

## Bromide-Chloride Anion Exchange Equilibria in Fused Salts

(II). Br-Cl Exchange Equilibria in Systems of  $\text{HCl}_{(g)}$ ,  $\text{HBr}_{(g)}$ ,  
 $\text{M}(\text{Cl-Br})$  where  $\text{M} = \text{Li, Na, K, Rb, Cs, Ca, and Mg}$

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The equilibrium  $\text{MeBr}_{(l)} + \text{HCl}_{(g)} = \text{MeCl}_{(l)} + \text{HBr}_{(g)}$ , where  $\text{M} = \text{Li, Na, K, Rb, Cs, Ca, and Mg}$ , respectively, has been studied at  $800^\circ\text{C}$  and at various ratios of  $P_{\text{HBr}}/P_{\text{HCl}}$ .

The equilibrium constant has been determined for each respective cation system. For the Mg and Ca chloride-bromide systems, the deviation from ideal solution was found to be negative, while for the Li, Na, and K system a positive deviation was obtained. These deviations are discussed in terms of the change in energy and entropy content on mixing the respective salts.

### I. EXPERIMENTAL

In a previous communication the equilibrium



was reported. In the present paper the investigation has been extended to a number of alkali and alkaline earth metals (Na, K, Rb, Cs, Ca, and Mg).

The apparatus and experimental procedures have been fully described previously<sup>1</sup>. The temperature of the present investigation was  $800^\circ\text{C}$ .

The pure potassium and sodium salts were of *pro analysi* grade from Merck, CsBr was obtained from Riedel de Haen, RbCl and CsCl from Merck and RbBr from Dr. Theodor Schuchardt, München.

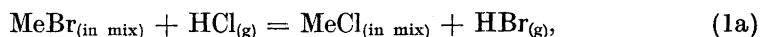
Although no further purification of these salts was effected, the pure salts were mixed with a small amount of ammonium chloride or bromide and fused in a platinum crucible. The melt was then poured on a platinum sheet from which appropriate size samples were taken.

Equilibrium was verified when the initial pure chloride and bromide of the respective cations approached the same final composition.

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## II. RESULTS

The equilibrium constant for the reaction



is given by

$$K = \frac{a_{\text{MeCl}} p_{\text{HBr}}}{a_{\text{MeBr}} p_{\text{HCl}}}$$

where Me represents a metal ion,  $a$  the activity and  $p$  the partial pressure. Introducing mole fractions ( $N$ ) and activity coefficients ( $\gamma$ ), one obtains

$$K = \frac{N_{\text{MeCl}} \gamma_{\text{MeCl}} p_{\text{HBr}}}{N_{\text{MeBr}} \gamma_{\text{MeBr}} p_{\text{HCl}}} = K' \frac{\gamma_{\text{MeCl}}}{\gamma_{\text{MeBr}}}$$

which defines the ideal equilibrium constant  $K'$ .

Taking logarithms one has

$$\ln K' = \ln K - (\ln \gamma_{\text{MeCl}} - \ln \gamma_{\text{MeBr}}) \quad (1b)$$

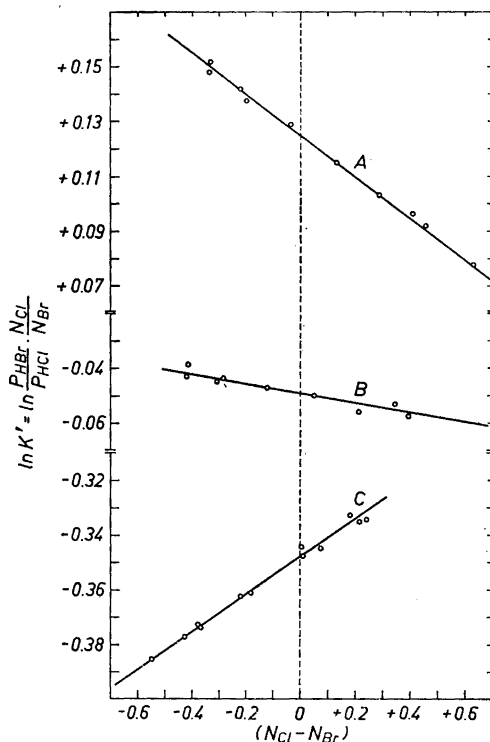


Fig. 1. The dependence of the equilibrium constant of the Br-Cl composition of the melt in the Li, Mg, and Ca systems. A:  $1/2 \text{MgBr}_2(\text{l}) + \text{HCl}_{(\text{g})} \rightleftharpoons 1/2 \text{MgCl}_2(\text{l}) + \text{HBr}_{(\text{g})}$ ; B:  $1/2 \text{CaBr}_2(\text{l}) + \text{HCl}_{(\text{g})} \rightleftharpoons 1/2 \text{CaCl}_2(\text{l}) + \text{HBr}_{(\text{g})}$ ; C:  $\text{LiBr}(\text{l}) + \text{HCl}_{(\text{g})} \rightleftharpoons \text{LiCl}(\text{l}) + \text{HBr}_{(\text{g})}$ .

