibility of the physical properties measured. The specific heat curves give us the best example of this; different investigators agree in general on the form of the curve, but often disagree seriously as to the exact values of the specific heat. The question of reproducibility is of particular importance when any given property is employed to differentiate between a gradual transition and a sluggish polymorphic inversion, for obvious reasons. It must be admitted, however, that this objection is largely of academic interest only, since the very nature of the methods of specific heat measurements at low temperatures is such as to assure the general correctness of the results.

In addition to the two types of transitions mentioned above, it is likely that there exists a third type in which a true polymorphic inversion is preceded by an abnormal change in specific heat and other properties. Quartz appears to belong to this mixed class; it is well known that its properties (specific heat, thermal expansion, optical properties) undergo large changes over a considerable temperature interval below the inversion point at 573° where the crystals suddenly change from trigonal to hexagonal symmetry. No other cases of this type appear to be known.

[2] Eucken and Karwat, *Z. physik. Chem.*, **112**, 467 (1924), HBr and HI; Giauque and Wiebe, THIS JOURNAL, **50**, 2193 (1928); **51**, 1441 (1929), HBr and HI; K. Clusius, *Z. physik. Chem.*, **3B**, 41 (1929), N_2, O_2, CO, CH_4.

[3] S. B. Hendricks, *Z. Krist.*, **67**, 465 (1928); **68**, 189 (1928); *Nature*, **126**, 167 (1930).

[4] L. Pauling, *Phys. Rev.*, **36**, 430 (1930).

[5] A. Smits, *Physik. Z.*, **31**, 172, 376, 435, 768 (1930).

The investigation reported in this and a following paper is concerned with a gradual transition in sodium nitrate. This substance occupies an apparently anomalous position among the nitrates of univalent metals. With the exception of lithium nitrate, which forms a trihydrate at ordinary temperature, all the other univalent nitrates exhibit one or more normal polymorphic inversions. Bridgman,[6] who studied these inversions under pressure, remarks upon the similarity of the phase diagrams and discusses the crystallographic analogies between the various forms encountered. Sodium nitrate is rhombohedral of the calcite type at ordinary temperature. This crystal type is found in anhydrous lithium nitrate, and as the high temperature modification of potassium nitrate and rubidium nitrate. None of these, however, appears to be completely isomorphic with sodium nitrate.

An unsuccessful search for an inversion in sodium nitrate has been made by Bridgman[6] and by Hissink.[7] Both investigators stopped at temperatures below that at which the gradual transition is completed.

In many respects the thermal behavior of sodium nitrate parallels that of ammonium chloride as already described. The specific heat begins to increase abnormally and reaches a peak value at 275°. Optical examination with a heating microscope fails to show any decided change between room temperature and the melting point, but the thermal expansion curve exhibits an abnormal course between 150 and 275°. The behavior is reproducible, and hysteresis phenomena are completely lacking. Studies have also been made of the solubility in water up to the melting point of the salt, and of the crystal structure at various temperatures.

The results are in good agreement with the postulate of intramolecular rotation[4] of the NO_3 ion at temperatures between 275° and the melting point, the deciding factor being the information gained from the analysis of the structure. This portion of the work, in collaboration with E. Posnjak and S. B. Hendricks, is published separately in a following paper. The results collected in the present article deal with the purely physicochemical determination of the gradual transition, and are independent of any postulate as to the nature of this phenomenon.

Part I. Thermal Capacity

In 1909 a paper was published by Goodwin and Kalmus[8] on the determination of specific heats and latent heats of melting for a number of salts, among which was included sodium nitrate. There is an anomaly in the course of the specific heat curve for the crystals of this substance, which was passed over unnoticed, but which certainly exceeds a reasonable

[6] P. W. Bridgman, *Proc. Am. Acad. Sci.*, **51**, 581 (1916).

[7] D. J. Hissink, *Z. physik. Chem.*, **32**, 537 (1900).

[8] Goodwin and Kalmus, *Phys. Rev.*, **28**, 1 (1909).

experimental error,[9] amounting to 5–10 cal./g. in the value of the total heat of the crystals. During the course of another investigation[10] I had occasion to take thermal analysis curves of sodium nitrate, and found an abnormal heat effect in approximately the same region as that exhibited by the results of Goodwin and Kalmus. The characteristics of this heat effect were different from those usually associated with normal polymorphic inversions, and hence a closer study was made of the phenomenon.

