# CHEMICAL EQUILIBRIUM IN MOLTEN SALT SOLUTIONS

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Abstract – The paper discusses two types of chemical equilibrium reactions (complex formation and acid-base reactions) in molten salt solutions. The thermodynamic and electrochemical methods for the study of complex formation in molten salt media are also discussed. Two types of acid-base equilibrium in ionic melts containing oxygen ions are considered.

## INTRODUCTION

In molten salt solutions, two types of chemical equilibrium reactions are of greatest interest: 1) complex formation reactions; 2) acid-base reactions. Many methods have been developed for the study of complex formation in molten salt systems. They may be divided into three groups: 1) thermodynamic methods; 2) electrochemical methods; 3) physicochemical nonequilibrium methods (Ref. 1-6). In this paper, thermodynamic and electrochemical methods are considered.

## THERMODYNAMICS

To thermodynamically characterize the complex formation in salt melts, we have proposed (Ref. 7) to use excessive thermodynamic functions. They are differences between the experimental and "ideal" values of the corresponding thermodynamic quantities

$$\Delta \bar{G}^{E} = \bar{G} - \bar{G}^{i} \tag{1}$$

$$\Delta \bar{S}^{E} = \bar{S} - \bar{S}^{i} \tag{2}$$

$$\Delta \bar{H}^{E} = \bar{H} - \bar{H}^{i} \tag{3}$$

$\bar{G}^{E}$, $\bar{S}^{E}$ and $\bar{H}^{E}$ are the excessive functions, $\bar{G}^{i}$, $\bar{S}^{i}$ and $\bar{H}^{i}$ the "ideal" values. The "ideal" values for molten salt systems can be calculated using Temkin's equation. For example, for $\bar{G}^{i}$ we have

$$\Delta \bar{G}^{i} = RT(N_{A}\ln N_{A} + N_{B}\ln N_{B} + N_{C}\ln N_{C} + N_{D}\ln N_{D}) \tag{4}$$

where $N_{A}$, $N_{B}$, $N_{C}$ and $N_{D}$ are the mole fractions of the molten salt system components. If we plot the excessive function against mole fraction, we obtain curves like those in Fig. 1.

The experimental values of thermodynamic functions are determined from emf measurements on **appropriate** chemical galvanic cells. By using this method, we have studied complex formation in many chloride systems. Some results of these studies are listed in Table 1. These data show that the most stable compounds are $Na_{2}BeCl_{4}$, $RbMgCl_{4}$ and $RbPbCl_{4}$. The composition of the most stable compounds can be established from the position of the minimum on $\bar{G}^{E}$N – N curves. After we had developed a platinum-oxygen reference electrode for ionic melts (Ref. 8), we studied the complex formation in molten oxide-salt systems. To this end, emf's of the chemical cells

$$Me \mid Me_{m}O_{n} - salt \mid Pt, O_{2}$$
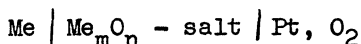
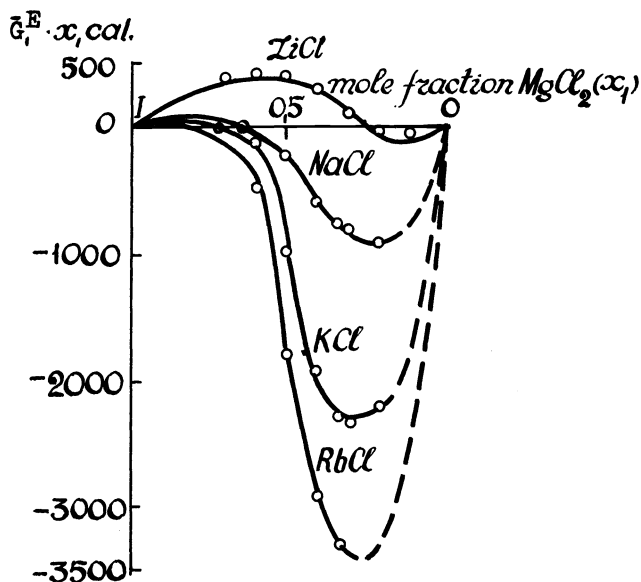were measured. Sodium metaphosphate and borax were investigated as molten

Fig. 1. The change in excessive partial isobaric potential as a function of the composition of molten lithium, sodium, potassium and rubidium chlorides containing magnesium chloride at 718 °C

