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THE MEASUREMENT OF HYDRATION HEATS FOR MAGNESIUM CHLORIDE WITH LOW WATER BY MEANS OF DSC

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Abstract

The heats of hydration reactions for $MgCl_2·4H_2O$ and $MgCl_2·2H_2O$ include two parts, reaction enthalpy and adsorption heat of aqueous vapor on the surfaces of magnesium chloride hydrates. The hydration heat for the reactions $MgCl_2·4H_2O+2H_2O \rightarrow MgCl_2·6H_2O$ and $MgCl_2·2H_2O+2H_2O \rightarrow MgCl_2·4H_2O$, measured by DSC-111, is –30.36 and –133.94 kJ mol^{-1}, respectively. The adsorption heat of these hydration processes, measured by head-on chromatography method, is –13.06 and –16.11 kJ mol^{-1}, respectively. The molar enthalpy change for the above two reactions is –16.64 and –118.09 kJ mol^{-1}, respectively. The comparison between the experimental data and the theoretical values for these hydration processes indicates that the results obtained in this study are quite reliable.

Keywords: adsorption heat, DSC, gas chromatography, hydration heat, magnesium chloride with low water

Introduction

Magnesium chloride is a basic material for the chemical industry [1, 2], and it has wide applications in metallurgy, architectural material and textile industry [3, 4]. It is also a material for fire-resistant material, cryogen and compound fertilizer productions [5, 6]. The fully dehydrated magnesium chloride is a good material for electrolytic metal magnesium production. Magnesium chloride has a strong adsorptive ability with water. So, it is also used as a drying agent. Many successful works have been done on the dehydration of bischophite [7–12]. But, the dehydration processes of magnesium chloride hydrates is actually inseparably connected with the hydration process. The later one will influence the dehydration process. The scientific research on its hydration process is not reported so far.

The hydration processes of magnesium chloride hydrates are accompanied with intensively exothermal phenomena. So, it is practicable that its calorific effects are measured by differential scanning calorimetry.

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The aims of this study are to investigate the thermal behavior of hydration processes for magnesium chloride hydrates and to obtain primary data for the research of both processes.

Speil equation [13] is widely used in heat measurement.

$$A=\int_{t_1}^{t_2}\Delta T\mathrm{d}t=\frac{m_a\Delta H}{g\lambda_S}=K(m_a\Delta H)=KQ_P \tag{1}$$

$$Q_P=\frac{A}{K} \tag{2}$$

In the above equation:

A – peak area of differential thermal curve, λ_S – thermal conductivity of the sample, ΔT – temperature difference between the sample and reference, K – coefficient, m_a – the mass of active material in the sample, ΔH – the enthalpy difference of per unit active material, g – coefficient connecting with the instrument.

It can be concluded from the above equation that constant pressure heat, Q_P, is linear to the peak area of the differential thermal curve, A.

Experimental

The experimental equipment diagram for measurement of hydration heats of magnesium chloride with low water is shown in Fig. 1, which consists of three parts, water vapor supplying system, reaction and reference tubes and DSC-111.

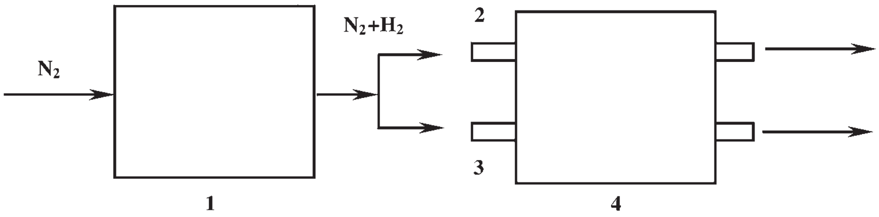

Fig. 1 Diagram for measurement of hydration heats of magnesium chloride with low water; 1 – water vapor supplying system; 2 – sample tube; 3 – reference tube; 4 – sample stove of DSC-111

The water vapor supplying system is a device, from which water steam is carried by N_2 through a tightly sealed up the water container, which is put in a carefully temperature controlled water bath. Adsorption and reference tubes are made of glass, with the same inner diameter as Φ6 mm and length of 20 cm, which are put in the sample stove of DSC-111 (SETARAM, made in France). A Karlvi thermal probe is used here.

