Russian Chemical Reviews **66** (7) 597 – 611 (1997) © 1997 Russian Academy of Sciences and Turpion Ltd

UDC 541.45 + 541.8 – 143

Oxo-acidity in ionic melts

V L Cherginets

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Abstract. The current state of research into the oxo-acidity in alkali metal nitrate, sulfate, and halide melts is analysed on the basis of the proposed classification of oxo-acidity reactions (Lux – Flood acid – base interactions). It is established that a considerable proportion of literature data on homogeneous acid – base equilibria are incorrect, since no account is taken in them of either the levelling of the acid (basic) properties by the solvent or of the error in the determination of the reaction stoichiometries. An explanation is proposed for the considerable scatter of data on the solubilities of oxides in ionic melts, which has been the principal inhibiting factor in the development of this field. The reactions of melts with gaseous acid and basic reagents are examined. The bibliography includes 171 references.

I. Introduction

Ionic melts are widely used in science and engineering as media for various processes such as electrolysis, electrochemical synthesis, the growing of single crystals, *etc*. The virtually complete dissociation of the solvents into constituent ions makes it possible to generate high current densities in electrolysis. In the absence of oxidants, for example H^+, it is possible to obtain in ionic melts products which cannot be isolated from aqueous solutions (alkali and alkaline earth metals, subions, *etc*.). From the standpoint of the protection of the environment, the application of fused salts as technological solvents is specially attractive, because their use does not entail the accumulation of liquid industrial waste.

The processes in solvent melts are appreciably influenced by the impurities present in the initial salt starting material or formed during the fusion of the solvents as a consequence of high-temperature hydrolysis or the interaction of the melt with the material of the container and the corrosive components of the atmosphere. Such impurities include impurity metal cations and various oxygen-containing anions (sulfates, carbonates, hydroxides). The strength of the effect of the anions on the processes in ionic melts depends mainly on the degree of their dissociation with formation of the oxide ion O^{2-} as one of the products.

V L Cherginets The Single Crystals Institute, National Academy of Sciences of Ukraine, prosp. Lenina 60, 310001 Kharkov, Ukraine. Fax (38-057) 232 02 73. Tel. (38-057) 230 79 95.
E-mail: cherginets@isc.kharkov.ua

Received 8 October 1996
Uspekhi Khimii **66** (7) 661 – 676 (1997); translated by A R Grzybowski

Reactions involving the transfer of oxide ions in ionic melts are usually regarded as acid – base interactions (oxo-acidity); their treatment is then based on the ideas proposed by Lux [1] and developed in the studies of Flood and coworkers:[2–4]

$$A + O^{2-} \rightleftharpoons B, \quad (1)$$

where A is an acid and B a base. The oxygen index pO, analogous to pOH in aqueous solutions, serves as a quantitative measure of the basicity (acidity) of fused media:

$$pO \equiv -\lg a_{O^{2-}} \sim -\lg m_{O^{2-}},$$

where $a_{O^{2-}}$ and $m_{O^{2-}}$ are the activity and molality of the oxide ions in the melt respectively.

Although studies on oxo-acidity have been carried out since 1939,[1] hitherto no attempt has been made to survey or treat systematically the results obtained and the available information about oxo-acidity in ionic melts consists of a set of scattered and frequently incorrect data. The present review is intended to fill the existing gap. It is possible to identify the following main trends in studies on oxo-acidity in ionic melts:

homogeneous (intrinsic acid – base) reactions;

dissolution and dissociation of oxides in melts;

interaction of melts with gaseous reagents, including high-temperature hydrolysis of the melts, elimination of oxygen-containing impurities, and dissociation of Lux – Flood bases (CO_3^{2-}, OH^-, *etc*.).

II. Homogeneous acid – base equilibria

1. Specific features of ionic melts as media for acid – base interactions

Ionic melts as media in which Lux – Flood acid – base interactions take place may be divided into two classes depending on the presence in them of constitutional oxygen ions (*i.e*. ions entering into the composition of the main components of the melts): oxygen-free and oxygen-containing. We shall consider the characteristic features of the acid – base interactions in melts of the types indicated.[5]

Oxygen-free melts do not contain constitutional oxygen and the 'pure' melt cannot therefore serve as a O^{2-} donor. However, as a consequence of the inevitable contamination of the melt by oxygen-containing impurities such as SO_4^{2-}, CO_3^{2-}, and OH^-, in practice oxygen-free melts nevertheless always contain a certain amount of oxide ions. The concentration of oxide ions in the 'pure' solvent melt is not constant but depends on the content of impurities and the degree of their dissociation with formation of O^{2-}, which increases in the sequence $SO_4^{2-} < CO_3^{2-} < OH^-$.

In the 'pure' oxygen-free melts, the pO is usually in the range 3–4.5. The use of even the strongest halogenating agents does not permit a significant decrease in the O^{2-} concentration and this is the 'inevitable fault' leading to errors in potentiometric measurements especially when small amounts of the test substances are added. However, in a number of instances the pO of the 'pure' halide melt is used as the 'internal standard' of the melts for the construction of acidity scales.[6–9]

In oxygen-containing melts, the acid–base reactions are more complex, since in this case a competing equilibrium acid–base autodissociation of the solvent-melt takes place. A characteristic feature of the oxygen-containing melts is the presence in the latter of not only the base but also of the solvent-acid. This renders oxygen-containing melts similar to low-temperature solvents with an intrinsic acid–base equilibrium.[10]

However, oxygen–containing melts also possess a series of characteristic features due to the relatively high temperature of the liquid state. Very often, the solvent-acid is volatile or unstable [1,11] and is gradually removed from the acid melt as a consequence of decomposition or evaporation, while the pO in such a solution gradually approaches the corresponding value for a neutral melt. For this reason, very frequently not only are the acid properties levelled off in oxygen-containing melts but an upper acidity limit is also established.

Thus it has been observed that the highest chromium and molybdenum oxides decompose a nitrate melt with evolution of NO_2 and with increase in temperature the e.m.f. of a cell with an oxygen electrode is appreciably reduced.[12] It has been suggested that the nitrogen(V) oxide and the corresponding anions are formed in the interaction of the oxides with the melt. Since the acids indicated are very strong, one may postulate that the process

$$2CrO_3 + NO_3^- \longrightarrow Cr_2O_7^{2-} + NO_2^+$$

is fully displaced to the right and that the acid strength is determined by the acid properties of the nitronium cation NO_2^+. The stability of the latter is low and, after the attainment of certain concentration, its reaction with the melt anions becomes fairly intense:

$$NO_2^+ + NO_3^- \longrightarrow 2NO_2 + \tfrac{1}{2}O_2. \qquad (2)$$

The kinetic methods for the determination of the acidity of the melt are based on this reaction. As reaction (2) occurs, the concentration of the nitronium cation diminishes and the rate of the process falls. Ultimately it becomes so low that a constant e.m.f. is observed in a series of consecutive measurements. This is in fact the upper acidity limit in the melt, which is independent of the type of acid. The above considerations make it possible to explain readily the temperature dependence observed by Shams El Din and El Hosary:[12] an increase in temperature leads not only to a decrease in the stability of the nitronium cation but also to an increase in the rate of process (2).

The presence of an upper acidity limit is also characteristic of sulfate melts, which is apparently associated with the limited solubility of SO_3 in the latter. This is indicated by the drift of the e.m.f. (pO) in the acid-containing melt towards the neutral point.[1]

2. Methods of investigation

Most diverse methods are used to investigate oxo-acidity and to estimate the acid properties of melts. The simplest is the indicator method, the essential feature of which has been described by Brough *et al.*[13] The behaviour of 11 acid–base indicators used in aqueous solutions has been investigated in the melts KNO_3–$LiNO_3$ at 210 °C and KSCN at 200 °C. The colour transitions of the indicators (Ind), associated with the change in the acidity of the medium on titration of an alkali or sodium peroxide with potassium pyrosulfate were examined:

$$2HInd + O^{2-} \rightleftharpoons 2Ind^- + H_2O. \qquad (3)$$

In the nitrate melt, only the colour of phenolphthalein changed (yellow → purple), whilst the remaining indicators were apparently oxidised. In the KSCN melt, which has no oxidative properties, colour transitions were observed for all the indicators investigated (Methyl Red, thymolphthalein, *etc.*).

The use of indicators for the investigation of acidity is limited primarily by their thermal instability and by their ready oxidisability at high temperatures. Since ionic melts do not as a rule contain water, the transition of the indicator to the protonated form [reaction (3)] is hardly possible (the yellowing of the solution in the reverse transition of phenolphthalein has been noted [13]). The indicator method can therefore be used only in the study of relatively low-temperature melts (< 250 °C).

