DIFFERENTIAL THERMAL ANALYSIS OF Na_2SO_4

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(Communicated by K. Banerjee, F.N.I.)

(*Received February 2; read May 27, 1955*)

The existence of anhydrous sodium sulphate in five polymorphic forms provides an interesting problem in X-ray crystallography. From the researches of many a worker and Kracek (1929), the existence of anhydrous sodium sulphate in three forms was found with certainty. These forms are (*a*) Thenardite or Na_2SO_4V, which separates above 32·5° C. from aqueous solution saturated at atmospheric pressure, (*b*) the form Na_2SO_4III, which appears when Na_2SO_4V, heated to high temperature, is cooled down to room temperature and (*c*) the hexagonal high temperature form Na_2SO_4II, which persists only at high temperature. Kracek and Gibson (1930), from the study of the salt in contact with its saturated solution in a pressure dilatometer, established the stable inversion.

$$Na_2SO_4I \rightleftarrows Na_2SO_4III \text{ at } 241^\circ C.$$
$$Na_2SO_4III \rightleftarrows Na_2SO_4IV \text{ at } 185^\circ C.$$

The inversion of Na_2SO_4IV to Na_2SO_4V could not be located with certainty because of the very small volume effect accompanying this change and that is why the 185° C. inversion actually represented the change $Na_2SO_4III \rightarrow Na_2SO_4V$. From the study of the heating and cooling curves of anhydrous Na_2SO_4, Kracek could identify the following phases:

Break	Phase Change	Temperature °C. Heating	Cooling
A	V $\rightarrow$ IV	197±2	
B	IV $\rightarrow$ III	210±2	
C	V $\rightarrow$ III	217±2	
D	IV $\rightleftarrows$ II	230±2	210, Irreversible in neutral.
E, K	II $\rightleftarrows$ I	238±2	234·5
F (H)	III $\leftrightarrows$ I	244±250	—
L	II $\rightleftarrows$ III	....	228

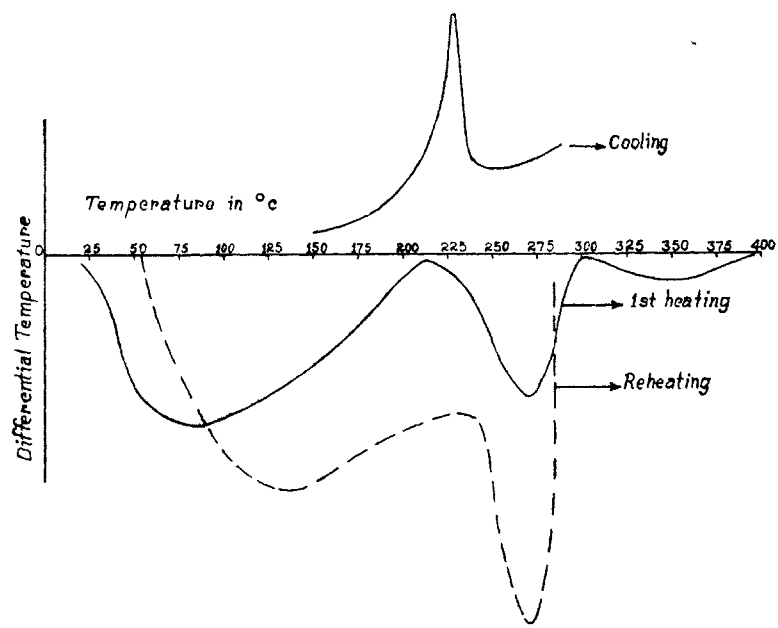
In the heating and cooling curves of Na_2SO_4, as obtained by Kracek, all the breaks can be seen there clearly.

Kracek and Kasanda (1930) could identify the high temperature hexagonal form of Na_2SO_4, i.e. Na_2SO_4II and also Na_2SO_4III from their X-ray diffraction study. But up to this time no definite information about the crystal structure of Na_2SO_4III was known. However, we (1953, 1954), by the application of Hesse (1945) and Stosick's (1949) method, have shown that Na_2SO_4III definitely belongs to the tetragonal crystal class with 16 molecules in the unit cell. While studying the crystal structure of Na_2SO_4III by X-ray diffraction method, we had carried out the differential thermal analysis of Na_2SO_4, the results of which are described below.

Experimental and Discussion

Sodium sulphate, used in this work, was prepared from Baker's 'Analyzed' anhydrous Na_2SO_4. The salt, dissolved in water, was precipitated again by pouring the warm solution into warm 95% alcohol. The solution was then filtered and the precipitate was freed from alcohol and water. Na_2SO_4, thus prepared, was then crushed into fine powders in an agate mortar. This powdered Na_2SO_4 was then used for differential thermal analysis.

The apparatus, used for this analysis, consisted of two micromaxes. One recorded the actual temperature of the furnace by means of a thermocouple inserted into a blank container, usually containing Al_2O_3, which do not transform even at high temperature. The other recorded any endothermic or exothermic reaction, occurring in the sample under investigations by means of another thermocouple, one end of which was dipped in the sample and the other end being dipped in the Al_2O_3 container. The furnace temperature was varied at regular interval, usually by 10° C. per minute and was kept constant by means of a powerstat. The powdered sample of Na_2SO_4 was placed in the second container. Both the Al_2O_3 and Na_2SO_4 containers were placed in the furnace. The thermo-e.m.f. developed due to the difference of temperature, which is also due to the heat of reaction, at the two ends of the thermocouple, was recorded by the usual potentiometric method. In our investigation, we actually used chromel-alomel thermocouple. The differential thermal curves during heating, cooling and reheating of Na_2SO_4 are given below.



Differential Thermal Curve of Na_2SO_4

Fig. 1

As it can be seen from the above Fig. 1, one peak at 90° C. was found during the first heating of Na_2SO_4. This peak was definitely due to the expulsion of occluded water. No breaks at 197° C. and 210° C. were found in this case. This was due to the fact that the first reaction in our case overlapped the other two.

The break which indicated the reaction $Na_2SO_4V \rightarrow Na_2SO_4III$ was also found by us at 215° C. During cooling, the peak, giving indications for the reaction $Na_2SO_4II \rightarrow Na_2SO_4III$ was also observed by us at 225° C. The curve, during reheating, is different from that found by Kracek (1929). In the present curve, the first peak was at 140° C. This peak may be due to the reaction $Na_2SO_4III \rightarrow Na_2SO_4IV$, which was not observed by Kracek, during reheating. The break at 230° C. clearly gave indications for the reaction of $Na_2SO_4IV \rightarrow Na_2SO_4II$.

Acknowledgements

The author wishes to express his sincerest gratitude to Prof. K. Banerjee, D.Sc., F.N.I., and to Dr. A. Bose, D.Sc., for their keen interest in the work. He is also grateful to the authorities of the Central Glass and Ceramic Research Institute for kindly permitting him to carry out the differential thermal analysis in their laboratories and to the Council of National Institute of Sciences of India for awarding him a research fellowship.

Abstract

The results of the differential thermal analysis of anhydrous sodium sulphate are described The transition temperatures for the various transformations, such as Na_2SO_4—Na_2SO_4III, Na_2SO_4II—Na_2SO_4III, Na_2SO_4III—Na_2SO_4IV and Na_2SO_4IV—Na_2SO_4II, have been found out clearly from the breaks of the curves.

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Issued October 7, 1955.