

On Carbonate Ion Dissociation in Molten Alkali Metal Halides at $\approx 800\text{ }^\circ\text{C}^\dagger$

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The carbonate ion dissociation equilibrium ($\text{CO}_3^{2-} = \text{CO}_2 + \text{O}^{2-}$, $\text{p}K = -\log K$) in molten sodium halides at $830\text{ }^\circ\text{C}$ was investigated using a potentiometric cell with a $\text{Pt}(\text{O}_2)|\text{ZrO}_2(\text{Y}_2\text{O}_3)$ membrane oxygen electrode reversible to O^{2-} . The consecutive increase of $\text{p}K$ values was observed in the sequence of sodium halides 2.67 ± 0.2 (NaCl), 2.88 ± 0.2 (NaBr), and 3.92 ± 0.2 (NaI). In contrast, in the sequences of K^+ - and Cs^+ -based chlorides, bromides, and iodides, which were studied earlier, minimal $\text{p}K$ values were obtained in bromide melts, that is, 2.22 ± 0.2 (CsCl), 1.20 ± 0.2 (CsBr), and 3.44 ± 0.2 (CsI); 3.2 ± 0.2 (KCl), 2.4 ± 0.2 (KBr), and 4.4 ± 0.2 (KI). Changes of the $\text{p}K$ values in the sequence $\text{Na} \rightarrow \text{K} \rightarrow \text{Cs}$ -based halides are caused, mainly, by different stabilities of corresponding carbonates (Na_2CO_3 , K_2CO_3 , and Cs_2CO_3). The acidity changes in the sequences of alkali metal halides are explained in terms of the complexation abilities of halide ions and alkali metal cations in the melts.

Introduction

Molten single alkali metal halides are often used in different engineering processes. They serve as starting materials for acoustic, optical (KCl, NaCl, CsBr), and scintillation crystal growth (CsI doped with TlI or NaI, NaI doped with TlI), as solvents for active metal deposition, as electrolytes for high-temperature power sources, and so forth. The quality of the final products is essentially dependent on the concentration of oxide-containing impurities in the liquid ionic media. The main oxygen admixtures, carbonates, act as weak Lux–Flood bases:¹

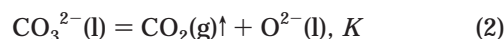


(where B is a base and A is the conjugated acid); that is, they are donors of oxide ions. The latter are fixed by depolarizators (mainly metal cations) in electrochemical processes that may lead to the electroactive particle concentration reduction and to the precipitation of metal oxides from melts. As to the single crystals, carbonate ions result in absorption bands in the IR region² and should be removed to achieve high optical parameters of the crystals. Nevertheless, carbonates were found to be appropriate for CsI doping³ and CsI (CO_3^{2-}) crystals are now considered among prospective scintillation materials. In this case, carbonate stability in the melt should be provided during the growth process.

Therefore, data on carbonate ion stability in alkali metal halide melts should be helpful for the development of both above-mentioned engineering applications. The behavior of carbonates dissolved in ionic melts is described by the dissociation constant, K , of CO_3^{2-} :

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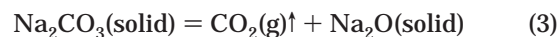


where l denotes liquid and g denotes the gaseous phase.

From the viewpoint of pure chemistry, it is interesting to study carbonate stability in the sequences $\text{CsCl} \rightarrow \text{CsBr} \rightarrow \text{CsI}$, $\text{KCl} \rightarrow \text{KBr} \rightarrow \text{KI}$, and $\text{NaCl} \rightarrow \text{NaBr} \rightarrow \text{NaI}$ to observe cation and anion effect on the melts' acidity, which may be estimated just by using eq 2.

