Enthalpies of Fusion of Intermediate Compounds, $KMgCl_3$, K_2MgCl_4, K_2BaCl_4, $KCaCl_3$, K_2SrCl_4, K_2LaCl_5, K_3PrCl_6, K_3NdCl_6, KGd_3Cl_{10}, and KDy_3Cl_{10}

Takeo HATTORI,* Kazuo IGARASHI, and Junichi MOCHINAGA

Department of Industrial Chemistry, Faculty of Engineering, Chiba University, Yayoi-cho, Chiba 260

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Synopsis. The enthalpies of fusion were measured on the intermediate compounds of the binary systems of KCl and some other chlorides. These were compared with the values calculated using C_p of the component salts according to the additivity. The enthalpies of fusion measured were in good agreement with calculated in K_2LaCl_5 and K_2BaCl_4.

Some intermediate compounds have been known in such binary systems of KCl and some rare earth chlorides as of KCl and alkaline earth chlorides. Enthalpies and entropies of fusion of these compounds are thermodynamically valuable on obtaining theoretical understanding of phase diagrams of these binary or ternary molten chloride systems. In the present work, heats of fusion were measured using a differential scanning calorimeter (DSC) on some intermediate compounds of the binary systems of KCl and some other chlorides and were compared with values calculated using C_p (heat capacity at constant pressure) of component salts.

Experimental

Starting raw materials used were KCl, alkaline earth chlorides ($MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$), and rare earth chlorides ($LaCl_3$, $PrCl_3$, $NdCl_3$, $GdCl_3$, and $DyCl_3$). In these chlorides, KCl, $CaCl_2$, $SrCl_2$, and $BaCl_2$, were of reagent grade and separately demoistured by heating under the reduced pressure of about 10^{-3} Torr† at slightly below their melting points for 5—10 h. These were then heated to the molten states and after cooling, they were sealed in test tubes in Ar atmosphere till use.

On the other hand, $MgCl_2$ and rare earth chlorides which were prepared according to the similar procedure in the previous paper,[1] were sublimated to purify at about 1000 °C for 8—10 h under vacuum using the apparatus described elsewhere.[2]

The chlorides were weighed in the mole ratios 1-1, 2-1, and 3-1 corresponding to the compositions $KMgCl_3$, $KCaCl_3$, K_2MgCl_4, K_2BaCl_4, K_2SrCl_4, K_2LaCl_5, K_3PrCl_6, K_3NdCl_6, KGd_3Cl_{10}, and KDy_3Cl_{10}. All kinds of mixtures were weighed in a dry box with purified N_2 gas and heated in a quartz tube ($15^{\phi}\times 300^{mm}$) at about 50 °C lower than the melting point in an electric furnace under vacuum, and then raised temperature to melt in Ar atmosphere. After melting thoroughly, the mixtures were solidified in the inclined quartz tube and kept in sealed test tubes.

These samples were ground to 100—300 mesh in an agate mortar in a dry box with purified N_2 gas. Enthalpies of fusion of the samples were measured using DSC on about 20 mg in a platinum pan ($5^{\phi}\times 5^{mm}$) in Ar atmosphere of a flow rate of 50 ml/min at heating rate of 10 °C/min. The enthalpy was measured from the equation

$$\Delta H = KA/M,$$

where ΔH is an enthalpy of fusion per unit weight of a sample, M a weight of a sample, A an area of peak on a recording chart, and K an apparatus constant. As the apparatus constant K was dependent on temperature, it was determined on calibration curve about heat of transition of some NBS-ICTA** standard materials, that is Ag_2SO_4 (transition temp: 412 °C, heat of transition: 6.09 cal/g), K_2SO_4 (583 °C, 11.13 cal/g), and K_2CrO_4 (665 °C, 12.62 cal/g).

Results and Discussion

The results obtained were summarized in Table 1. Experimental enthalpies were measured from endothermic peaks of DSC curves. The calculated values were derived as follows.