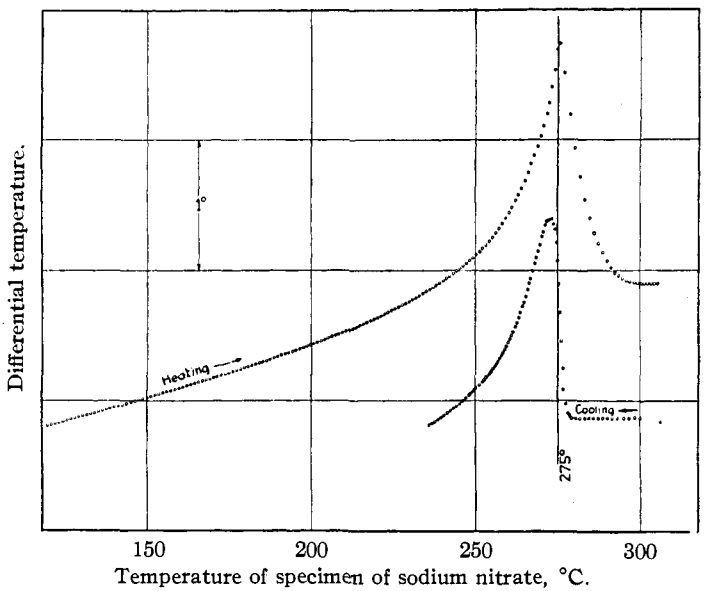

Fig. 1.—Differential heating and cooling curves for sodium nitrate. Note the absence of location of the beginning of the heat effect and its sharp termination on the heating curve.

The accessory apparatus used for thermal analysis was the same as in my earlier work. In order to secure maximum sensitivity and freedom from minor fluctuations of the differential temperature, the furnace was provided with a hollow copper block within which the sample of sodium nitrate contained in a platinum thimble crucible was suspended upon the thermocouple, which was immersed in the salt, but protected from corrosive attack by a capsule made from platinum tubing 1.5 mm. in diameter. The reference thermocouple was located in a well in the copper block. This arrangement has proved to be entirely satisfactory in that the differential temperature readings were perfectly steady. Readings were made to within 0.2 microvolt, using copper–constantan couples, which corresponds to a sensitivity of 0.005°, far in excess of what was actually needed. The thermocouples were calibrated with accepted standards.

The sodium nitrate used for the experiments was recrystallized, starting with the best C. P. material available. About 2.5 g. of the salt was used in each experiment.

[9] The melting points quoted in their Table II, p. 12, for sodium nitrate and potassium nitrate are transposed.

[10] F. C. Kracek, *J. Phys. Chem.*, **34**, 225 (1930).

Single crystals were produced by melting the samples in place in the furnace and slowly cooling. It may be mentioned, however, that single crystals and crystal aggregates showed no difference in behavior.

Typical results of the thermal analysis experiments are shown in Figs. 1 and 2. The important feature of these curves is that, on heating, the rise in the differential temperature ceases sharply at 275.5°, but on cooling, heat begins to be evolved by the sample at a temperature which is higher, namely, about 279°. This is contrary to all experience with normal polymorphic inversions,[11] in which the heat effect on cooling, in conse-

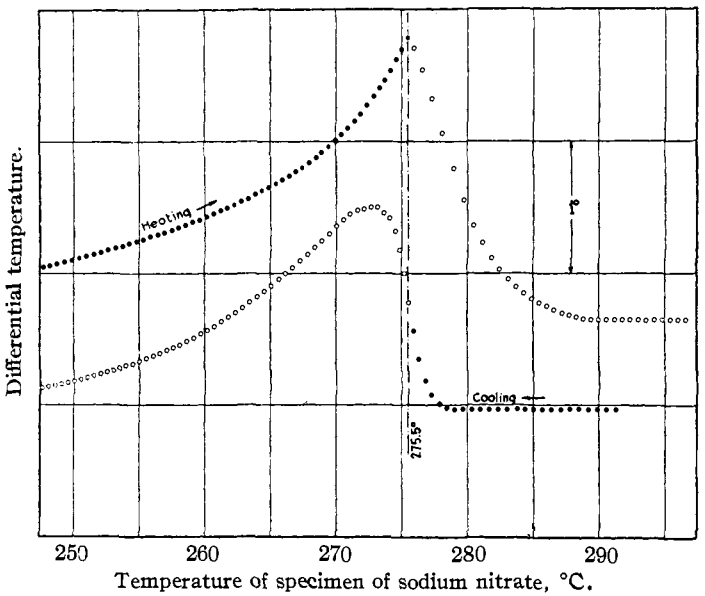

Fig. 2.—Differential heating and cooling curves for sodium nitrate near the peak of the curve. Compare the black circle curves with the curve of the expansion coefficient in Fig. 6.

quence of hysteresis, however slight in amount, always begins at a temperature which is *lower* than that at which the heat effect begins on heating. The second unusual feature of these curves is that *no point of beginning* of the heat effect can be located on the heating curve. The heat capacity increases gradually as temperature rises to 275.5°, and then suddenly decreases sharply to a normal value, within 2 or 3 degrees, as shown by the contour of the recovery curve, and the beginning of the heat effect on cooling. Just below 275.5° the increase in heat capacity is rapid, but it does not have the character of a latent heat, for in the latter case we should expect in a single crystal a fall in the temperature of the sample with a rising

[11] Consult *J. Phys. Chem.*, **34**, 225 (1930), for typical heating and cooling curves obtained with potassium nitrate.

differential temperature, with a heat effect which is so prompt. While these experiments do not yield an absolute value for the heat capacity, they nevertheless furnish relative values, and they describe the character of the behavior as exactly as could be done with a strictly calorimetric procedure.

