

## Enthalpies of Mixing in the Ternary Systems CaCl<sub>2</sub>—MeCl—MeBr—CaBr<sub>2</sub> where Me is Na, K and Rb

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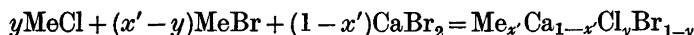
Calorimetric measurements are reported for enthalpies of mixing in the liquid reciprocal systems CaCl<sub>2</sub>—CaBr<sub>2</sub>—MeCl—MeBr where Me=Na, K and Rb. When these results are combined with the enthalpies of mixing for the binary systems, ternary excess enthalpies between 0 and -60 cal/equivalent with an uncertainty of ± 2 cal/equivalent are obtained.

In recent articles Kleppa and Toguri,<sup>1</sup> Meschel and Kleppa<sup>2-4</sup> and Meschel, Toguri and Kleppa<sup>5</sup> have discussed in some detail the enthalpies of mixing in ternary, reciprocal fused salt mixtures, *i.e.*, systems which contain two cations (A,B) and two anions (X,Y). It was shown by Kleppa and Toguri on the basis of a simple thermodynamic cycle, that the enthalpy change associated with the formation of the ternary mixture A<sub>x</sub>B<sub>1-x</sub>X<sub>y</sub>Y<sub>1-y</sub> where *x* and *y* represent ionic fractions may be written as a sum of six contributions:

$$\Delta H_{\text{tern}}^{\text{M}} = (1-x)y \Delta H^{\circ} + x\Delta H_{\text{A(XY)}} + (1-x)\Delta H_{\text{B(XY)}} + y\Delta H_{\text{(AB)X}} + (1-y)\Delta H_{\text{(AB)Y}} + \Delta H^{\text{E}} \quad (1)$$

In this expression  $\Delta H^{\circ}$  represents the standard enthalpy change for the reciprocal reaction, AX + BY = AY + BX. The next four terms represent contributions from the four binary systems (A,B)X, (A,B)Y, A(X,Y) and B(X,Y). The last term is a ternary excess enthalpy which is characteristic of the ternary mixture proper.

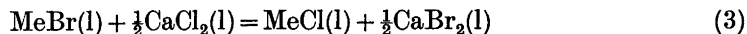
Let us now consider the formation of one mole of the ternary liquid mixture Me<sub>x</sub>Ca<sub>1-x</sub>Cl<sub>y</sub>Br<sub>1-y</sub>. Here *x*' denotes the equivalent fraction of the monovalent ion Me<sup>+</sup> and *y* is the ionic fraction of Cl<sup>-</sup> ions in solution. This mixture can be formed from any three of the four salts, CaCl<sub>2</sub>, CaBr<sub>2</sub>, MeCl and MeBr. We may thus write



In analogy with eqn. 1 it can readily be shown that the enthalpy change associated with this reaction is

$$\begin{aligned} \Delta H_{\text{tern}}^{\text{equiv}} &= (1-x')y\Delta H^{\circ, \text{equiv}} + x'\Delta H_{\text{Me(ClBr)}}^{\text{equiv}} \\ &+ (1-x')\Delta H_{\text{Ca(ClBr)}}^{\text{equiv}} + y\Delta H_{\text{(MeCa)Cl}}^{\text{equiv}} \\ &+ (1-y)\Delta H_{\text{(MeCa)Br}}^{\text{equiv}} + \Delta H^E, \text{equiv} \end{aligned} \quad (2)$$

In this expression  $\Delta H^{\circ, \text{equiv}}$  is the enthalpy change of the reciprocal reaction



The four terms with coefficients  $x'$ ,  $1-x'$ ,  $y$ , and  $1-y$  are the enthalpy changes associated with the formation of one equivalent of each of the considered binary mixtures. The last term is the equivalent ternary excess enthalpy which can be defined through the following relations (see Fig. 1)

$$\Delta H^E, \text{equiv} = \Delta H_{57}^{\text{equiv}} - y\Delta H_{14}^{\text{equiv}} - (1-y)\Delta H_{26}^{\text{equiv}} \quad (4a)$$

$$= \Delta H_{68}^{\text{equiv}} - x'\Delta H_{12}^{\text{equiv}} - (1-x')\Delta H_{34}^{\text{equiv}} \quad (4b)$$