TABLE 1. Thermodynamic characterization of complex formation in molten chlorides

| Molten salt system | Temperature (°C) | Mole fraction | Thermodynamic excess quantities | | |
|---|---|---|---|---|---|
| | | | $\Delta \bar{H}^E$ (J/mol) | $\Delta \bar{G}^E$ (J/mol) | $\Delta \bar{S}^E$ (J/mol deg) |
| $MgCl_2$-LiCl | 718 | 0.33 | -600000 | +1975 | 21.7 |
| $MgCl_2$-NaCl | " | 0.33 | -624000 | -9450 | 21.6 |
| $MgCl_2$-KCl | " | 0.33 | -624000 | -29000 | 21.6 |
| $MgCl_2$-RbCl | " | 0.33 | - | -41600 | - |
| $PbCl_2$-LiCl | 550 | 0.405 | -335000 | -175 | 4.05 |
| $PbCl_2$-NaCl | " | 0.551 | -342000 | -1890 | 1.07 |
| $PbCl_2$-KCl | " | 0.344 | -351000 | -9480 | 3.70 |
| $PbCl_2$-RbCl | " | 0.403 | -354000 | -10950 | 6.06 |
| $PbCl_2$-NaCl-KCl | 500 | 0.48 | -330000 | -5660 | 25.2 |
| $CuCl$-$PbCl_2$-NaCl-KCl | " | 0.40 | -115800 | -1590 | 16.6 |
| $AgCl$-$PbCl_2$-NaCl-KCl | " | 0.32 | -3620 | +2270 | 2.00 |
| $BiCl_3$-$PbCl_2$-NaCl-KCl | 430 | 0.30 | -326000 | -4680 | 18.8 |
| $BeCl_2$-NaCl | 500 | 0.32 | - | -31300 | - |

salt ligands. Previous to that, the emf of the chemical cell

$$Me \mid Me_mO_n \mid Pt, O_2$$
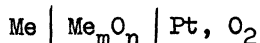
had been studied. The results of these studies are given in Table 2. In five systems investigated, a noticeable chemical interaction takes place as evidenced by a great difference between concentrations and activities and by large values of excessive isobaric potentials. The strongest chemical interaction takes place in the systems: bismuth oxide-borax and bismuth oxide-sodium metaphosphate. The plot of $N\Delta\bar{G}$ against N shows that in the

TABLE 2. Thermodynamic characterization of molten systems on the basis of emf measurements on galvanic cells

| Oxide | Concentration (mole fraction) | Sodium metaphosphate | | | Borax | | |
|---|---|---|---|---|---|---|---|
| | | Temperature (°C) | Activity of the oxide | Excessive isobaric potential (kJ/mol) | Temperature (°C) | Activity of the oxide | Excessive isobaric potential (kJ/mol) |
| Lead oxide | 0.01 | 800 | $1.4 \times 10^{-6}$ | -98.6 | 950 | $1.4 \times 10^{-3}$ | -22.0 |
| | 0.05 | " | $8.2 \times 10^{-6}$ | -106.2 | | $0.35 \times 10^{-2}$ | -27.0 |
| | 0.10 | " | $1.9 \times 10^{-5}$ | -98.8 | | $0.5 \times 10^{-2}$ | -31.0 |
| | 0.20 | " | $1.05 \times 10^{-4}$ | -94.2 | | $0.85 \times 10^{-2}$ | -31.0 |
| | 0.30 | " | $8 \times 10^{-4}$ | -74.7 | | $0.98 \times 10^{-2}$ | -33.0 |
| | 0.01 | 900 | $1.8 \times 10^{-6}$ | -94.6 | 900 | $0.2 \times 10^{-2}$ | -22.0 |
| | 0.05 | | $0.8 \times 10^{-6}$ | -100.2 | | $0.3 \times 10^{-2}$ | -27.0 |
| | 0.10 | | $7.8 \times 10^{-5}$ | -98.6 | | $0.43 \times 10^{-2}$ | -31.0 |
| | 0.20 | | $3.3 \times 10^{-5}$ | -85.6 | | $0.96 \times 10^{-2}$ | -31.0 |
| | 0.30 | | $2.3 \times 10^{-4}$ | -74.8 | | $0.98 \times 10^{-2}$ | -32.0 |
| Bismuth oxide | 0.01 | 860 | $0.03 \times 10^{-10}$ | -225.0 | 920 | $0.66 \times 10^{-2}$ | -7.5 |
| | 0.03 | | $0.3 \times 10^{-8}$ | -150.0 | | $0.14 \times 10^{-1}$ | -3.7 |
| | 0.05 | | $0.12 \times 10^{-7}$ | -143.8 | | $0.38 \times 10^{-1}$ | -2.5 |
| | 0.10 | | $0.3 \times 10^{-6}$ | -136.0 | | $10^{-1}$ | -3.0 |
| Nickel oxide | 0.05 | 900 | $0.21 \times 10^{-2}$ | -8.35 | | | |
| | 0.01 | | $0.44 \times 10^{-2}$ | -7.78 | | | |
| | 0.05 | | $0.72 \times 10^{-2}$ | -18.40 | | | |
| | 0.10 | | $0.98 \times 10^{-2}$ | -22.58 | | | |