The experimental materials are $MgCl_2·3.98H_2O$ and $MgCl_2·1.95H_2O$ with a graininess of 30~80 mesh, which are obtained from pure $MgCl_2·6H_2O$ after dehydration in the fluid system [14]. The compositions of the samples are given in Table 1.

Table 1 The compositions of the samples in mass%

Sample	$MgCl_2$	MgO	H_2O	Molar ratio
$MgCl_2{\cdot}3.98H_2O$	57.01	0	42.99	3.98
$MgCl_2{\cdot}1.95H_2O$	72.07	1.37	26.56	1.95

The hydration reactions of magnesium chloride hydrates are as follows:

$$MgCl_2{\cdot}4H_2O+2H_2O \rightarrow MgCl_2{\cdot}6H_2O \quad (1)$$

$$MgCl_2{\cdot}2H_2O+2H_2O \rightarrow MgCl_2{\cdot}4H_2O \quad (2)$$

The experimental conditions, for reaction (1) and reaction (2), are shown in Table 2.

Table 2 Experimental conditions for reaction (1) and reaction (2)

Content	Reaction (1)	Reaction (2)
Sample mass/mg	82.30	78.20
Temperature range/°C	10~700	10~700
Temperature increase rate/K min^{-1}	10	10
Carrying gas	$N_2(g)$	$N_2(g)$
Assumed temperature/°C	60	80
Experimental temperature/°C	50	70
Stable temperature/°C	54.99	75.31
Temperature of water bath/°C	21.3	21.2
Fluid rate of nitrogen/mL min^{-1}	69.4	65.79

In order to measure the adsorption heats of magnesium chloride hydrates to water, a gas chromatograph is used meanwhile.

The water vapor is carried by nitrogen gas into analytic column in the gas chromatography, GC-9AM, made in Japan, along with a data processor, C-R4A. The analytic chromatographic column is GDX 301, Φ 3.0 mm×1.0 m, to which magnesium chloride reactor is connected. The referential chromatographic column is GDX 301, Φ 3.2 mm×3.6 m.Temperature of the column chamber is ranged from 40 to 90°C. The injector temperature is 85°C, while TDC, 100°C. Total pressure is 4.9 atm, while the pressure for chamber 1 and chamber 2 is 1.2 and 1.1 atm respectively. Current intensity of monitor is 80 mA. The fluid rate of carrier gas for chamber 1 and 2 is 90 and 45 mL min^{-1}, respectively.

Results and discussion

The results for thermal analysis

The thermal fluid curve of the dehydration processes for $MgCl_2{\cdot}3.98H_2O$ and $MgCl_2{\cdot}1.95H_2O$, recorded by DSC-111, is shown in Figs 2 and 3, respectively, from

