

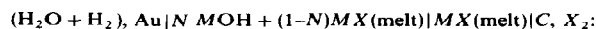
HYDROLYSIS OF MOLTEN ALKALI CHLORIDES, BROMIDES AND IODIDES

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Abstract—An electrochemical technique has been developed for studying equilibrium of the hydrolytic reactions of molten alkali chlorides, bromides, and iodides with exception of lithium salts. It consists of measuring the emf of the cells with gaseous electrodes



$$\varepsilon = \varepsilon^0 + \frac{RT}{F} \ln \frac{P_{H_2}^{1/2} \cdot P_{X_2}^{1/2}}{P_{H_2O}} a_{MOH},$$

this emf being connected with the equilibrium constant by the equation:

$$\ln K = -\frac{F}{RT} \varepsilon - \frac{\Delta G_{HX}^0}{RT} + \ln \frac{P_{H_2}^{1/2} \cdot P_{X_2}^{1/2}}{P_{H_2O}} a_{MOH}.$$

Here $X = \text{Cl, Br or I}$, $M = \text{Na, K, Rb or Cs}$, P_{H_2} , P_{X_2} and P_{H_2O} are pressures of the indicated gases on the electrodes, a_{MOH} and ΔG_{HX}^0 are activity of the hydroxides in melts under investigation and standard Gibbs energy of reactions $\frac{1}{2}H_2(g) + \frac{1}{2}X_2(g) \rightleftharpoons HX(g)$. As the hydrolysis results in forming diluted solutions of MOH in molten MX, one may use the conditional equilibrium constant of reactions $H_2O(g) + MX(\text{melt}) \rightleftharpoons MOH(\text{melt}) + HX(g)$

$$K^* = \frac{K}{f_{MOH}^*} = \frac{P_{HX}}{P_{H_2O}} N_{MOH}$$

with a_{MX} being equal to 1. Here N_{MOH} and f_{MOH}^* are the mole fraction and limiting value of the activity coefficient of MOH in the melts at $N_{MOH} \rightarrow 0$. The equilibrium hydrolytic constant has been determined as a function of temperature. Expressions are obtained for its temperature dependence, this increases as temperature rises and the ionic potential of alkali cations decreases in the series from Na^+ to Cs^+ . Other things being equal, the hydrolysability of molten alkali halides diminishes in going from chlorides to iodides. The solutions of MOH in molten MX are shown to be close to a perfect mixture.

INTRODUCTION

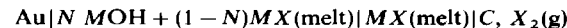
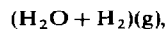
The electrolytes on the base of molten alkali halides are widely used in electrochemical and thermodynamical investigations, electrolytic production and refining of many metals. When operations are carried out in open electrolytic cells, the contents always become contaminated with hydroxides formed by hydrolysis. Hydroxide ions interact with cations of multivalent metals to give, as a rule, their high-melting oxides which are very slightly soluble in molten alkali halides. This is an undesirable phenomenon resulting in uncontrollable composition changes in electrolytes and contaminating them by oxide sludges which can interfere with normal electrode processes. To have control over it, one has to know the equilibrium hydrolytic constant for the base melts (alkali halides) as a function of their ionic composition and temperature.

In the literature available there are only one or two publications [1-3] the authors of which have investigated the hydrolytic reaction of solid and molten sodium chloride and iodide by the dynamic chemical method. The present writers approached the problem

by an electrochemical route, making use of cells with gaseous water-hydrogen and chlorine electrodes which had been developed and test-operated beforehand. The experimental observations and their discussion are given in this paper.

EXPERIMENTAL

The cells with gaseous water-hydrogen and halogen electrodes



can be used for studying hydrolytic reactions of molten alkali halides and determining the activity of alkali hydroxides dissolved in them. On the electrodes proceeds reactions: $OH^-(\text{melt}) + \frac{1}{2}H_2(g) \rightleftharpoons H_2O(g) + e^-$ and $\frac{1}{2}X_2(g) + e^- \rightleftharpoons X^-(\text{melt})$. Their equilibrium potentials are

$$E_{H_2O+H_2} = E_{H_2O+H_2}^0 + \frac{RT}{F} \ln \frac{P_{H_2O}}{P_{H_2}^{1/2} \cdot a_{OH^-}}$$

and

$$E_{X_2} = E_{X_2}^0 + \frac{RT}{F} \ln \frac{P_{X_2}^{1/2}}{a_{X^-}}$$

The emf of the cells is

$$\begin{aligned} \varepsilon &= E_{X_2} - E_{H_2O+H_2} \\ &= E_{X_2}^0 - E_{H_2O+H_2}^0 + \frac{RT}{F} \ln \frac{P_{H_2}^{1/2} \cdot P_{X_2}^{1/2}}{P_{H_2O}} \frac{a_{OH^-}}{a_{X^-}} \\ &= \varepsilon^0 + \frac{RT}{F} \ln \frac{P_{H_2}^{1/2} \cdot P_{X_2}^{1/2}}{P_{H_2O}} a_{MOH}, \end{aligned}$$

because $a_{MX} = 1$ (the halogen electrodes are dipped in molten individual alkali halides) and $a_{OH^-} = a_{MOH}$ if alkali cations are the same in MOH and MX . The standard emf is connected with the standard Gibbs energy of the reactions which takes place in the cells $\frac{1}{2}H_2(g) + \frac{1}{2}X_2(g) + MOH(melt) = MX(melt) + H_2O(g)$, by the equation $\Delta G_1^0 = -F\varepsilon^0$. Hence

$$\Delta G_1^0 = -F\varepsilon + RT \ln \frac{P_{H_2}^{1/2} \cdot P_{X_2}^{1/2}}{P_{H_2O}} a_{MOH}.$$

