

## DEHYDRATION KINETICS OF SODIUM THIOSULPHATE PENTAHYDRATE IN THERMAL ENERGY STORAGE

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**Abstract**—The kinetics of dehydration of sodium thiosulphate pentahydrate have been determined by the thermogravimetric technique. The data have been analysed using Freeman and Carroll's [5] graphical technique and Zsako's [6] standard deviation calculation method. The energy of activation and order of the reaction for different transitions have been determined. The enthalpies of various transitions have been calculated from weight-loss data. The results show that the energy of activation is proportional to the enthalpy of transition in this system.

Energy storage  
pentahydrate

Thermal energy storage  
Dehydration kinetics.

Phase-change materials

Sodium thiosulphate

### NOMENCLATURE

$E$  = Energy of activation, kJ/mol  
 $\Delta H$  = Enthalpy of transition  
 $n$  = Order of reaction  
 $R$  = Gas constant,  $8.314 \times 10^3$  J/K mol  
 $T$  = Temperature, K  
 $\Delta T$  = Temperature difference  
 $t$  = Time, s  
 $w$  = Weight loss with time  
 $w_c$  = Weight loss on completion of reaction  
 $w_t$  = Weight loss at time  $t$ , ( $w_c - w$ )  
 $x$  = Concentration  
 $Z$  = Frequency factor

### INTRODUCTION

Solar energy is intermittent in nature. A low-cost storage unit is essential for its optimum utilization. Phase-change materials, particularly salt hydrates show great promise for energy storage applications [1, 2]. Salt hydrates have high heats of fusion and relatively low cost. However, they suffer from problems such as supercooling and phase segregation [1]. The use of nucleating and thixotropic thickening agents has been suggested [3, 4] to eliminate supercooling and phase segregation, respectively. In order to provide a sufficient driving force for rapid heat transfer, a temperature swing of 10–20° above the melting point is essential during the charging of the storage system. However, hydrated salts tend to lose an appreciable quantity of water of hydration when subjected to repeated cycles of charging and discharging over these extended temperature swings.

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This loss of water of hydration results in the degradation of the storage material which reduces the energy density of the storage system. Hence, this necessitates evaluation of the dehydration characteristics of salt hydrates for an optimum design of the storage system. The present study describes the kinetics of dehydration of the salt-hydrate, sodium thiosulphate pentahydrate in the temperature interval 323–423 K.

### EXPERIMENTAL

The sodium thiosulphate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) was recrystallized with double-distilled water. The melting point of the material was checked by heating and cooling curves. Thermogravimetric studies were carried out on Derivatograph, MOM Budapest type Paulik, Paulik & Erdy. A known amount of recrystallized  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  was taken in a calorimetric crucible and heated from room temperature to 523 K at a heating rate of 5 K/min.

### RESULTS AND DISCUSSION

The various reactions which occur as a result of heating salt-hydrates melting, dissociation and dehydration. DTA/TG curves of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  are shown in Fig. 1. The first endotherm in the DTA curve is due to the melting of the salt-hydrate. The second and third endotherms in the DTA are due to the formation of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  and anhydrous  $\text{Na}_2\text{S}_2\text{O}_3$ , respectively. Melting and dehydration of

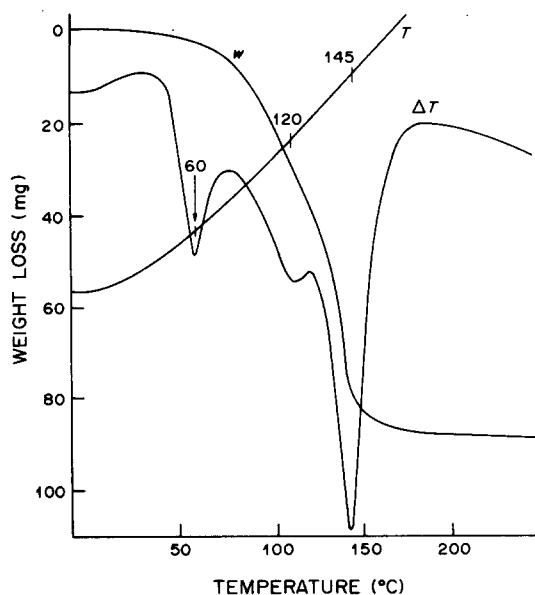
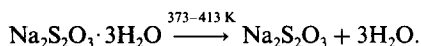
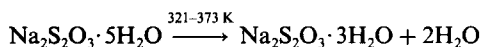


Fig. 1. DTA ( $\Delta T$ ), heating ( $T$ ) and weight loss ( $w$ ) curves for  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ .

the  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  occurs concomitantly, and complete dehydration occurs at 413 K. A small hump on the TG curve at 373 K indicates a metastable intermediate corresponding to the composition  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  (on the basis of weight-loss calculations). Hence, stepwise dehydration of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  may be summarized as