As for studies of carbonate ion stability in ionic melts, some works in nitrate melts^{4–6} should be mentioned, where authors attempted to determine whether carbonate was a strong Lux base or a weak base. Frederics et al.⁴ and Kust⁵ performed electrochemical studies of carbonate solutions in nitrate melts and found that the CO_3^{2-} ion underwent complete dissociation in the said melts. In contrast, Zambonin et al.⁶ showed that carbonate ions in nitrate melts are stable: A solution of Na_2CO_3 in a nitrate melt was kept in an inert atmosphere. Then a sample of the cooled solution was dissolved in water, and a standard titration procedure of this solution with acid in the presence of phenolphthalein and methyl orange showed that there was no appreciable decomposition of CO_3^{2-} according to eq 2.

When carbonates are dissolved in melts at temperatures of $\approx 727\text{ }^\circ\text{C}$, the dissociation process becomes more appreciable, although thermochemical calculations of the reaction



give K values of the order of 10^{-8} ($\text{p}K \approx 8$). Practical investigations^{7,8} performed in the $\text{KCl} + \text{NaCl}$ equimolar mixture, however, show that $\text{p}K$ values are ≈ 5 (5.16^7 and 4.89^8) at $700\text{ }^\circ\text{C}$ and ≈ 3.5 (3.6^7 and 3.4^8) at $800\text{ }^\circ\text{C}$.

There are no other published data on carbonate behavior in individual alkali metal halides. This problem was partially solved in our previous works where sequences of potassium and cesium⁹ halides were studied. The purpose of the present work is to study carbonate behavior in

molten sodium halides and to estimate relative acidic properties of molten alkali metal halides at $\approx 800^\circ\text{C}$.

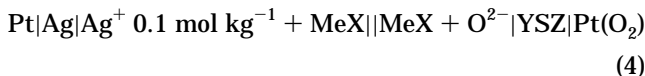
Experimental Section

Reagents. Sodium halides used as solvents were of Reakhim "extra pure for single crystals" (NaCl, NaI) and Reakhim "pure for analysis" (NaBr) quality, and they were used without purification. NaOH was of Reakhim "pure for analysis" quality; preliminarily, it was melted and held in an argon flow for 1 h to remove absorbed water and, after cooling, it was ground to provide addition of small amounts (of the order of 0.001–0.003 g) of NaOH to the melts studied.

Argon was of extra pure quality, and carbon dioxide was of reagent quality. The gases were dried by zeolite and then bubbled through the melt.

Anhydrous magnesium chloride was obtained by mixing $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ with NH_4Cl of reagent quality in the proportion 1:2, calcining this mixture at 400°C (addition of NH_4Cl suppresses hydrolysis), and melting at 742°C . Then the MgCl_2 melt was cooled to room temperature and kept in a dry atmosphere.

The Essence of the Experiment. The studies of reaction 2 in molten alkali metal halides (MeX) consist in the addition of KOH (for Cs^+ - and K^+ -based halides) or NaOH (for Na^+ -based halides) in the melt saturated by CO_2 ($p = 0.1$ MPa). Under these conditions, the hydroxides were completely transformed to carbonates; the equilibrium concentrations of O^{2-} ($m_{\text{O}^{2-}}$) were determined from potentiometric data. The potentiometric cell



(hereafter YSZ is a solid electrolyte $0.9\text{ZrO}_2 + 0.1\text{Y}_2\text{O}_3$, molar fractions) with a membrane oxygen electrode $\text{Pt}(\text{O}_2)|\text{YSZ}$ was preliminarily calibrated with known amounts of the hydroxides to obtain calibration E - $p\text{O}$ plots

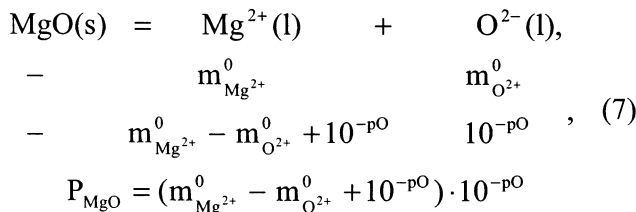
$$E = E^0 + [RT/(zF)]p\text{O} \quad (5)$$

where $p\text{O} = -\log m_{\text{O}^{2-}}$; equilibrium constants of (2) were calculated on the basis of initial and equilibrium O^{2-} concentrations according to the following equation:

$$K = (m_{\text{O}^{2-}} p_{\text{CO}_2}) / (m_{\text{O}^{2-}}^0 - m_{\text{O}^{2-}}) \quad (6)$$

where $m_{\text{O}^{2-}}^0$ and p_{CO_2} were the initial molality of the oxide ion donor and the partial pressure of carbon dioxide, respectively.

