Chloride-Bromide Exchange Equilibria in Binary Molten Salts

The Experimental Method. The System LiCl, LiBr, HCl, HBr

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The equilibrium LiBr(l) + HCl(g) = LiCl(l) + HBr(g) has been
studied at 800°C and at various ratios of p_{HBr}/p_{HCl}. The equilibrium
constant was found to vary with the composition of the salt melt.
The ideal equilibrium constant was found to be $\ln K_{800°C} = + 0.35$.
  The variation of $\ln K$ with composition corresponds to a positive
deviation from ideality in the binary system LiCl-LiBr.

The development of the theory of molten salt mixtures and a critical evalua-
tion of existing theories have been limited by the lack of experimental data.
For example, the exploration of the effect of such factors as charge, radius, and
polarizability of ions on the deviation from ideality in fused salt systems are
still in the embryonic stage. It was anticipated that from a study of anion
exchange equilibria, some new information might be obtained about these
effects.

The experimental work was started by B. Saether and the techniques were
subsequently improved during the time that O. Fykse, A. Block-Bolten and
J. Toguri worked on the project. The data to be presented here originate from
the last period only.

From an investigation of the equilibrium reaction of the type

$$MeBr(l) + HCl(g) = MeCl(l) + HBr(g)$$
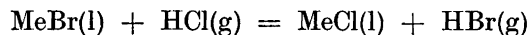
one can determine the values of $p_{HBr} \cdot N_{MCl}/p_{HCl} \cdot N_{MBr}$ as a function of the
composition of the fused salt mixture. (N = molefraction, p = partial
pressure.) Assuming the (Br-Cl) mixture to form regular solutions, the energy
of mixing of pure MeCl and MeBr may be estimated where Me might be either
a single cation or a mixture of several cations. Further the validity of the
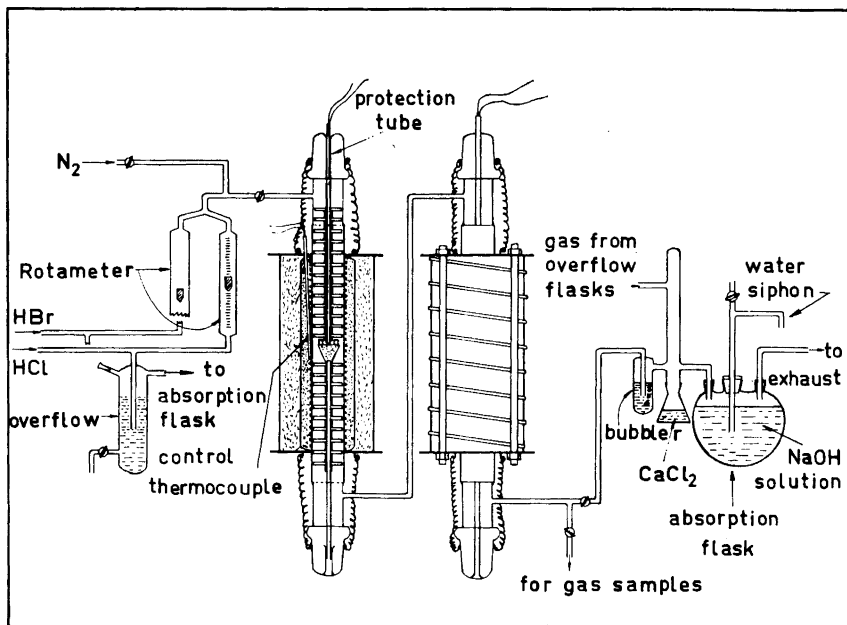regular solution equation may be checked by such measurements.

Fig. 1. Apparatus.

In the present paper a detailed account of the experimental procedure is given together with results for the system LiCl-LiBr. Results for the other alkali and alkaline earth systems will be presented in a following communication.

EXPERIMENTAL

The experimental procedure which seemed to be most suitable for the equilibrium studies, was the flow method. The components HCl and HBr were taken from cylinders at a constant flow rate, mixed and passed over the liquid salt mixtures, which were maintained at a constant temperature, until equilibrium was established.