The results of these experiments on the abnormal increase in the heat capacity, which extends for at least 100° below the temperature at which the peak of the curve is reached, favor the conclusion that the change which takes place in the crystals of sodium nitrate is not that of a typical inversion from one modification to another, but rather a gradual alteration instead of an abrupt one in the properties of the same physical phase.

Part II. Thermal Expansion of Sodium Nitrate

The measurements of the volume change which a polymorphic substance undergoes during the transition from one crystal phase into another is important from the standpoint of thermodynamics since the ratio of the heat of inversion to the volume change per unit mass enters into the calculation of the slope of the transition curve in consequence of the Clapeyron equation. In addition to the quantitative consequences of such measurements, there is obtained usually a considerable amount of pertinent information regarding the characteristics of the transition, particularly with respect to the promptness and the rate with which it proceeds. In typical rapid polymorphic transitions the crystals expand uniformly and reproducibly up to the inversion point. At the inversion point the rate of transition is zero, so that it is necessary to raise the temperature some distance beyond that point by an amount dependent upon the characteristics of the substance, for the inversion to proceed. It is well recognized that the growth of nuclei of the new crystal phase is an important factor in determining the rate. Once initiated, the rapid inversions proceed readily to completion, usually within a few degrees above the equilibrium temperature. On cooling, the phenomena are reversed, so that ordinarily there is a hysteresis band extending on both sides of the transition point; within this band the volume measurements are not reproducible. After the volume change of transition is completed, the substance once more exhibits a normal expansion, which is not necessarily the same above and below the transition point.

The expansion of sodium nitrate does not proceed in the manner outlined above through the transition region, and in this respect the salt again differs from typical polymorphic behavior. The measurements were made with a mercury-in-glass dilatometer, and they gave, with suitable auxiliary measurements, values of the specific volume of the salt at various temperatures.

The apparatus is shown diagrammatically in Fig. 3. The dilatometer was made of Pyrex glass, in the simple form indicated.[12] The bulb of the dilatometer was in an

[12] Compare Kracek and Gibson, *J. Phys. Chem.*, **34**, 188 (1930).

air-bath thermostat heated by electric current, and controlled by a bare five-junction copper–constantan thermocouple which operated a special potentiometer controller. The temperature control was sensitive to ±0.05° at any given setting. The air was kept in motion by a propeller fan rotated at about 800 r. p. m.; this fan maintained the whole enclosure at a uniformly distributed temperature. The reading thermocouple of copper–constantan (calibrated) was fastened to the dilatometer bulb by two clips, and was enclosed in a small porcelain tube, partly for protection, and partly to give it a thermal lag somewhat comparable with that of the contents of the dilatometer.

The exposed portion of the dilatometer was of heavy capillary Pyrex tubing. The reading portion of the capillary was in vertical position, and was placed against a mirror which had a scale engraved upon it. The readings were made with the aid of a cathetometer to avoid parallax, and were recorded to 0.1 mm. Corrections were made for the exposed stem to reduce all the readings to 25°, which was the approximate temperature of the room.

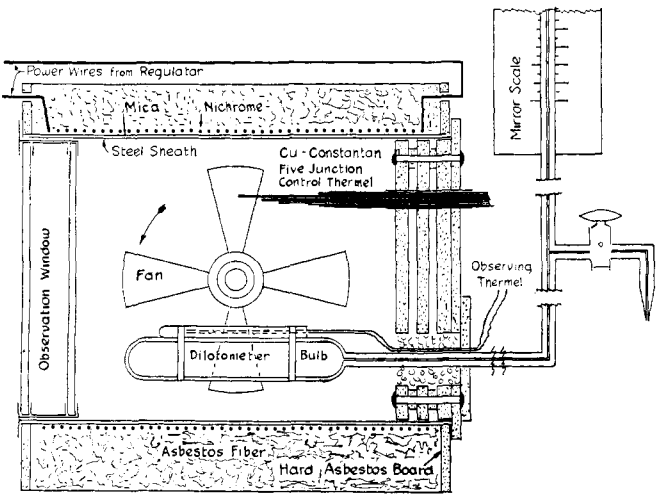

Fig. 3.—The thermostat as used with the dilatometer.

The capillary was calibrated with a weighed thread of mercury in the usual manner, against the same portion of the scale employed in making the observations. The results of the calibration were integrated to give the cubical contents of the capillary from a reference mark to any given reading of the meniscus. The capillary was fairly uniform in cross section.

Filling the Dilatometer.—The bulb of the dilatometer was provided with a side tube through which a known amount of the salt was introduced. This side tube was later sealed off at the entrance to the bulb. Some trouble was experienced at first owing to liberation of occluded moisture by the crystals; this persisted even when the salt was fused before introduction into the bulb. It was found necessary to melt the salt in the bulb under vacuum. The salt used had been recrystallized, and was quite free from all impurities. It was first fused in a platinum dish, then crushed, and screened to remove all dust smaller than 30-mesh. A known amount of this preparation was introduced into the bulb, which was then evacuated and heated to melt the salt. After evolution of bubbles had ceased, the bulb was cooled while still evacuated and mercury was introduced, care being taken to avoid any trapped bubbles of air.

