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A STUDY ON THE THERMODYNAMIC PROPERTIES AND DEHYDRATION REACTION KINETICS OF SOME SALT-HYDRATES

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Abstract

Correlations were determined between heat capacity and temperature and phase change enthalpy of $Ba(OH)_2 \cdot 8H_2O$. The phase diagram and DSC curve of the binary system $Na_2CO_3 \cdot 10H_2O$-$Na_2HPO_4 \cdot 12H_2O$ were determined The kinetics of the dehydrating reaction of $Ba(OH)_2 \cdot 8H_2O$, $Na_2CO_3 \cdot 10H_2O$ and $Na_2HPO_4 \cdot 12H_2O$ were measured and theoretically analyzed by TG.

Keywords: DSC, kinetics, TG, thermal analysis, thermodynamics

Introduction

Recently, the energy crisis that people are facing has become more and more serious, hence it is important to find effective and cheap energy storage system and to develop new energy sources [1]. Inorganic phase change storage energy materials consist of inorganic salt hydrates and their eutectic mixture [2, 3].

In this paper the thermodynamic properties of some inorganic salt hydrates are determined, and the kinetics of their thermal dehydration reaction are studied.

Experimental

Determinations of the thermodynamic properties of $Ba(OH)_2 \cdot 8H_2O$

Specific heats

The specific heats were determined with an RD-I Series Heat Conducting Automatic Calorimeter, and a computer for handling the data, using α-Al_2O_3 as reference substance. The specific heats of solid $Ba(OH)_2 \cdot 8H_2O$ were determined from 288.25 to 340.15 K. The relationship between the specific

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heats and temperature was represented by: $C=a_o+a_1T+a_2T^2$. The coefficients a_o, a_1, a_2 were evaluated by linear regression using the LSQ method [14]. Numerically: $C/(\mathrm{J{\cdot}K^{-1}{\cdot}g^{-1}}=-23.027+144T/\mathrm{K}-2.089{\cdot}10^{-4}T^2/\mathrm{K}^2$; at ambient temperature $T=293.15$ K, $C=1.234$ $\mathrm{J{\cdot}K^{-1}{\cdot}g^{-1}}$.

Enthalpy of phase change of $Ba(OH)_2{\cdot}8H_2O$

First, the enthalpy of phase change of $Ba(OH)_2{\cdot}8H_2O$ $\Delta_s^lH_m$ was determined with an RD-I Series Heat Conducting Automatic Calorimeter, ($\Delta_s^lH_m$ (351.15 K) $=291.29$ $\mathrm{J{\cdot}g^{-1}}$) and then the DSC curve of the compound was recorded (Fig. 1) with a DuPont 9900 Thermal Analysis System (USA). The sample weight was 8.7500 mg and the heating rate 2 $\mathrm{deg{\cdot}min^{-1}}$. The enthalpy was found to be $\Delta_s^lH_m$ (351.15 K)$=290.50$ $\mathrm{J{\cdot}g^{-1}}$.