A diagram of the apparatus is shown in Fig. 1. Two ordinary resistance furnaces were utilized (see Fig. 1). With these furnaces a constant temperature zone ($\pm$ 1°C) of 6 cm was readily obtained. A control thermocouple, placed between the windings of the furnace and insulation, was connected to a Kent two point controller which regulated the temperature. The actual temperature was determined by a chromel-alumel thermocouple protected by an alumina sheath, and placed into the sample holder as shown in the diagram. Baffles made from dense porcelain were used to minimize heat losses as well as to insure mixing of the gases utilized.

The system is essentially an all glass construction. A ceramic to glass seal connects the Haldenwanger High Temperature Porcelain furnace tube to the apparatus. Minimum number of stopcocks were utilized, and where required, stopcocks with teflon were used. All joints were lubricated with Florube grease. This grease was not attacked by the HCl and HBr gases.

The flow of HCl and HBr was controlled by means of rotameter tubes with tantalum floats obtained from Rotameter Manufacturing Co. Ltd. The pressure was regulated by means of a sealed overflow tube containing Shell Risella oil 27 which was found to be chemically inert.

A line supplying purified nitrogen was added to the system to permit flushing of the system.

The samples were contained in platinum cups 1 cm in diameter by 1 cm in height. Platinum lids with holes were used to cover the sample in order to minimize possible transfer of salts from one crucible to another crucible *via* the gas phase.

A flask containing NaOH solution served to absorb the HCl and HBr. To prevent moisture from entering into the system, a $CaCl_2$ trap was placed between the absorption flask and bubbler with Shell Risella oil 27. The latter also served this function.

The cylinders of anhydrous HBr and HCl gases were obtained from Matheson Co. Inc., East Rutherford N. J., U.S.A. The analysis of these gases are as follows.

HBr — 99.9 %, contains no free bromine or moisture,
the principle impurity being nitrogen.

HCl — 99.3 %, inerts 0.2 %, CO_2 0.5 %.

The LiCl used throughout this investigation was Fisher certified Reagent grade.

All experiments reported in this communication were carried out at 800 $\pm$ 2°C, which corresponds to an error of $\pm$ 0.02 in ln K_K. The course of a typical experiment was as follows: Samples of approximately 0.5 g of pure LiCl were placed into platinum crucibles. The crucibles with their lids were then placed into the furnace and the system flushed with N_2 gas for approximately 4 h. During this period the furnace temperature was raised to 800°C. At this point the N_2 flow was stopped and the HCl and HBr gas flow of desired HBr/HCl ratio was started. The total flow rate used throughout the present study was of the order of 100 — 200 ml/min, a rate sufficient to prevent thermal diffusion errors. The experiments were then allowed to continue for 5 — 6 h, a period of time found to be sufficient for establishing equilibrium. Although rotameters were used, the actual ratio of HBr/HCl was determined for each experiment by sampling the gas after it has passed through the reaction zone. A number of gas samples were taken at various periods during the experiment. After the equilibration period, the HBr and HCl gas mixture was exchanged with nitrogen and the system flushed. Then the furnace temperature was decreased.

The ratio of Br/Cl in the salt mixtures was determined by chemical analysis. This was accomplished by titrating potentiometrically with $AgNO_3$. The equivalent point was determined according to a method worked out by Lydersen (to be published).

Table 1. Summary of results.

Gas phase		Salt mixture				
% Br	p_{HBr}/p_{HCl}	% Br	N_{Cl}/N_{Br}	K'	ln K'	$N_{Cl}-N_{Br}$
69.85	2.317	77.30	0.294	0.680	-0.385	-0.546
63.07	1.708	71.34	0.402	0.686	-0.377	-0.427
60.43	1.527	68.92	0.451	0.689	-0.373	-0.378
59.91	1.494	68.48	0.460	0.688	-0.374	-0.370
52.08	1.087	60.96	0.640	0.696	-0.362	-0.219
50.10	1.004	59.03	0.694	0.697	-0.361	-0.181
41.19	0.700	49.71	1.012	0.709	-0.344	$+0.006$
40.68	0.686	49.26	1.030	0.706	-0.348	$+0.015$
37.98	0.612	46.37	1.157	0.708	-0.345	$+0.073$
33.07	0.494	40.80	1.451	0.717	-0.333	$+0.184$
31.56	0.461	39.20	1.551	0.715	-0.335	$+0.216$
30.29	0.434	37.78	1.647	0.716	-0.335	$+0.244$
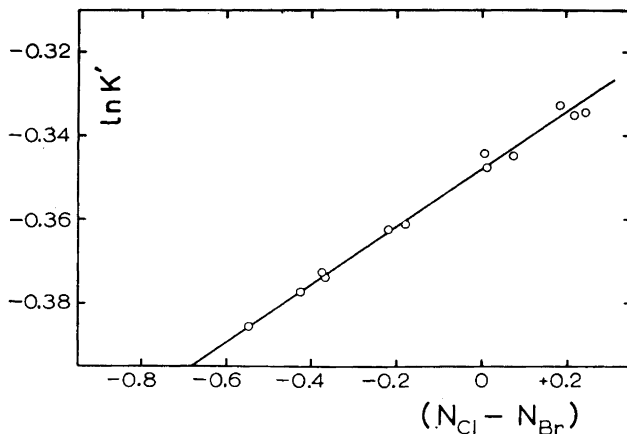
Fig. 2. $\ln K' = \ln N_{\mathrm{Cl}} p_{\mathrm{HCl}} / N_{\mathrm{Br}} p_{\mathrm{HBr}}$ in dependence of $(N_{\mathrm{Cl}} - N_{\mathrm{Br}}.)$