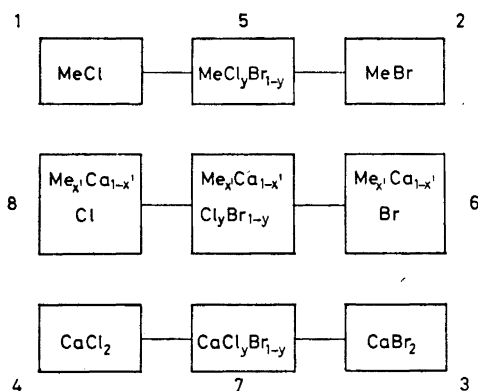


Fig. 1. Schematic diagram showing the formation of 1 equivalent of the ternary mixture  $\text{Me}_x\text{Ca}_{1-x}\text{Cl}_y\text{Br}_{1-y}$  from the pure salts.

There are several different paths which may be adopted in order to obtain information on  $\Delta H^E, \text{equiv}$

In the present investigation two types of calorimetric measurements have been performed, namely:

- (1) Quasi-binary mixing of type 1-3 and 2-4.
- (2) Quasi-binary mixing of type 6-8.

Together with information on the enthalpy of mixing from the four binary systems 1-2, 2-3, 3-4 and 4-1 we can calculate  $\Delta H^E, \text{equiv}$ .

## EXPERIMENTAL

*Apparatus.* All calorimetric experiments reported in the present work were performed in a single unit microcalorimeter suitable for work up to 1100°C. Apart from its single (rather than twin) construction, this apparatus is similar to the one used by Hersh and Kleppa<sup>6</sup> at temperatures up to 800°C. In the absence of a twin construction the furnace surrounding the calorimeter is equipped with a Leeds and Northrup proportional temperature controller giving a stable temperature ( $\pm 0.1^\circ\text{C}$ ) in the furnace system. The calorimeter assembly is heavily lagged with respect to the furnace so as to avoid as far as possible short-term drifts resulting from slight variations in the controlled temperature.

The temperature-sensing device of this calorimeter consists of a 54 + 54 junction Pt/Pt 13 %Rh thermopile, the output of which is amplified by means of a Leeds and Northrup 9835-B DC amplifier and recorded on a Leeds and Northrup type H-Azar recorder. The emf *versus* time curves were integrated by means of an Ott precision planimeter. In this way the area between curve and base line, which is proportional to the total heat, could be determined with a precision of about 0.3 %.

All experiments were performed in fused silica containers under an excess pressure of 10 mmHg of pure dry nitrogen to avoid moisture to enter the system. For further details a paper by Hersh and Kleppa<sup>6</sup> should be consulted.

*Salts.* The sources of, major impurities in, and over-all purity of the salts used in the present work are given in Table 1. Calcium bromide was made from the carbonate and

Table 1. Source and purity of salts.

Salt	Made from	Supplier	Over-all purity in weight per cent	Major impurities by spectroscopic analysis in weight per cent
CaCl <sub>2</sub>	CaCO <sub>3</sub>	Mallinckrodt Chem. Works	100.0 ± 0.1	Mg, Sr, Na 0.1, others < 0.01
CaBr <sub>2</sub>		»	100.0 ± 0.1	Sr 0.05, Na 0.01
NaCl		Fischer Scientific Comp.	100.0 ± 0.1	Ca 0.01, others < 0.01
NaBr		Mallinckrodt Chem. Works	100.0 ± 0.1	K (0.05 - 0.2)
KCl		Fisher Scientific Comp.	100.0 ± 0.1	< 0.005
KBr		»	100.0 ± 0.1	< 0.005
RbCl		Kawecki Chem. Comp.	100.1 ± 0.1	Na, K, Cs 0.05
RbBr		»	100.2 ± 0.2	Na, K, Cs 0.02

