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THERMODYNAMIC STUDY OF THE MOLTEN SALT BINARY SYSTEM $KHSO_4$–$NaHSO_4$

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Abstract

The partial molar enthalpies of mixing of $NaHSO_4$ and $KHSO_4$ have been measured at 528 K by dropping samples of pure compounds into molten mixtures of $NaHSO_4$ and $KHSO_4$ in Calvet calorimeter. From these values the molar enthalpy of mixing has been deduced.

The same method has been used for the determination of the heat capacity of the two pure compounds in the solid and liquid states.

The phase diagram of this system has been confirmed by conductometric and thermal analysis methods.

By an optimization method the excess entropy of the liquid mixtures was also calculated.

Keywords: catalysis, ionic melts, thermodynamics

Introduction

The vanadium based catalyst used industrially for SO_2 oxidation is a supported liquid phase (SLP) catalyst with the catalytic melt distributed in the pores of a kieselguhr support. The catalytic melt is well described by the model melt–gas system $M_2S_2O_7$–M_2SO_4–$MHSO_4$–V_2O_5/SO_2–O_2–SO_3–H_2O–N_2 (*M*=alkali) at 400–500°C.

For years we have been concentrating on optimizing the composition of the alkali mixture in order to find superior catalysts with low temperature of deactivation as well as applying the catalytic system on removal of SO_x from power plant off-gases, in this case the oxidation of SO_2 to SO_3 is followed by condensation of H_2SO_4 as a commercial product [1].

In this connection, knowledge of thermodynamic properties of the solvent components is useful for the design of improved catalysts.

The present paper concerns our experimental results (heat of mixing of the liquid mixtures, heat capacity of the pure components and phase diagram), obtained for the binary $KHSO_4$–$NaHSO_4$ system. This system is probably interesting because it

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presents an eutectic point with a low temperature of melting [2], and can be used as solvent for dissolve the other salts, V_2O_5, $M_2S_2O_7$, etc.

Experimental

Chemicals

$KHSO_4$ and $NaHSO_4$ were from Merck (suprapur 99%). These chemicals were dried at 110°C and stored in a drybox and also kept in sealed ampules until use [3, 4].

Thermal measurements

Heat capacity and partial molar enthalpies are obtained by drop of samples in the Pyrex cell loaded at the bottom of the Pyrex calorimeter tube. The temperature of the Calvet microcalorimeter was regulated to within ±0.2°C. The calibration of the calorimeter was realized after each experiment by dropping gold samples in the experimental cell.

Differential enthalpic analysis (DEA) was performed in the Calvet calorimeter. The very low heating rate (10°C h^{-1}) was controlled by a linear temperature programmer (Eurotherm). The calibration constant is a function of the temperature and of the state, solid or liquid, of the mixtures. Therefore we have determined its value before and after melting.

Results

Heat capacity

The heat capacity of $NaHSO_4$ or $KHSO_4$ is obtained by measuring the difference of the enthalpy of the sample, $H(T)–H(T_0)$ between the room temperature, T_0, and the experimental temperature, T.

To obtain C_p we assume that $H(T)$ is equal to: $H(T)=a+bT+cT^2$. Therefore

$$H(T)-H(T_0)=b(T-T_0)+c(T^2-T_0^2) \text{ and } C_p=b+2cT$$

The difference, $H(T)–H(T_0)$, is measured for several temperatures and the coefficients b and c are obtained from the experimental values by linear regression.

To obtain the heat capacity of the liquid compound we must substract the enthalpic variation from the heat of melting of the samples and the enthalpic variation of the solid samples between the room temperature and its melting point.