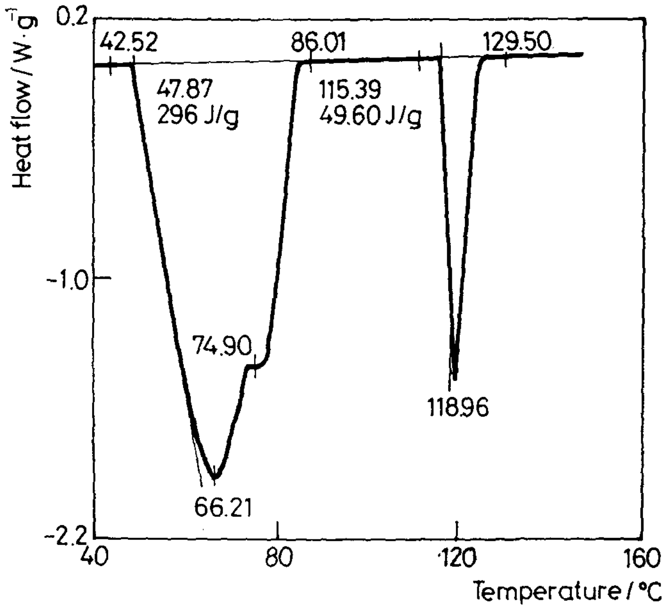

Fig. 1 The DSC curve of $Ba(OH)_2{\cdot}8H_2O$

Binary system of $Na_2CO_3{\cdot}10H_2O$-$Na_2HPO_4{\cdot}12H_2O$

Phase diagram of the binary system

The solidification points of the binary system were determined by DSC 20.00 g mixtures of $Na_2CO_3{\cdot}10H_2O$ and $Na_2HPO_4{\cdot}12H_2O$ were weighed, containing $Na_2HPO_4{\cdot}12H_2O$ mass fractions of 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80 and 0.90. In addition, 20.00 g of pure $Na_2CO_3{\cdot}10H_2O$ and

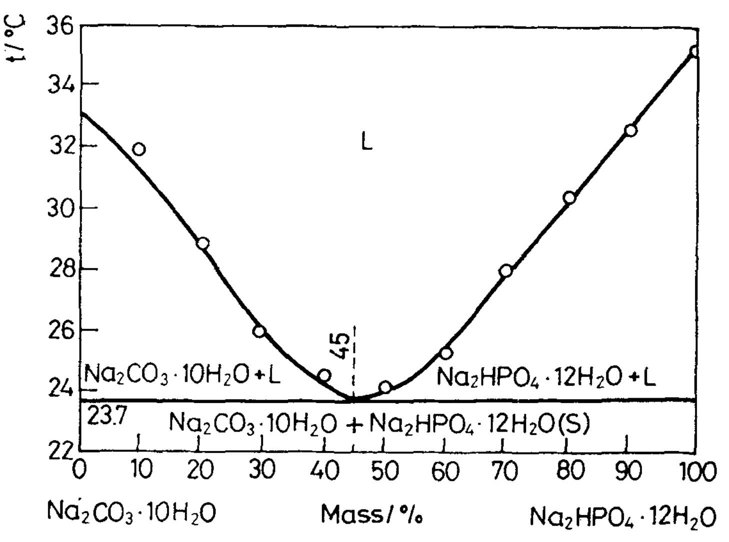

Fig. 2 The phase diagram of $Na_2CO_3\cdot10H_2O$–$Na_2HPO_4\cdot12H_2O$

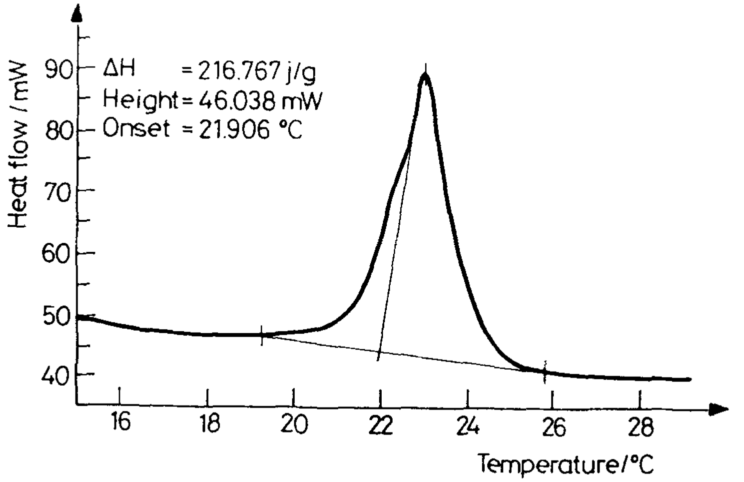

Fig. 3 The DSC curve of 0.45 (mass) $Na_2HPO_4\cdot12H_2O$

$Na_2HPO_4\cdot12H_2O$ each were weighed. The 11 samples were placed in separate test tubes and the cooling curves of the samples were determined. From the temperatures of phase change derived from the cooling curves, the phase diagram of the system $Na_2CO_3\cdot10H_2O$–$Na_2HPO_4\cdot12H_2O$ was constructed (Fig. 2). Figure 2 indicates that the eutectic point is at a mass fraction of $Na_2HPO_4\cdot12H_2O$ of 0.45 in the binary system. 20 g of a mixture containing a mass fraction of $Na_2HPO_4\cdot12H_2O$ of 0.45 was weighed and its phase change temperature was found to be 23.7°C.