Besides CO_2 dissociation, we determined the solubility products of MgO :



(where s denotes the solid phase, $m_{\text{Mg}^{2+}}^0$ is the initial Mg^{2+} molality, P_{MgO} is the solubility product, and $pP_{\text{MgO}} \equiv -\log P_{\text{MgO}}$) in molten KCl and CsCl at 800°C and in NaCl at 830°C . The essence of this experiment consisted in the following. An amount of MgCl_2 corresponding to a molality of 0.03 – $0.05 \text{ mol} \cdot \text{kg}^{-1}$ was added to the melt studied. Then

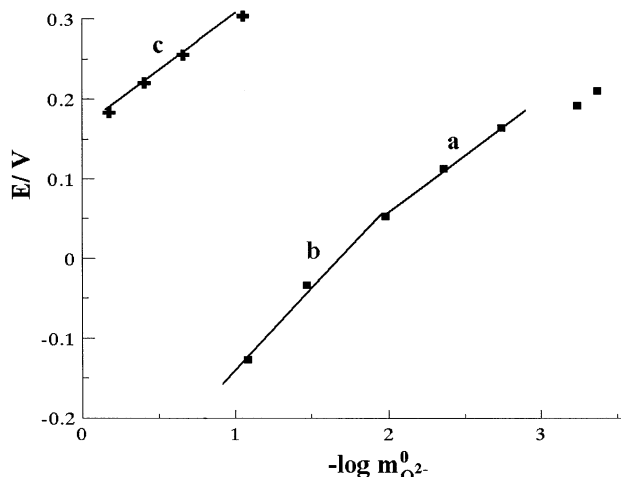


Figure 1. The dependence of emf vs initial oxide ion molalities $-\log m_{\text{O}_2}^0$, the potentiometric cell with oxygen electrode $\text{Pt}(\text{O}_2)|\text{YSZ}$ in molten NaCl at 830°C in Ar (a,b) and in CO_2 (c).

amounts of Lux base NaOH (KOH) were added to the melt (in this moment, the concentrations were described by the first string under eq 7). Such additions led to a shift of this reaction to the left. The measured electromotive force (emf) allowed us to determine equilibrium $p\text{O}$ (equilibrium concentrations were described by the second string under eq 7) and to calculate P_{MgO} according to the third string under eq 7. Since the solubilities of MgO in molten alkali metal halides usually are too small,¹⁰ all the additions of NaOH lead to precipitation of MgO , that is, all the obtained solutions of MgO are saturated.¹¹ The set of pP_{MgO} was used to calculate the average magnitude. A comparison of pP_{MgO} in the melts studied with the known values for the melts of the same anion composition, that is, KCl + NaCl and CsCl + KCl + NaCl eutectic allows us to estimate relative acidities of the melts studied. It should be emphasized that there are no data on MgO solubilities in molten alkali metal halides at 800°C .

Results and Discussion

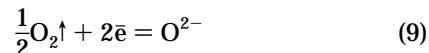
Features of Calibration Plots. The typical calibration plot and data obtained in a CO_2 atmosphere are presented in Figure 1.