Previously we have measured the temperature and enthalpy of fusion of the two salts

$$\Delta_{fus}H(KHSO_4)=16.2 \text{ kJ mol}^{-1} \text{ (this work) and } T_{fus}(KHSO_4)=208°C \text{ [3]}$$

$$\Delta_{fus}H(NaHSO_4)=17.3 \text{ kJ mol}^{-1} \text{ (this work) and } T_{fus}(NaHSO_4)=182°C \text{ [4]}$$

The experimental values of the enthalpic variations at different temperatures for each salts in the solid and liquid state are listed in Table 1. In this table we can see that the number of determinations for $KHSO_4$ in the solid state is greater than for $NaHSO_4$, this is due to the fact that a solid–solid transition of $KHSO_4$ occurs at 178°C [3] or 164 and 181°C [5].

Table 1 Enthalpy variation of $KHSO_4$ and $NaHSO_4$ *vs.* *T*

Salts	T/°C	ΔH/kJ mol^{-1}	State
$NaHSO_4$	81	7.10	solid
	120	11.62	solid
	168	17.85	solid
	209	43.45	liquid
	228	45.81	liquid
	255	54.86	liquid
	258	57.48	liquid
$KHSO_4$	79	7.10	solid
	119	12.12	solid
	158	18.54	solid
	169	22.69	solid
	186	23.93	solid
	198	26.26	solid
	205	28.42	solid
	208	44.72	liquid
	227	50.07	liquid
	245	53.25	liquid
	254	60.30	liquid
	256	59.66	liquid

In order to determine with accuracy the temperature and enthalpy of solid–solid transition of $KHSO_4$ we made a thermal analysis with a slow rate heating (5°C h^{-1}). We obtained a thermal effect at 178°C and another one with an offset temperature at 208°C. The enthalpy variations associated are: 2.11 and 16.2 kJ mol^{-1} respectively.

Table 2 Heat capacity of $KHSO_4$ and $NaHSO_4$:$C_p=b+2ct$ (*t* in °C)

Salts	Temperature range /°C	C_p		State
		b/J mol^{-1} K^{-1}	$2c$/J mol^{-1}	
$NaHSO_4$	25–180	124.7 (±2.3)	0	solid
	185–270	246.1 (±12.2)	0	liquid
$KHSO_4$	25–200	90.6 (±0.6)	0.56 (±0.04)	solid
	210–270	287.0 (±14.3)	0	liquid

The enthalpy of melting obtained in this work is little different from the one obtained earlier by DSC [3]. We think that the value obtained here is more correct because in DSC measurements the salt is loaded in a small Pyrex crucible sealed by flame. This operation can cause the partial decomposition of the salt.

No difference between the heat capacity of the two solid phases of $KHSO_4$ has been found. The values obtained are presented in Table 2.

Heat of mixing

The liquid partial molar enthalpies of $KHSO_4$ and $NaHSO_4$ were obtained by dropping samples of each compound, at room temperature, in the experimental crucible containing a melt mixture at T. The measurements have been done at T=255°C for five compositions:

$$x(KHSO_4)=0,\ 0.485,\ 0.522,\ 0.545,\ 1.$$

For obtain the heat of mixing, we must substract to the measured thermal effect, the term $H(T)–H(T_0)$ of the dropped compound. This term has already been measured prior to the experiments and the results have been used for the determination of the heat capacity. Results are listed in Table 3.

Table 3 Measured partial molar enthalpy of liquid $KHSO_4$ and $NaHSO_4$ at 255°C

$x(KHSO_4)$	$\Delta_{mix}H(NaHSO_4)$/J mol^{-1}	$\Delta_{mix}H(KHSO_4)$/J mol^{-1}
0	–	–3993
0.485	–1002	–1315
0.522	–1001	–1173
0.545	–1157	–1099
1	–6644	–

We have assumed that the variation of the molar heat of mixing, $\Delta_{mix}H$, *vs*. the composition of the melt is given by the analytical expression:

$$\Delta_{mix}H=x(1–x)[A+Bx]$$

where $x=x(KHSO_4)$.

