THERMAL STUDIES ON PHASE TRANSITIONS IN SOME SODIUM, POTASSIUM, AND SILVER COMPOUNDS

M. J. ADAMS AND J. E. HOUSE, JR.
Department of Chemistry
Illinois State University, Normal, Illinois 61761

ABSTRACT. — Enthalpies of the phase transitions in solid potassium nitrite, potassium thiocyanate, sodium nitrite, and silver nitrate have been determined using differential scanning calorimetry. The corresponding enthalpies are 199 ± 2, 397 ± 4, 299 ± 33, and 555 ± 5 cal/mole respectively. The enthalpies determined for the phase transitions in silver nitrate and sodium nitrite are in good agreement with previously reported values while those for potassium thiocyanate and potassium nitrite do not agree with older values. Observations are presented on the thermal changes in $Na_2Cr_2O_7 \cdot 2H_2O$ during dehydration.

A large number of phase transitions are known to occur when salts are heated in the solid state (Rao and Rao, 1967). Of particular note are the familiar phase transitions in solid ammonium halides. However, because of the difficulty in studying the thermal changes during these transitions, there is frequently disagreement on the enthalpy change associated with the phase changes. Therefore, even for some common compounds, the enthalpies are not accurately known. Accordingly, we have determined the enthalpies associated with transitions in solid potassium thiocyanate, potassium nitrite, sodium nitrite, and silver nitrate. As a result of the attempted study of phase transitions in sodium dichromate, the kinetics and thermal changes accompanying the dehydration of sodium dichromate dihydrate have been determined.

METHODS AND MATERIALS

All compounds used were of reagent grade and were used without further chemical purification. These crystalline compounds were freshly ground to a fine powder before use. The $Na_2Cr_2O_7 \cdot 2H_2O$ was finely powdered and a sample placed in an oven at 110° for several days to determine the total amount of water of hydration present. The calculated weight loss for dehydration is 12.08% and the observed weight loss was 12.16%.

Enthalpies of the phase transitions and the dehydration of $Na_2Cr_2O_7 \cdot 2H_2O$ were determined using a Perkin-Elmer Differential Scanning Calorimeter, Model DSC-1B. The instrument was calibrated against the fusion of metallic tin with a heat of fusion of 14.5 cal/g. The system was purged with dry nitrogen at a flow rate of 15 cc/min. Samples of about 2-5 mg weighed to six decimal places were used and the endothermic peak areas were determined by graphical integration.

Results and Discussion

The enthalpy changes obtained for the phase transitions studied are shown in Table 1. The compounds studied were chosen because of the approximate nature of values previously reported or because there were large discrepancies between two or more reported values. It is readily apparent that the values obtained in this study agree well with one or more previously reported values for the phase transitions in silver nitrate and sodium nitrite. It is also obvious that the older values for transitions in potassium thiocyanate and potassium nitrite are greatly different from those in this work and outside our limits of error. The limits of error for the experimental procedures used in this work make it possible to unequivocally eliminate some of the previously reported values which were determined by techniques much less accurate than differential scanning calorimetry. The physical nature of the transitions in these compounds has been discussed in the references in Table 1 and will not be reviewed here.

It was hoped that the phase transitions in $Na_2Cr_2O_7$ could also be studied (Popov and Galchenko, 1951). However, only peaks of variable size and at irregular temperatures could be obtained between 385-500°K. The reason for this behavior is not known. In several thermograms, peaks corresponding to phase transitions were found at 420, 434, and 443°K, but these were not present in all runs.

It has been possible to study carefully the dehydration of $Na_2Cr_2O_7 \cdot 2H_2O$. Previously, only a qualitative study of the dehydration has been reported (Erday, *et al.*, 1966) and no kinetic or thermodynamic values were reported. These workers reported that the two moles of water of crystallization are removed by 300°C. In all our runs, the dehydration was complete by 120°C and was accompanied by an enthalpy change of 15.9 ± 0.8 kcal/mole. Using the procedure of Thomas and Clarke (1968), we have determined the activation energy for the dehydration to be 15.0 ± 0.8 kcal/mole.

Table 1. Enthalpy Changes for Phase Transitions.

Compound	Transition Temperature, °C	Number of Determinations	Enthalpy Change, cal/mole: This Work[a]	Literature	Reference
KSCN	140	4	397 ± 4	530	b
$NaNO_2$	160	5	299 ± 33	~285, ~250	c, d
KNO_2	40	5	199 ± 2	~100	d
$AgNO_3$	160	3	555 ± 5	584, 561, 920	e, f, g

[a] Given as average value ± average deviation from the mean.
[b] Sakiyama, *et al.*, 1963
[c] Nomura, 1961
[d] Rao and Rao, 1966A
[e] Janz and Kelly, 1963
[f] Reinsborough and Wetmore, 1967
[g] Rao and Rao, 1966B

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