The hydrolytic reactions $H_2O(g) + MX(melt) \rightleftharpoons MOH(melt) + HX(g)$ can be considered in terms of thermodynamic formalism as a difference of the reactions $\frac{1}{2}H_2(g) + \frac{1}{2}X_2(g) \rightleftharpoons HX(g)$ (ΔG_2^0) and the above mentioned one. Thus the standard Gibbs energy can be found by the equation $\Delta G^0 = \Delta G_2^0 - \Delta G_1^0$

$$\Delta G^0 = \Delta G_2^0 + F\varepsilon - RT \ln \frac{P_{H_2}^{1/2} \cdot P_{X_2}^{1/2}}{P_{H_2O}} a_{MOH}.$$

On the other hand, $\Delta G^0 = -RT \ln K^0$ where K^0 is the desired equilibrium constant of the hydrolytic reactions. Hence

$$\begin{aligned} \ln K^0 &= \ln \frac{P_{HX} \cdot a_{MOH}}{P_{H_2O} \cdot a_{MX}} = -\frac{\Delta G_2^0}{RT} - \frac{F}{RT} \varepsilon \\ &+ \ln \frac{P_{H_2}^{1/2} \cdot P_{X_2}^{1/2}}{P_{H_2O}} \frac{a_{MOH}}{a_{MX}}. \end{aligned}$$

The equation enables it to be calculated from the emf measured at the fixed pressures of the gases on the electrodes and hydroxide activity in melts under study, with ΔG_2^0 , being found from the available literature on the thermodynamic properties of hydrogen, halogens and hydrogen halides[4].

The diluted solutions of MOH in MX being the product of hydrolyzing molten alkali halides, one may use a conditional equilibrium constant:

$$K^* = \frac{K^0}{f_{MOH}^*} = \frac{P_{HX}}{P_{H_2O}} N_{MOH} \text{ with } a_{MX} \approx 1.$$

Here N_{MOH} and f_{MOH}^* are the mole fraction and limiting value of the activity coefficient of MOH in the melts at $N_{MOH} \rightarrow 0$.

$$\ln K^* = -\frac{\Delta G_2^0}{RT} - \frac{F}{RT} \varepsilon + \ln \frac{P_{H_2}^{1/2} \cdot P_{X_2}^{1/2}}{P_{H_2O}} N_{MOH}.$$

The bromine and iodine electrodes are much more complicated in construction and operation as compared with the chlorine one. Therefore it was used instead of them in the cells with melts of $MOH + MBr$

and $MOH + MI$:

$(H_2O + H_2)$,

$Au|N MOH + (1 - N)MX(melt)|MCl(melt)|C, Cl_2$,

where $X = Cl, Br$ or I and $M = Na, K, Rb$ or Cs , with alkali cations being the same in both their electrode compartments. The emf of such cells is converted to that of the cells with the bromine or iodine electrodes by making use of the potential differences E_{X_2/Cl_2} between them and the chlorine electrode[5, 6]. In such a case

$$\begin{aligned} \ln K^* &= -\frac{\Delta G_2^0}{RT} - \frac{F}{RT} (\varepsilon - E_{X_2/Cl_2}) \\ &+ \ln \frac{P_{H_2}^{1/2} \cdot P_{Cl_2}^{1/2}}{P_{H_2O}} N_{MOH}. \end{aligned}$$

The measurements were made with the cells shown in Fig. 1. The chlorine electrode did not differ in its construction from those used in our previous investigations[7]. The gas was released from it under atmospheric pressure measured to an accuracy of ~ 60 Pa.

The water-hydrogen electrode was a gold wire dipped in the melts of $MOH + MX$ under study. They were placed in an aluminum test tube the thin wall of which served as a porous diaphragm securing the electric contact by ionic conduction between the electrolytes in the electrode and intermediate compartments of the cells. Its gas space was filled with a mixture of hydrogen and water vapour. It was shown that aluminum and gold did not react with melts containing up to ~ 10 mol% MOH under the atmosphere of

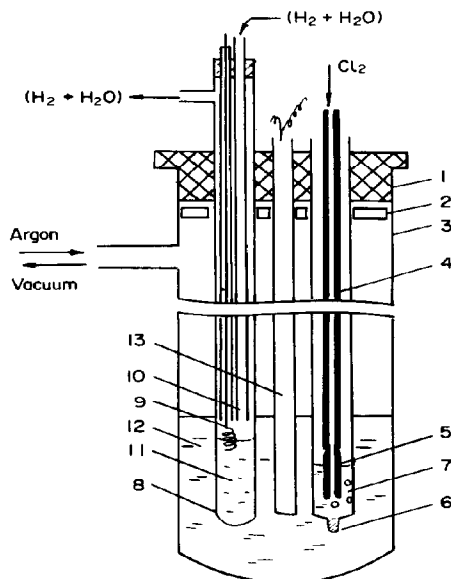


Fig. 1. Experimental device: (1) rubber plug, (2) fluoroplastic thermal screen, (3) quartz test tube, (4) graphite tube, (5) tip of spectral-purity carbon, (6) porous asbestos diaphragm, (7) melt of MCl , (8) aluminum test tube, (9) gold wire in aluminum capillary, (10) nickel tube, (11) melt of $MOH + MX$ under investigation, (12) melt of MCl , (13) thermocouple quartz jacket.