system lead oxide-sodium metaphosphate, the most stable complex corresponds to the composition $PbO \cdot 6NaPO_3$ (Fig. 2).
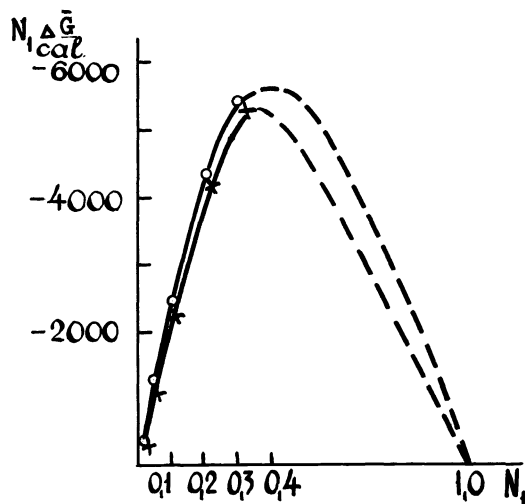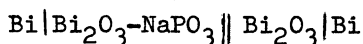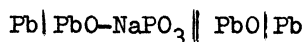


Fig. 2. A plot of $N \Delta \bar{G}$ against $N$ for the system lead oxide-sodium metaphosphate: oo - 800 °C; xx - 900 °C

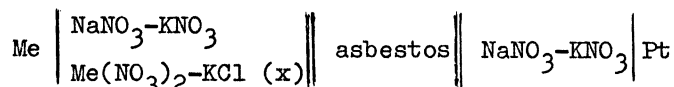We studied the complex formation in the same molten systems by emf measurements on the concentration cells
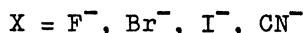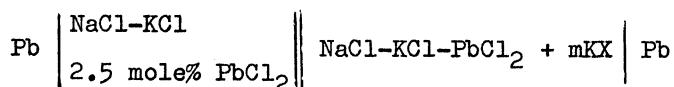
$$Pb \mid PbO-NaPO_3 \parallel PbO \mid Pb$$

$$Bi \mid Bi_2O_3-NaPO_3 \parallel Bi_2O_3 \mid Bi$$

Complex formation in such systems can be inferred from the plots of $\Psi$ against $1/N_1$, where $\Psi$ is the emf and $N_1$ the mole fraction of the oxide. The bends on these plots correspond to the composition of complex compounds. In such a way, the complex compounds (Ref. 8-10): $PbO \cdot 6NaPO_3$; $Bi_2O_3 \cdot 4NaPO_3$ were determined. The formation of these compounds was confirmed by X-ray investigations (Ref. 11).

### ELECTROCHEMISTRY

We have also studied complex formation in the systems metal chlorides-potassium chloride in molten sodium nitrate-potassium nitrate as solvent. As metal chlorides we used cadmium, lead and nickel chlorides. To this end, we have measured emf's of the concentration cells

$$Me \left| \begin{array}{c} NaNO_3-KNO_3 \\ Me(NO_3)_2-KCl \ (x) \end{array} \right| \left| \ asbestos \ \right| \left| \begin{array}{c} NaNO_3-KNO_3 \end{array} \right| Pt$$

In the left half-cell, the concentration of the ligand (potassium chloride) was varied. The step stability constants of complex species were calculated from the data obtained by potentiometric measurements. This method was also used to study the complexation of lead ions by fluoride, bromide, iodide and cyanide ions as ligands in molten alkali chlorides as supporting electrolytes. To this end, emf's of the concentration cells

$$Pb \left| \begin{array}{c} NaCl-KCl \\ 2.5 \ mole\% \ PbCl_2 \end{array} \right| \left| \ NaCl-KCl-PbCl_2 + mKX \ \right| Pb$$

$$X = F^-, \ Br^-, \ I^-, \ CN^-$$

were measured.