The application of spectroscopic methods for the study of the basicity of melts has been described.[14,15] Duffy *et al.*[14] constructed an 'optical' basicity scale for metallurgical slags relative to CaO adopted as the standard. The optical basicity was determined by estimating the changes in the frequencies of the spectral lines (the $^1S_0 \rightarrow {}^3P_1$ transition) of the Tl^+, Pb^{2+}, and Bi^{3+} cations in a basic medium. X-Ray fluorescent spectroscopic study of the Na_2O–B_2O_3–Al_2O_3, Na_2O–B_2O_3–SiO_2, and Na_2O–SiO_2–Al_2O_3 melts showed that the relative acidity of the oxides diminishes in the sequence $B_2O_3 > SiO_2 > Al_2O_3$.[15] The spectroscopic methods require as a rule the use of cooled (quenched) specimens, which may affect the validity of the results obtained in view of the discrepancy between the temperature of the melt investigated and the temperature at which the acid (basic) properties are estimated.

There are data obtained in the study of the basicity of melts by measuring the solubility in the latter of acid gases.[16,17] The solubility of sulfur(VI) oxide in sodium phosphates has been determined by a gravimetric method and a correlation has been established between the basicity of the melt and the solubility of the acid gas in the latter.[16] Iwamoto [17] used CO_2 and H_2O in order to determine the basicity. However, such methods are applicable only to basic melts, because the acids present in stable acid melts displace the indicator acid gas. Furthermore, the products of the interaction of the acid gas with basic melts are stable, which leads to an irreversible change in the properties of the latter.

The so called 'kinetic' method has been proposed for the estimation of the acidity of alkali metal nitrate melts. The interaction of nitrate melts with pyrosulfate ions [18,19]

$$S_2O_7^{2-} + NO_3^- \rightleftharpoons 2SO_4^{2-} + NO_2^+$$

leads to the formation of the nitronium cation, which subsequently interacts with nitrate ions in accordance with Eqn (2). The latter reaction is the slowest and the overall acidity of the medium can be inferred from its rate:

$$T_A = [S_2O_7^{2-}] + [NO_2^+].$$

The interaction of dichromate ions with chlorate ions in the KNO_3–$NaNO_3$ melt involves the occurrence of two reactions:[20,21]

$$Cr_2O_7^{2-} + ClO_3^{2-} \rightleftharpoons 2CrO_4^{2-} + ClO_2^+,$$

$$ClO_2^+ + Cl^- \longrightarrow Cl_2\uparrow + O_2\uparrow. \qquad (4)$$

Reaction (4) is rate-limiting. The rate of evolution of chlorine is proportional to the quantity

$$T_A = [Cr_2O_7^{2-}] + [ClO_2^+].$$

The interaction of bromate ions with dichromate in a nitrate melt has been studied.[22] The cations investigated can be arranged in the sequence $BrO_2^+ < ClO_2^+ < NO_2^+$ in terms of their acidity. We suggest that the introduction of the overall quantity T_A by the above investigators [18–24] unjustifiably complicates the analysis of the results, because the acidity of nitrate melts is determined solely by the concentration (activity) of NO_2^+ ions and the rates of the rate-limiting reactions (2) and (4) depend only on the concentrations of the cations NO_2^+ and ClO_2^+ respectively.

The kinetic method has been used also to investigate the acidity of the Cu^{2+} and Co^{2+} cations in the KNO_3-NaNO_3 melt at temperatures in the range 325–375 °C.[23,24] The acidity was determined from the rate of reaction (2). The nitronium cation was formed in solution *via* the reaction

$$M^{2+} + NO_3^- \rightleftharpoons MO + NO_2^+,$$

$M^{2+} = Cu^{2+}, Co^{2+}$.

The acidity of the cations of these metals was found to be close to that of the dichromate ion and the cations investigated by Duke and coworkers.[18–22] Evidently Slama [23,24] made a definite error in the estimation of the acidity of the cations, because the degree of binding of the oxide ions O^{2-} by the latter is determined not only by their active properties but also by the formation of a new phase — the corresponding oxides, which are virtually insoluble in the test melt.

The deficiencies of the methods described prevent their wide-scale employment for the investigation of the oxo-acidity of metals over a wide temperature range.

The method based on the e.m.f. of cells with transport in which an oxygen indicator electrode, reversible with respect to O^{2-} ions, is employed is the most promising. The ectrochemical cells can be represented as follows in a general form:

Reference electrode | melt + O^{2-} | O^{2-} electrode.

In the familiar potentiometric studies, it has been postulated that the diffusion potential is zero. Either a metallic electrode (*i.e.* a metal immersed in a solution of the salt of the corresponding cation at a definite concentration) or an oxygen electrode immersed in a solution with a known or constant concentration of oxide ions (concentration cells) have been used as reference electrodes.

3. Nitrate melts

Since a large number of publications have been devoted to studies of the oxo-acidity of nitrate melts, these systems are traditionally regarded as most thoroughly investigated. The relatively low melting points of both individual alkali metal nitrates and of their mixtures permit the employment of comparatively simple experimental apparatus. Potentiometric studies in nitrate melts reduce mainly to the determination of the acid–base equilibrium constants.

The greatest number of publications concern the studies of the oxo-acidity of the KNO_3 melt at 350 °C.[12,25–49] The results of the determination of the constants for the addition of the oxide ion to higher oxides and anions of Group V elements (P, As, V) have been published.[25–30] All the oxides investigated react with the nitrate melt to form the salts of the corresponding meta-acids:

$$R_2O_5 + NO_3^- \rightleftharpoons 2RO_3^- + NO_2^+.$$

Reaction (2) displaces the equilibrium to the right. Nitrogen(IV) oxide is evolved until the e.m.f. decreases to ~ 0.5 V, which, judging from the results of other studies, corresponds to the upper limit of acidity in the KNO_3 melt.[25–30] According to these data,[25–30] the acid–base product for the solvent is $\sim 10^{-16}$. As the titrant Na_2O_2 is added, the following reactions take place consecutively in the melt:

$$2RO_3^- + O^{2-} \rightleftharpoons R_2O_7^{4-},$$

$$R_2O_7^{4-} + O^{2-} \rightleftharpoons 2RO_4^{3-}.$$

R = P, As, V.

The acid properties of the oxide intensify in the sequence $V_2O_5 < P_2O_5 < As_2O_5$.

Apart from these reactions, the equilibria which according to Shams El Din *et al.*[25–27] are established when the ions HPO_4^{2-}, $H_2PO_4^-$, $HAsO_4^{2-}$, and $H_2AsO_4^-$, added to the melt are titrated have also been investigated. The equilibrium constants of the reactions

$$2H_2RO_4^- + O^{2-} \rightleftharpoons 2HRO_4^{2-} + H_2O, \quad (5)$$

$$2HRO_4^{2-} + O^{2-} \rightleftharpoons 2RO_4^{3-} + H_2O. \quad (6)$$

were determined. However, even pure salts, incorporating the corresponding anions, decompose at temperatures very appreciably below 350 °C, forming the corresponding meta- and pyro-salts.[50] In the absence of water vapour, equilibria (5) and (6) cannot therefore occur.

The study of the acid properties of the highest oxides of Group VIB,[12,31,32] showed that chromium(VI) and molybdenum(VI) oxides react with the nitrate melt, forming the dichromate and trimolybdate ions respectively. After the cessation of the evolution of NO_2, the e.m.f. is close to 0.5 V, which agrees with the values obtained for the oxides of Group V elements.[25–30] The products of the interaction of chromium and molybdenum oxides with the melt are titrated in one stage and the final products of the neutralisation reactions are the chromate and the molybdate respectively. Tungsten(VI) oxide is a weaker acid and does not decompose the pure melt. Its titration takes place in one stage and the product is tungstate ions. The acidity of the oxides investigated increases in the sequence $WO_3 < MoO_3 < CrO_3$.

The published equilibrium constants K[12,25–40] cannot be called correct because the calculated values vary during titration within the limits of several orders of magnitude of pK. This occurs either owing to the incorrect selection of the participants in the equilibrium (the stoichiometry) or because the authors did not calibrate in an 'acid' medium the oxygen electrode $Pt(O_2)$ employed.

It has been established by the method involving the titration of the corresponding carbonates by dichromate [34] and metaphosphate [35] ions, *i.e.*

$$M_{n/2}CO_3 \downarrow + A \longrightarrow \tfrac{n}{2}M^{n+} + CO_2 \uparrow + B$$

that the acidity of the cations increases in the sequence K^+, $Na^+ < Li^+$, $Ba^{2+} < Sr^{2+} < Ca^{2+} < Pb^{2+}$. Although this sequence agrees satisfactorily with the electronegativity series of the metals, nevertheless this method for the examination of acidity must be regarded as unsuccessful because the acids employed by the investigators for the titration not only eliminate oxide ions from the carbonates but can also form insoluble chromates and phosphates with the majority of the cations. The formation of complexes or precipitates is demonstrated by the position of barium in this series, the acidity of which is comparable to the acidity of potassium and sodium and is appreciably lower than the acidity of lithium. This might have influenced also the positions of a number of other alkaline earth metals in the series considered.