$\text{H}_2\text{O} + \text{H}_2$ whereas the surface of platinum became lusterless, its electrode potential was poorly reproducible and ~ 50 mV more positive than that of gold.

Hydrogen was produced by electrolysis. It was passed through a trap with an activated carbon cooled at -195°C to remove traces of oxygen and saturated with water vapour in a thermostat at $40\text{--}50^\circ\text{C}$. The temperature of water in it was maintained constant within 0.5°C at present values. The partial pressure of the water vapour in its mixtures with hydrogen was varied from 7300 to 15700 Pa. They were fed into the gas space of the electrode through a fluoroplastic tube heated above the water condensation points and released out of it through a waterlock. The partial pressures of H_2O and H_2 in their mixtures were calculated at a total pressure of one atmosphere, making use of the most reliable data on the temperature dependence of saturation vapour pressure for H_2O [8].

Alkali halides were purified from traces of hydrolysis products and other impurities which could react with hydroxides, by zone melting. The hydroxide ions were introduced into the melts by adding samples of alkali hydroxides (NaOH and KOH) or reducing water vapour on an auxiliary nickel cathode: $\text{H}_2\text{O}(\text{g}) + \text{e}^- = \text{OH}^-(\text{melt}) + \frac{1}{2}\text{H}_2(\text{g})$. Other electrode reactions can also take place at higher current densities: $\text{H}_2\text{O}(\text{g}) + 2\text{e}^- = \text{O}^{2-}(\text{melt}) + \text{H}_2(\text{g})$ and $M^+(\text{melt}) + \text{e}^- = M^0(\text{melt})$. However their products (oxide ions and solutions of alkali metals in their molten halides) react with water vapour to give hydroxide ions. A gold cathode is quite unacceptable for this purpose because of forming alloys of gold with alkali metals. The hydroxide concentration was controlled coulometrically and checked by chemical analysis.

The capsulated gas electrodes were immersed in a molten chloride of the same alkali metal. It was in a wide quartz tube. Its gas space was filled with argon to exclude the possibility of an explosion in case hydrogen penetrates from the water-hydrogen electrode through its wall. The cell arranged in a massive high-temperature steel block was heated in an electric furnace with controlled temperature. It was measured with a Pt-PtRh thermocouple in a quartz jacket dipped in the melt in the middle compartment, and could be maintained constant within 2°C at set values.

The emf was measured with a digital voltmeter the inner input resistance of which was $10\text{ M}\Omega$ to an accuracy of 2.5 mV whereas the inner resistance of the cells was about $300\ \Omega$. So the potential ohmic drop in them was negligible (of the order of 10^{-4} V) in comparison with the emf ($\sim 2\text{ V}$). Its values were assumed to be reliable if they had remained constant within random errors of measurements for an hour and longer, with temperature and partial pressures of the gases on the electrodes being unchanged.

The experimental values of the emf include a thermo-emf between carbon and gold leads to the electrodes of the cells. It was measured in a massive metal block with two narrow channels in which a precise Pt-PtRh and Au-C thermocouples were inserted. The carbon was of the same type as the lead to the chlorine electrode. The thermo-emf has an opposite sign against the electrode potential difference to be determined.

$$\varepsilon = \varepsilon_{\text{exp}} - \varepsilon_T$$

Its temperature dependence can be approximated by an equation

$$\varepsilon_T = -0.977 + 5.79 \times 10^{-3} \Delta T \pm 0.003\text{ mV}$$

on the confidence level of 0.95. Here ΔT is a temperature difference between the hot and cold junctions of the Au-C thermocouple.

The thermo-emf taken account, the experimental emf values of the cells in question contain another electric potential jump on the diaphragm separating the melts of MX and $\text{MX} + \text{MOH}$. It arises from differences in the mobilities of ions X^- and OH^- diffusing in the opposite directions through diaphragm pores owing to their chemical-potential gradients $d\mu_{\text{X}^-}$ and $d\mu_{\text{OH}^-}$. That is the so-called diffusion potential:

$$\begin{aligned} E_{\text{dif}} &= -\frac{1}{F} \left(\int_{N_{\text{MX}}-1}^{N_{\text{MX}}} t_{\text{X}^-} d\mu_{\text{MX}} + \int_{N_{\text{MOH}}=0}^{N_{\text{MOH}}} t_{\text{OH}^-} d\mu_{\text{MOH}} \right) \\ &= -\frac{RT}{F} \left[\int_1^{N_{\text{MX}}} t_{\text{X}^-} \left(\frac{df_{\text{MX}}}{f_{\text{MX}}} + \frac{dN_{\text{MX}}}{N_{\text{MX}}} \right) \right. \\ &\quad \left. + \int_0^{N_{\text{MOH}}} t_{\text{OH}^-} \left(\frac{df_{\text{MOH}}}{f_{\text{MOH}}} + \frac{dN_{\text{MOH}}}{N_{\text{MOH}}} \right) \right] \end{aligned}$$

where t_{X^-} and t_{OH^-} are transport numbers of the indicated ions, f_{MX} and f_{MOH} , N_{MX} and N_{MOH} are activity coefficients and molar fractions of MX and MOH in the electrolyte of the $\text{H}_2\text{O} + \text{H}_2$ electrode.