For the case of variable ligand concentrations and constant complexing ion concentration, the equation

$$\frac{dE}{d\ell n[X]} = -\bar{n} \ \frac{RT}{zF} \tag{5}$$

is valid. Here $\bar{n}$ is the coordination number. It follows from the graphical solution of equation (5) that fluoride and iodide ions form one complex each and the cyanide ion forms two compounds with lead ion. Bromide ion forms no compounds with lead ions. The complexity function was also found from the known equation

$$\Delta E = RT/zF \ \ln \mathcal{P} \tag{6}$$

The same complexes were also investigated by potentiodynamic method. Current-potential curves were taken for a pure solvent, for lead chloride solutions without ligands and with ligand additives. From the experimental data, the values of the function $\mathcal{P}$ were found using the equations

$$\Delta E = f([kX]) \tag{7}$$

$$2.3 \log i_p'/i_p = f([kX]) \tag{8}$$

$$\mathcal{P} = \sum_{i=0}^{i} \beta_i [X]^i \tag{9}$$

Some potentiodynamic curves are shown in Fig. 3. Some results of these investigations are listed in Table 3. In molten nitrates, nickel forms four complexes with chloride. In molten chlorides, lead forms the most stable complex with iodide. $i_p'$ and $i_p$ are the peak currents from Fig. 3, $\beta_i$ is the stability constant.
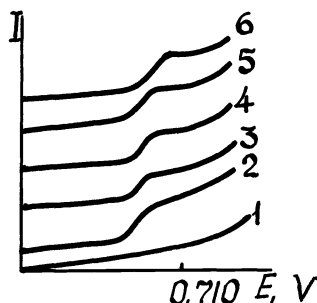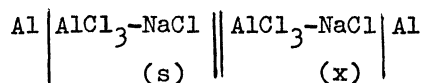
Fig. 3. Potentiodynamic curves: 1 – sodium chloride-potassium chloride melt (supporting electrolyte); 2 – supporting electrolyte + 4x10$^{-3}$ mol of lead chloride; 3-6 – supporting electrolyte + 4x10$^{-3}$ mol + 5x10$^{-2}$, 3x10$^{-2}$, 4x10$^{-2}$ mol of potassium iodide respectively. These values are given for 1000 g of supporting electrolyte.

TABLE 3. Complex formation of the systems KCl-MeCl$_2$ (Me = Cd, Ni, Pb) in molten nitrates. Complexation of Pb$^{2+}$ by the F$^-$, I$^-$ and CN$^-$ ligands in molten chlorides

| Metal ion | Potentiometric method | | | | | | | Potentiodynamic method | |
|---|---|---|---|---|---|---|---|---|---|
| | ligand | solvent | $\beta_1$ | $\beta_2$ | $\beta_3$ | $\beta_4$ | $\Sigma\beta_i$ | $\bar{n}$ | $\beta_1$ |
| Cd$^{2+}$ | Cl$^-$ | NaNO$_3$-KNO$_3$ | 90 | | | | 90 | | |
| Ni$^{2+}$ | Cl$^-$ | NaNO$_3$-KNO$_3$ | 6 | 4 | 14 | 16 | 40 | | |
| Pb$^{2+}$ | Cl$^-$ | NaNO$_3$-KNO$_3$ | 21 | 6 | – | – | 27 | | |
| Pb$^{2+}$ | F$^-$ | NaCl-KCl | 26 | | | | | 0.28 | 32 |
| Pb$^{2+}$ | I$^-$ | NaCl-KCl | 43 | | | | | 0.56 | 37 |
| Pb$^{2+}$ | CN$^-$ | NaCl-KCl | 17 | | | | | 1.89 | 19 |

Polarographic method

| Cd$^{2+}$ | Cl$^-$ | NaNO$_3$-KNO$_3$ | 38 | | | | 38 |
|---|---|---|---|---|---|---|---|
| Ni$^{2+}$ | Cl$^-$ | NaNO$_3$-KNO$_3$ | 5.5 | 6 | 15 | 14 | 40 |
| Pb$^{2+}$ | Cl$^-$ | NaNO$_3$-KNO$_3$ | 21 | 3 | | | 24 |

Interesting results were obtained when studying complex formation in the molten aluminium chloride-sodium chloride system. The concentration cells

$$\text{Al} \left| \begin{matrix} \text{AlCl}_3\text{-NaCl} \\ \text{(s)} \end{matrix} \right\| \left. \begin{matrix} \text{AlCl}_3\text{-NaCl} \\ \text{(x)} \end{matrix} \right| \text{Al}$$

have been investigated. In the left half-cell, there is a saturated sodium chloride solution and in the right one variable sodium chloride concentration (x).