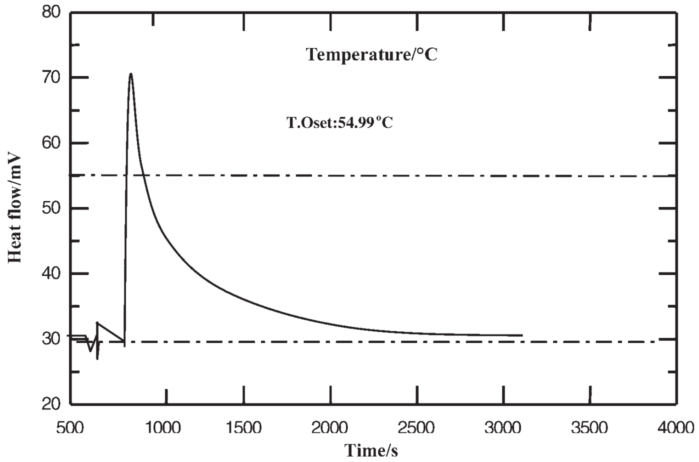

Fig. 2 DSC-111 thermal fluid curve of $MgCl_2 \cdot 3.98H_2O$

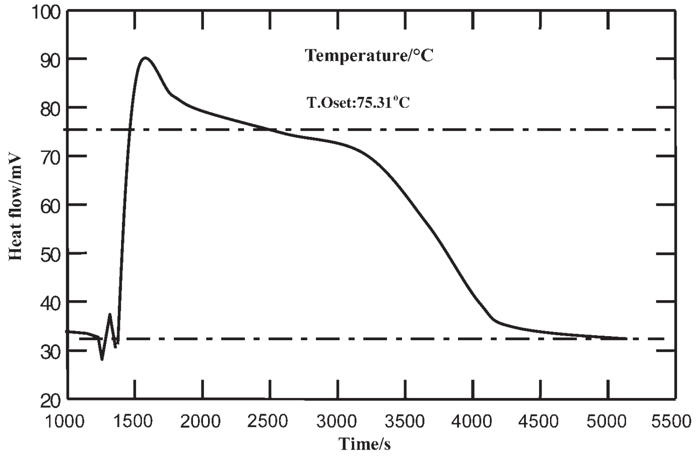

Fig. 3 DSC-111 thermal fluid curve of $MgCl_2 \cdot 1.95H_2O$

which the area of thermal fluid curve for the blank assay has been subtracted. The thermodynamics data are given in Table 3.

Table 3 Calorific effect data for the hydration processes of $MgCl_2 \cdot 4H_2O$ and $MgCl_2 \cdot 2H_2O$

Reaction	Q_P/J g^{-1}	Q_P/kJ mol^{-1}
(1)	–181.220	–30.26
(2)	–1022.433	–133.94

From Table 3, it is easy to find that magnesium chloride with two moles water gives out more extensive heat than that with four moles water does.

Results for gas chromatography analysis

Actually, the data given in Table 3 include reaction heat and adsorption heat. In order to obtain the hydration heat for magnesium chloride with low water, gas chromatographic thermodynamics study on their hydration processes has been carried out.

The adsorptive capacity of adsorbent has the relationship to the area of chromatographic curves [15].

$$\Gamma=\frac{KF'_{\mathrm{C}}}{\mu_1 w}A_{\mathrm{C}} \tag{3}$$

In the above equation, Γ is adsorptive capacity of adsorbent over unit mass adsorbate. A_{C} is the area of chromatography curve. K is the constant of TCD. w is the mass for adsorbate. F'_{C} is the calibrated fluid rate of carrier gas, while, μ_1 is moving speed of data recording paper.

$$F'_{\mathrm{C}}=j\frac{P_0-P_{\mathrm{W}}}{P_0}\frac{T_{\mathrm{C}}}{T_{\mathrm{r}}}F_{\mathrm{C}} \tag{4}$$

In Eq. (4), P_0 and P_{W} is saturated aqueous vapor pressure at experimental temperature and atmospheric pressure, respectively, while j is a coefficient [16]. T_{C} and T_{r} is chromatographic column temperature and room temperature, respectively.

The hydration processes of $MgCl_2\cdot3.98H_2O$ and $MgCl_2\cdot1.95H_2O$ under certain temperature and water vapor partial pressure were measured by gas chromatography