The first two points refer to the initial stage of calibration where the molality of residual oxygen admixtures ($m_{\text{O}^{2-}}^0$) is comparable with the initial molality of NaOH and

$$\log(m_{\text{O}^{2-}}^0 + m_{\text{O}^{2-}}^0) \approx \log(m_{\text{O}^{2-}}^0) \quad (8)$$

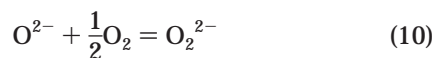
Therefore, these points cannot be considered as calibration data. Subsequent additions of NaOH in an Ar atmosphere result in a dependence consisting of two linear sections, sections a and b in Figure 1.¹² Such a two-sectional structure is caused by the so-called "peroxide function" which has been discussed by Cherginets et al.¹³

The slope of section c in Figure 1 is close to $1.15 RT/F$, which agrees with the generally accepted electrode process of oxygen reduction:

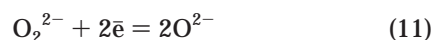


The inflection in the calibration plot arises at a constant for each melt and temperature at a given oxide ion concentration; the increase of oxide ion concentration gave rise to the second plot, Figure 1b, with the slope $2.3 RT/F$. The appearance of this section in E - $p\text{O}$ plots is usually

connected with the so-called peroxide function, that is, the formation of peroxide ions on the inner electrode surface (Pt|O₂|YSZ) owing to the interaction of excess O²⁻ with O₂,



and the peroxide is reduced at the oxygen electrode surface:



In this case, only one electron is consumed for the formation of one oxide ion in the melt.

As seen from Figure 1, the pO value at the point of inflection in Na⁺-based melts (pO ≈ 2) is appreciably less than similar values in low-acidic melts KCl + NaCl (pO ≈ 3 at 700 °C) and CsCl + KCl + NaCl (pO ≈ 4 at 600 °C, pO ≈ 3 at 700 °C).¹² Such a shift agrees with the expected one since a temperature rise causes a decrease of peroxide ion stability at elevated temperatures.

When finishing calibration at pO ≈ 1, it becomes possible to study carbonate dissociation immediately. For this purpose, CO₂ should be passed through the melt instead of Ar. Indeed, passing CO₂ through the melts leads to a shift of reaction 2 to the left and practically all entered oxide is fixed in CO₃²⁻. The first and obvious result is the equilibrium constant which is calculated according to eq 6. Besides, a plot *E*-pO obtained in a CO₂ flow gives evidence of reversibility of the Pt(O₂)|YSZ electrode to O²⁻ at high pO values (Figure 1c). In the case of a NaCl melt, this process results in emf values lying above the inflection point. Subsequent additions of the base under CO₂ pressure result in plot with a slope of 1.15 *R**T*/*F* proper to this emf range for *E*-pO plots.

Transformation of eq 6 leads to the following formulas:

$$K m_{\text{O}_2^{2-}}^0 - K m_{\text{O}_2^{2-}} = m_{\text{O}_2^{2-}} p_{\text{CO}_2} \quad (12)$$

$$K m_{\text{O}_2^{2-}}^0 = (K + p_{\text{CO}_2}) m_{\text{O}_2^{2-}} \quad (13)$$

$$m_{\text{O}_2^{2-}}^0 = \frac{K + p_{\text{CO}_2}}{K} m_{\text{O}_2^{2-}} \quad (14)$$

Taking into account that $K \ll p_{\text{CO}_2}$, $p_{\text{CO}_2} = 1$, and $K = \text{const}$, the following may be obtained:

$$-\log m_{\text{O}_2^{2-}} \equiv \text{pO} = -\log m_{\text{O}_2^{2-}}^0 + \text{p}K \quad (15)$$

and

$$\left(\frac{\partial E}{\partial \text{pO}}\right)_{p,T} = \left(\frac{\partial E}{\partial (-\log m_{\text{O}_2^{2-}}^0 + \text{p}K)}\right)_{p,T} = \left(\frac{\partial E}{\partial (-\log m_{\text{O}_2^{2-}}^0)}\right)_{p,T} \quad (16)$$

This means that the slope of Figure 1c should coincide with the *E*-pO slope in the corresponding emf range (plot 1). This result gives us evidence that the Pt(O₂)|YSZ electrode maintains its reversibility to oxide ions according to eq 9 at O²⁻ concentrations considerably lower than those which may be achieved by direct Lux base addition.