In the melts under investigation, the most probable equilibria are

$$\text{Al}_2\text{Cl}_6 + \text{Cl}^- \rightleftharpoons \text{Al}_2\text{Cl}_7^- \ (\text{K}_1) \tag{10}$$

$$\text{Al}_2\text{Cl}_7^- \rightleftharpoons \text{AlCl}_4^- + \text{AlCl}_3 \ (\text{K}_2) \tag{11}$$

$$2\text{AlCl}_4^- \rightleftharpoons \text{Al}_2\text{Cl}_7^- + \text{Cl}^- \ (\text{K}_3) \tag{12}$$

After the concentration of one of any species has been determined as a function of the melt composition, the concentrations of other species can be calculated from equations (10), (11) and (12). The equilibrium constants have the following values: $K_1 = (3 \pm 0.1) \times 10^8$; $K_2 = (2.6 \pm 0.1) \times 10^4$; $K_3 = (7.8 \pm 0.2) \times 10^8$. This method is described in greater detail in Ref. 12 . In addition to potentiometric and potentiodynamic methods, we used polarography and chronopotentiometry for the study of complex formation in molten salt systems. With ionic melts, polarography is based on the application of solid electrodes. Therefore, we had to derive appropriate equations, which could permit the use of polarography with solid electrodes to study the complex formation in molten salt systems (Ref. 13). These equations are:

$$(\varphi' - \varphi'') = RT/nF \ln \mathcal{P} - RT/nF \ln i_d'/i_d'' \tag{13}$$

$$(\varphi' - \varphi'') = RT/nF \ln \mathcal{P} \tag{14}$$

$$(\varphi' - \varphi'') = RT/nF \ln \mathcal{P} - RT/\alpha nF \ln i_d'/i_d'' \tag{15}$$

$$(\varphi_p' - \varphi_p'') = RT/nF \ln \mathcal{P} - RT/nF \ln i_p'/i_p'' \tag{16}$$

$$(\varphi_p' - \varphi_p'') = RT/nF \ln \mathcal{P} \tag{17}$$

$$(\varphi_p' - \varphi_p'') = RT/\alpha nF \ln \mathcal{P} - RT/\alpha nF \ln i_p'/i_p'' \tag{18}$$

$\mathcal{P}$ is the complexity function, $i_d$ the limiting current, $i_p$ the peak current. A prime denotes the quantities that pertain to processes in the absence of ligand and a double prime in its presence. These equations permit determination of the function $\mathcal{P}$ by the shift of polarograms with adding a ligand.

Equations (13-18) describe different cases: reversible processes with and without depolarization, irreversible processes with and without depolarization. As is seen from Table 3, the agreement between the values obtained by potentiometric and polarographic methods is quite satisfactory. When studying the electrode kinetics in some ionic melts by chronopotentiometry, we detected kinetic currents, which indicate a chemical reaction, i.e., complex formation (Ref. 14). An example of such ionic melt is the system lithium chloride-potassium chloride-sodium tungstate. In this system exists the equilibrium

$$WO_4^{2-} \rightleftharpoons WO_3 + O^{2-} \tag{19}$$
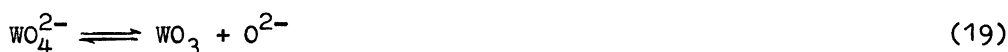
The species $WO_4^{2-}$ may be regarded as a complex ion, for which the stability constant may be given by the expression

$$K = \left[WO_3\right]\left[O^{2-}\right] / \left[WO_4^{2-}\right] \tag{20}$$

To interpret the results of chronopotentiometric measurements, the following equations may be used:

$$i_k = nF \left\{ kD\left[WO_3\right]/K\left[O^{2-}\right] \right\}^{1/2} \tag{21}$$

$$\mu = (D/kK)^{1/2} \tag{22}$$

$$\tau = \frac{\mu^2}{D} \tag{23}$$

$i_k$ is the kinetic current, k the rate constant of electrode reaction, D the diffusion coefficient, K the equilibrium constant, and $\mu$ the reaction layer thickness. All these quantities can be determined from experimental data. The life time ( $\tau$ ) of a complex species can be calculated from equation (23). For the $WO_4^{2-}$ and $CdBr_3^-$ species we found:

$$\tau_{WO_4^{2-}} = 2.04 \ s; \ \tau_{CdBr_3^-} = 1.4 \times 10^{-2} \ s$$

The complexity function is usually determined by the expression

$$\varphi = \frac{C}{[Me^{n+}]} \tag{24}$$

C is the total concentration, $[Me^{n+}]$ the concentration of "free" ions. Until recently, the discharge of a complex ion was considered to be preceded by its dissociation, e.g.,

$$PbCl_4^{2-} \rightleftharpoons Pb^{2+} + 4Cl^- \tag{25}$$

$$Pb^{2+} + 2e \longrightarrow Pb \tag{26}$$

In ionic melts, a direct discharge of complex species often takes place, e.g.