Table 1. Experimental and calculated enthalpies of fusion of the intermediate compounds in binary component salts

End components Against KCl	Intermediate compounds (mp/K)	Enthalpies of fusion / kcal mol^{-1}	
		Exptl	Additive value
$MgCl_2$	K_2MgCl_4(688)	8.9	21.4
$MgCl_2$	$KMgCl_3$ (754)	7.9	15.7
$BaCl_2$	K_2BaCl_4(932)	16.4	15.8
$CaCl_2$	$KCaCl_3$(1021)	16.6	13.0
$SrCl_2$	K_2SrCl_4(865)	13.6	14.6
$LaCl_3$	K_2LaCl_5(902)	25.0	25.4
$PrCl_3$	K_3PrCl_6(938)	20.1	30.7
$NdCl_3$	K_3NdCl_6(961)	22.6	30.8
$GdCl_3$	KGd_3Cl_{10}(833)	13.5	
$DyCl_3$	KDy_3Cl_{10}(830)	19.9	

In each binary system, the heat capacities of the end component salts at their melting points were extrapolated to the melting point of the corresponding intermediate compound. The enthalpy values for the compound were estimated from those for the binary compounds by the relation

$$\Delta H_{C,T} = a\Delta H_{A,T} + b\Delta H_{B,T}, \quad (aA + bB \rightarrow A_aB_b = C) \quad (1)$$

where ΔH is heat of fusion and T the melting point of the compound C. And

$$\Delta H_{A,T} = \Delta H_{A,mp} + \int_{mp}^{T} \Delta C_p dT, \quad (2)$$

where, ΔC_p is represented by the relation in the reaction A(s)=A(l),

$$\Delta C_p = C_p(l) - C_p(s). \quad (3)$$

The melting points, heats of fusion, and heat capacities

† 1 Torr=133.322 Pa.

** NBS-ICTA: National Bureau of Standard-International Circular Thermal Analysis.

TABLE 2. HEAT CAPACITIES (C_p), HEATS OF FUSION (L_f), AND MELTING POINTS OF THE SUBSTANCES USED

Substance	Mp/°C	L_f/kcal mol^{-1}	$C_p=a+bT+cT^2$/cal deg^{-1}mol^{-1}			
			a	10^3 b	10^{-5} c	Temp range/K
KCl (s)	772	6.35±0.1	9.89	5.20	0.77	298—mp
KCl (l)			16.00	—	—	mp—1200
$MgCl_2$ (s)	714	10.3 ±0.3	18.90	1.42	−2.06	298—mp
$MgCl_2$ (l)			22.10	—	—	mp—1500
$BaCl_2$ (s)	962	4.0 ±0.1	26.61	—	—	1198—mp
$BaCl_2$ (l)			24.96	—	—	mp—1339
$CaCl_2$ (s)	772	6.8 ±0.1	17.18	3.04	−0.60	600—mp
$CaCl_2$ (l)			24.70	—	—	mp—1700
$SrCl_2$ (s)	873	3.8 ±0.2	18.2	2.44	—	298—mp
$SrCl_2$ (l)			26.2	—	—	
$LaCl_3$ (s)	855	13.0±0.2	22.4	9.4	—	
$LaCl_3$ (l)			32	—	—	
$PrCl_3$ (s)	786	12.1±0.2	21.8	8.4	—	
$PrCl_3$ (l)			32	—	—	
$NdCl_3$ (s)	760	12.0±0.2	22.8	7.4	—	
$NdCl_3$ (l)			31	—	—	
$GdCl_3$ (s)	609	9.6				
$DyCl_3$ (s)	654	7				

of the end component chlorides were shown in Table 2.[3-5]

In the systems of KCl–$LaCl_3$ and KCl–$BaCl_2$, the experimental enthalpies of the compounds of K_2LaCl_5 and K_2BaCl_4 were in good agreement with the calculated and value of K_2SrCl_4 were relatively good. These compounds were all 2 : 1 in mole ratio.

The deviation of the experimental enthalpies from the additivity were very small, especially in K_2LaCl_5 and the experimental were only 0.4 kcal/mol lower than the calculated.

Holm *et al.*[6] studied the binary system of KCl–$MgCl_2$ using a drop-calorimeter and reported that the melting points and enthalpies of fusion of the compounds were 705 K, 10.75 kcal/mol and 755 K, 10.33 kcal/mol in K_2MgCl_4 and $KMgCl_3$, respectively.

References

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