Dissociation Constants of Carbonate Ions in Molten Sodium Halides. The data of Figure 1c presented in the previous section allow us not only to check the oxygen electrode function at high pO but also to calculate the constant of eq 2 according to eq 6. An example of the treatment of the calibration results obtained in NaCl melt is presented in Table 1 (results of parallel studies coincide

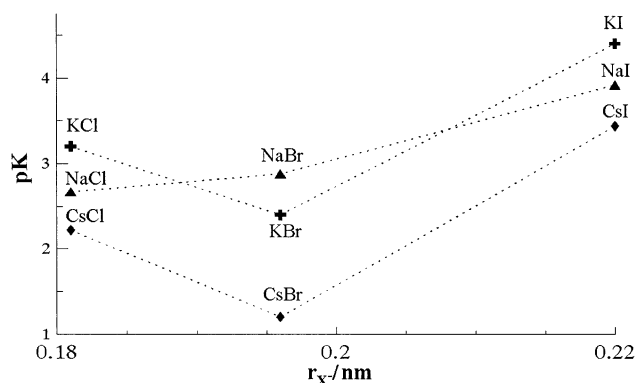


Figure 2. The dependence of p*K* of eq 2 vs anion radius in molten potassium (crosses, 800 °C), cesium (rhombus, 800 °C), and sodium (triangles, 830 °C) halides.

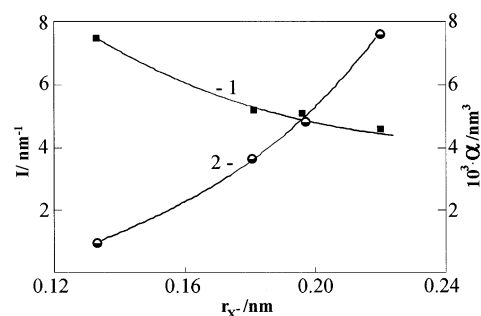


Figure 3. The dependence of formal ionic moments, *I*, and polarization, α , versus radii of halide ions.

Table 1. Results of Carbonate Ion Dissociation Study in Molten NaCl at 830 °C

calibration plot: $E = -0.235(\pm 0.02) + 0.146(\pm 0.01)\text{pO}$, V			
$-\log m_{\text{O}_2^{2-}}^0$	<i>E</i> , V	pO	p <i>K</i>
1.08	0.302	3.67	2.59
0.66	0.255	3.35	2.69
0.41	0.220	3.11	2.70
0.18	0.183	2.86	2.68
$\text{p}K = 2.67 \pm 0.06$			

within a standard deviation of 0.1–0.2). Similarly, equilibrium constants in the other sodium halides were calculated; they are p*K* = 2.88 ± 0.2 (NaBr) and p*K* = 3.92 ± 0.2 (NaI). It is interesting to present these results (Figure 2) together with p*K* obtained in molten cesium and potassium halides;⁹ the accuracy of all the constants presented does not exceed ±0.2 (standard deviations).

The carbonate stability increases in the sequence NaCl → NaBr → NaI, whereas there are no consecutive p*K* increases in the similar sequences of cesium and potassium halide changes of p*K* of eq 2. Carbonate stability decreases from iodide to chloride melts via the chloride melt.⁹

One of the possible explanations of the observed effect consists of the following. Alkali metal halide melts are known to be built from ionic complexes, and equilibrium between “free” and fixed ions occurs in the melts. The halide melt acidities are dependent on the relative free cation concentration (Cs⁺, K⁺, Na⁺). Owing to the fixation into complexes, cation concentrations differ in different halide melts. The complexation ability of anions is known to increase together with the increase of their ionic moment and polarization.¹⁴ As is seen from Figure 3, curve 1, the formal ionic moments decrease in the sequence Cl⁻ → Br⁻ → I⁻; in contrast, in the mentioned sequence polarization increases (curve 2). Therefore, bond energies of halide complexes should achieve minimal values within this

sequence. According to the mention of Smirnov,¹⁴ who studied mainly sodium-based melts, this minimum is observed for chloride melts, which agrees with the data obtained for molten sodium halides.