$$SiF_6^{2-} + 4e \longrightarrow Si + 6F^- \tag{27}$$

In these cases, the experession (24) loses its physical meaning since there are no $Me^{n+}$ species in the ionic melt. Therefore, we proposed another expression for the complexity function in ionic melts:

$$\theta = [MeX_i] / [MeX_m] \tag{28}$$

where $[MeX_i]$ is the concentration of the total number of species containing Me, $[MeX_m]$ the concentration of electrochemically active species. On the basis of chronopotentiometric measurements, we have established a relation between the function $\theta$ and the electrode overpotential $\eta$ (Ref. 15):

$$\eta = \frac{1-\alpha}{\alpha} \ \frac{RT}{zF} \ \ln \theta \tag{29}$$

Electrochemical methods give the most comprehensive information on the complex formation in ionic melts.

### ACID-BASE EQUILIBRIUM

Interesting chemical interactions in ionic melts are acid-base equilibria. This type of equilibria was first studied by H. Lux (Ref. 16). Later on, such equilibria were studied by many investigators (Ref. 17, 18). We have studied acid-base equilibria of two types:

$$MO_{n/2} \rightleftharpoons M^{n+} + n/2 \ O^{2-} \tag{30}$$

$$MO_{n/2+1}^{2-} \rightleftharpoons MO_{n/2} + O^{2-} \tag{31}$$

These studies may be divided into two groups: a) study of complex formation in acid-base equilibria; b) study of the effect of acid-base equilibria on electrochemical kinetics. The former problem was partly considered above. Besides this, using potentiometric method, the equilibria

$$CO_3^{2-} \rightleftharpoons CO_2 + O^{2-} \tag{32}$$

$$P_2O_7^{4-} \rightleftharpoons 2PO_3^- + O^{2-} \tag{33}$$

$$PO_4^{3-} \rightleftharpoons PO_3^- + O^{2-} \tag{34}$$

in different supporting electrolytes have been studied. A platinum-oxygen electrode was used as the indicator electrode and emf's of galvanic cells of the type

$$Pt \ \bigg| \ MO_{n/2+1}^{2-}-NaCl-KCl \ \bigg\| \ NaCl-KCl-PbCl_2 \ \bigg| \ Pb$$
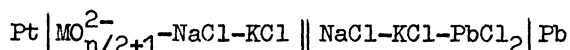
were measured. The concentration of oxygen ions was determined using the equation

$$E = const + RT/nF \ln\left[O^{2-}\right] \qquad (35)$$

In these experiments, sodium hydroxide was used as the oxygen ion donor. On the basis of experimental data, the plots

$$\varphi - \left[O^{2-}\right]; \quad \varphi - \left[CO_3^{2-}\right]; \quad \varphi - \left[P_2O_7^{4-}\right]; \quad \varphi - \left[PO_4^{3-}\right]$$

were made. These are straight lines with different slopes. All of them are shifted relative to the reactions (32), (33) and (34) towards more positive potential values by the addition of oxygen ion donor. The chemical activity of the anion increases in the order

$$CO_3^{2-} < P_2O_7^{4-} < PO_4^{3-} < PO_3^{-}$$
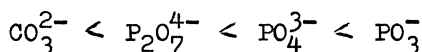
As a result of potentiometric measurements, titration curves are obtained when adding oxygen ions to the starting melts containing metaphosphate or pyrophosphate ions. The first curve bend indicates that the reaction proceeds by the mechanism (33). A further addition of oxygen ions leads to equation (34). When the oxygen ions are in large excess, one more weak bend is observed, which is due to the reaction

$$PO_3^{-} + 2O^{2-} \rightleftharpoons PO_3^{-} \cdot 2O^{2-} \qquad (36)$$
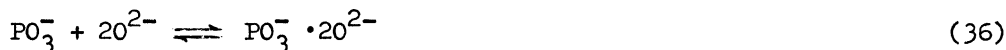
The corresponding potentiometric titration curves are shown in Fig. 4. The results of the determination of the constants for some acid-base equilibria are given in Table 4.
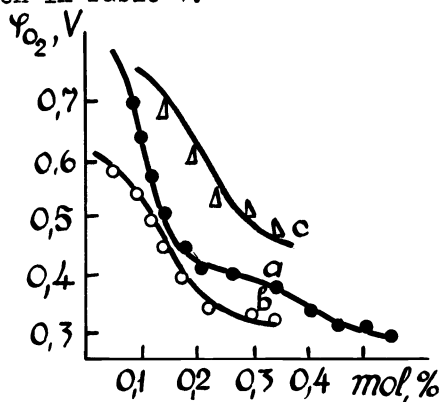