The relative Lux–Flood base strengths in nitrate melts have been investigated.[36,37] The bases investigated were separated into two groups: the oxide ions (OH^-, O^{2-}, and O_2^{2-}) and the carbonate ions [CO_3^{2-}, HCO_3^-, $(COO)_2^{2-}$, CH_3COO^-, $HCOO^-$]. The first group includes the bases,which,according to the authors,dissociate fully in the melt with formation of oxide ions. The second group is made up of weak bases. Since they all decompose at the experimental temperature (350 °C) with formation of the carbonate ion, the differences between separate representatives of this group are confined to their reducing properties: by reducing nitrate ions, organic acid salts promote the accumulation in the melt of excess amounts of oxide and carbonate ions compared with the stoichiometric concentrations. The majority of the bases investigated are therefore unsuitable for quantitative studies.

There exists the view [37] that oxide ions are present in nitrate melts in the form of pyronitrate ions, which are strong bases with strengths comparable to that of carbonate ions. From the contemporary point of view, the existence of the pyronitrate ion is doubtful, because the coordination number of nitrogen with respect to oxygen cannot exceed 3, whilst in the hypothetical

pyronitrate it is 4. It has been shown [33] that the pyronitrate ion is not formed in basic melts. Oxide ions can be stabilised in the melt solely by virtue of the formation of silicate ions in the reaction with the material of the container (Pyrex).

The communications of Shams El Din and Gerges [39,40] also contain data on the behaviour of oxygen electrodes in nitrate melts. The 'anomalous' behaviour of the platinum oxygen electrode has been attributed to the 'peroxide' function of oxygen gas electrodes. On the other hand, a satisfactory reversibility is characteristic of metal oxide electrodes (of the second kind).

Experimental study of the acid–base equilibria involving phosphates and molybdates led to the conclusion that heteropolyacids are formed in nitrate melts.[41,42] This has been confirmed by the results of cryoscopic studies.[43] Certain characteristic features of the potentiometric titration method in melts have been described.[44,45] The automatic titration method consists of the following features:[44] a rod of the solidified solution of $K_2Cr_2O_7$ in the test melt is lowered at a uniform rate, by means of a special device, into the melt containing the base and the pen recorder measures the e.m.f.'s. This method makes it possible to estimate only the concentration of the acid in the test melt (to within 3.5% according to the authors). The thermodynamic characteristics could not be determined because the measured e.m.f. does not correspond to equilibrium.

With increase in the acidity of the oxide, the decomposition temperature of the nitrate melt falls.[46] This has been explained by the decrease in the activation energy for the decomposition reaction as a result of the binding of the oxide ions formed by acids. However, the observed phenomenon can be explained also, without resorting to kinetic ideas, by the shift of the decomposition equilibrium towards the formation of oxide ions and nitrogen oxides in accordance with the Le Chatelier rule. The affinity of the oxide decreases in the sequence $SiO_2 > TiO_2 > ZrO_2 > Al_2O_3 > MgO$.

A study of the possibility of using a series of metal oxide oxygen electrodes ($Nb|Nb_2O_5$, $Ta|Ta_2O_5$, $Zr|ZrO_2$) in potentiometric studies [47–49] made it possible to construct the following acidity series in the potassium nitrate melt at 350 °C: $NH_4VO_3 > NaPO_3 > NaH_2PO_4 > K_2Cr_2O_7 > K_2HPO_4 > Na_4P_2O_7 > NaH_2AsO_4 > K_2CO_3 > Na_2O_2$.

The presence in this series of certain acids, the existence of which is doubtful, shows that the authors did not always take into account the real processes occurring in the melt. Thus it is quite clear that ammonium metavanadate should decompose to the oxide V_2O_5, which is partly reduced by ammonia, whilst acid salts decompose to the corresponding pyro- and meta-salts. The above acidity series cannot therefore by regarded as uncontroversial.

4. Sulfate melts

The intrinsic acid–base dissociation equilibrium is established in sulfate melts:

$$SO_4^{2-} \rightleftharpoons SO_{3,\,solv} + O^{2-}. \quad (7)$$

Such systems have been investigated to a much smaller extent than the nitrate melts, which can be explained by the relatively high melting points of both the individual sulfates and their eutectic mixtures. Another possible cause is the very low stability of the acid solutions in such melts. Indeed, reaction (7) should lead to the formation in the melt of SO_3, which is a gas at the melting points of the known eutectic mixtures of alkali metal sulfates. The sulfate melts may contain SO_3 as a result of the formation of polysulfates, for example the pyrosulfate $SO_3 \cdot SO_4^{2-}$. According to reference data,[50,51] the decomposition temperatures of pure pyrosulfates do not exceed 460 °C and in solution they should be even lower. Under the conditions of continuous renewal of the atmosphere over the melt, *i.e.* in an argon or nitrogen stream, the process involving the evaporation of the acid SO_3 from the sulfate melt, *i.e.*

$$SO_{3,\,solv} \rightleftharpoons SO_{3,\,gas} \quad (8)$$

should be displaced fully to the right according to the Le Chatelier rule and equilibrium cannot be attained in acid solutions. From the standpoint of the study of oxo-acidity, the eutectic mixture of potassium, lithium, and sodium sulfates (0.135 : 0.78 : 0.085) with a melting point of 512 °C may prove to be the most promising.[52] In this case, studies may be carried out at lower temperatures than in the classical study [1] and hence acid and basic solutions will be more stable.

The oxygen electrode $Pt(O_2)$ has been calibrated and an acidity scale has been constructed [1] in the $K_2SO_4–Na_2SO_4$ melt at 800 °C. The study of the thermal stability of the pyrosulfate showed that the enhancement of the acidity of the cations of the melt lowers the decomposition temperature of the latter.[3]

Measurements of the acidity of centimolar solutions of sodium pyrosulfate and peroxide showed that the extent of the acidity scale in the $K_2SO_4–Li_2SO_4–Na_2SO_4$ melt at 550 °C amounts to 10 pO units.[53,54] Hence it is easy to determine the acid–base product for the solvent: it is 10^{-14}. The range of stability of the VO^{2+} ion is pO = 8.5–10.6.

In conclusion of the topic of oxo-acidity in sulfate melts, one should mention the study [55] in which the potentiometric titration of MoO_3, $Cr_2O_7^{2-}$, PO_3^-, $P_2O_7^{4-}$, and V_2O_5 with sodium carbonate in the $K_2SO_4–Li_2SO_4–Na_2SO_4$ melt was achieved at 625 °C. The e.m.f. jump was observed at an acid : carbonate molar ratio of 1 : 1. In the case of vanadium oxide, the ratio was 1 : 3. There is no information about the equilibrium constant.

5. Silicate melts

The studies of silicate melts are as a rule of applied importance and these systems are widely used in industry (slags, glasses, *etc.*).

A number of studies [56–58] have been devoted to the dependence of the acidity of silicate melts on their composition. Together with SiO_4^{4-}, the polyanions $(SiO_3)_3^{6-}$ and $(SiO_{2.5})_6^{6-}$ exist in the $PbO–SiO_2$ system ($N_{SiO_2} = 0–0.6$) at 1100–1200 °C.[56] A decrease in the ratio Na_2O/SiO_2 in fused glasses diminishes the basicity, whereas magnesium oxide hardly affects the basicity of the melt.[57] The study was carried out with the aid of the $Ag(O_2)$ oxygen electrode in concentration cells.