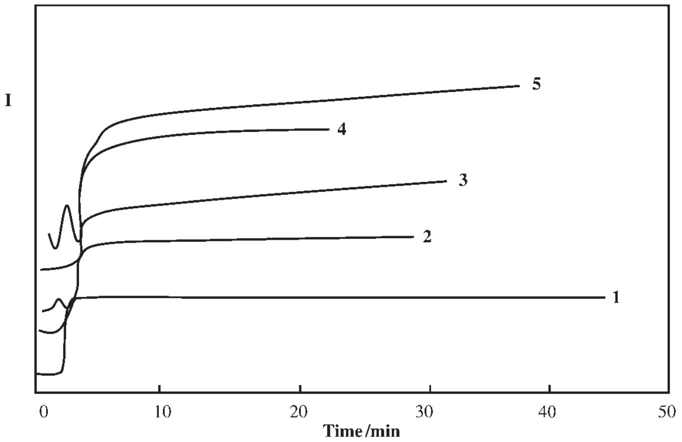

Fig. 4 The hydration gas chromatography curves for $MgCl_2\cdot3.98H_2O$ at 60°C
curve 1: P_{H_2O}=1.12, $T_{\mathrm{water\text{-}bath}}$=20.2°C; curve 2: P_{H_2O}=1.53, $T_{\mathrm{water\text{-}bath}}$=24.05°C; curve 3: P_{H_2O}=1.46, $T_{\mathrm{water\text{-}bath}}$=24.0°C; curve 4: P_{H_2O}=1.29, $T_{\mathrm{water\text{-}bath}}$=20.03°C; curve 5: P_{H_2O}=1.83, $T_{\mathrm{water\text{-}bath}}$=24.0°C

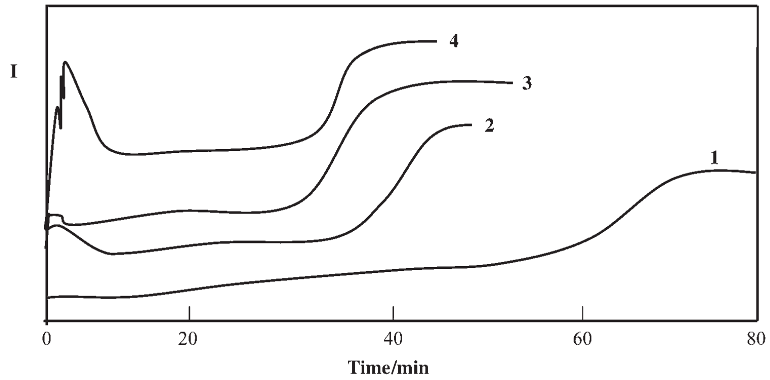

Fig. 5 The hydration gas chromatography curves for $MgCl_2 \cdot 1.95H_2O$ at 70°C
curve 1: P_{H_2O}=1.29, $T_{water\text{-}bath}$=24.0°C; curve 2: P_{H_2O}=1.46, $T_{water\text{-}bath}$=24.0°C;
curve 3: P_{H_2O}=1.53, $T_{water\text{-}bath}$=20.02°C; curve 4: P_{H_2O}=1.83, $T_{water\text{-}bath}$=24.0°C

and shown in Figs 4 and 5, from which, data for adsorption isotherms are obtained and listed in Tables 4 and 5, and plotted in Figs 6 and 7 correspondingly.

These adsorption isotherms are in good agreement with the Boltzman equation. All the data, in Fig. 7, are nearly located on the curves for Boltzman equation.

Table 4 Data of adsorption isotherms for $MgCl_2 \cdot 3.98H_2O$

No.	P_{H_2O}/kP$_a$	Γ/mol kg^{-1}				
		60°C	55°C	50°C	45°C	40°C
1	1.12	0	0.89	1.94	2.73	3.59
2	1.29	2.03	2.74	3.72	4.75	5.37
3	1.46	2.29	4.15	5.02	5.66	6.29
4	1.53	2.61	4.49	5.73	6.20	7.63
5	1.83	2.82	4.91	6.10	6.27	8.27

Table 5 Data of adsorption isotherms for $MgCl_2 \cdot 1.95H_2O$

No.	P_{H_2O}/kP$_a$	Γ/mol kg^{-1}		
		70°C	80°C	90°C
1	1.12	13.36	11.86	3.49
2	1.29	15.51	13.23	8.74
3	1.46	17.73	14.08	12.83
4	1.53	18.31	14.49	13.21
5	1.83	19.15	14.68	14.00