Enthalpy of phase change

Considering the data in Fig. 2, 10.900 mg sample with a mass fraction of $Na_2HPO_4 \cdot 12H_2O$ of 0.45 was cycled three times through melting and freezing to have its DSC curve determined using PERKIN-ELMER 7 Series Thermal Analysis System (USA) (Fig. 3). The heating rate was 2 deg·min^{-1}, the enthalpy of phase change of the eutectic was 216.767 kJ·kg^{-1}.

Kinetics

The simple equations of a dehydration reaction are:

$$\frac{d\alpha}{dt} = Ae^{-E/RT}(1 - \alpha)^n \qquad (1)$$

$$\frac{d\alpha}{dT} = \frac{A}{\varphi} e^{-E/RT}(1 - \alpha)^n \qquad (2)$$

The kinetics of the reaction were studied by means of PERKIN-ELMER 7 Series Thermal Analysis System (USA). The operating conditions were: $Ba(OH)_2 \cdot 8H_2O$ mass 12.632 mg, heating rate 2.5 deg·min^{-1}; $Na_2CO_3 \cdot 10H_2O$ mass 19.919 mg, $Na_2HPO_4 \cdot 12H_2O$ weight 16.074 mg, heating rate 2 deg·min^{-1}. An empty crucible was used as reference. The TG curves of $Ba(OH)_2 \cdot 8H_2O$, $Na_2CO_3 \cdot 10H_2O$ and $Na_2HPO_4 \cdot 12H_2O$ are shown in Figs 4, 5 and 6.

Results and discussion

1. The relationship between the specific heats of solid $Ba(OH)_2 \cdot 8H_2O$ and temperature measured is:

$$C/(J \cdot K^{-1} \cdot g^{-1}) = -23.027 + 144T/K - 2.089 \cdot 10^{-4} T^2/K^2$$

At ambient temperature T=293.15 K, C=1.234 J·K^{-1}·g^{-1}. The enthalpy of phase change for $Ba(OH)_2 \cdot 8H_2O$ is: $\Delta_s^l H_m$ (351.15 K)=291.29 J·g^{-1} (determined with an RD-I Series Heat Conduct Automatic Calorimeter, China) and $\Delta_s^l H_m$ (351.15 K)=290.50 J·g^{-1} (determined with a DuPont 9900 Thermal Analysis System, USA). The enthalpies determined are similar, hence the results can be considered as reliable.

2. The phase diagram of the binary system $Na_2CO_3 \cdot 10H_2O$–$Na_2HPO_4 \cdot 12H_2O$ was constructed. Fractions of 0.45 (mass) $Na_2HPO_4 \cdot 12H_2O$ and 0.55