The platinum oxygen electrode is satisfactorily reversible in the $PbO–SiO_2$, $Na_2O–CaO–SiO_2$, and $MO–PbO–SiO_2$ silicate melts, where M is an alkali earth metal cation.[59]

The application of the membrane oxygen electrode for the monitoring of the acidity of fused silicates during glass making has been described.[60] The study of the basicity of $Na_2O–Al_2O_3–SiO_2$ melts by an e.m.f. method showed that Al_2O_3 exhibits weaker acid properties than SiO_2.[61]

Under the conditions of the corrosion of the glasses $Na_2O \cdot x\text{-}Al_2O_3 \cdot 2SiO_2$ ($x = 0–0.4$) in alkaline earth metal nitrate melts, the degree of interaction of the melt with the silicate increases with decrease in the radius of the alkaline earth metal cation, *i.e.* with intensification of its acidity.[62]

The influence of the charge and radius of the cation in the oxides Tl_2O, PbO, CdO, ZnO, and Bi_2O_3 on the basicity of the lead metasilicate melt has been investigated potentiometrically at 800, 850, and 900 °C.[63]

6. The equimolar KCl–NaCl mixture

The reversibility of the oxygen gas electrode $Pt(O_2)$ in chloride melts has been investigated and the constants for the acid–base equilibria involving chromium(VI), molybdenum(VI), and tungsten(VI) oxides and anions have been determined at 700 °C.[64–69] The constants for the addition of the oxide ion to chromium oxide and sodium metaphosphate have been found.[64–66] It has been established that the titration of CrO_3 proceeds in accordance with the scheme

$$2CrO_3 + O^{2-} \rightleftharpoons Cr_2O_7^{2-},$$

$$Cr_2O_7^{2-} + O^{2-} \rightleftharpoons 2CrO_4^{2-},$$

and the equilibrium constant is 2.88×10^3 for the first stage and 1.4×10^{-1} for the second.

The metaphosphate ions are also titrated in two stages:

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

$$P_2O_7^{4-} + O^{2-} \rightleftharpoons 2PO_4^{3-}.$$

The equilibrium constants for the first and second stages are $(2.88 \pm 1.2) \times 10^3$ and $(2.5 \pm 1.4) \times 10$ respectively.

An excess of the titrant (O^{2-}) leads to the formation of basic phosphates, to which the authors attribute the composition $PO_3^- \cdot 2O^{2-}$. When sodium carbonate is used as the titrant, basic products are not formed. The Ba^{2+} and Li^+ cations exhibit appreciable acid properties in a chloride melt; the equilibrium constants for the addition of the oxide ion are 8.1×10^3 and 3.53×10^2 respectively.

The study of the acid properties of MoO_3 and the corresponding anions showed that the equilibrium constants for the addition of the oxide ion, *i.e.*

$$2MoO_3 + O^{2-} \rightleftharpoons Mo_2O_7^{2-},$$

$$Mo_2O_7^{2-} + O^{2-} \rightleftharpoons 2MoO_4^{2-}$$

are 5×10^4 and 880 ± 880 respectively.[67]

Two studies[68,69] were devoted to the determination of the constants of the acid–base equilibria involving a tungsten(VI) oxo-compound. The titration of tungsten oxide in the melt is also a two-stage process:

$$2WO_3 + O^{2-} \rightleftharpoons W_2O_7^{2-},$$

$$W_2O_7^{2-} + O^{2-} \rightleftharpoons 2WO_4^{2-}$$

with the equilibrium constants 1460 ± 390 and 880 ± 880 respectively. The platinum oxygen electrode exhibits a satisfactory reversibility with respect to oxide ions in a chloride melt.[69] The slope of the E–pO relation is close to $2.3RT/2F$ (F is the Faraday), which corresponds to the electrode process

$$\tfrac{1}{2}O_2 + 2e \rightleftharpoons O^{2-}.$$

The above results served as the basis for further electrochemical studies on electrochemical reduction reactions of Group VI metals.[70–72] The theoretical foundations and principles of controlling electrochemical processes involving the isolation of metals and their compounds with nonmetals (carbides, borides, silicides) from ionic melts have been developed.[73]

In a study of the acid–base equilibria in $CaWO_4$ solutions, the solubility of CaO in the KCl–NaCl melts at 1000 K was found to be ~ 0.084 mol.%.[74] The solubility of scheelite in a chloride melt at 1000 K is $10^{-3.5}$ mol kg^{-1}. The equilibrium constant for the reaction

$$WO_3 + O^{2-} \rightleftharpoons WO_4^{2-}$$

is ~ 10.

According to Combes and Tremillon,[74] the polyanion $W_3O_{10}^{2-}$ ($pK = 12.7$) is formed on reverse titration. Thus the titration curve is not reversible. The results may be accounted for by the elimination of WO_3 from acid chloride melts in the form of the oxide chloride. Under the conditions of reverse titration, the substance used as the titrant is lost in an uncontrolled manner. These considerations apply also to other studies in which titration involving the transition from a base to an acid was resorted to in the investigation of the acid properties of the oxo-compounds of Group VI elements.

The acid–base equilibria in solutions of phosphorus(V) oxo-compounds have been investigated at 700 °C with the aid of the membrane oxygen electrode $Pt(O_2)|ZrO_2(Y_2O_3)$.[75] In the melt with the ratio $Na_2O : P_2O_5 = 1.67 - 3$, the polyphosphate ions are formed:

$$P_nO_{3n+1}^{-(n+2)} + PO_4^{3-} \rightleftharpoons P_{n+1}O_{3n+5}^{-(n+5)}.$$

The corresponding equilibrium constants have been determined. The solubilities of the polyphosphates formed have been found by the cryoscopic method.

The titration of V_2O_5 takes place in two stages:[76]

$$V_2O_5 + O^{2-} \rightleftharpoons 2VO_3^-,$$

$$2VO_3^- + O^{2-} \rightleftharpoons V_2O_7^{4-}.$$

The pK for the first and second stages are -9.3 ± 0.3 and -8.3 ± 0.3 respectively.

The acid–base properties of certain higher oxides and oxo-anions in chloride melts at 700 °C have been investigated in a series of studies.[77–81] The results, presented in Table 1, agree satisfactorily with the analogous data obtained with the aid of the membrane oxygen electrode $Pt(O_2)|ZrO_2$. The application of the platinum oxygen electrode leads to pK values which are lower by approximately 3–4 orders of magnitude. In chloride melts, the $Cr_2O_7^{2-}$ ion is unstable and decomposes with formation of equimolar amounts of CrO_3 and CrO_4^{2-}.[79]

Table 1. The constants of certain acid–base equilibira in KCl–NaCl and NaI melts.[77–81]

Equilibrium	−pK		
	m [a]	N [b]	mol.%
KCl–NaCl melt, 700 °C			
$2PO_3^- + O^{2-} \rightleftharpoons P_2O_7^{4-}$	8.01 ± 0.1	10.67	6.67
$PO_3^- + O^{2-} \rightleftharpoons PO_4^{3-}$	5.93 ± 0.1	7.26	5.26
$PO_3^- + 2O^{2-} \rightleftharpoons PO_5^{5-}$	7.24 ± 0.1		
$CrO_3 + 2O^{2-} \rightleftharpoons CrO_5^{4-}$	8.41 ± 0.1	9.77	7.77
$Cr_2O_7^{2-} + O^{2-} \rightleftharpoons 2CrO_4^{2-}$	7.18 ± 0.1	7.18	7.18
$2CrO_4^{2-} + O^{2-} \rightleftharpoons Cr_2O_9^{6-}$	1.60 ± 0.2	4.26	0.26
$MoO_3 + O^{2-} \rightleftharpoons MoO_4^{2-}$	8.32 ± 0.2	9.65	7.65
$MoO_3 + 2O^{2-} \rightleftharpoons MoO_5^{4-}$	9.71 ± 0.3	11.37	7.37
$WO_3 + O^{2-} \rightleftharpoons WO_4^{2-}$	9.31 ± 0.2	10.64	8.64
$WO_3 + 2O^{2-} \rightleftharpoons WO_5^{4-}$	10.67 ± 0.5	13.33	9.33
$B_4O_7^{2-} + O^{2-} \rightleftharpoons 4BO_2^-$	4.82 ± 0.1	2.16	4.16
$BO_2^- + O^{2-} \rightleftharpoons BO_3^{3-}$	2.37 ± 0.2	3.17	1.70
$V_2O_5 + O^{2-} \rightleftharpoons 2VO_3^-$	6.95 ± 0.2	6.95	6.95
$V_2O_5 + 2O^{2-} \rightleftharpoons V_2O_7^{4-}$	12.23 ± 0.1	14.89	10.96
$V_2O_5 + 3O^{2-} \rightleftharpoons 2VO_4^{3-}$	12.30 ± 0.1	14.96	10.96
$V_2O_5 + 5O^{2-} \rightleftharpoons 2VO_5^{5-}$	13.88 ± 0.5	19.20	11.20
$2GeO_2 + O^{2-} \rightleftharpoons Ge_2O_5^{2-}$	4.18 ± 0.4	6.84	2.84
NaI melt, 700 °C			
$2VO_3^- + O^{2-} \rightleftharpoons V_2O_7^{4-}$	5.40 ± 0.3	7.10	4.10
$V_2O_7^{4-} + O^{2-} \rightleftharpoons 2VO_4^{3-}$	1.68 ± 0.3	1.68	1.68
$B_4O_7^{2-} + O^{2-} \rightleftharpoons 4BO_2^-$	5.02 ± 0.8	3.37	5.37

[a] In units of molality. [b] In units of normality.