hydrogen bromide. After neutralization of the carbonate with acid, the water solution containing the calcium bromide was heated until most of the excess water had evaporated. The salt was then separated from the solution by filtration. By desolving the salt and repeating the evaporation and filtering process pure salt ready for drying was obtained. The drying device consisted of a 6 cm o.d. and 30 cm long pyrex tube with a pyrex fritted disc at the bottom. At the top of the tube was a standard taper 45/50 ground joint. 250 - 500 g of salt was added to a fused silica cylinder which fitted into the pyrex tube. The pyrex tube was placed in a furnace and slowly heated from room temperature to 450°C over a period of 20 - 60 h. Pure dry nitrogen or pure dry hydrogen halide was passed through the salt bed. Hydrogen halide was used only to dry the calcium salts. Before the salts were used they were finally fused under vacuum.

All the salts were analyzed for cation impurities by a semi-quantitative spectrographic method. All the salts were also tested for neutrality with phenolphthalein and the hydroxide content was determined if the salts were basic. The over-all purity was determined in the following manner: About 4 mmol of the salts were dissolved in distilled deionized water. By passing this solution through a cation exchange column and titrating the resulting solution with standardized 0.1 N sodium hydroxide solution, the total content of alkali or alkaline earth halide in the sample could be determined.

*Procedure.* In the course of the present investigation only liquid-liquid experiments were carried out. The salts were maintained in an inert atmosphere of pure dry nitrogen gas which was passed through the silica liner at a flow-rate sufficient to keep an over-pressure of 10 mmHg in the liner when the outlet was closed.

Prior to each calorimetric experiment the fused silica liner with its content was preheated to a temperature about 50°C above that of the calorimeter proper. This served to reduce the thermal disturbance which was associated with the introduction of the loaded liner into the calorimeter. In typical runs the mixing experiment was carried out in 1½ h after the liner had been introduced. By preheating the liner adjustment of the liquid levels in the breakoff and test tube could also be obtained. This is important

when measuring small heat effects because of the vertical temperature gradient in the calorimeter. This gradient was for the present work about  $0.05^{\circ}\text{C}$  per cm over 18 cm. The actual mixing operation was initiated by breaking a fine tip of a break-off silica tube. Stirring was achieved by moving the break-off tube up and down in a silica tube containing the salt mixture. Corrections to the enthalpy of mixing from the breaking of the tip and stirring were negligible for the present work. All weighings of the hygroscopic salts were carried out in a dry box. The weighed samples of the salts to be mixed were transferred from the dry box to the fused silica envelope. The total time of exposure of the sample to air was of the order of 30 sec. The calibration of the calorimeter was carried out by dropping, from room temperature into the apparatus at working temperature, small pieces of pure 2 mm o.d. Pt wire weighing a total of about 0.5 g. The evaluation of the resulting endothermic heat effect was based on Kelley's equation for the heat content of platinum.<sup>7</sup> During its fall into the calorimeter, the platinum wire picked up some heat. The magnitude of this effect was determined in separate experiments, by carrying out calibrations with platinum wires of different diameters. Extrapolation to zero surface area showed that, for 2 mm o.d. wires, this pickup of heat represented 0.5 % at  $690^{\circ}\text{C}$ , 1.5 % at  $800^{\circ}\text{C}$ , and 3 % at  $900^{\circ}\text{C}$ .