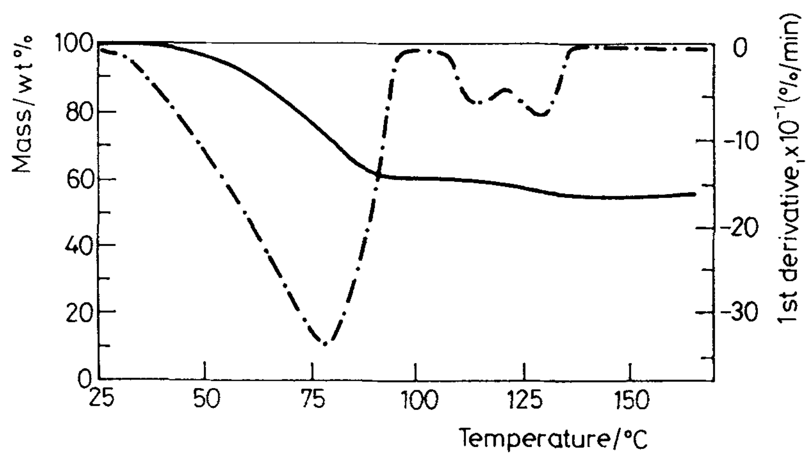

Fig. 4 The TG (DTG) curve of $Ba(OH)_2{\cdot}8H_2O$

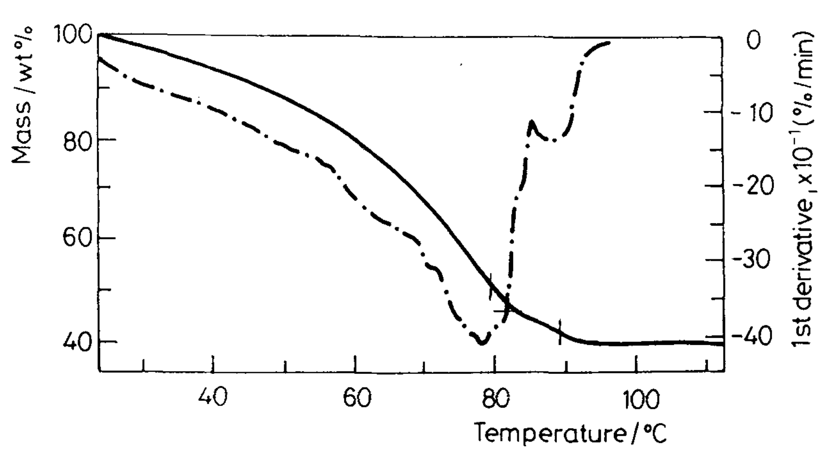

Fig. 5 The TG (DTG) curve of $Na_2CO_3{\cdot}10H_2O$

(mass) $Na_2CO_3{\cdot}10H_2O$ form a eutectic mixture at 23.7°C, the enthalpy of phase change being 216.767 $kJ{\cdot}kg^{-1}$.

3. There are three platforms in TG curve of $Ba(OH)_2{\cdot}8H_2O$, showing the eight molecules of water are lost in two steps, in the first step seven molecules of water, in the second step one molecule of water being lost:

$$Ba(OH)_2{\cdot}8H_2O_{(S)} \xrightarrow{35\sim110^{\circ}C} Ba(OH)_2{\cdot}H_2O_{(S)} + 7H_2O_{(g)}$$

$$Ba(OH)_2{\cdot}H_2O_{(S)} \xrightarrow{110\sim150^{\circ}C} Ba(OH)_2{\cdot}H_2O_{(g)}$$

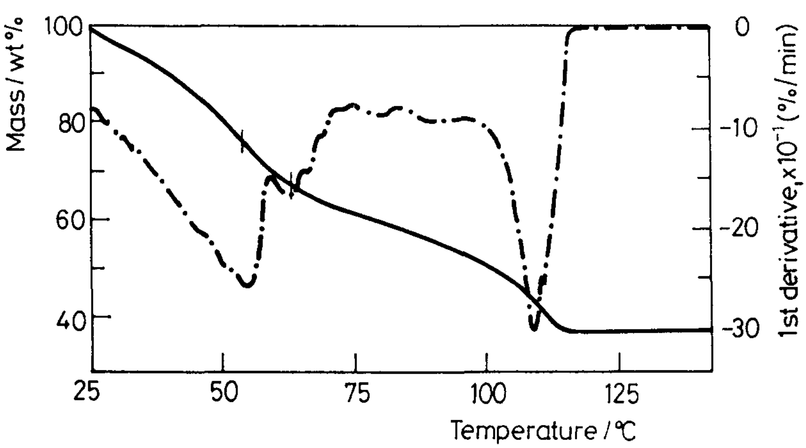

Fig. 6 The TG (DTG) curve of $Na_2HPO_4{\cdot}12H_2O$

The reaction activation energy E, and reaction order n of the two steps of dehydration reactions were obtained from TG and DTG curves by using the LSQ method.