7. Other alkali metal halide melts

Empirical acidity series in KCl and CsI melts at 700 °C have been quoted.[6,7] The practical value of these studies is that the $SO_4^{2-}/S_2O_8^{2-}$, $WO_4^{2-}/W_2O_7^{2-}$, and $PO_4^{3-}/P_2O_7^{4-}$ buffer solutions proposed by the authors, which have satisfactorily reproducible pO values, may be used as standard solutions for the calibration of oxygen electrodes in alkali metal halide melts.

The acidity series in the sodium iodide melt at 700 °C have been constructed by Rybkin and Banik.[8] The authors conclusion that the carbonate and hydroxide ions are bases of equal strength cannot be regarded as correct, since the acidity scales were constructed using solutions in which the contents of the test reagents were the same (0.01 mol kg^{-1}), whereas it follows from the equations

$$2OH^- \rightleftharpoons H_2O\uparrow + O^{2-}, \quad (9)$$

$$CO_3^{2-} \rightleftharpoons CO_2\uparrow + O^{2-} \quad (10)$$

that the amount of hydroxide should be twice as great. One mole of O^{2-} may be formed from 1 mol of CO_3^{2-}, whereas only 0.5 mol of O^{2-} may be obtained from 1 mol of OH^-. Indeed, in another study by the same workers it was shown that the hydroxide ion is a stronger base than the carbonate.[82]

Certain results of the study of the acid properties of boron(III) and vanadium(V) oxo-compounds in the NaI melt at 700 °C, carried out by Cherginets,[81] are presented in Table 1.

The comparative Lux–Flood base strengths (OH^-, CO_3^{2-}, SO_4^{2-} in the NaI melt at 700 °C have been established by titration with sodium pyrophosphate.[82,83] The first of these bases reacts with the acid in proportions of 2:1, whilst the others are neutralised in proportions of 1:1. Depending on the e.m.f. jump at the point of equivalence, the bases investigated can be arranged in the sequence $OH^- > CO_3^{2-} > SO_4^{2-}$ in terms of the decrease in basicity. The equilibrium constants have not been quoted.

In a number of instances, the substances introduced into the melt actually exist in the latter in another form. For example, potassium nitrate and nitrite decompose to the oxides at the experimental temperature.[6,7]

This applies also to pyro- and per-sulfates[6,7] and also to acid phosphates.[8] The acidity of the pyrophosphate in an iodide melt is much higher than that of the metaphosphate ion according to the data of Rybkin and Banik.[8] However, the titration of phosphorus oxo-compounds proceeds in accordance with the scheme

$$PO_3^- \longrightarrow P_2O_7^{4-} \longrightarrow PO_4^{3-},$$

and the acidity of the pyrophosphate should therefore be lower, because in the conjugate pair 'metaphosphate–pyrophosphate' the latter is the base. The frequently observed lack of correlation between the pH of aqueous solutions of salts and the pO of the analogous solutions in the melt (this usually applies to phosphorus oxo-compounds) is due to the difference between the processes occurring during neutralisation. The neutralisation of phosphoric acid in aqueous solutions proceeds in stages in accordance with the scheme

$$H_3PO_4 \xrightarrow{OH^-} H_2PO_4^- \xrightarrow{OH^-} HPO_4^{2-} \xrightarrow{OH^-} PO_4^{3-}.$$

The analogous sequence in melts assumes the form

$$\tfrac{1}{2}P_2O_5 \xrightarrow{\frac{1}{2}O^{2-}} PO_3^- \xrightarrow{\frac{1}{2}O^{2-}} \tfrac{1}{2}P_2O_7^{4-} \xrightarrow{\frac{1}{2}O^{2-}} PO_4^{3-}.$$

A correlation should therefore be sought between the acidities of an aqueous solution of the anion and a solution of the corresponding anhydro-acid in the melt. The salts $NaPO_3$ and $Na_4P_2O_7$ can be readily obtained by pyrolysing the corresponding acid salts, but the reverse processes hardly occur in aqueous solutions and the above substances exist as the salts of the independent acids HPO_3 and $H_4P_2O_7$. On the other hand, in the case of meta- and pyro-arsenates, which exhibit a greater tendency to hydrolyse, a correlation between the pH of the aqueous solutions of these anhydro-compounds and the pO of the solutions in the melt should be observed. Thus the breakdown of the correlation in the case of phosphorus oxo-compounds is only apparent, because it is induced solely by kinetic limitations.

Analysis of literature data makes it possible to discover also a fundamental inaccuracy which has arisen in the studies of oxo-acidity in nitrate melts, in particular in KNO_3. As a constituent of this melt, the NO_3^- ion is capable of dissociating with formation of O^{2-} in accordance with the equation

$$NO_3^- \rightleftharpoons NO_2^+ + O^{2-},$$

which is thus the equation of the intrinsic acid–base dissociation of the solvent.[84] In the potassium nitrate melt, there is a possibility of the levelling off of both acid properties,[84] *i.e.*

$$A\square + NO_3^-(NO_2^+ : O^{2-}) \longrightarrow A[:]O^{2-} + NO_2^+, \quad (11)$$

and basic properties (as has been observed by De Andrade *et al.*),[85] *i.e.*

$$O^{2-} + 2K^+ \rightleftharpoons K_2O. \quad (12)$$

This implies that acids stronger than NO_2^+ and bases stronger than K_2O cannot exist. According to Eqn (11), the acid–base titration curves for solutions of strong acids of equal concentration should be identical. This permits a fresh look at the results obtained in earlier studies.[39–42]

We shall consider the potentiometric titration data for solutions of oxo-acids (Fig. 1). The curves presented virtually coincide (despite some difference between the initial concentrations of the acid). This means that the process

$$NO_2^+ + O^{2-} \rightleftharpoons NO_3^-,$$

occurred in all cases, whereas the above investigators[39–42] performed their calculations on the basis of reaction equations with other stoichiometric coefficients, which in fact led to an appreciable drift in the calculated equilibrium constants.

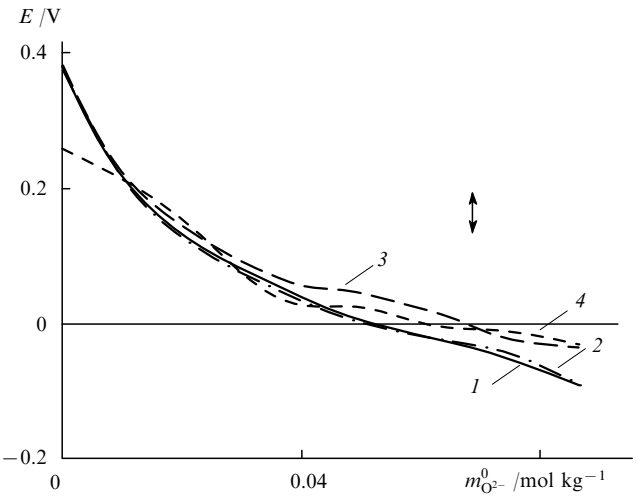


Figure 1. Potentiometric titration curves for solutions of the oxo-acids CrO_3 (*1*), MoO_3 (*2*), WO_3 (*3*), and PO_3 (*4*) at concentrations of ~0.1 mol kg^{-1} in the KNO_3 melt at 350 °C (according to data in Refs 39–42). The arrow indicates the error in the measurement of the e.m.f.

The levelling of the acid strengths in oxygen-containing melts makes the latter an unsuitable medium for the determination of the equilibrium constants for processes involving strong acids. The melts of alkali metal halides, in which this phenomenon is not observed, are more suitable for this purpose. Since the physicochemical properties of ionic melts (ionic densities, charges, and radii)† are usually similar, the application of the acidity scale obtained for one melt in order to characterise another melt is more justified than, for example, the use of different low-temperature molecular solvents, the physicochemical properties of which (relative permittivity, donor–acceptor properties) differ extremely significantly.

† The radii of the NO_3^- and Cl^- ions are 0.165 and 0.167 nm respectively.[10]

III. The solubilities of oxides in alkali metal halide melts

The dissolution of oxides in alkali metal halide melts is accompanied by the interaction of the ions of the oxides with those of the melt (solvation). These interactions are superimposed on the oxide dissociation process and lead to the formation of halo-complexes and oxides of the alkali metals. Furthermore, part of the molecular oxide also dissolves. Thus the following equilibria are established in a saturated solution of the oxide:

$$MO_{solid} \rightleftharpoons MO_{solution}, \quad (13)$$

$$MO_{solution} \rightleftharpoons M^{2+} + O^{2-}, \quad (14)$$

$$M^{2+} + n\mathrm{Hal}^{-} \rightleftharpoons \mathrm{MHal}_n^{2-n}, \quad (15)$$

$$O^{2-} + 2\mathrm{Kt}^{+} \rightleftharpoons \mathrm{Kt}_2O, \quad (16)$$

where Kt^+ is the cation of the melt (Cs^+, K^+, and Na^+).