After the conclusion of the measurements the salt was dissolved out, an aliquot portion of the solution evaporated to dryness, carefully fused and weighed. This determination gave 18.824 g. of sodium nitrate, compared with 18.835 g. by direct weighing of the salt introduced into the bulb. The glass showed no evidence of attack by the salt during the fusion, and the salt showed no evidence of decomposition.

The Experimental Procedure.—The thermostat was brought up to the desired temperature and readings were taken of the position of the mercury meniscus in the capillary at five-minute intervals until three successive readings showed no change. The thermostat was then readjusted to another temperature and readings were taken as before. In this fashion a series of determinations was obtained at successively higher temperatures, followed by a series with descending temperatures. At the end of the first cycle another set of observations was begun, allowing thirty to sixty minutes at each constant temperature, to ascertain whether any secular changes were taking place. The readings in all cases remained unchanged during the whole time the temperature was held constant at each point, proving definitely that each final reading represented equilibrium conditions. At a few points in the neighborhood of 275° the temperature was held constant for several hours.

During the first cycle of readings a slight readjustment took place, probably owing to more intimate penetration of the mercury into the cracks in the block of salt in the bulb. In all the succeeding cycles the readings fell reproducibly 3.1 mm. below those for the first cycle. The readings of the first cycle were disregarded. The position of the mercury meniscus at 25° was 8.9 mm. below the zero of the scale at the end of the first cycle, and remained unchanged thereafter.

The data obtained in these experiments were converted by calculation to give the specific expansion of sodium nitrate from 25°. For this calculation it was necessary to know (a) the total volume of the bulb, the weight of sodium nitrate and the weight of mercury in the bulb at 25°, (b) the specific volume of sodium nitrate at 25°, equal to 0.4426 cc./g. [calculated from Andreae, *Z. physik. Chem.*, **82,** 109 (1913)], (c) the specific volume of mercury at the temperature of the experiment (taken from "International Critical Tables," Vol. II, p. 457), (d) the cubic expansion coefficient of the Pyrex bulb, equal to 9.6×10^{-6}, taken from measurements by the Corning Glass Works, in addition to (e) the effective diameter of the capillary.

The greatest source of uncertainty in Δv_a lies in the correction for the expansion of the glass bulb, which accounts roughly for 10% of Δv_a. Some error is also introduced by the assumption that the temperature of the mercury in the capillary at the point of emergence from the thermostat dropped sharply from t to the temperature of the room. These factors introduce systematic errors which may affect the absolute accuracy of the value of Δv_a by as much as 2%, but which do not affect the relative precision of the calculated values, so that a graph of Δv_a *vs.* t°C. has the same relative precision as the original readings of the mercury meniscus.

The results of the dilatometric experiments are collected in Table I, arranged in the order in which the readings were taken. Figures 4 and 5

TABLE I

THERMAL EXPANSION OF SODIUM NITRATE MEASURED WITH A DILATOMETER

Series II

Temperature was held constant about thirty minutes at each point

t, °C.	Position of meniscus corrected to 25°, mm.	Specific expansion of $NaNO_3$ from 25° cc./g.
25.0	−8.9	0.0
102.5	66.6	0.00573
114.8	78.4	.00663
135.5	97.7	.00814
173.2	134.1	.01109
188.2	149.8	.01241
199.2	161.8	.01347
215.2	180.1	.01511
233.8	204.2	.01741
251.1	230.4	.02011
264.8	252.8	.02272
269.1	261.5	.02380
272.0	269.0	.02475
276.2	281.1	.02630
280.6	286.8	.02690
286.2	292.5	.02748
293.1	299.3	.02812
298.1	304.8	.02860
275.5	280.3	.02620
270.2	264.3	.02417
265.3	253.7	.02283
25.0	−8.8	....

Series III

Temperature was held constant thirty to sixty minutes at each point, with the exception of a period of twelve hours at 208.0°. At the end of the second day's run, held overnight at about 265°

t, °C.	Position of meniscus corrected to 25°, mm.	Specific expansion of $NaNO_3$ from 25°, cc./g.
25.0	−8.8	0.0
104.8	68.7	.00589
125.5	87.4	.00742
155.1	115.9	.00960
165.2	126.0	.01041
176.8	137.9	.01140
177.1	138.3	.01143
182.3	143.6	.01186
189.3	151.0	.01248
197.7	160.3	.01330
206.1	170.4	.01422
208.0	172.4	.01440
222.4	189.4	.01595
241.0	214.3	.01847
257.6	240.2	.02127
262.8	249.3	.02231
267.9	259.4	.02353
270.8	266.0	.02436
272.9	271.8	.02511
275.0	278.1	.02597
276.4	280.8	.02628
282.9	289.1	.02716
294.0	300.8	.02825
299.3	305.7	.02867
288.0	294.4	.02765
278.4	284.3	.02663
274.2	276.4	.02570
269.3	262.0	.02386
268.4	260.4	.02366
269.0	261.5	.02380
269.1	261.8	.02383

Series IV

After preceding series temperature was held at about 265° overnight, then adjusted to 269.1° and successive readings were taken holding thirty to sixty minutes at constant temperature at each point