Results obtained for cesium and potassium halides are not subject to this rule. The reason is that the stability of the alkali metal cation–halide anion complex is dependent on the nature of both ions. Alkali metals are divided in two analytical groups, (Na, Li) and (K, Rb, Cs). Some properties of cations belonging to different groups differ considerably. Hence, such a difference may be observed for alkali metal halide melts based on Na⁺ cations and, on the other hand, Cs and K cations. The running of the sequences of the p*K* shows that this actually takes place.

The above-mentioned sequence for molten cesium halides is placed accurately 1 log *K* unit lower than that for the corresponding potassium halide melts (see Figure 2). Such a shift of p*K* values leads to the assumption that its cause lies in the difference of thermal stability of Cs₂CO₃ and K₂CO₃. It is known that the decomposition pressure over Cs₂CO₃ is ~10 times as much as that of K₂CO₃;¹⁵ therefore, this fact easily explains the p*K* shift.

On the Relative Acidities of Molten Alkali Metal Halide Melts. The obtained values of p*K* of eq 2 allow us to estimate the relative acidic properties of molten alkali metal halides. Indeed, the increase of acidic properties of ionic melts results in more strong fixation of oxide ions, which are formed as a product of acid–base reaction by cations of the melt. This effect leads to the shift of reaction 2 to the right, while the degree of the equilibrium (and p*K*) shift may be considered as a measure of relative melt acidity. However, p*K* of eq 2 may serve as the correct measure of acidity only in the case of molten salts of the same cation composition, that is, KCl → KBr → KI, since it has been shown that p*K* values of eq 2 in molten KCl and CsCl differ by 1, although their acidities are close.⁹ Therefore, to estimate acidic properties of molten alkali halides we should estimate acidities of melts of the same anion composition. Chlorides are the most appropriate for this purpose, and their acidities may be estimated by the oxide solubility method.^{16,17}

The oxobasicity index of the melt (as a measure of acidity) is equal to the difference of solubility products (p*P*) of the same oxide (e.g., MgO) in different melts. If we use MgO solubility data and CsCl + KCl + NaCl eutectic as a reference melt (such a melt was proposed as a standard one by Cherginets et al.⁹), calculations should be performed by the following formula:

$$pI_L = pP_{N,MgO,CsCl+KCl+NaCl} - pP_{N,MgO,L} \quad (17)$$

where $pP_{N,MgO,CsCl+KCl+NaCl}$ and $pP_{N,MgO,L}$ are $-\log P_{MgO}$ calculated in molar fractions in the reference CsCl + KCl + NaCl melt and in the melt studied (L). As for MgO solubility studies, p*P* values in the molar fraction scale are 11.44 (CsCl + KCl + NaCl), 11.74 (KCl), and 11.40 (CsCl), which confirms that the said melts possess close acidic properties. This may be explained within the framework of Pearson's concept of "hard" and "soft" acids and bases.¹⁸ The division of acids and bases to hard and soft is performed on the basis of their polarization properties: hard reagents are small particles of low polarization, and soft ones are relatively big particles with considerably higher polarization.¹⁸ Alkaline metal cations are hard acids; moreover, the ionic radii of K⁺ and Cs⁺ are close (0.133 and 0.169 nm,¹⁹ respectively). Therefore, the above-mentioned melts have close acidities (the higher acidity of

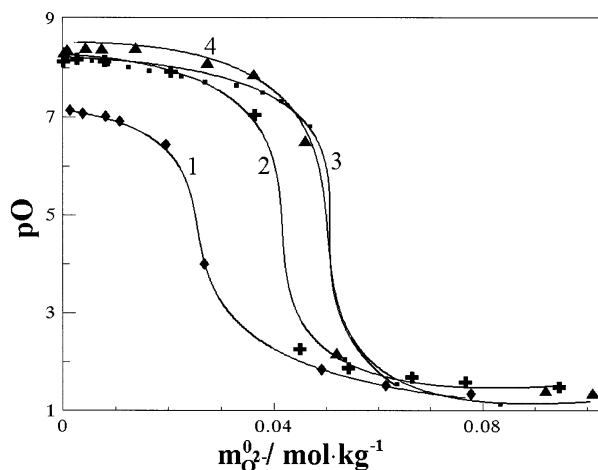


Figure 4. The dependence of p*O* vs $m_{O^{2-}}^0$ for the titration of MgCl₂ with NaOH ($\equiv (1/2)O^{2-}$) in molten NaCl (1, 830 °C), CsCl + KCl + NaCl (2, 800 °C), KCl (3, 800 °C), and CsCl (4, 800 °C).