Since the formation of complexes between the anions of the melt and various cations proceeds to approximately the same extent, one may postulate that the dependence of the solubility of the oxide on the nature of its constituent metal is determined primarily by the degree of interaction of the metal cation and the oxide ions in the melt, which is an acid – base process as defined by Lux and Flood.

According to Lux and Flood, the equilibrium constant of reaction (1) may serve as a quantitative measure of the acidity of the chemical compound or ion. If all the participants of this reaction are in the dissolved state, then the equilibrium established in the homogeneous system may be regarded as of the acid – base type. However, the solubility of the majority of oxides in melts is limited (the excess oxide precipitates). Thus, the oxide ions are eliminated from the melt not only as a result of the reaction with the cationic acid but also as a result of the formation of another phase (*i.e.* a deposit of the oxide). In the study of the solubilities of oxides in melts by potentiometric titration, one must therefore take into account equilibrium (13). It follows from Eqns (13)–(16) that the binding of the oxide ions by the metal cations is in general a heterogeneous process, as a result of which a new phase (the metal oxide) is formed. In this case, the affinity of the cation M^{2+} cannot be unambiguously related to the completion of the $M^{2+} + O^{2-}$ interaction in the melts. The solubility of the oxide (Σs_{MO}) in the melt can be determined, taking into account its incomplete dissociation, as the sum of the activities (concentrations) of the metal cations and the undissociated oxide:

$$\Sigma s_{MO} = a_{M^{2+}} + a_{MO}, \quad (17)$$

where $a_{M^{2+}}$ and a_{MO} are respectively the activity of the metal cation and of the undissociated oxide in the saturated solution.

Since the concentration of the undissociated oxide in the saturated solution is as a rule extremely difficult to determine, in practice the solubility product P_{MO} is used as the characteristic of the solubility of the oxide:

$$P_{MO} = a_{M^{2+}} a_{O^{2-}}. \quad (18)$$

According to the Law of Mass Action, in the region of saturation of the solution the dissociation constant of the oxide can be expressed in the form

$$K_{MO} = \frac{a_{M^{2+}} a_{O^{2-}}}{a_{MO}}. \quad (19)$$

Comparison of Eqns (18) and (19) leads to the expression

$$K_{MO} = \frac{P_{MO}}{a_{MO}}. \quad (20)$$

The complete set of the constants characterising the equilibria in the saturated solution of the oxide can be obtained, provided that two parameters of Eqn (20) out of three have been found. Owing to the lack of well developed and generally accepted methods for the determination of activity coefficients and their dependence on the concentrations of the corresponding species in fused salts, in practice the calculation of concentration parameters is usually resorted to.

1. Methods for the investigation of the solubilities of oxides in melts

In the study of the solubilities of oxides in oxygen-containing and halide melts, different versions of the isothermal saturation and potentiometric titration methods are usually employed.

The isothermal saturation method consists in the successive addition of the test oxide to the solvent melt until the formation of a saturated solution. The instant of saturation is established both with the aid of potentiometric measurements [85,86] and by a titrimetric procedure (by determining the concentration of the metal forming the oxide in a sample of the melt).[87] The final result is the determination of the 'total' solubility in accordance with Eqn (17), which, when account is taken of Eqns (18) and (20), may be expressed in the form

$$\Sigma s_{MO} = P_{MO}^{1/2} + \frac{P_{MO}}{K_{MO}}. \quad (21)$$

Naturally, if the potentiometric method with a precalibrated electrode system is used to monitor the degree of saturation, then, knowing the amount of added oxide and the equilibrium molality of the oxide ion in the melt, the parameters of its dissociation can be determined separately. However, this case is more of an exception. Furthermore, in order to obtain a representative selection it is necessary to carry out a series of experiments, which requires much time and a considerable expenditure of reagents.

The method involving the analysis of melt samples [87] is used fairly widely, but it may lead to distortion of the results as a consequence of the contamination of the sample by suspended oxide particles. It is therefore necessary to take measures to prevent the formation of suspensions in the melt, which greatly complicates the technique of the measurement.

The isothermal saturation method is very convenient in studies over a range of temperatures, but it can hardly be used to determine the solubilities of oxides of the type MgO, NiO, Al_2O_3, *etc.*, which are extremely sparingly soluble in nitrate and halide melts. As a rule, the data obtained in such investigations do not permit the simultaneous estimation of the solubility product of the oxide and its dissociation constant with the exception of limiting cases where the oxide is either fully dissociated or, conversely, is hardly dissociated. Since the 'pure' melt itself contains oxide ions, in the determination of the solubility errors may arise which become especially pronounced if the solubility is comparable to the concentrations of the oxide ion in the 'pure' solvent melt.

The potentiometric titration method is applicable over a much wider range. It makes it possible to determine the solubility product and in many instances (when an unsaturated solution region is present on the titration curve) also to calculate the dissociation constants of oxides in melts. Potentiometric studies are as a rule carried out in cells with transport, but this does not lead to significant experimental errors, because the potentials of liquid compounds in melts are insignificant.[88]

2. The KCl – LiCl melt (0.405 : 0.595)

The solubility of the Fe(II, III) oxides in the KCl – LiCl (0.405 : 0.595) melt has been investigated.[89,90] Potentiometric and diffractometric studies showed that, on precipitation by the donor of oxide ions (CO_3^{2-}, pure FeO is formed, whereas trivalent iron is deposited as the $LiFeO_2 - Li_yFe_{1-y}O$ solid solution. The solubility products of the iron oxides FeO, Fe_3O_4, and Fe_2O_3 are $10^{-5.4}$, $10^{-36.3}$, and $10^{-29.16}$ respectively. The Fe^{3+} cations oxidise the chloride melt with liberation of chlorine. An evident disadvantage of these studies is the use of sodium carbonate,

known *a priori* to be incompletely dissociated, as the base, which undoubtedly influenced the calculated solubility products. Furthermore, it is not comprehensible how it was possible to obtain Fe_2O_3 by deposition if the corresponding cation is unstable in the chloride melt.

The qualitative study of the solubilities of oxides in the KCl–LiCl melt at ~ 500 °C was based on the visual monitoring of the solubility.[91,92] KOH was added to a solution of the chloride of the test metal in the melt. If the oxide was not then precipitated, it was regarded as soluble (CdO, PbO, BaO, CaO, Ag_2O). Otherwise the oxide was regarded as sparingly soluble (CoO, NiO, ZnO) or insoluble (MgO, BeO, Al_2O_3). Copper(II) oxide proved to be unstable in chloride melts and its dissolution was accompanied by the reduction of Cu^{2+} ions to Cu^+. The chlorides of certain other metals in the highest oxidation states, for example $TiCl_3$, $FeCl_3$, and $AuCl_3$, behave similarly. The addition of the corresponding metal chlorides to a melt containing other oxides led to the dissolution of the latter as a result of the occurrence of reactions of the type

$$2CuCl_2 + ZnO\downarrow \longrightarrow ZnCl_2 + 2CuCl + \tfrac{1}{2}O_2\uparrow.$$

A significant difference between the solubilities of the oxide in 'the powder form' or prepared *in situ*, *i.e.* by adding KOH to a solution of the corresponding chloride, has been noted. The solubilities of CaO and CdO obtained by the latter method are much higher.

Saturated solutions of various oxides have been investigated polarographically.[93,94] The degree of interaction of the oxide with the melt was inferred from the potential, the shift of the polarogram, and the change in its form compared with theoretical data. It has been established that, in the electrochemical reduction of a cation, the stage involving the acid–base dissociation of the corresponding oxide is rate-limiting. The stability constants of the oxides were found to have the following values (in mol.%): CoO — $(9.9\pm1.9)\times10^3$, NiO — $(6.8\pm0.8)\times10^3$, PbO — $(3.4\pm1.3)\times10^3$, and Bi_2O_3 — $(8.7\pm3.5)\times10^3$. The equilibrium constant for the formation of the plumbate ion from PbO is $(2.0\pm1.6)\times10^2$. Cadmium, copper, and silver oxides were fully dissociated under the experimental conditions, which agrees with other data.[91,92]

The estimation of the solubilities of a series of oxides was undertaken in order to elucidate the possibility of using the corresponding metal oxide electrodes (electrodes of the second kind) as indicator oxygen electrodes.[95] The solubilities of the oxides at 500 °C were found to have the following values (in mol kg^{-1}): NiO — 3.3×10^{-4}, BiOCl — 6.8×10^{-4}, PdO — 9.4×10^{-3}, PtO — 3.32×10^{-2}, and Cu_2O — 3.8×10^{-2}.