269.1	261.7	0.02382
271.2	267.1	.02451
273.0	272.1	.02515
274.8	277.7	.02587
275.9	280.6	.02625
278.5	284.4	.02665
281.9	288.0	.02703
284.9	291.1	.02733
287.6	293.8	.02760
285.7	291.7	.02740
281.2	287.4	.02696
277.7	283.2	.02653
276.2	280.4	.02624
274.7	278.6	.02585
273.6	275.1	.02560
270.1	264.1	.02412
266.6	256.4	.02316
25.0	−8.9	....

give a graphical representation of the total expansion per gram of sodium nitrate from 25 to t°C. plotted against the temperature. These figures show the relative precision and the reproducibility of the results. Figure 4 contains data for the third series only; Fig. 5, on the other hand, contains data for series II, III and IV without distinction except for that between ascending or descending order with respect to temperature, the ascending points being marked with open circles, the descending ones with black circles.

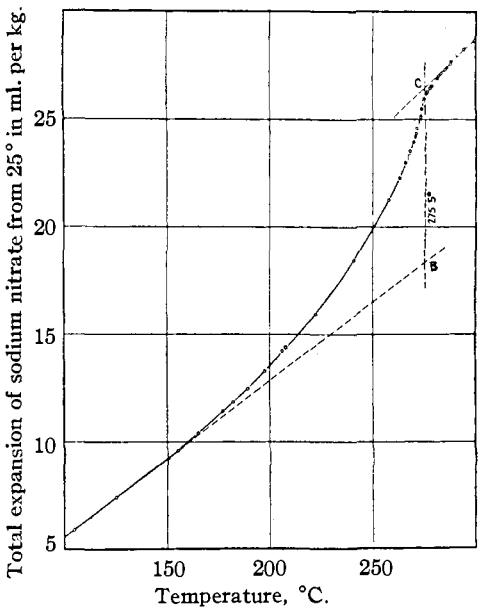

Fig. 4.—The expansion curve of sodium nitrate from 100° upward. The open and the black circles differentiate between ascending and descending sequence of constant temperatures. The distance BC is a measure of the anomalous expansion. Note the gradual character of the curve.

The value of the expansion coefficient $\alpha = 1/v_a \times \Delta v_a/\Delta t$ was obtained at a number of even temperatures from large scale graphs of Figs. 4 and 5. This is represented in Fig. 6. It should be noted that the curve of total expansion does not break sharply, but is rounded in the neighborhood of 275°; the peak of the α-curve of Fig. 6 falls close to 275.5° in agreement with the location of the peak on the differential heating curve of Fig. 2.

The amount of the anomalous expansion was determined from Fig. 4, as the distance BC on the graph, corresponding to 0.00811 cc./g. or 1.73% of the specific volume at 275°. It must be remembered that this does *not* represent a transition volume change in the usual sense, since the curve represents equilibrium values of expansibility at each temperature.

Extrapolation of the total expansion curve to 309.5°, the melting point of sodium nitrate, yields 0.02963 cc./g. from 25°. The specific volume at 25°, from Andreae's measurements of the density, is 0.44262 cc./g. Jaeger's[13] and Goodwin and Mailey's[14] measurements on the density of fused sodium nitrate yield $\rho = 1.915 \pm 0.015$, or 0.5223 ± 0.0050 for the specific volume of liquid sodium nitrate at the melting point. We obtain from these, in round numbers, 0.0500 ± 0.005 cc./g. for the change of volume

[13] F. M. Jaeger, *Z. anorg. allgem. Chem.*, **101**, 16 (1917).

[14] Goodwin and Mailey, *Phys. Rev.*, **25**, 469 (1907).

during melting, corresponding approximately to 9% of the volume of the liquid.

The most important features of the expansion curve are its complete reproducibility with rising and falling sequence of constant temperatures, the absence of a noticeable break in the curve where the anomalous expansion begins, and the slight round of the curve at 275°. The expansion coefficient rises gradually to a peak value near 275.5°, as has already been pointed out, and then quite rapidly diminishes to a nearly steady value beyond 280°. The character of the expansion curve precludes definitely the possibility of speaking of a finite transition volume change; it adds weight to the results on thermal analysis which indicate that there is no finite latent heat of transition.