Here, adsorption heat can be defined by Clausius–Clapeyron equation as follows [17]:

$$Q=RT^2\left[\frac{\partial\ln(P/P^0)}{\partial T}\right]_q=-R\left[\frac{\partial\ln(P/P^0)}{\partial(1/T)}\right]_q \tag{5}$$

Selecting Q as 3.63, 4.47 and 13.50, 13.31 mol kg^{-1} from Fig. 6 and Fig. 7 respectively, we obtain the corresponding equilibrium partial pressure of aqueous va-

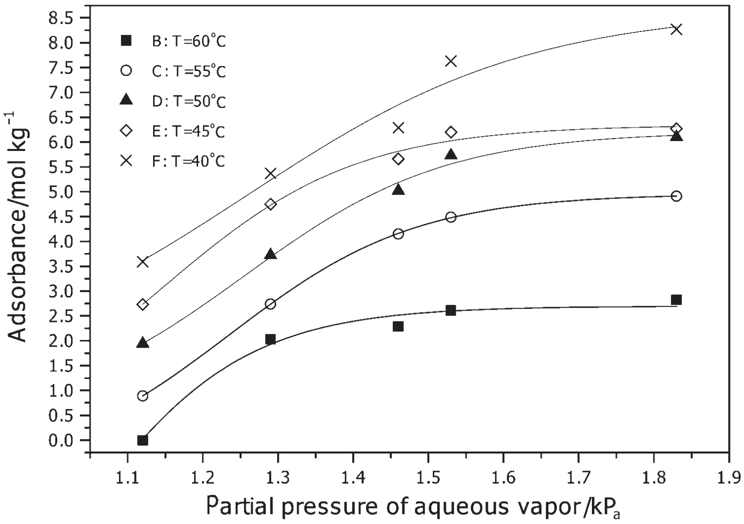

Fig. 6 The abdsorption isotherm of $MgCl_2\cdot3.98H_2O$ to aqueous vapor

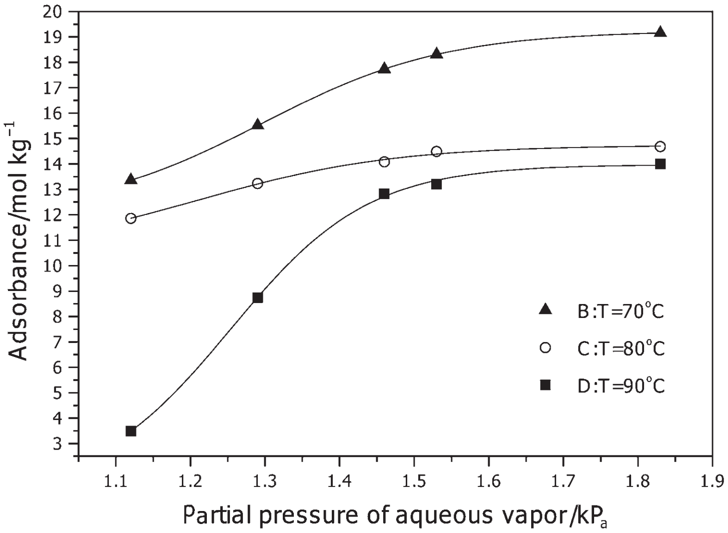

Fig. 7 The adsorption isotherm of $MgCl_2\cdot1.95H_2O$ to aqueous vapor

por, P. There is a linear relationship between $\ln(P/P^0)$ and $1/T$ (show in Figs 8 and 9). The adsorption heat equals to minus R times the slope of line.

From Figs 8 and 9, we get the adsorption heats of magnesium chloride hydrates, which are shown in Table 6.