3. The KCl–NaCl melt (0.50 : 0.50)

The study of the solubilities of CaO, SrO, and BaO over the range of temperatures from T_m to 900 °C was carried out by an isotopic method.[96] Together with the KCl–NaCl melt, the pure individual potassium and sodium chlorides were also used as the solvent. The solubilities of the oxides increased in the sequence CaO < SrO < BaO. The solubility products of the oxides in the KCl and KCl–NaCl melts were found to be similar and somewhat lower than in the NaCl melt. Comparison of the experimental data with the results of thermodynamic calculations showed that the solution contains simultaneously both the molecular oxide MO and the M^{2+} and O^{2-} ions formed on its dissociation.

In an analogous investigation,[87] the solubilities of the oxides in the temperature range 700–810 °C were determined by measuring the concentrations of the metal cations in the solidified melt specimen using the complexometric titration method. Comparison of the observed solubility products with theoretical estimates made it possible to calculate the activity coefficients of the oxide ions in the saturated solutions studied. The quantities obtained can hardly be regarded as correct, because they are influenced significantly by the incomplete dissociation of the oxides in the melt and by the deviations from ideality of the solution induced by the presence of doubly charged alkaline earth metal cations and O^{2-}. The contribution of each of these components was not estimated separately.

The acid properties of the Ca^{2+}, Li^+, and Ba^{2+} cations have been investigated[97] at 700 °C and the constants for the acid–base equilibria

$$2Li^+ + O^{2-} \rightleftharpoons Li_2O,$$

$$Ba^{2+} + O^{2-} \rightleftharpoons BaO,$$

were found as 353 mol.% and 81 mol.% respectively. It follows from these data that all the cations investigated are appreciably acid.

The acidity of the cations of the main subgroup elements weakens with increase in the atomic number of the element, whereas in the Group B elements and in transition series such behaviour is not observed.[9] Careful analysis of the data of Ovsyannikova and Rybkin[9] showed, however, that the weakening of the acid properties occurs also in the Zn–Cd diad. Although the above study can in fact be regarded as systematic, it is difficult to extract from it any quantitative data for the estimation of the solubilities of the oxides, since the additional equilibrium (7) is superimposed on the main acid–base equilibrium (14) in the KCl–NaCl melt, because all the cations investigated were added to the melt in the form of sulfates and the influence of this equilibrium was not estimated quantitatively. The use of sulfates should evidently lead to the formation of a deposit and the evolution of SO_3 from the solutions containing the most acid cations.

Furthermore, the results of the above workers[9] are in direct conflict with the phenomenon of the levelling of basic properties described in the preceding section. According to potentiometric data, the content of O^{2-} at equilibrium in the $BaSO_4$ solution is ten times higher than in the K_2SO_4 and Na_2SO_4 solutions at the same concentration. The concentrations were found to be higher to a somewhat lesser extent in solutions containing Cs^+ (by a factor of 3.2), Sr^{2+} (by a factor of 2), and Rb^+ (by a factor of 1.2). It follows from the equation

$$MO + 2Na^+ \rightleftharpoons M^{2+} + Na_2O$$

that, when the metal cation in the melt based on sodium salts is a weaker acid than Na^+, the equilibrium should be displaced to the right and the basicity of O^{2-} is limited by the basicity of Na_2O in the corresponding melt. The addition to the melt of a small amount of a compound with cations less acid than Na^+ should therefore induce the same effect as the addition of an equivalent amount of the corresponding sodium salt (since the authors investigated solutions at a concentration of 0.01 mol kg^-, $M^{n+}/Na = 0.0026/n$). However, the results obtained in the above study[9] conflict with this conclusion.

The solubilities of ZnO, HgO, NiO, and SrO have been investigated by the potentiometric titration method, with the initial transition from the acid to the base and then from the base to the acid.[98] The characteristics corresponding to the solubility product and the dissociation constant were calculated from the experimental data. Unfortunately the average values of the calculated parameters of the equilibria are not quoted in the above study[98] (the averaging was carried out by Combes *et al.*[99]). It was found that the calculated values of K_{MO} and P_{MO} for the forward and reverse titrations differ significantly. This constitutes yet another piece of evidence in support of the need to apply a single research technique in the search for correlations. In the sequence MgO < NiO < ZnO < SrO, the solubility increases. In a later study,[9] a somewhat different series of cations was found. However, preference should be given to the results obtained by the potentiometric titration method.

The solubilities of a series of oxides in the KCl–NaCl melt at 1000 K have been investigated also in other studies.[85,99–101] Two steps were observed on the Mg^{2+} titration curve: the first corresponded to the formation of Mg_2O^{2+} and the second to the

formation of MgO.[99] Although the potentiometric studies of the solubilities of MgO in this and analogous chloride melts have been frequently performed, no one else observed a similar phenomenon. There is usually only one e.m.f. jump, corresponding to the reaction

$$Mg^{2+} + O^{2-} \rightleftharpoons MgO\downarrow.$$

The use of BaO for the titration of alkaline earth metal cations cannot be regarded as correct either, because in this case the substances precipitated are not the individual oxides but their solid solutions with BaO, the solubility of which differs from that of the pure oxide. The principal result of the studies quoted is the conclusion that the solubilities of the oxides increase in the series of alkaline earth metals MgO < CaO < BaO (the solubility of MgO was measured by the potentiometric method and those of the remaining two oxides were found by the isothermal saturation method). The temperature dependence of the solubility of zirconium(IV) oxide in the KCl – NaCl melt assumes the form [102]

$$N_{ZrO_2} = (-5.7 \pm 3.1) \times 10^{-6} + (7 \pm 3) \times 10^{-9}\, T.$$

The solubility of ZrO_2 at 700 °C is insignificant even in an acid medium, so that the use of membrane electrodes based on stabilised ZrO_2 should not lead to an appreciable contamination of the test melt by zirconium(IV) compounds.

The solubilities of 11 oxides of s^2 and $3d$ metals at 700 °C have been investigated (Table 2)[103, 104] The existence of a correlation between the solubilities of the oxides and the crystal-chemical radii of the cations r was established:

$$pP_{MO} = pP_{r\to\infty} + \frac{k}{r^2}. \qquad (22)$$

In a number of instances, the results obtained by different workers [98–101, 103, 104] agree well with one another, which can be accounted for by the virtually identical experimental conditions (the method for the determination of the solubility, the titrant, the molality of the cation, *etc.*). However, the discrepancies are usually fairly considerable. Such a scatter of the results has not so far been accounted for and the impossibility of a systematic treatment of the results naturally did not promote the development of studies on the solubilities of oxides in alkali metal halide melts.

Solubility data can be divided into two groups depending on the method for their determination (Fig. 2); within each group, the solubilities of one oxide have similar values. A fairly unexpected result of the comparison of the available literature data is the conclusion that the solubilities of oxides found by the isothermal saturation method are as a rule several orders of magnitude lower than the values calculated from potentiometric data, although in the former case one determines Σs_{MO} and in the latter only s_M^{2+}.

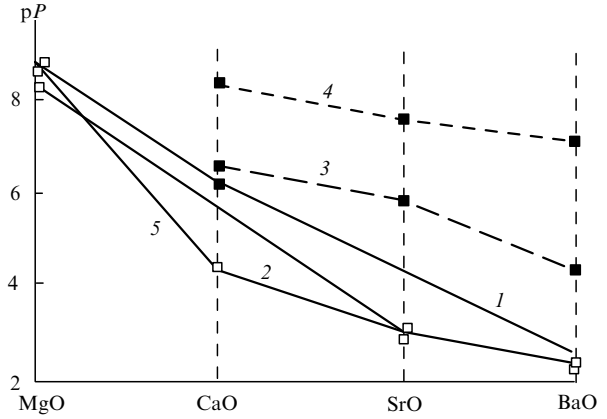


Figure 2. The solubilities of alkaline earth metal oxides in the KCl – NaCl melt measured by the isothermal saturation (open squares) and potentiometric titration (filled squares) methods: (*1*) according to the data of Combes and coworkers;[85, 99–101] (*2*) according to the data of Delimarskii *et al.*;[98] (*3*) according to the data of Shapoval and Tsiklauri;[97] (*4*) according to Volkovich's data;[87] (*5*) according to the data of Chergi-nets and coworkers [104, 110] (at 700 °C).

The higher solubility in melts of oxides prepared *in situ* was first noted by Delarue,[91, 92] although no explanation of the results was given.