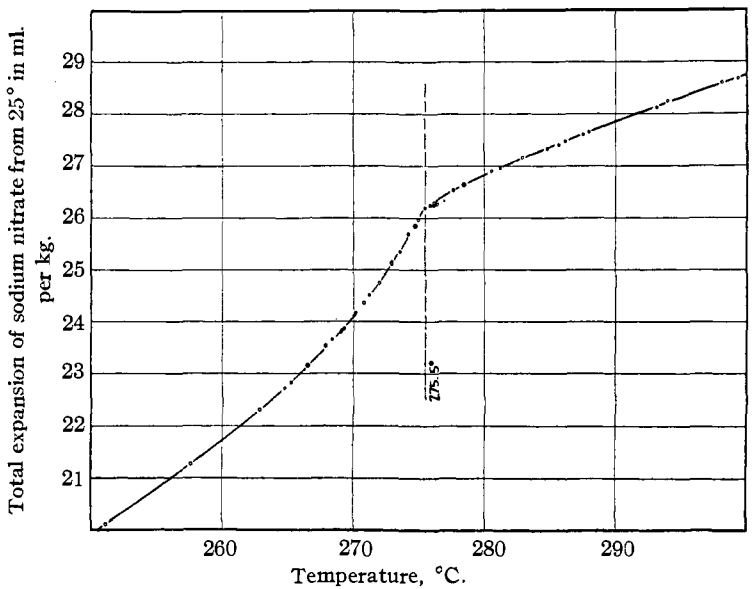

Fig. 5.—The expansion curve of sodium nitrate near 275°. Note the reproducibility of the curve as indicated by the open and black circles which differentiate between rising and falling sequence of constant temperatures, and the absence of a sharp break at 275°.

Part III. Optical Examination

Sodium nitrate at ordinary temperature is optically uniaxial and negative, $\omega = 1.5874$, $\epsilon = 1.3361$. Observation with a microscope equipped with a heating stage[15] shows that the optical character remains unchanged up to the melting point of the salt. The anomalous volume change described in the preceding chapter is clearly observable under the microscope,

[15] A very compact heating stage built by Mr. C. J. Ksanda of this Laboratory was used.

particularly during cooling, but it is *not* accompanied by an alteration in the optical character. No attempt was made to measure the change in the magnitude of the refractive indices with temperature, but it can be stated with confidence that the birefringence does *not* change suddenly at 275°, the only point at which a sharp change could be expected.

The results of these observations lead to the conclusion that crystalline sodium nitrate does not pass through a change of phase during the gradual transition, the same crystal phase persisting up to the melting point.

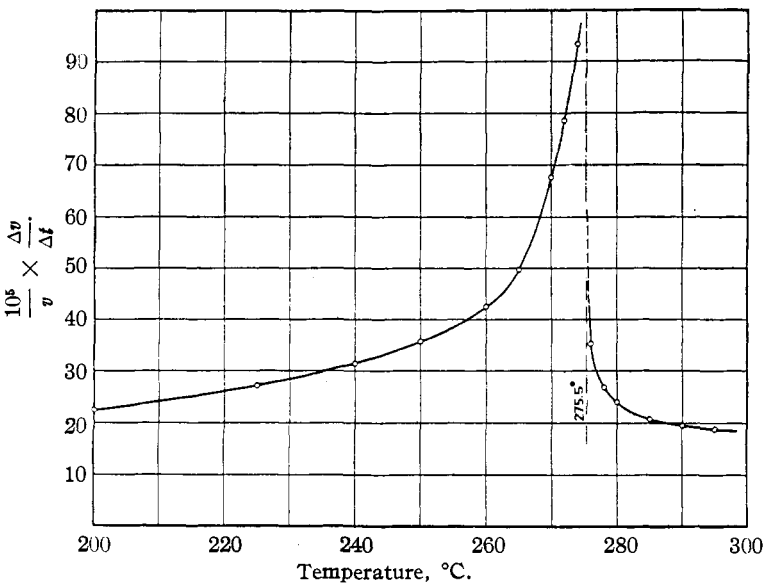

Fig. 6.—Curve of the expansion coefficient of sodium nitrate. Compare with Fig. 2.

Part IV. Solubility in Water up to the Melting Point of Sodium Nitrate

The solubility was determined by the synthetic method in sealed tubes of Pyrex glass, the reliability of the method having already been tested with other systems.[16] The thermostat and accessory apparatus used with the dilatometer (see Fig. 3) were also used in the solubility work, with appropriate modifications. The fan shaft of Fig. 3 is hollow, to allow for the introduction of a smaller shaft which is provided with an arm to carry and rotate the solubility tube. Transparent windows are provided at both ends of the thermostat, for visual observation. The thermocouples are introduced through an opening in one of the windows, the thermocouple for reading the temperature of the thermostat being arranged to hang free in the immediate neighborhood of the rotating solubility tube. The junction

[16] F. C. Kracek, *J. Phys. Chem.*, **35**, 417, 947 (1931).

of this couple is enclosed in a small mass of alundum to provide an appropriate thermal lag. The fan is rotated at about 800 r. p. m., the solubility tube at about 30 r. p. m., just fast enough to keep the contents of the tube well stirred. Under these conditions the temperature control is sensitive to about $\pm 0.05°$.