The solutions of alkali hydroxides in molten alkali halides are close to perfect mixtures. Consequently, $f_{\text{MX}} = 1$ and

$$E_{\text{dif}} = \frac{RT}{F} (t_{\text{X}^-}^* - t_{\text{OH}^-}^*) N_{\text{MOH}}$$

Here $t_{\text{X}^-}^* = t_{\text{X}^-}/N_{\text{MX}}$ and $t_{\text{OH}^-}^* = t_{\text{OH}^-}/N_{\text{MOH}}$ are partial transport numbers. Unlike t_{X^-} and t_{OH^-} , they do not change much with the MOH concentration in the melts $\text{MOH} + \text{MX}$ and therefore could be taken as factors outside the integral signs.

So

$$E_{\text{dif}} = 8.617 \times 10^{-5} T (t_{\text{X}^-}^* - t_{\text{OH}^-}^*) N_{\text{MOH}}, \text{ V.}$$

As $1 \geq (t_{\text{X}^-}^* - t_{\text{OH}^-}^*) \geq -1$, the diffusion potential at $1000\text{--}1200\text{ K}$ and $N_{\text{MOH}} = 10^{-2}$ does not exceed the experimental error (2–3 mV).

It will be noted that this estimation of the diffusion potential is also valid for the cells with the chlorine electrode instead of the bromine or iodine one. Their emf and the experimental values of the potential difference $E_{\text{Br}_2/\text{Cl}_2}$ or $E_{\text{I}_2/\text{Cl}_2}$ include the same potential jump caused by the diffusion of ions Br^- or I^- and Cl^- through porous diaphragms. It is eliminated when one takes the difference of $\varepsilon - E_{\text{Br}_2/\text{Cl}_2}$ or $\varepsilon - E_{\text{I}_2/\text{Cl}_2}$, but there remains a contribution of the potential jump which arises from the diffusion of ions OH^- and Cl^- , Br^- or I^- having different mobilities.

Detailed analysis of experimental-error sources in measuring equilibrium values of the emf, the gas pressures on electrodes and temperature, in determining alkali hydroxide concentrations in the electrolytes of the cells, as well as in the literature thermodynamic data used in calculations, has shown that relative error in determining $\ln K^*$ did not exceed 6%.

THE EQUILIBRIUM CONSTANT FOR THE HYDROLYTIC REACTIONS OF MOLTEN ALKALI CHLORIDES

The hydrolysis of molten lithium chloride results in the formation of comparable amounts of its hydroxide and oxide, which makes it difficult to interpret the experimental observations. Therefore one had to confine oneself to determining the equilibrium constant as a function of temperature for the hydrolytic reactions of molten NaCl, KCl and CsCl among the products of which alkali hydroxides predominate over their oxides. It has been calculated from the experimental data by an equation

$$\ln K^* = 0.737 - \frac{11605}{T} (\varepsilon - 0.973) + \ln \frac{P_{H_2}^{1/2} \cdot P_{Cl_2}^{1/2}}{P_{H_2O}} N_{MOH},$$

on assumption that $\Delta G_2^0 = -94679 - 6.13T$, J mol⁻¹ HCl. The variables entering in it varied within 1033–1242 K, 1.850–2.460 V, 84660–94070, 96530–102270 and 7370–12340 Pa; $(0.86-2.32) \times 10^{-2}$, respectively, for T , ε , P_{H_2} , P_{Cl_2} , and P_{H_2O} , N_{MOH} .

To minimize the experimental error originating from the gas pressure variations on the electrodes and the changes in composition of the melts as a consequence of volatilisation of their components, the duration of the experiments did not exceed 4 h. One could measure the emf of the cells at one–three temperatures during this time under otherwise equal conditions, (P_{H_2} , P_{Cl_2} , P_{H_2O} and N_{MOH}).

The experimental values of the equilibrium constant are represented in Fig. 2 as plots of $\ln K^*$ against $1/T$. They can be approximated by the following empirical equations derived from the experimental data by the least-squares technique on the confidence level of 0.95.

$$\ln K^* = (9.306 \pm 1.104) - \frac{25294 \pm 1297}{T} \pm 0.383 \quad (\text{NaCl})$$

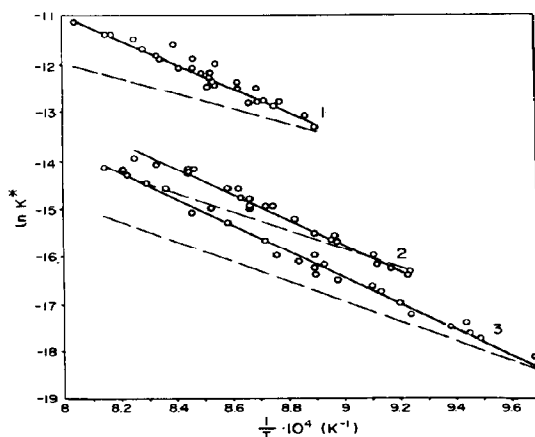


Fig. 2. Temperature dependence of conditional equilibrium constant for hydrolytic reactions of molten NaCl(1), KCl(2), and CsCl(3).

$$\ln K^* = (8.368 \pm 0.587) - \frac{26796 \pm 670}{T} \pm 0.304 \quad (\text{KCl})$$

$$\ln K^* = (8.014 \pm 0.515) - \frac{27173 \pm 579}{T} \pm 0.356 \quad (\text{CsCl}).$$

The hydrolysis of molten NaCl had been studied earlier[1] by the independent dynamic chemical method. The equilibrium hydrolytic constant was found to be on the order of 10^{-6} to 10^{-5} at 1075–1223 K, which is in close agreement with that determined by the electrochemical technique.