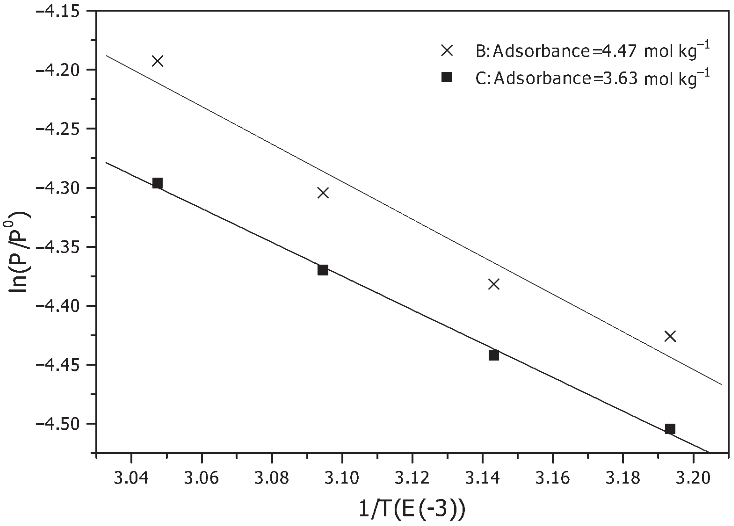

Fig. 8 The diagram of $\ln(P/P^0)$ to $1/T$ for the isotherms of $MgCl_2 \cdot 3.98H_2O$, when adsorbances are 4.47 and 3.63 mol kg^{-1}

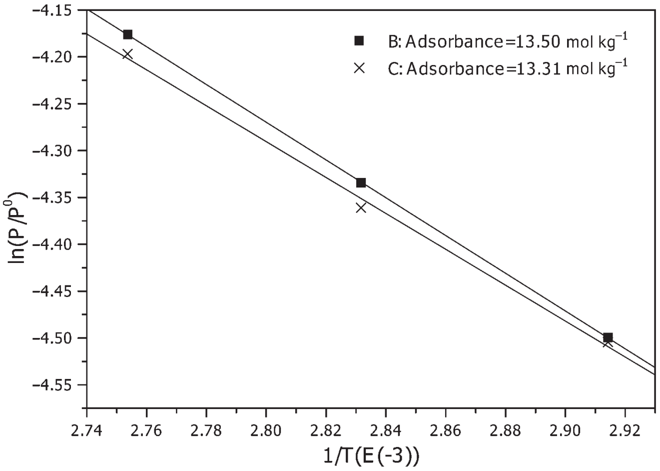

Fig. 9 The diagram of $\ln(P/P^0)$ to $1/T$ for the isotherms of $MgCl_2 \cdot 1.95H_2O$, when adsorbances are 13.50 and 13.31 mol kg^{-1}

Table 6 Adsorption heats of magnesium chloride hydrates to aqueous vapor

Adsorbent	Adsorbance Γ/mol kg^{-1}	Adsorption heats Q/KJ mol^{-1}
$MgCl_2 \cdot 3.98H_2O$	3.63	–13.06
	4.47	–14.17
$MgCl_2 \cdot 1.95H_2O$	13.31	–15.59
	13.50	–16.61

The average adsorption heat for $MgCl_2 \cdot 4H_2O$ and $MgCl_2 \cdot 2H_2O$ to aqueous vapor is –13.62 and –15.85 kJ mol^{-1}, respectively. Assume that the adsorption heats are constant within a small temperature range, so the molar enthalpy changes for the reaction (1) and reaction (2), which are mentioned ahead, are deduced:

Reaction (1): $\Delta rH_{327.7,m}= -30.26 - (-13.62)= -16.64$ kJ mol^{-1}
Reaction (2): $\Delta rH_{373.46,m}= -133.94-(-15.85)= -118.09$ kJ mol^{-1}

Theoretical values

The theoretical values of enthalpy changes for those hydration processes are deduced under the following three assumptions.

1. Aqueous vapor was treated as perfect gas;
2. The pressure influence was neglected;
3. All the materials involved in above reactions are at normal state.