From the experimental results (liquid partial molar enthalpies) we have obtained by linear regression the A and B coefficients.

$$A=–3953(\pm 183)\ \text{J mol}^{-1} \text{ and } B=–2494(\pm 75)\ \text{J mol}^{-1}$$

The minimum of the curve representing $\Delta_{mix}H$ *vs*. $x(KHSO_4)$ is obtained for $x(KHSO_4)=0.56$, $\Delta_{mix}H=–1318$ J mol^{-1}

Phase diagram

According to literature, this phase diagram [2] shows just one eutectic point at $x(KHSO_4)=0.465$ melting at t=125°C.

In order to have more information, we made three thermal measurements at the compositions: $x(KHSO_4)=0.396$, 0.509, 0.543.

The melting temperature of the eutectic that we have obtained is equal to 130°C. The results are listed in Table 4.

Table 4 Thermal analysis results of some mixtures $KHSO_4$–$NaHSO_4$

$x(KHSO_4)$	T liquidus/°C	T solidus/°C
0.396	145	131
0.509	141	130
0.543	145	130

From the melting curve obtained for $x(KHSO_4)=0.543$, we have deduced the heat exchanged during the melting. By taking into account during this process the enthalpy of melting of $KHSO_4$ and $NaHSO_4$ at the eutectic temperature, that means corrected with the heat capacity of the pure salt, we have deduced the enthalpy of mixing at this composition:

$$\Delta_{mix}H[x(KHSO_4=0.543)]=-1221 \text{ J mol}^{-1}.$$

This value is in good agreement with the one obtained from the above mentioned expression (–1317 J mol^{-1}).

Assessment

From the thermodynamic functions obtained for the pure compounds, the enthalpy of mixing and by considering the liquid solution as regular, we can calculate the phase diagram. This calculation gives an eutectic temperature very low and the two liquidus

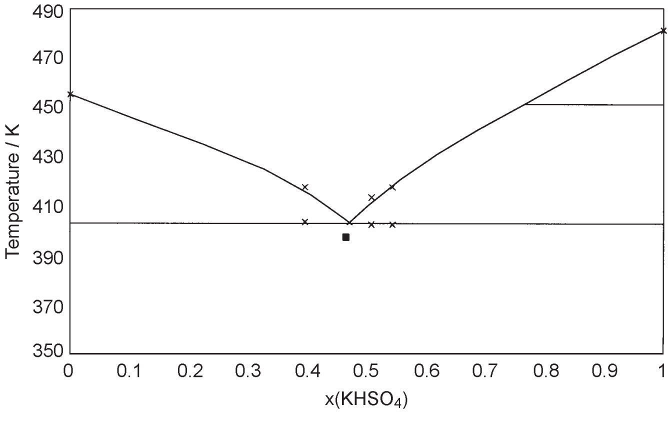

Fig. 1 Phase diagram of the $KHSO_4$–$NaHSO_4$ system; – calculated; x – this work; ■ – [2]

lines do not fit the experimental points. The misfit is probably due to the fact that the liquid solution is not regular.

Therefore we have introduced in our calculation an excess term for the entropy:

$$\Delta S^{ex}=Wx(1-x)$$

where W is obtained by optimization calculation. W=–15.6 J mol^{-1} K^{-1}.

The Gibbs free enthalpy is given by the analytic expression:

$$\Delta G^{ex}=x(1-x)[-3953+15.6T-2494x]$$

The calculated phase diagram and the experimental point are shown in Fig. 1. The agreement is very good.

Conclusions

In this work we have determined the temperature and enthalpy of solid–solid or solid–liquid transitions of $KHSO_4$ and $NaHSO_4$ and the heat capacity of these compounds, both in the solid and liquid state.

The phase diagram has been confirmed to be a simple eutectic point type.

From the measured liquid partial molar enthalpies of the two pure salts, the enthalpy of mixing has been deduced in the entire composition range and the excess entropy has been optimized from all experimental data.

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