The hydrolysability of molten alkali chlorides falls from NaCl to CsCl as the ionic potential of their cations decreases. That is a direct consequence of weakening their polarizing action on H₂O molecules in the melts, which hinders their splitting into ions of OH⁻ staying in them and H⁺ forming covalent HCl molecules expelled from them.

There is a linear relation of $\ln K^*$ to the inverse of the nominal crystallochemical radii of alkali cations ($1/r_{M^+}$) (see Fig. 3). By making use of it one can estimate the equilibrium constant for the hydrolytic reaction of molten RbCl. It turns out to be 8.3×10^{-8} , 2.4×10^{-7} , 6.4×10^{-7} and 1.6×10^{-6} , respectively, at 1100, 1150, 1200 and 1250 K.

The equilibrium hydrolytic constant known, one can quantitatively evaluate an extent of purifying molten alkali chlorides from their hydroxides by blowing hydrogen chloride through them, depending on the HCl and H₂O partial pressures in the gas phase. Given in Table 1 are the molar fractions of MOH in the molten MCl which are in equilibrium with the gas bubbles at indicated temperatures and ratios of P_{H_2O}/P_{HCl} . In reality, the efficiency of the purification procedure is dependent in a large measure on conditions of conducting the experiments, in particular, the partial pressure of H₂O in the gas flow and its velocity.

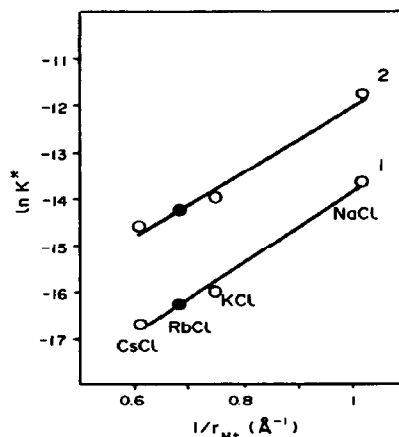


Fig. 3. Relation of $\ln K^*$ to the inverse of nominal crystallochemical radii of alkali cations for their chlorides at 1100(1) and 1200 K (2).

Table 1. The molar fraction of alkali hydroxide in molten chlorides which are in equilibrium with the gas phase ($\text{HCl} + \text{H}_2\text{O}$)

$P_{\text{H}_2\text{O}}/P_{\text{HCl}}$	N_{NaOH}		N_{KOH}	
	1100 K	1200 K	1100 K	1200 K
10^3	1.1×10^{-3}	7.7×10^{-3}	1.1×10^{-4}	8.6×10^{-4}
1	1.1×10^{-6}	7.7×10^{-6}	1.1×10^{-7}	8.6×10^{-7}
10^{-3}	1.1×10^{-9}	7.7×10^{-9}	1.1×10^{-10}	8.6×10^{-10}
	N_{RbOH}		N_{CsOH}	
	1100 K	1200 K	1100 K	1200 K
10^3	8.3×10^{-5}	6.4×10^{-4}	5.7×10^{-5}	4.4×10^{-4}
1	8.3×10^{-8}	6.4×10^{-7}	5.7×10^{-8}	4.4×10^{-7}
10^{-3}	8.3×10^{-11}	6.4×10^{-10}	5.7×10^{-11}	4.4×10^{-10}

THE EQUILIBRIUM CONSTANT FOR THE HYDROLYTIC REACTIONS OF MOLTEN ALKALI BROMIDES

The measurements were carried out with cells in which the chlorine electrode was substituted for the bromine one. Therefore the potential difference between them had to be eliminated from the measured emf. This difference had been determined earlier[5] as a function of temperature for all the pairs of alkali bromides and chlorides with the same cations including these.

$$E_{\text{Br}_2/\text{Cl}_2} = -0.434 + 10.3 \times 10^{-5} T \pm 0.002 \text{ V}$$

(in NaBr and NaCl)

$$E_{\text{Br}_2/\text{Cl}_2} = -0.302 + 3.7 \times 10^{-5} T \pm 0.001 \text{ V}$$

(in KBr and KCl)

$$E_{\text{Br}_2/\text{Cl}_2} = -0.254 + 1.9 \times 10^{-5} T \pm 0.001 \text{ V}$$

(in CsBr and CsCl).

The conditional equilibrium constant has been computed from the experimental data by an equation:

$$\ln K^* = 0.797 - \frac{11605}{T} (\varepsilon - E_{\text{Br}_2/\text{Cl}_2} - 0.560) + \ln \frac{P_{\text{H}_2}^{1/2} \cdot P_{\text{Cl}_2}^{1/2}}{P_{\text{H}_2\text{O}}} N_{\text{MOH}},$$

with standard Gibbs energy of the reaction $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Br}_2(\text{g}) = \text{HBr}(\text{g})$ being $\Delta G_2^0 = -54063 - 6.625T$, J mol^{-1} HBr. The variables entering in the equation varied within 1060–1242 K, 1.910–2.400 V, 84720–94550, 98590–102320 and 7370–15730 Pa, $(0.17\text{--}1.28)10^{-2}$, respectively, for T , ε , P_{H_2} , P_{Cl_2} and $P_{\text{H}_2\text{O}}$, N_{MOH} .