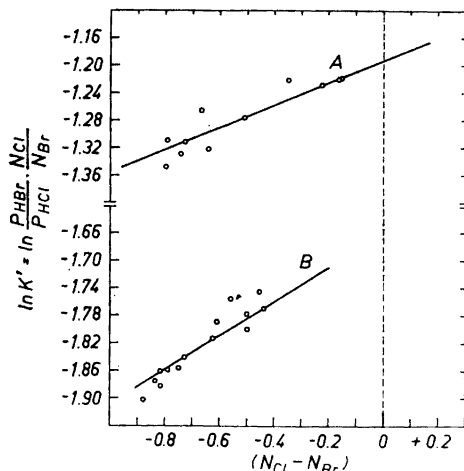


Fig. 2. The dependence of the equilibrium constant for the Br—Cl composition of the melt in the K and Na systems.

A:  $\text{NaBr(l)} + \text{HCl(g)} \rightleftharpoons \text{NaCl(l)} + \text{HBr(g)}$ ; B:  $\text{KBr(l)} + \text{HCl(g)} \rightleftharpoons \text{KCl(l)} + \text{HBr(g)}$ .

If the activity coefficients can be expressed by the equation for regular solutions:

$$RT \ln \gamma_{\text{MeBr}} = b N_{\text{MeCl}}^2 \quad (2)$$

$$RT \ln \gamma_{\text{MeCl}} = b N_{\text{MeBr}}^2 \quad (3)$$

one obtains

$$\ln K' = \ln K + b/RT (N_{\text{Cl}} - N_{\text{Br}}) \quad (4)$$

where

$$N_{\text{Cl}} = N_{\text{MeCl}} \text{ and } N_{\text{Br}} = N_{\text{MeBr}}$$

Plotting experimental values of  $\ln K'$  as a function of  $(N_{\text{Cl}} - N_{\text{Br}})$ , a straight line should result if the requirements inherent in eqn. (2) and (3) are valid. Further,

$$\ln K = \ln K' \text{ for } N_{\text{Br}} = N_{\text{Cl}} = 0.5$$

and  $b/RT$  is given by the slope of the straight line.

Figs. 1, 2 and 3 show  $\ln K'$  as a function of  $(N_{\text{Cl}} - N_{\text{Br}})$  for the systems investigated. It appears that the function is linear for the Li-, Na-, K-, Ca-, and Mg-systems.

For systems containing Rb and Cs, the concentration region is too narrow to permit any certain conclusion about linearity.

The change in free enthalpy for reaction (1a), with all components in their standard state (pure fused salts, gas at one atmosphere pressure), is given by  $\Delta G_T^\circ = -RT \ln K$ , cf. Table 1.

Data for the heat content and the entropy of these compounds at high temperatures are still incomplete and the available data are partly inaccurate.

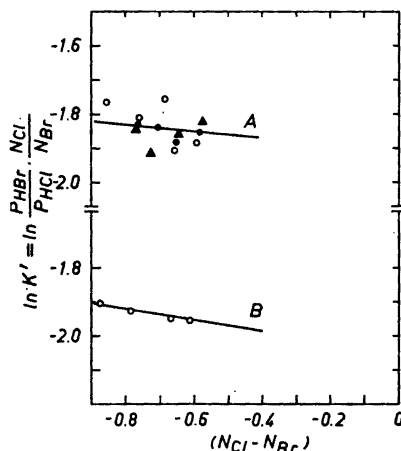
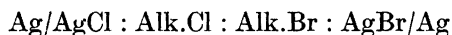


Fig. 3. The dependence of the equilibrium constant for the Br-Cl composition of the melt in the Rb and Cs systems.  $\circ$  Samples starting with pure RbCl;  $\blacktriangle$  samples starting with pure RbBr;  $\bullet$  average value between RbCl and RbBr.  
 A:  $\text{RbBr}_{(l)} + \text{HCl}_{(g)} \rightleftharpoons \text{RbCl}_{(l)} + \text{HBr}_{(g)}$ ; B:  $\text{CsBr}_{(l)} + \text{HCl}_{(g)} \rightleftharpoons \text{CsCl}_{(l)} + \text{HBr}_{(g)}$ .

From the data compiled in JANAF Therm Tables (1960) for the potassium system, which is one of the better known systems,  $\Delta G^{\circ}_{1073^{\circ}\text{K}}$  is equal to 3530 kcal, in very good agreement with our measurements ( $3500 \pm 80$  kcal). For the lithium system, however, according to the JANAF compilation  $\Delta G^{\circ}_{1073^{\circ}\text{K}} = 1550$  kcal, a value which we surmise to be considerably in error.

The present values of  $\Delta G^{\circ}_{1073^{\circ}\text{K}}$  may also be compared with values obtained from some preliminary measurements of galvanic cells of the type <sup>2</sup>:



with the cell reaction:

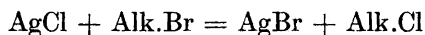


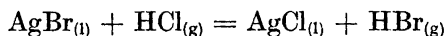
Table 1. Experimental equilibrium constants and free enthalpy change for the reaction  $\text{MeBr} + \text{HCl} = \text{MeCl} + \text{HBr}$  at  $800^{\circ}\text{C}$ .