## RESULTS

1. *Binary mixtures.* The three binary mixtures NaCl–NaBr, KCl–KBr, and RbCl–RbBr have been investigated by Kleppa, Hersh and Toguri<sup>8</sup> and by Melnichak.<sup>9</sup> The enthalpy of mixing for the  $\text{CaCl}_2$ – $\text{CaBr}_2$  system was determined during the present investigation. For these four binary common cation systems the molar enthalpy,  $\Delta H^M$ , of mixing was fitted by an expression of the following type:

$$\Delta H^M = y(1-y)(a+by) \quad (5)$$

where  $y$  is the ionic fraction of  $\text{Cl}^-$  ions in the mixture. The constants  $a$  and  $b$  were determined by the methods of least squares. A summary of the results obtained by Melnichak<sup>9</sup> for the three alkali halide mixtures and the present data for the calcium chloride-calcium bromide mixtures are given in Table 2. In Fig. 2 the enthalpy interaction parameter,  $\Delta H^M/y(1-y)$ , for the binary

Table 2. Summary of molar enthalpy of mixing,  $\Delta H^M$ , data for the four binary mixtures Na, K, Rb, Ca(Cl–Br). ( $\Delta H^M = y(1-y)(a+by)$ , cal/equiv.  $y$  is the mol fraction of  $\text{Cl}^-$  ions in solution.)

System	$^{\circ}\text{C}$	$a$ cal/mol	$b$ cal/mol	$\Delta H_{x'=0.5}^{\text{equiv}}$ cal/equiv
NaCl–NaBr	811	70	25	20.6
KCl–KBr	811	35	26	12
RbCl–RbBr	731	29	11	8.6
$\text{CaCl}_2$ – $\text{CaBr}_2$	812	273	0	34.2

$\text{CaCl}_2$ – $\text{CaBr}_2$  is plotted *versus* concentration. The six binary charge-unsymmetrical common anion systems  $\text{CaCl}_2(\text{Br}_2)$ – $\text{NaCl}(\text{Br})$ ,  $\text{CaCl}_2(\text{Br}_2)$ – $\text{KCl}(\text{Br})$  and  $\text{CaCl}_2(\text{Br}_2)$ – $\text{RbCl}(\text{Br})$  were investigated previously.<sup>10</sup>

The molar enthalpy of mixing for these systems was fitted by an expression of the following form:

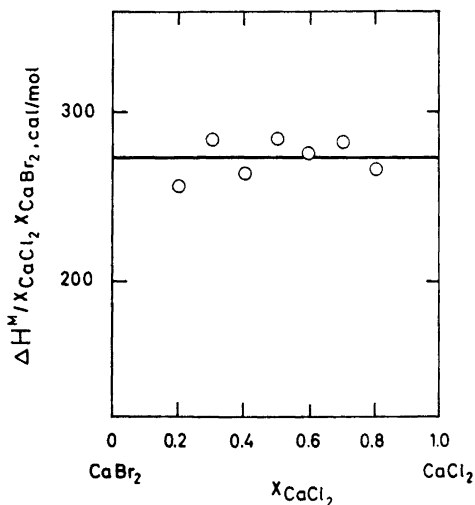


Fig. 2. Molar enthalpy of mixing interaction parameter,  $\Delta H^M/x_{\text{CaCl}_2}x_{\text{CaBr}_2}$ , at 812°C in the liquid mixture  $\text{CaCl}_2-\text{CaBr}_2$ .

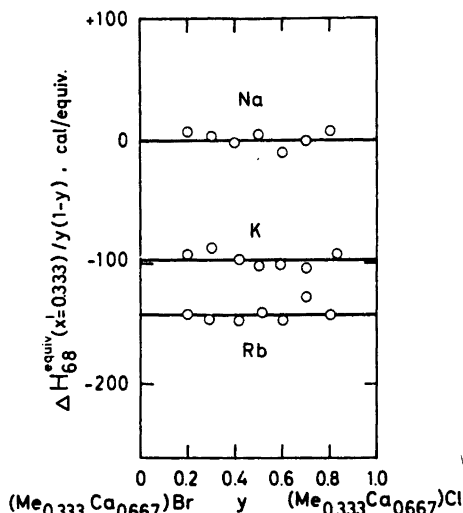


Fig. 3. Equivalent enthalpy of mixing interaction parameters,  $\Delta H_{68}^{\text{equiv}}/y(1-y)$ , at 812°C, 812°C and 894°C in the quasi-binary mixtures  $(\text{Me}_{0.333}-\text{Ca}_{0.667})\text{Br}-(\text{Me}_{0.333}-\text{Ca}_{0.667})\text{Cl}$  where Me is Na, K, and Rb, respectively.