The values of the equilibrium hydrolytic constant for molten NaBr, KBr and CsBr are shown in Fig. 4 where $\ln K^*$ is plotted against $1/T$. The linear polytherms are described by the following equations on the confidence level of 0.95

$$\ln K^* = (3.506 \pm 0.560) - \frac{19786 \pm 657}{T} \pm 0.300$$

(NaBr)

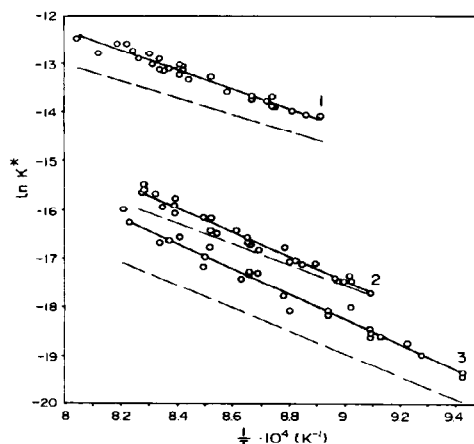


Fig. 4. Temperature dependence of conditional equilibrium constant for hydrolytic reactions of molten NaBr(1), KBr(2), and CsBr(3).

$$\ln K^* = (5.596 \pm 0.679) - \frac{25661 \pm 785}{T} \pm 0.321$$

(KBr)

$$\ln K^* = (5.626 \pm 0.763) - \frac{26588 \pm 865}{T} \pm 0.392$$

(CsBr).

As with the chlorides, the hydrolysability of molten alkali bromides diminishes from NaBr to CsBr, being smaller for the salts with the same cations. That can be explained by a lower bond energy of the atoms in covalent molecules of HBr compared to that in HCl.

There is a linear relation of $\ln K^*$ to $1/r_M$, where r_M is a crystallochemical radius of alkali cations (see Fig. 5). It enabled the equilibrium hydrolytic constant of molten RbBr to be found equal to 1.33×10^{-8} , 3.72×10^{-8} , 9.61×10^{-8} and 2.30×10^{-7} , respectively, at 1100, 1150, 1200 and 1250 K.

In Table 2 the molar fractions are given for alkali hydroxides in molten bromides which are in equilibrium with the gas phase ($\text{HBr} + \text{H}_2\text{O}$) under indicated conditions. They help in judging the extent of contamination of the melts by the hydroxides.

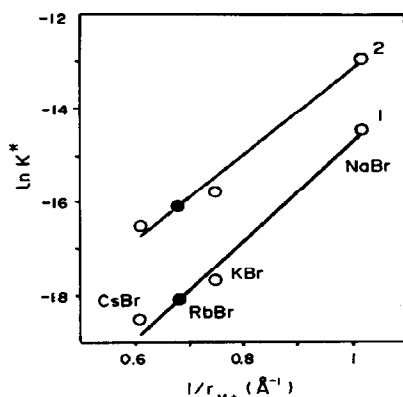


Fig. 5. Relation of $\ln K^*$ to the inverse of nominal crystallochemical radii of alkali cations for their bromides at 1100 K (1) and 1200 K (2).

THE EQUILIBRIUM CONSTANT FOR THE HYDROLYTIC REACTIONS OF MOLTEN ALKALI IODIDES

The measurements were also made with cells in which the iodine electrode was replaced with the chlorine one. On conversion to the emf of the cells with iodine electrode one must know the potential difference between them. This has been measured earlier [6] as a function of temperature for the salt pairs and can be expressed with the following equations:

$$E_{I_2/Cl_2} = -0.801 + 0.4 \times 10^{-5} T \pm 0.001 \text{ V} \quad (\text{NaI/NaCl})$$

$$E_{I_2/Cl_2} = -0.747 + 4.0 \times 10^{-5} T \pm 0.001 \text{ V} \quad (\text{KI/KCl})$$

$$E_{I_2/Cl_2} = -0.658 + 2.9 \times 10^{-5} T \pm 0.001 \text{ V} \quad (\text{CsI/CsCl}).$$

The conditional equilibrium constant has been calculated from the experimental observations by an

equation

$$\ln K^* = 0.866 - \frac{11605}{T} (\varepsilon - E_{I_2/Cl_2} - 0.070) + \ln \frac{P_{H_2}^{1/2} \cdot P_{Cl_2}^{1/2}}{P_{H_2O}} N_{MOH},$$

with standard Gibbs energy of the reaction $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) = HI(g)$ being $\Delta G_2^0 = -6802 - 7.199 T$, $J \text{ mole}^{-1} HI$. The variables in the equation varied in our experiments within 1054–1224 K, 1.970–2.410 V, 86030–94480, 97460–101860 and 7370–12960 Pa, $(0.18\text{--}1.54) \times 10^{-2}$, respectively, for T , ε , P_{H_2} , P_{Cl_2} and P_{H_2O} , N_{MOH} .