E_1=58.08 kJ·mol^{-1} n_1=0.5 simple reaction

E_2=26.42 kJ·mol^{-1} n_2=0 interface reaction

4. From the TG and DTG curves of $Na_2CO_3{\cdot}10H_2O$ it can be concluded that ten molecules of water are lost in two steps, in the first step nine molecules of water, in the second step one molecule of water being lost

$$Na_2CO_3{\cdot}10H_2O_{(s)} \xrightarrow{25\sim83^\circ C} Na_2CO_3{\cdot}10H_2O_{(s)} + 9H_2O_{(g)}$$

$$Na_2CO_3{\cdot}H_2O_{(s)} \xrightarrow{83\sim98^\circ C} Na_2CO_{3(s)} + H_2O_{(g)}$$

The reaction activation energy E, reaction order n and frequency factor A of the two steps of dehydration were obtained from the TG and DTG curves and using the LSQ method.

E_1=36.068 kJ·mol^{-1} n_1=0 A_2=234.088 interface reaction

E_2=172.732 kJ·mol^{-1} n_2=0.5 A_2=4.83×10^{22} interface reaction

5. From the TG and DTG curves of $Na_2HPO_4{\cdot}12H_2O$ it can be concluded that 12 molecules of water are lost in three steps, in the first step five molecules

of water, in the second step five molecules of water and in the third step two molecules of water are lost:

$$Na_2HPO_4\cdot 12H_2O_{(s)} \xrightarrow{25\sim 57^\circ C} Na_2HPO_4\cdot 7H_2O_{(s)} + 5H_2O_{(g)}$$

$$Na_2HPO_4\cdot 7H_2O_{(s)} \xrightarrow{57\sim 105^\circ C} Na_2HPO_4\cdot 2H_2O_{(s)} + 5H_2O_{(g)}$$

$$Na_2HPO_4\cdot 2H_2O_{(s)} \xrightarrow{105\sim 115^\circ C} Na_2HPO_{4(s)} + 2H_2O_{(g)}$$

The reaction activation energy E, reaction order n and frequency factor A of three steps of dehydration were obtained from the TG and DTG curves using the LSQ method.

$E_1=37.054\ kJ\cdot mol^{-1}$ $n_1=0$ $A_1=1080.47$

$E_2=-43.487\ kJ\cdot mol^{-1}$ $n_2=0$ $A_2=5.78\times\cdot 10^{-9}$

$E_3=124.19\ kJ\cdot mol^{-1}$ $n_3=0.5$ $A_3=5.197\times 10^{14}$

References

1 S. Kakac, E. Paykong and Y. Yener, Storage of solar thermal energy, NATO ASI Ser.; Ser.E, 1989, p. 167.
2 S. Kranse and R. Tamme, J. Solar Eng., 226 (108) 1986.
3 Lao Yunliang and Shen Zhongnan, Weapons Industry J., 21 (1983) 4 (China).
4 Zhang Xiaodi, Appl. Regres. Anal., Zhejiang University Publishing House (China).

Zusammenfassung — Es wurden Beziehungen zwischen der Wärmekapazität, der Temperatur und der Phasenumwandlungsenthalpie von $Ba(OH)_2\cdot 8H_2O$ ermittelt. Weiterhin wurde das Phasendiagramm und die DSC-Kurve des binären Systems $Na_2CO_3\cdot 10H_2O$-$Na_2HPO_4\cdot 12H_2O$ bestimmt. Mittels TG wurde die Dehydratationsreaktion von $Ba(OH)_2\cdot 8H_2O$, $Na_2CO_3\cdot 10H_2O$ und $Na_2HPO_4\cdot 12H_2O$ gemessen und theoretisch ausgewertet.