Fig. 4. Potentiometric titration curves:
a – 0.25 mol% $PO_3^{-}$ + $O^{2-}$; b – 0.15 mol% $P_2O_7^{4-}$ + $O^{2-}$;
c – 0.25 mol% $PO_3^{-}$ + $CO_3^{2-}$

Using potentiometric titration, the acidic properties of magnesium, strontium, zinc and nickel ions in the molten sodium chloride-potassium chloride eutectic at 700 °C have been studied. A zirconium oxygen electrode was employed in these measurements. The stoichiometry of acid-base reaction was determined from the relation

$$\bar{n} = \left[O_0^{2-}\right]\left[O^{2-}\right]/\left[Me^{2+}\right] \qquad (37)$$

where $\left[O_0^{2-}\right]$ and $\left[O^{2-}\right]$ are the overall and equilibrium concentrations of oxygen ions. The concentration constants calculated from the equation

$$K_n = \bar{n}/\left[O^{2-}\right](1 - \bar{n}) \qquad (38)$$

TABLE 4. Acid-base equilibrium constants for carbonate and phosphate ions in the NaCl-KCl melt at 700 °C

| Acid-base reaction | Equilibrium constant values | |
|---|---|---|
| | from experimental data | from relations between constants |
| $CO_2 + O^{2-} \rightleftharpoons CO_3^{2-}$ | $2.5 \pm 0.5$ | |
| $2PO_3^- + O^{2-} \rightleftharpoons P_2O_7^{4-}$ | $(2.9 \pm 1.2) \times 10^3$ | |
| $P_2O_7^{4-} + O^{2-} \rightleftharpoons 2PO_4^{3-}$ | $(2.5 \pm 1.4) \times 10$ | |
| $PO_3^- + O^{2-} \rightleftharpoons PO_4^{3-}$ | $(5.6 \pm 2.7) \times 10^2$ | $(2.7 \pm 2.5) \times 10^2$ |
| $PO_3^- + 2O^{2-} \rightleftharpoons PO_3^- \cdot 2O^{2-}$ | $7.98 \times 10^4$ | |
| $PO_3^- + PO_4^{3-} \rightleftharpoons P_2O_7^{4-}$ | $5.2 \pm 4.6$ | $(1.1 + 1.2) \times 10$ |
| $PO_3^- + CO_3^{2-} \rightleftharpoons PO_4^{3-} + CO_2$ | $(0.5 + 0.1) \times 10^2$ | $(1.1 + 1.2) \times 10^2$ |

and from the equilibrium ratio

$$K = [MeO] \big/ [Me^{n+}] \, [O^{2-}] \tag{39}$$

are close to each other. On the basis of the studies of the equilibria

$$Me^{2+} + O^{2-} \rightleftharpoons MeO \quad (Me = Mg, Sr, Zn, Ni) \tag{40}$$
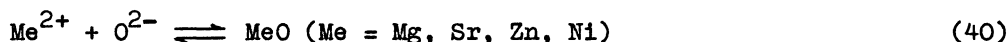
the acidic properties of cations were found to decrease in the order (Ref. 19):

$$Mg^{2+} > Ni^{2+} > Zn^{2+} > Sr^{2+}$$
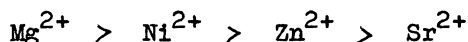
To elucidate the effect of acid-base reaction on the electrochemical kinetics in ionic melts, we have carried out chronopotentiometric and polarographic investigations. In particular, the reduction of carbonate ion in sodium chloride-potassium chloride eutectic as supporting electrolyte has been studied. In this melt, the equilibrium (40) exists. A two-step reduction of carbonate ion was established. To judge by the transition time ratio, the reduction of carbonate oxide agrees well with the following mechanism