System:	ln K		$\Delta G^{\circ}_{1073^{\circ}\text{K}}$ kcal	
Li (Cl, Br)	-0.348	$\pm 0.002$	-0.743	$\pm 0.004$
Na (Cl, Br)	-1.19	$\pm 0.01$	-2.54	$\pm 0.02$
K (Cl, Br)	-1.64	$\pm 0.04$	-3.50	$\pm 0.08$
Rb (Cl, Br)	-1.85		-4.0	
Cs (Cl, Br)	(-1.9)		(-4.1)	
Ca (Cl, Br)	-0.049	$\pm 0.002$	-0.105	$\pm 0.004$
Mg (Cl, Br)	+0.125	$\pm 0.002$	+0.267	$\pm 0.004$

Table 2. Comparison of the free enthalpy change obtained in the present investigation with other available values.

System:	$\Delta G^{\circ}_{1073^{\circ}\text{K}}$ in cal		
	From exchange measurement	From EMF measurement	From previous thermodynamic data
Li (Cl, Br)	740	780	1550
Na (Cl, Br)	2540	2530	
K (Cl, Br)	3500	3540	3530
Rb (Cl, Br)	4000	3880	
Cs (Cl, Br)	4100	4150	

A few of the liquid junction potentials have been checked and found to be small. From these data, one may subtract the free enthalpy change at 1073°K for the reaction:



which is known to be 6800 kcal from Kelley's data<sup>3</sup>. This difference will give the free enthalpy change for reaction (1a) and the respective values may be compared with the data for  $RT \ln K$  obtained from eqn. 4. This comparison is shown in Table 2.

For the first three systems the agreement is fairly good. For the Cs- and Rb-containing systems, the accuracy of the exchange measurements were not sufficient to permit a reliable extrapolation to  $N_{\text{Cl}} = N_{\text{Br}}$  in order to obtain  $\Delta G^{\circ}_{1073^{\circ}\text{K}}$ .

## DISCUSSION

The data from the exchange equilibria also show the manner in which the deviations from ideal behaviour for chloride-bromide mixtures vary with the cation present. The Mg- and Ca-containing systems show negative deviations, and the Li-, Na- and K-containing systems show positive deviations increasing in the above order, *cf.* Table 3. For the Rb- and Cs-containing systems measurements are less accurate, *cf.* Fig. 3, but the deviations from ideal behaviour seem to be much smaller than the deviation for the K-containing system.

The present measurements of the equilibrium constant as a function of temperature were not of the precision required to determine the deviations from ideal entropy of mixing. This is frequently the case for thermodynamic studies based on free energy measurements alone. However, one should be aware of the possibility of deviations from the ideal entropy of mixing. In a solid solution of the KCl-KBr (1:1) system, *e.g.*, the vibrational entropy of mixing was found to be 0.11 e.u. per mole of mixture<sup>13</sup>.

If it is assumed that the entropy of mixing is ideal for the present systems, the *b*-values in Table 3 would represent change in heat content by the process

Table 3. Experimental values of  $b$  from the equilibrium  $MBr + HCl = MCl + HBr$  at 800°C.

System	$b$ , cal
Li (Cl, Br)	+ 150
Na (Cl, Br)	+ 350
K (Cl, Br)	+ 530
Ca (Cl, Br)	- 40
Mg (Cl, Br)	- 160

of mixing. However, some preliminary calorimetric measurements by Kleppa, Hersh and Toguri<sup>14</sup> give the following values for the same heat of mixing parameter for alkali chloride — bromide mixtures: Li(Cl—Br) 50 cal, Na(Cl—Br) 90–110 cal, K(Cl—Br) 60 cal, Rb(Cl—Br) 50 cal, Cs(Cl—Br) 30 cal.

This discloses the interesting property of these systems that the major part of the positive deviation from ideality can be attributed to a negative term in the entropy of mixing. These excess entropies of mixing for  $N_{Cl} = \frac{1}{2}$  are  $-0.02$ ,  $-0.06$  and  $-0.11$  e.u. per mole of mixtures for the systems Li(Cl—Br), Na(Cl—Br) and K(Cl—Br), respectively. The composition dependence of this entropy term is further given by the equation

$$\Delta S_{\text{excess}} = \text{Constant } N_{Cl} N_{Br}$$

indicating that the extra entropy contribution (similar to energy contributions) is connected to nearest or next nearest neighbour interaction.

Though similar behaviour has been observed for mixtures of organic molecules, it is not known to the authors that this has been found for simple mixtures of fused salts, and the reason for this is apparently the difficulty in measuring the entropy with sufficient accuracy.

The definition of the ideal entropy of mixing for fused salts is generally based on the following conditions:

1) Structural conformity for mixture and components, and a configurational entropy determined uniquely by a random distribution of ions with charges of the same sign.

2) No change in the total vibrational entropy by the process of mixing.

It is too early to decide whether the observed excess entropy should be related to structural changes which could be described as change in size and number of holes or vacancies, or if the excess entropy should be attributed to changes in the vibrational entropy created by the change in the environment of the ions by the mixing process.

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