$$\Delta H^M = x(1-x)(a + bx + cx^2 + dx^3) \quad (6)$$

where  $x$  is the mol fraction of the alkaline earth salt in the mixture. The constants  $a$ ,  $b$ ,  $c$ , and  $d$  were determined by the methods of least squares. A summary of the results are given in Table 3.

Table 3. Summary of molar enthalpy of mixing,  $\Delta H^M$ , data for some binary alkali-calcium chloride and bromide systems. ( $\Delta H^M/x(1-x) = a + bx + cx^2 + dx^3$ , kcal/mol  $x$  is the mole fraction of the alkaline earth salt in the mixture S.D. is the standard deviation.)

System	°C	$a$ kcal/mol	$b$ kcal/mol	$c$ kcal/mol	$d$ kcal/mol	S.D. kcal/mol
$\text{CaCl}_2-\text{NaCl}$	810	-4.482	1.602			0.070
$\text{CaCl}_2-\text{KCl}$	810	-10.447	3.257			0.159
$\text{CaCl}_2-\text{RbCl}$	890	-10.897	0.253	1.829		0.225
$\text{CaBr}_2-\text{NaBr}$	810	-4.589	1.657			0.034
$\text{CaBr}_2-\text{KBr}$	810	-9.263	1.801			0.192
$\text{CaBr}_2-\text{RbBr}$	810	-9.484	-10.901	26.877	-16.798	0.166

2. The quasi-binaries  $(\text{Me}_x\text{Ca}_{1-x})\text{Cl}-(\text{Me}_x\text{Ca}_{1-x})\text{Br}$  at equimolar concentration of  $\text{Me}^+$  and  $\text{Ca}^{2+}$  ( $x'=0.333$ ). The experimental enthalpies of mixing,  $\Delta H_{68}^{\text{equiv}}$ , which is obtained by adding  $y$  equivalents of  $(\text{Me}_{0.333}\text{Ca}_{0.667})\text{Cl}$  to

$1-y$  equivalents of  $(\text{Me}_{0.333}\text{Ca}_{0.667})\text{Br}$  to form one equivalent of the mixture  $\text{Me}_{0.333}\text{Ca}_{0.667}\text{Cl}_y\text{Br}_{1-y}$  are presented in graphical form in Fig. 3 for  $\text{Me}=\text{Na}$ ,  $\text{K}$ , and  $\text{Rb}$ . This graph gives  $\Delta H_{68}^{\text{equiv}}(x'=0.333)/y(1-y)$  plotted *versus* ionic fraction of  $\text{Cl}^-$  ions in solution,  $y$ . We can observe that the enthalpies of mixing for anion mixing are small for the ternary mixtures as well as for the above binary mixtures. The energetic asymmetries in  $\Delta H_{68}^{\text{equiv}}$  when plotted *versus*  $y$ , is within the experimental scatter. We accordingly have at the equimolar  $\text{Me}^+ - \text{Ca}^{2+}$  composition

$$\Delta H_{68}^{\text{equiv}}(\text{Me}=\text{Na})=y(1-y)(1.3 \pm 10), \quad \text{cal/equiv} \quad (7a)$$

$$\Delta H_{68}^{\text{equiv}}(\text{Me}=\text{K})=y(1-y)(-98 \pm 10), \quad \text{cal/equiv} \quad (7b)$$

$$\Delta H_{68}^{\text{equiv}}(\text{Me}=\text{Rb})=y(1-y)(-143 \pm 10), \quad \text{cal/equiv} \quad (7c)$$

3. *The quasi-binaries*  $\text{MeCl} - \text{CaBr}_2$ ,  $\text{MeBr} - \text{CaCl}_2$ . For the present six quasi-binary systems we carried out only two measurements at  $x'=0.5$  for each system. This was done to determine the enthalpy change for the reciprocal reaction eqn. (3) and to compare the values obtained for  $\Delta H^{E,\text{equiv}}$  from the 68 mixing with the values from 13 and 24 mixings. The experimental results obtained are presented in Table 4.