The values of the equilibrium constant for the hydrolytic reactions of molten sodium, potassium and cesium iodides are represented in Fig. 6 where $\ln K^*$ are plotted against $1/T$. The experimental polytherms can be approximated by the following equations

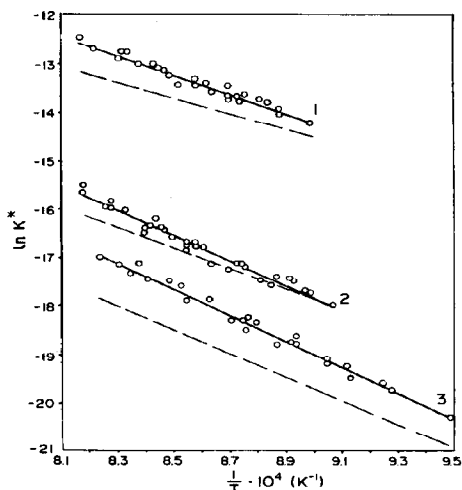


Fig. 6. Temperature dependence of conditional equilibrium constant for hydrolytic reactions of molten NaI(1), KI(2), and CsI(3).

Table 2. The molar fraction of alkali hydroxides in molten bromides which are in equilibrium with the gas phase ($HBr + H_2O$)

P_{H_2O}/P_{HBr}	N_{NaOH}		N_{KOH}	
	1100 K	1200 K	1100 K	1200 K
10^3	5.1×10^{-4}	2.3×10^{-3}	2.0×10^{-5}	1.4×10^{-4}
1	5.1×10^{-7}	2.3×10^{-6}	2.0×10^{-8}	1.4×10^{-7}
10^{-3}	5.1×10^{-10}	2.3×10^{-9}	2.0×10^{-11}	1.4×10^{-10}
	N_{RbOH}		N_{CsOH}	
	1100 K	1200 K	1100 K	1200 K
10^3	1.3×10^{-5}	9.6×10^{-5}	8.8×10^{-6}	6.6×10^{-5}
1	1.3×10^{-8}	9.6×10^{-8}	8.8×10^{-9}	6.6×10^{-8}
10^{-3}	1.3×10^{-11}	9.6×10^{-11}	8.8×10^{-12}	6.6×10^{-11}

derived on the confidence level of 0.95.

$$\ln K^* = (4.054 \pm 0.723) - \frac{20315 \pm 841}{T} \pm 0.305 \quad (\text{NaI})$$

$$\ln K^* = (5.652 \pm 0.702) - \frac{2612 \pm 816}{T} \pm 0.336 \quad (\text{KI})$$

$$\ln K^* = (5.30 \pm 0.571) - \frac{2699 \pm 650}{T} \pm 0.329 \quad (\text{CsI})$$

The values determined by us are in good agreement with those found by the independent dynamic chemical method for molten NaI[2].

In the series of molten alkali iodides the same change in their hydrolysability is observed as with the chlorides and bromides: it decreases from sodium to caesium salts, being the smallest among them with an exception of NaI, the equilibrium hydrolytic constant of which is a little bigger than that of NaBr in the temperature range under study.

A linear relation of $\ln K^*$ to $1/r_{M^+}$ is also valid for these melts (see Fig. 7). By making use of it, the

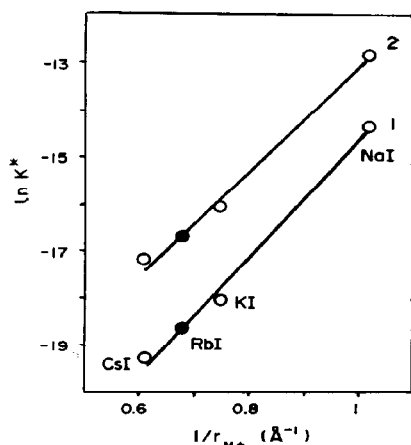


Fig. 7. Relation of $\ln K^*$ to the inverse of nominal crystallo-chemical radii of alkali cations for their iodides at 1100(1) and 1200 K (2).

equilibrium hydrolytic constant was estimated for molten RbI. It has been found to be 8.22×10^{-9} , 2.41×10^{-8} , 6.27×10^{-8} , and 1.51×10^{-7} , respectively, at 1100, 1150, 1200 and 1250 K.

To illustrate the hydrolysability of molten alkali iodides in Table 3 the molar fractions of alkali hydroxides in them are cited when the melts are in equilibrium with the gas phase ($\text{HI} + \text{H}_2\text{O}$) under given conditions.

Among molten alkali chlorides, bromides and iodides, with the exception of lithium salts, molten NaCl displays the biggest hydrolysability and molten CsI the smallest one. But it is well known that the latter is the most unstable towards the free air action which is a result of reactions of the atmospheric oxygen with iodide anions: $\text{O}_2(\text{g}) + 4\text{I}^-(\text{melt}) = 2\text{O}_2^{2-}(\text{melt}) + 2\text{I}_2(\text{g})$, $\text{O}_2(\text{g}) + 2\text{I}^-(\text{melt}) = \text{O}_2^{2-}(\text{melt}) + \text{I}_2(\text{g})$, or $\text{O}_2(\text{g}) + \text{I}^-(\text{melt}) = \text{O}_2^-(\text{melt}) + \frac{1}{2}\text{I}_2(\text{g})$. Naturally, this conclusion must be verified by direct experimental investigations of the cells $\text{I}_2(\text{g}), \text{C}|\text{MI}(\text{melt})|\text{NMO}_2 + (1-N)\text{MI}(\text{melt})|\text{Pt}, \text{O}_2(\text{g})$ with water being fully excluded.