Kirchhoff equation is available in these processes.

$$\Delta_r H^0_{T,m} = \Delta H^0_{298.15,m} + \int_{298.15}^{T} \Delta_r C_{p,m} \mathrm{d}T \quad (6)$$

With the help of physical chemistry data [18], we get the theoretical standard molar enthalpy changes for above reactions.

$$\Delta_r H^0_{327.7,m} = -18.22 \text{ kJ mol}^{-1};\ \Delta_r H^0_{373.46,m} = -134.12 \text{ kJ mol}^{-1}$$

Table 7 gives the comparison of the experimental data and standard molar reaction enthalpy for reaction (1) and reaction (2).

Table 7 The comparison of the experimental data and theoretical values

Reaction equation	Reaction temperature/ °C	Experimental data, $\Delta_r H_{T,m}$/ KJ mol^{-1}	Theoretical data, $\Delta_r H^0_{T,m}$/ KJ mol^{-1}	Errors/%
$MgCl_2 \cdot 4H_2O+2H_2O \rightarrow MgCl_2 \cdot 6H_2O$	54.99	–16.64	–18.22	8.67
$MgCl_2 \cdot 2H_2O+2H_2O \rightarrow MgCl_2 \cdot 4H_2O$	75.31	–118.09	–134.12	11.95

It is found from Table 7 that the error between the experimental results and theoretical values of the hydration processes for $MgCl_2 \cdot 4H_2O$ and $MgCl_2 \cdot 2H_2O$ is 8.67 and

11.95%, respectively. It is acceptable, because the later one was based on three assumptions given above, meanwhile the former one used materials with 3.98 and 1.95 molar water, rather than 4 and 2 molar water, which were under experimental state.

Conclusions

We measured thermodynamic data concerning the hydration processes for the magnesium chloride with low water using DSC and gas chromatography methods .The results obtained by two different methods are in good agreement, which means the data we obtained in this study are relatively reliable and can be used as primary data for the study of dehydration and hydration processes for magnesium chloride hydrates.

We use DSC method in this study, rather than DTA , because the former one's basic line of thermal fluid curve is relatively more stable than that of the latter one, and has slight influence from thermal resistant, which does not greatly change with the temperature variations.

The thermodynamic data, concerning the hydration processes for $MgCl_2{\cdot}H_2O$ and $MgCl_2$ are not obtained in this work, because these processes are usually accompanied by many side-reactions. In order to avoid them, protection gas, usually HCl (*g*), needed in the reaction system, which would cause a bad influence on the experimental instrument. This work remains for further studies.

References

1 Q. Gou, Chemical Engineering of Shanxi, 3 (1997) 22.
2 P. Shen, Environmental Protection, 10 (1998) 20.
3 D. Tie, J. Construction Engineering of Shenyang, 6 (1990) 88.
4 H. Wang, Printing and Dyeing, 19 (1993) 46.
5 G. Zhang, Overseas Animal Husbandry, 3 (1989) 33.
6 Y. Dong, Feed and Animal Husbandry, 6 (1992) 29.
7 X. Chen, J. Middle South College of Mining Industry, 1 (1979) 15.
8 J. Chen, J. Sea, Lake and Chemical Industry, 4 (2000) 17.
9 H. Moscowitz, Ind. Eng. Chem. Prod. Dev., 17 (1978) 156.
10 Y. Kirsh and S. Yariv, J. Thermal Anal., 32 (1987) 392.
11 J. Chen, J. Sea, Lake and Chemical Industry, 5 (2000) 4.
12 J. Chen, J. Sea and Lake Salt and Its Chemical Industry, 6 (1998) 19.
13 Ding, Enyong, Liang, Xuehai, Fenxi Huaxue, 21 (1993) 660.
14 J. Chen, J. Qinghai University, 5 (1999) 5.
15 Zh. Ye, Chemical Adsorption Separation Process, Press of Petrochemical Engineering, Beijing 1989, p. 68.
16 Science and Technology University of Chengdu, Handbook for Anal. Chem., Press of Chem. Ind., Beijing, 5 (1985) 195.
17 R. Aa. Beebe, P. L. Evans and T. C. W. Kleinsteuber, J. Phys. Chem., 4 (1966) 1009.
18 Handbook of Phys. Chem. 55th ed., New York 1989, p. 352.