Table 4. Quasi-binary mixing  $\text{MeCl} - \text{CaBr}_2$  and  $\text{MeBr} - \text{CaCl}_2$  where  $\text{Me}=\text{Na}$ ,  $\text{K}$ , and  $\text{Rb}$

System	Temperature °C	Ionic fraction of $\text{Me}^+$ in final mixture, $x_{\text{Me}^+}$	$\Delta H^M$ , cal/mol
NaCl + CaBr <sub>2</sub>	812	0.666	-1630
		0.666	-1630
NaBr + CaCl <sub>2</sub>	812	0.667	-157
		0.667	-163
KCl + CaBr <sub>2</sub>	812	0.667	-3330
		0.667	-3240
KBr + CaCl <sub>2</sub>	812	0.667	-870
		0.667	-840
RbCl + CaBr <sub>2</sub>	894	0.667	-3760
		0.667	-3800
RbBr + CaCl <sub>2</sub>	894	0.666	-930
		0.667	-955

#### DISCUSSION

In view of eqn. (4b) and eqns. (7a, 7b, 7c) we can now derive the ternary excess enthalpies at equimolar  $\text{Me}^+ - \text{Ca}^{2+}$  composition,  $x'=0.333$ , along the quasi-binary section (68).

$$\Delta H^{E,\text{equiv}}(\text{Me}=\text{Na})=-100y(1-y), \quad \text{cal/equiv} \quad (8a)$$

$$\Delta H^{E,\text{equiv}}(\text{Me}=\text{K})=-180y(1-y), \quad \text{cal/equiv} \quad (8b)$$

$$\Delta H^{E,\text{equiv}}(\text{Me}=\text{Rb})=-230y(1-y), \quad \text{cal/equiv} \quad (8c)$$

The asymmetries in the ternary excess terms have been neglected because of the relative large uncertainty,  $\pm 10$  cal/mol, in the determination of the quasi-binary enthalpy interaction parameter,  $\Delta H_{68}^{\text{equiv}}$  ( $x' = 0.333$ )/ $y(1-y)$  (see Fig. 3).

In view of eqn. (2) we can further calculate the equivalent ternary excess enthalpy at  $x' = y = 0.5$  from the 13 and 24 quasi-binary mixing experiments. In Table 5 the ternary excess enthalpy per equivalent of ternary mixture,

Table 5. Equivalent ternary excess enthalpy,  $\Delta H^{E,\text{equiv}}$ , for the three ternary mixtures  $\text{CaCl}_2 - \text{CaBr}_2 - \text{MeCl} - \text{MeBr}$  where  $\text{Me} = \text{Na}, \text{K},$  and  $\text{Rb}$ .

System	Temperature °C	Type of mixing	Equivalent fraction of $\text{Me}^+$ ions $x'$	$\Delta H^{E,\text{equiv}}$ cal/equiv
$\text{CaCl}_2 - \text{CaBr}_2 -$	812	13 and 24	0.500	-30
$\text{NaCl} - \text{NaBr}$		68	0.333	-25
$\text{CaCl}_2 - \text{CaBr}_2 -$	812	13 and 24	0.500	-70
$\text{KCl} - \text{KBr}$		68	0.333	-45
$\text{CaCl}_2 - \text{CaBr}_2 -$	894	13 and 24	0.500	0
$\text{RbCl} - \text{RbBr}$		68	0.333	-60