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One can calculate the equilibrium constant for the hydrolytic reactions of molten alkali chlorides, bromides and iodides

$$K^0 = e^{-\Delta G^0/RT} = \frac{P_{\text{HX}} a_{\text{MOH}(\text{melt})}}{P_{\text{H}_2\text{O}} a_{\text{MX}(\text{melt})}}$$

from the data available in literature[4] on the thermodynamic properties of their components, and thus find the activity coefficient f_{MOH}^* of alkali hydroxides dissolved in their molten halides at $N_{\text{MOH}} \rightarrow 0$ that is $a_{\text{MX}} \rightarrow 1$.

$$f^* = K^0/K^*$$

The results of the K^0 calculations are shown in Fig. 2, 4 and 6 with dashed lines. The values of f_{MOH}^* found in such a way are given in Table 4.

The activity coefficients of NaOH, KOH and CsOH in their dilute solutions in corresponding molten alkali chlorides, bromides, and iodides are in proximity of zero order (they vary from 0.30 to 0.59 at 1250 K, and from 0.82 to 2.11 at the melting points of the salts), which suggests that the solutions in question are close

Table 3. The molar fraction of alkali hydroxides in molten iodides which are in equilibrium with the gas phase ($\text{HI} + \text{H}_2\text{O}$)

$P_{\text{H}_2\text{O}}/P_{\text{HI}}$	N_{NaOH}		N_{KOH}	
	1100 K	1200 K	1100 K	1200 K
10^3	5.5×10^{-4}	2.6×10^{-3}	1.4×10^{-5}	1.0×10^{-4}
1	5.5×10^{-7}	2.6×10^{-6}	1.4×10^{-8}	1.0×10^{-7}
10^{-3}	5.5×10^{-10}	2.6×10^{-9}	1.4×10^{-11}	1.0×10^{-10}
	N_{RbOH}		N_{CsOH}	
	1100 K	1200 K	1100 K	1200 K
10^3	8.2×10^{-6}	6.3×10^{-5}	4.4×10^{-6}	3.4×10^{-5}
1	8.2×10^{-9}	6.3×10^{-8}	4.4×10^{-9}	3.4×10^{-8}
10^{-3}	8.2×10^{-12}	6.3×10^{-11}	4.4×10^{-12}	3.4×10^{-11}

Table 4. The activity coefficient of alkali hydroxides in their dilute solutions in molten alkali halides at their melting points and 1250 K

Solution	T, K	f_{MOH}^*	T, K	f_{MOH}^*
NaOH + NaCl	1074	1.20	1250	0.40
NaOH + NaBr	1020	0.82	1250	0.48
NaOH + NaI	934	1.54	1250	0.48
KOH + KCl	1044	1.40	1250	0.40
KOH + KBr	1007	1.38	1250	0.57
KOH + KI	954	2.11	1250	0.59
CsOH + CsCl	919	1.80	1250	0.30
CsOH + CsBr	910	0.94	1250	0.37
CsOH + CsI	905	0.87	1250	0.35

Table 5. Gibbs energy (in kJ/mole MOH) of molten alkali hydroxides

MOH	MX	1100 K			1200 K		
		$-\Delta G_{MOH(MX)}^*$	$-\Delta G_{MOH(av)}^*$	$-\Delta G_{MOH}^{\circ}[4]$	$-\Delta G_{MOH(MX)}^*$	$-\Delta G_{MOH(av)}^*$	$-\Delta G_{MOH}^{\circ}[4]$
NaOH	NaCl	540.8			567.2		
	NaBr	544.3	542.7	540.6	566.2	566.4	559.8
	NaI	543.0			565.7		
KOH	KCl	556.9			583.5		
	KBr	556.8	556.6	556.5	581.3	581.9	577.5
	KI	556.2			581.0		
CsOH	CsCl	581.2			609.8		
	CsBr	582.7	582.4	576.9	609.3	609.7	600.5
	CsI	583.3			609.9		

to ideal mixtures. Being below or above unity the activity coefficient of any component of solutions must tend to 1 as temperature rises. Its calculated values seem to be inconsistent with their general thermodynamic conception. The unreliability of the thermodynamic properties of molten alkali hydroxides used in the calculations is most likely to be a cause of the contradiction.

If the solutions of MOH in molten MX are supposed to be perfect mixtures one can estimate more probable values of Gibbs energy for individual molten NaOH, KOH and CsOH by making use of more reliable thermodynamic data[4] for other components of the reactions: $H_2O(g) + MX(melt) \rightleftharpoons MOH(melt) + HX(g)$ and their conditional equilibrium constant determined experimentally.

$$\Delta G_{MOH(melt)}^* = -RT \ln K^* + \Delta G_{MX(melt)}^{\circ} + \Delta G_{H_2O(g)}^{\circ} - \Delta G_{HX(g)}^{\circ}$$

The average experimental values of $\Delta G_{MOH(av)}^*$ are juxtaposed with ΔG_{MOH}° available in literature[4]. The

discrepancy between them reaches $\sim 2\%$ for CsCl. (See Table 5).

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