$$CO_2 + 2e \longrightarrow CO_2^{2-} \tag{41}$$

$$CO_2^{2-} + 2e \longrightarrow C + 2O^{2-} \tag{42}$$

Using the well-known equation

$$\tau^{1/2} = \pi^{1/2} nFCD^{1/2}/2i - \pi^{1/2} D^{1/2}/2ki \tag{43}$$

and chronopotentiometric data, plots of $i\tau^{1/2}$ against $i$ and $\tau^{1/2}$ against $1/i$ were made, which are shown in Fig. 5. The first plot (a) has a bend, the second plot is a straight line with a negative intercept. These two facts indicate a kinetic process besides electrode reactions. This kinetic process is an acid-base reaction. To calculate the electrochemical kinetic parameters, the chronopotentiometric equation

$$\varphi = 0.193/\alpha \, n_a \, \lg(nkC/i) + 0.193/\alpha \, n_a \, \lg 1 - (t/\tau)^{1/2} \tag{44}$$

was used. For the electrochemical characteristics of carbonate anion we found: $\alpha = 0.5$; $n_a = 1$; $k = (6.7 \pm 0.5) \times 10^{-3}$ cm/s (Ref. 20 & 21).
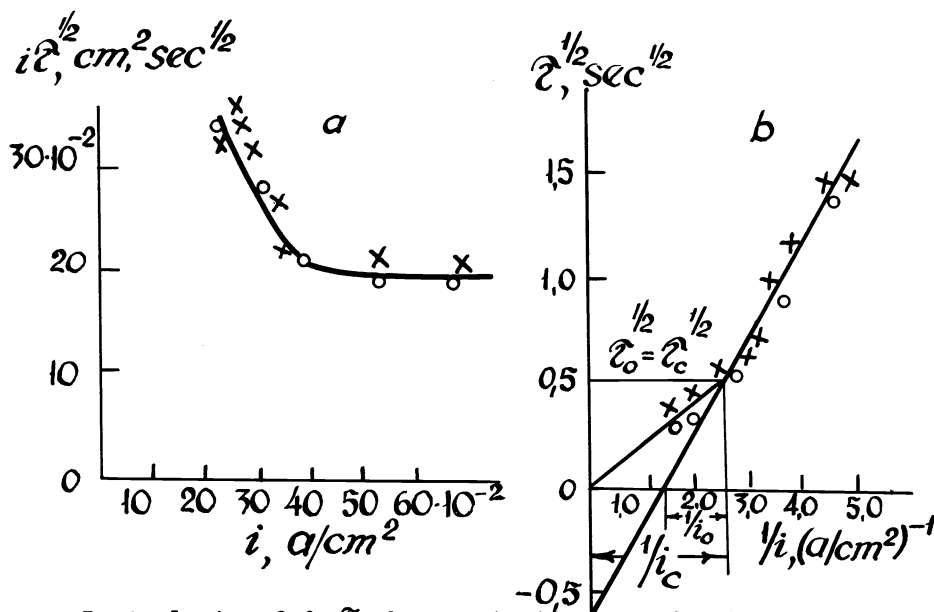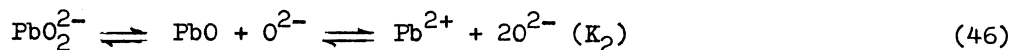
The equilibrium

$$PbO \rightleftharpoons Pb^{2+} + O^{2-} \quad (K_1) \tag{45}$$
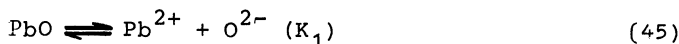
Fig. 5. Analysis of $\varphi - \tau$ chronopotentiograms for the NaCl-KCl melt, containing $10^{-4}$ mol/cm$^3$ Li$_2$CO$_3$ at 700 °C:

a) $i\tau^{1/2} - i$; b) $\tau^{1/2} - 1/i$

in the lithium chloride-potassium chloride system has been studied by the polarographic method. In an alkaline melt, such equilibria as

$$PbO_2^{2-} \rightleftharpoons PbO + O^{2-} \rightleftharpoons Pb^{2+} + 2O^{2-} \quad (K_2) \quad (46)$$

also occur. In this case, the equation

$$\varphi_{1/2} = RT/\alpha nF \ln K_2 - RT/\alpha nF \ln K_1 - RT/\alpha nFpO - RT/\alpha nF \ln i_d/i \quad (47)$$

is valid (Ref. 22). Equation (47) permits calculation of some electrochemical kinetic parameters as well. Besides, it indicates an effect of acid-base equilibria on electrochemical kinetics. Thus, chronopotentiometric and polarographic methods can be successfully used for the study of acid-base reactions in ionic melts.

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