The loss of water of hydration with a rise in temperature was analysed by Freeman and Carroll's [5] technique in which the basic rate equations,  $-dx/dt = kx^n$  and  $k = Z \exp(-E/RT)$ , are used to

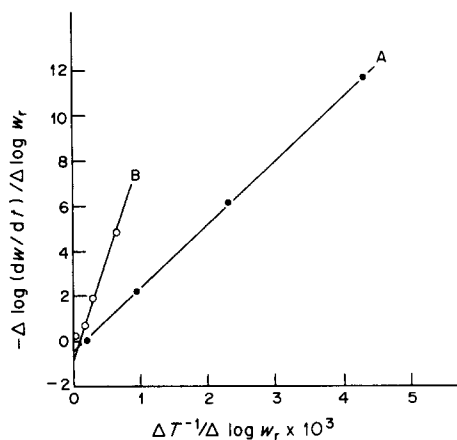


Fig. 2. Plot of  $-\Delta \log(dw/dt)/\Delta \log w_r$  vs  $\Delta T^{-1}/\Delta \log w_r$ .

Table 1. Kinetic parameters of dehydration

| (A) First transition: $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} \rightarrow \text{Na}_2\text{S}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + 2\text{H}_2\text{O}$ |                         |           |
|---|-------------------------|-----------|
| $\Delta H = 49.79 \text{ kJ/mol}$ $T_{(\text{final})} = 373 \text{ K}$  |                         |           |
|   | Freeman and Carroll [5] | Zsako [6] |
| Order of reaction ( $n$ )   | 0.45                    | 0.33      |
| Energy of activation, $E$ (kJ/mol)  | 55.88                   | 58.60     |
| (B) Second transition: $\text{Na}_2\text{S}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \rightarrow \text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$                          |                         |           |
| $\Delta H = 153.20 \text{ kJ/mol}$ $T_{(\text{final})} = 413 \text{ K}$   |                         |           |
|   | Freeman and Carroll [5] | Zsako [6] |
| Order of reaction ( $n$ )   | 1.0                     | 1.0       |
| Energy of activation, $E$ (kJ/mol)  | 173.51                  | 184.18    |

derive the expression

$$-(E/R)\Delta T^{-1}/\Delta \log w_r = \Delta \log(-dw/dt)/\Delta \log w_r - n \quad (1)$$

Fig. 2 shows a plot of  $\Delta \log(dw/dt)/\Delta \log w_r$  vs  $\Delta T^{-1}/\Delta \log w_r$  for both steps of the dehydration process. The energy of activation and order of reaction, as calculated from the slope and intercept, respectively, are reported in Table 1.

A computer program based on Zsako's [6] method of standard deviation for calculation of the energy of activation and order of the reaction was also developed. Table 1 shows that the energy of activation and order of the reaction obtained by this method are comparable to those obtained by Freeman and Carroll's method. The deviation in the values calculated by these methods can be attributed to the inaccuracy of the graphical techniques.

The enthalpy of transition for these two steps has been calculated from weight-loss data. Figure 3 shows that there is a linear correlation between  $\log w$  and the inverse of the absolute temperature ( $T^{-1}$ , K).

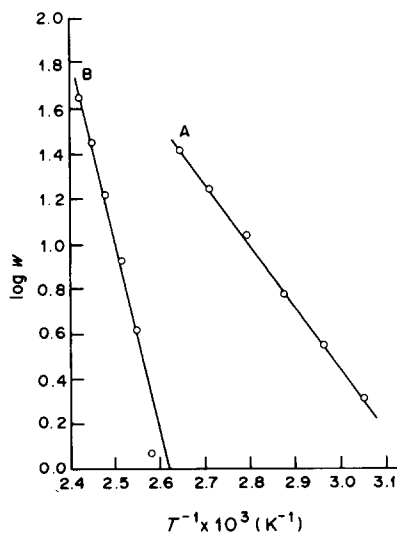


Fig. 3. Plot of  $\log w$  vs  $T^{-1} \times 10^3 \text{ K}^{-1}$ .

The first and second transitions are represented by lines A and B, respectively. The value of  $\Delta H$  has been calculated from the expression,

$$\log w = -\Delta H/2.303 RT + C. \quad (2)$$

This is similar to the expression given by Stepin *et al.* [7]. The  $\Delta H$ -values calculated from the slope of the linear plot in Fig. 3 for both steps are reported in Table 1. The results in Table 1 show that the ratio of the energy of activation of the first and second transition is almost comparable to the ratio of the enthalpy of transition for these steps.

### CONCLUSION

It can be concluded from this study that the dehydration of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  takes place in two steps, with the formation of metastable intermediate  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . The energy of activation of the first step, which results in formation of the trihydrate is less than that for formation of the anhydrous salt. The low activation energy of the first step is responsible for the partial loss of water of

crystallization when  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  is subjected to repeated cycles of melting and freezing over moderate temperature swings above the melting point in a storage system. The results obtained by the methods of Freeman–Carroll [5] and Zsako [6] are comparable.

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