The results of the individual solubility experiments are given in Table II. The supersolubility limits[17] were also determined in several of the experiments; the temperature of spontaneous crystallization is in general 4°

TABLE II

DETERMINATIONS OF SOLUBILITY OF SODIUM NITRATE IN WATER

Expt.	Grams of Water	Grams of $NaNO_3$	r_w[a]	r_m[b]	$NaNO_3$, % Weight	$NaNO_3$, % Mole	t, °C.
16	2.5192	4.1794	1.6590	0.35160	62.39	26.01	94.05
17	3.2924	6.1186	1.8584	.39385	65.02	28.26	106.80
18	3.5975	7.1976	2.0007	.42401	66.78	29.78	114.90
15	2.0543	5.0425	2.4546	.52021	71.05	34.22	136.90
1	2.2501	6.4247	2.8553	.60512	74.06	37.70	151.60
2	1.7556	5.9874	3.4105	.72278	77.33	41.95	168.90
3	1.4843	5.6214	3.7872	.80263	79.11	44.53	178.00
4	1.4471	5.8784	4.0622	.86090	80.25	46.26	183.80
5	1.2897	6.5597	5.0862	1.0779	83.57	51.88	201.60
6	0.8925	5.8163	6.5169	1.3811	86.70	58.00	218.90
7	.9096	6.5353	7.1848	1.5227	87.78	60.36	224.70
8	.7477	7.3838	9.8754	2.0929	90.81	67.67	242.25
14	.5867	7.3266	12.4880	2.6465	92.59	72.58	253.55
13	.5409	8.0582	14.898	3.1573	93.71	75.95	260.90
9	.4499	6.9026	15.343	3.2515	93.88	76.48	261.75
10	.3883	7.4794	19.262	4.0822	95.07	80.32	270.00
11	.2134	8.6472	40.521	8.5876	97.59	89.57	289.20
12	.1466	8.5451	58.289	12.353	98.31	92.51	295.35
..	....	....	....	....	100.0	100.0	309.5

[a] r_w = g. of $NaNO_3$ per g. of H_2O. [b] r_m = moles of $NaNO_3$ per mole of H_2O.

below the solubility curve for this system. Figure 7 represents the data obtained, together with the more significant results from the literature. Below the normal boiling point the solubility curve passes smoothly through the points established by Berkeley,[18] in continuation of the results obtained in this study, and hence no determinations were made below 90°. At higher temperatures we have determinations by Étard,[19] who apparently failed to attain complete saturation in most of his experiments.

The solubility curve at the higher temperatures is shown in Fig. 8, in a $1/T$ *vs.* log N_2 plot, to bring out the trend of the solubility results as fully as possible. It will be seen that a smooth curve, with a very slight reverse S curvature, fits the results better than one with a sharp break at 275.5°.

[17] Miers and Isaacs, *J. Chem. Soc.*, **89**, 413 (1906).

[18] Berkeley, *Phil. Trans. Roy. Soc.*, **203A**, 189 (1904).

[19] Étard, *Ann. chim. phys.*, **2**, 503 (1894).

No exact conclusions can be drawn from the solubility curve regarding the nature of the gradual transition, other than that the solubility results do not vitiate the conclusions obtained from the other types of evidence, to the effect that the same physical crystalline phase of sodium nitrate persists

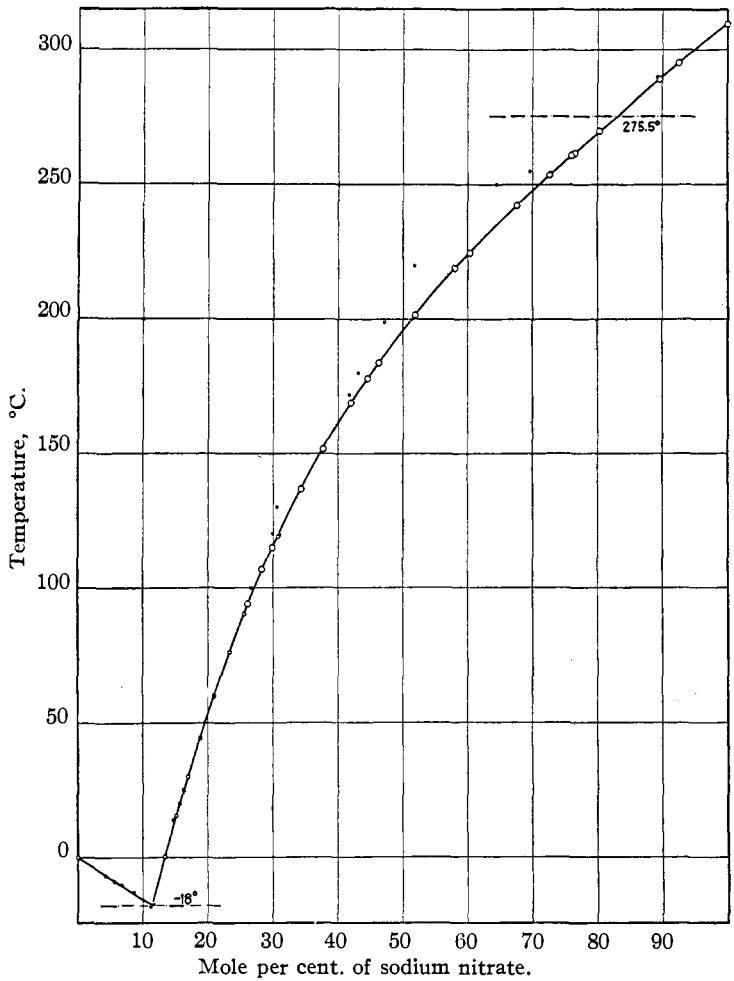

Fig. 7.—The solubility of sodium nitrate in water. The larger open circles by Kracek. The small black circles above 100° are by Étard. Results below 100° by Berkeley and others.

up to the melting point. These solubility results are hence published more for their intrinsic value rather than as a deciding criterion for the gradual transition. To attempt drawing more definite conclusions from these solubility data would necessitate ascribing much higher accuracy to these results than they warrant.