RESULTS

The experiments were conducted at 800°C over a $p_{\mathrm{HBr}} / p_{\mathrm{HCl}}$ range of approximately 0.43—2.32. The results are tabulated in Table 1.

The equilibrium concerned in this study is

$$\mathrm{LiBr(l)} \; + \; \mathrm{HCl(g)} \; = \; \mathrm{LiCl(l)} \; + \; \mathrm{HBr(g)} \tag{1}$$
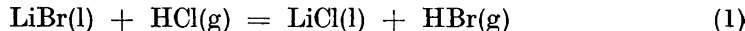
for which the equilibrium constant is

$$K_a = (p_{\mathrm{HBr}} / p_{\mathrm{HCl}}) \times (a_{\mathrm{LiCl}} / a_{\mathrm{LiBr}}) = \underbrace{(p_{\mathrm{HBr}} / p_{\mathrm{HCl}}) \times (N_{\mathrm{Cl}} / N_{\mathrm{Br}})}_{K'} \times (\gamma_{\mathrm{LiCl}} / \gamma_{\mathrm{LiBr}}) \tag{2}$$

where N_{Br} and N_{Cl} are ionic fractions of the respective Br^- and Cl^- ions in the melt, and γ is the activity coefficient.

On the assumption of regular solution, and symmetrical activity functions of composition, the acitivity coefficients can be replaced by expression of the following type.

$$RT \; \ln \; \gamma_{\mathrm{LiBr}} \; = \; b_{\mathrm{Li}} N_{\mathrm{Cl}}^2 \tag{3}$$

where b_{Li} is a constant.

Hence

$$\ln K' = \ln \frac{p_{\mathrm{HBr}}}{p_{\mathrm{HCl}}} \cdot \frac{N_{\mathrm{Cl}}}{N_{\mathrm{Br}}} = \frac{b_{\mathrm{Li}}}{RT} (N_{\mathrm{Cl}} \; - \; N_{\mathrm{Br}}) + \ln K_a \tag{4}$$

In eqn. (4) the ratio $p_{\mathrm{HBr}} / p_{\mathrm{HCl}}$ and all the concentration terms are known experimentally. Thus by plotting $\ln \left[p_{\mathrm{HBr}} / p_{\mathrm{HCl}} \times N_{\mathrm{Cl}} / N_{\mathrm{Br}} \right]$ against $(N_{\mathrm{Cl}} - N_{\mathrm{Br}})$ a straight line with slope equal to b/RT should be obtainable. $\ln K'$, the ideal equilibrium constant, should then correspond to the intercept of the experimental line at $(N_{\mathrm{Cl}} - N_{\mathrm{Br}}) = 0$.

The present results are plotted in this manner, as shown in Fig. 2 and in Table 1. From a least square analysis, the following values are obtained for the equilibrium constant

$$\ln K_a = 0.348 \pm 0.005$$

From this the value $b_{Li} = 150 \pm 25$ kcal/mole is obtained.

The positive value of b_{Li} corresponds to an endothermic heat of mixing for pure liquid LiCl with pure liquid LiBr.

However, the significance of this data will be discussed in a following communication which will also report the results for other alkali bromide-chloride systems.