$\Delta H^{E,\text{equiv}}$ , obtained by 13 and 24 mixing is given together with the excess ternary enthalpy obtained by 68 mixing. There is good agreement between the two sets of data for the sodium and potassium systems. For the  $\text{CaCl}_2 - \text{CaBr}_2 - \text{RbCl} - \text{RbBr}$  ternary, however,  $\Delta H_{0.5}^{E,\text{equiv}}$  (13 and 24) = 0 cal/equiv while  $\Delta H_{0.333}^{E,\text{equiv}}$  (68) = -60 cal/equiv. The disagreement between these two sets of measurements is probably due to the greater experimental uncertainty in the determination of the ternary excess enthalpy by the quasi-binary experiments 13 and 24 compared to the 68 experiments. Anion-common-cation mixing yields as mentioned above, small enthalpies of mixing and is thus more reliable to use for the determination of  $\Delta H^{E,\text{equiv}}$  than cation-common-anion mixing where the enthalpies of mixing may be uncertain by as much as  $\pm 50$  cal/mole (see Table 4).

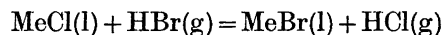
The equivalent ternary excess enthalpy is defined through eqns. (4a) and (4b) above, which are symmetrical in the four equivalent fractions. It may thus be expected that the leading term in  $\Delta H^{E,\text{equiv}}$  should depend on composition through the product of the four equivalent fractions. On the basis of this postulate the ternary excess enthalpy in these three reciprocal ternary systems may be described by the following expressions:

$$\text{Na-system: } \Delta H^{E,\text{equiv}} = -x'(1-x')y(1-y)400, \text{ cal/equiv}$$

$$\text{K-system: } \Delta H^{E,\text{equiv}} = -x'(1-x')y(1-y)720, \text{ cal/equiv}$$

$$\text{Rb-system: } \Delta H^{E,\text{equiv}} = -x'(1-x')y(1-y)920, \text{ cal/equiv}$$

From the data presented in Table 4 the enthalpy change associated with reciprocal reactions of the type described by eqn. (3) can be calculated. Toguri, Flood and F orland<sup>11</sup> measured Br-Cl exchange equilibria of the type



for Me=Li, Na, K, Rb, Cs, Mg, and Ca. By combining the data of Toguri *et al.* Gibbs energy change for reciprocal reactions of type (3) can be calculated for Me=Na, K and Rb. From the present enthalpy measurements and the data of Toguri *et al.* we can further calculate the corresponding entropy changes. These entropy changes can then be compared with the changes in volume associated with these reactions. Values for the specific density of the salts are given by Klemm.<sup>12</sup> The data are compiled in Table 6. The entropy

Table 6. Gibbs energy-, enthalpy-, entropy- and volume-changes for the reaction  
 $\text{MeBr(l)} + \frac{1}{2}\text{CaCl}_2(\text{l}) = \text{MeCl(l)} + \frac{1}{2}\text{CaBr}_2(\text{l})$

Alkali metal	$\Delta G^\circ_{1073^\circ\text{K}}$ cal/equiv	$\Delta H^\circ_{1085^\circ\text{K}}$ cal/equiv	$\Delta S^\circ_{1073^\circ\text{K}}$ cal/equiv deg.	$\Delta V_{1073^\circ\text{K}}$ cm <sup>3</sup> /equiv
Na	2440 ± 20	2200 ± 30	- 0.2	- 1.4
K	3400 ± 80	3650 ± 70	0.2	- 2.3
Rb	3900	4260 ± 50	0.3	- 1.5

data in Table 6 show that there is a significant change in entropy by reactions of type (3). When calculating the entropy of mixing for a system containing a mixture of the four salts in eqn. (3), it is common to use a lattice model and consider the configurational entropy only. The present results show that other contributions to the entropy of mixing have to be taken into account in a more thorough calculation. Furthermore we can observe an increase in entropy for reaction (3) for the potassium and rubidium systems, while the volume change associated with these reactions is negative. From free volume theory, however, one would generally expect a decrease in volume to be associated with a decrease in entropy.

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