Part V. Discussion

In transitions of this type the phase change, if we can speak of it as such, must take place gradually, rather than discontinuously, as is the case in normal polymorphic transformations. We cannot write down an expression for the entropy difference between the "phases" when the heat of transition is zero, that is, the Gibbs zeta potential is the same for the two "phases"; even though there may be a considerable difference in properties of the substance at two different temperatures, there can be no

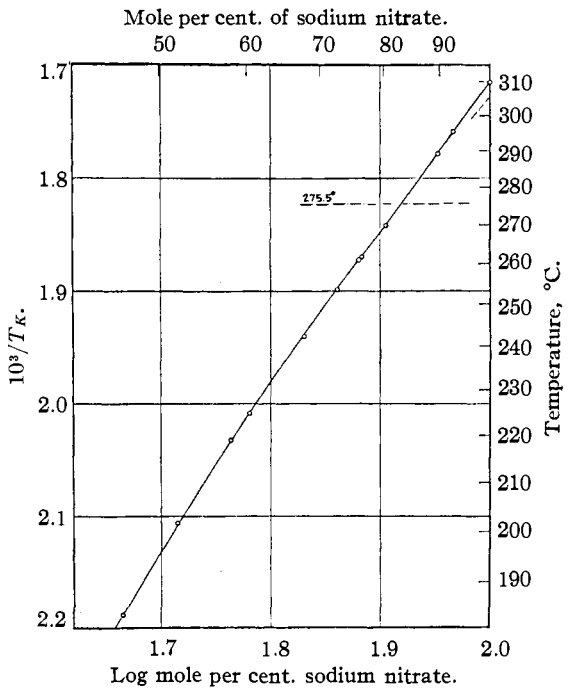

Fig. 8.—$10^3/T$ *vs.* log N_2 graph of solubility of sodium nitrate in water between 180° and the melting point. Note the slight reverse S curvature in the neighborhood of 275°.

finite change at any one given temperature. Strictly speaking, there would be only one phase undergoing abnormal alteration in properties gradually, but the major portion of the transformation may be accomplished over a comparatively narrow range of temperature, as in the case of sodium nitrate near 275°. Similarly, the expression $\Delta H/(T\Delta v)$, which determines the pressure variation of the transition temperature in the Clapeyron equation, is indeterminate, since it has a value of 0/0. The effect of pressure then cannot be calculated, but it should be possible to determine it experimentally; since the anomalous expansion is positive in

sodium nitrate, it is to be expected that the temperature of the completion of the gradual transition should rise with increasing pressure.[20] All the experimental results quoted are in good accord with the view advanced here, to wit, that the gradual transition represents an anomalous change in the properties of a single phase. The rounding of the expansion curve in the neighborhood of 275° (see Fig. 5) appears to be of special significance in this respect. From the standpoint of thermodynamics, it is the Le Chatelier rule, and not the Clapeyron equation, which must be applied.

The most completely investigated other case of the gradual transition is that of the ammonium salts, in which, as already mentioned, the transitions end at temperatures between −50 and −30°. Simon and Bergmann[1] have recently published data on the thermal expansion of the chloride, bromide and phosphate. Their curve for ammonium chloride is very similar to the curve for sodium nitrate, and, although they make no statement with regard to the reproducibility of the curve for a given specimen, it is very probable that it represents equilibrium conditions. The curves for the bromide and phosphate exhibit gradual contractions over a range of temperatures. Simon ascribes the transitions in the ammonium salt to the ammonium ion, but offers no adequate suggestion as to the mechanism. On Pauling's theory the gradual transition in the ammonium salts is due to the initiation of rotation of the ammonium ion in the crystal. There is a possible objection to this in the case of ammonium bromide and the phosphate in view of the contraction encountered with these salts.

The physical conditions in the case of sodium nitrate are such that the above objection to intramolecular rotation of the nitrate ion does not hold. This question will be considered in more detail in the paper which will deal with the structure of sodium nitrate at various temperatures.

The principal conclusion that can be drawn from the physico-chemical study reported in this paper is that sodium nitrate undergoes a gradual transformation accompanied by a change in the specific heat and volume in a manner such that there is at no point a finite discontinuity in the properties of the substance.

Summary

Crystalline sodium nitrate undergoes a gradual transition which ends at 275.5°. The characteristics of the transition differ from those of a normal polymorphic inversion in that there is no finite discontinuity in the properties of the substance during the transition. The results on thermal capacity and expansion, optical properties and solubility in water are presented and discussed in comparison with the behavior of normal inversions.

WASHINGTON, D. C.

[20] Since this was written Professor Bridgman has announced the determination of the effect of pressure on the gradual transitions in ammonium chloride and ammonium bromide.