Table 2. Results of Potentiometric Titration of Mg²⁺ (0.026 mol·kg⁻¹) with O²⁻ in Molten NaCl at 830 °C

$m_{O^{2-}}^0$	<i>E</i> , V	p <i>O</i>	p <i>P</i>	$m_{O^{2-}}^0$	<i>E</i> , V	p <i>O</i>	p <i>P</i>
0.0013	0.660	7.14	8.75	0.0268	0.327	4.00	
0.0038	0.654	7.08	8.74	0.0491	0.050	1.84	
0.0081	0.647	7.02	8.77	0.0614	-0.015	1.52	
0.0108	0.637	6.92	8.74	0.0777	-0.053	1.34	
0.0195	0.586	6.44	8.63				

the CsCl + KCl + NaCl melt is explained by the presence of Na⁺, a cation of higher acidity).

To find the place of molten sodium halides among other alkaline metal halides, the MgO solubility product should be determined. For this purpose, we performed potentiometric titration of Mg²⁺ cations with NaOH additions in molten NaCl. The obtained and calculated parameters are presented in Table 2 (the results of other experiments are the same without considerable deviations; we present results of the "most successful attempt"). According to values from column 4, the average p*P* (molalities) may be estimated as 8.75 ± 0.03, which corresponds to a p*P* equal to 11.22 in the molar fraction scale (the value 8.63 drops out). The results of potentiometric titration of Mg²⁺ in chloride melts at ~800 °C presented in Figure 4 show that NaCl differs from the other said melts. This is caused, mainly, by the higher acidity of NaCl as compared with CsCl + KCl + NaCl, CsCl, and KCl, since according to ref 18 Na⁺ is more hard than K⁺ or Cs⁺, and the radius of Na⁺ is considerably smaller (0.095 nm¹⁹).

MgO solubility grows in the sequence KCl → CsCl + KCl + NaCl → NaCl, that is, it increases together with the increase of Na⁺ concentration in the melts (it is equal to 0 in KCl, 0.3 in CsCl + KCl + NaCl, and 1 in NaCl, molar fractions) that results in the acidity increase.

All the above results allow us to construct an acidity scale for alkali metal halide melts at 800 °C. For this purpose, oxobasicity indices,¹⁶ p*I*_L, were determined as the difference of p*P* versus the CsCl + KCl + NaCl melt (in the set of chloride melts). Then, using KCl, NaCl, and CsCl as reference melts for chloride–bromide–iodide sequences, oxobasicity indices were estimated as the differences of p*K* of eq 2 between the corresponding halide and chloride melt (e.g., p*I*_L for NaBr was estimated as p*K*_{NaBr} – p*K*_{NaCl}).

As is seen from the data in Figure 5, iodide melts form a group with close oxobasicity indices (–1), whereas the acidic properties of chloride and bromide melts are more scattered (within 0.6 for chlorides and within 1 for bro-

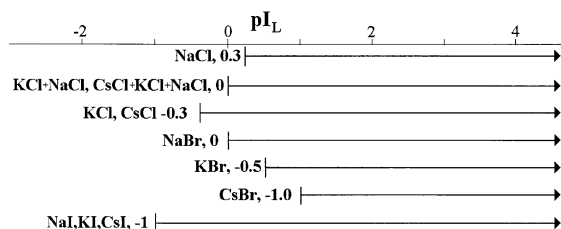


Figure 5. The acidity scale of molten alkali metal halides at ≈ 800 °C built on the oxobasicity indices (pI_L) data.

mides). In all the melts studied, the acidity level varies within $2 pI_L$ units.

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