The solubility of any substance depends on the size of its crystals in contact with the solution. For substances dissolving in the form of molecules, this dependence is expressed by the Ostwald – Freundlich formula:[105]

$$\frac{RT}{M}\ln\frac{S_1}{S_2} = \frac{2\sigma}{d}\left(\frac{1}{r_2} - \frac{1}{r_1}\right),$$

where S_1 and S_2 are the solubilities of the crystals with the radii r_1 and r_2 respectively, M is the molecular weight, d the density, and σ the surface energy.

For dissociating substances, the analogous equation assumes the form

$$\frac{RT}{M}\ln\frac{P_1}{P_2} = \frac{2\sigma}{d}\left(\frac{1}{r_2} - \frac{1}{r_1}\right),$$

where P_1 and P_2 are the corresponding solubility products.

In particular, it follows from the equations presented that an increase in crystal size leads to a diminution of solubility. For this reason, larger particles should be deposited from concentrated solutions than from dilute solutions. The increase in the size of crystals in a concentrated solution of the cation can be explained

Table 2. The values of pP_{MO} and pK_{MO} for certain oxides in alkali metal halide melts (on the mole fraction scale).[103, 104]

Oxide	KCl – NaCl (700 °C)		CsCl – KCl – NaCl (600 °C)		CsCl – KCl – NaCl (700 °C)		CsBr – KBr (700 °C)		CsI (700 °C)
	pP	pK	pP	pK	pP	pK	pP	pK	pP
BaO	4.66		4.75		~4.5		5.16		4.98
SrO	5.44	2.30	5.81	2.71	5.54	2.14	6.82	2.45	6.28
CaO	6.72		7.73	3.71	6.86	2.99	9.93	3.76	7.50
MgO	11.62		12.68		11.68		12.76		
MnO	9.13		9.73		9.49		10.70		
CoO	10.24		10.92		10.50		11.33		
NiO	11.38		12.60		11.42		12.71		
Cu_2O	6.53		6.95	3.29	6.35	2.59			
ZnO	9.28		8.80		8.15		11.03		
CdO	7.35		7.54		7.09		9.35		8.00
PbO	7.47	4.47	8.21	5.08	7.04	4.03	8.52	5.81	7.80

by the ageing of the oxide — recrystallisation, which is faster when the concentrations of the reactants increase.

Under the conditions of oxidative titration, a finely dispersed metal oxide is formed and begins to 'age' as a consequence of the occurrence of recrystallisation, *i.e.* of the increase in the size of the crystals and the decrease in the surface energy σS, which leads to a decrease in solubility (solubility products). The recrystallisation is promoted by prolonged maintenance at a high temperature and for a high concentration of the corresponding ions in solution. The first case obtains, in particular, when studies are performed by the isothermal saturation method, where the oxide is subjected to preliminary heat treatment or sintering and the pellets obtained are kept in the melt for several hours. In the second case, the transfer of the substance from small to large crystals is evidently accelerated.

We may note that the solubilities of the oxides quoted by Delimarskii *et al.*[98] are somewhat higher than those obtained by the present author. This can apparently be accounted for by the fact that the study of Delimarskii *et al.*[98] was carried out in more dilute solutions (0.01 mol kg^{-1}), where ageing is somewhat slower. A significant disadvantage of dilute solutions is the very marked change in the concentration of the cation during the period of the investigation and hence the poor reproducibility of the results. The measurement of the solubility of NiO in the KCl – NaCl melt may serve as an example. Titration of a solution at a concentration of 0.01 mol kg^{-1} yields $pP_{NiO} = 7.95 \pm 0.20$ (Delimarskii *et al.*[98] obtained 8.32), whereas at a concentration of 0.05 mol kg^{-1} we have $pP_{NiO} = 9.03 \pm 0.06$. However, in this case too the values of pP differ by an order of magnitude. The results quoted[98, 101, 103, 104] for magnesium and barium oxides were obtained by titrating solutions at a concentration of 0.05 mol kg^{-1} and they agree very well with our data. In the vicinity of the equivalence point, the values of pP_{MO} frequently decrease slightly. This is apparently also caused by the difference between the dimensions of the crystals deposited from the melt.

4. The solubilities of the oxides in other alkali metal halide melts

The solubilities of the oxides of s^2 and $3d$ metals in the CsCl – KCl – NaCl (0.455 : 0.245 : 0.30, eutectic) melt have been investigated at 600 and 700 °C (Table 2).[106–111] A method for the separation of the regions of existence of unsaturated and saturated solutions of the oxides, ensuring that the calculated dissociation constants and solubility products of the oxides respectively are correct, has been proposed and justified. The solubilities of the oxides in lithium-free chloride melts at the same temperature are identical (in mole fractions) and the temperature variation agrees with the Schroeder equation.

The solubilities of the oxides in the $2CsBr \cdot KBr$ melt at 700 °C are lower than in the analogous system with the Cl^- ion.[112–114] Thus, SrO which is moderately soluble in chloride melts, becomes sparingly soluble in the bromide melt, whilst the sparingly soluble calcium and cadmium oxides become virtually insoluble. The range of oxides the solubilities of which can be investigated in the CsI melt[115] is still narrower than in the case where systems with other halide ions are employed (Table 2). The results of the investigations have shown that the iodide melt occupies an intermediate position between the chloride and bromide melts as regards the solubilities of the oxides in it.

The linear dependence of pP on r^{-2} holds for all the alkali metal melts investigated.[106–115] This makes it possible to employ the relations indicated (Table 3) for the estimation of the solubility products of the oxides from the cationic radii. Furthermore, on the basis of the results quoted,[110, 111] it is possible to calculate the solubilities of the oxides also at other temperatures by means of the Schroeder equation. When one halide anion of the melt is replaced by another, the degree of association of the melt ions changes, which exerts a decisive influence on the solubilities of the oxides.

Table 3. The coefficients of Eqn (22) for alkali metal halide melts (95% confidence limits).

Melt	T/°C	$pP_{r\to\infty}$	k
KCl – NaCl	700	1.8 ± 0.9	0.053 ± 0.01
CsCl – KCl – NaCl	600	1.7 ± 2.0	0.057 ± 0.01
CsCl – KCl – NaCl	700	1.7 ± 0.3	0.054 ± 0.02
CsBr – KBr	700	3.2 ± 1.8	0.053 ± 0.01
CsI	700	2.65 ± 0.58	0.052 ± 0.01

The study of the solubility of ZrO_2 in the potassium metaphosphate melt and in $KCl - KPO_3$ mixtures at 800 °C showed that the solubility of zirconium oxide reaches 1.34 mass % in pure KPO_3 and 3.25 mass % in the equimolar $KCl - KPO_3$ mixture.[116] The increase in the solubility of ZrO_2 with decrease in the KPO_3 concentration is caused, according to the authors, by the depolymerisation of the latter and by the enhancement of the acid properties of the melt. At a KCl concentration above 60 mol.%, the solubility of ZrO_2 falls sharply, apparently owing to the decrease in the acidity of the melt because the intensification of the dissociation of the metaphosphate under these conditions is no longer compensated by the decrease in the concentration of the acid.

The solubilities of nickel and thorium(IV) oxides in the KF – LiF melt at 550 °C have been studied potentiometrically using a membrane oxygen electrode.[117, 118] The solubility product of NiO is 1.3×10^{-6}, which is appreciably higher than in the chloride melt. The solubility of NiO apparently increases as a result of the formation of stable fluoride complexes of Ni^{2+}.

The solubility products (in mole fractions) of Co_3O_4, NiO, and Y_2O_3 at 1100 K in the NaCl melt are $(0.99 - 3.3) \times 10^{-11}$, $(1.9 - 4.9) \times 10^{-12}$, and $(1.4 - 2.2) \times 10^{-36}$, while those in the Na_2SO_4 melt are $(0.8 - 2.2) \times 10^{-10}$, $(1.6 - 8) \times 10^{-11}$, and $(4.5 - 6.4) \times 10^{-31}$ respectively.[119, 120] The excess titrant leads to the formation of the anionic oxo-complexes NiO_2^-, CoO_2^-, and YO_2^- in the melt.

The solubility products of zinc oxide and K_2ZnO_2 in the potassium chloride melt at 800 °C are 2.3×10^{-8} and 3.2×10^{-12} respectively.[121]

A number of studies have been devoted to oxo-acidity in alkali metal chloride melts to which cations with a high acidity have been added: $MgO - BaCl_2 - CaCl_2 - NaCl$,[122] $CaO - CaCl_2 - KCl - NaCl$,[123] $CeCl_3 - KCl - NaCl$,[124] and $ZnO - NaCl - ZnCl_2$[125, 126] The cationic acids influence significantly the acid – base processes in ionic melts as a result of the binding of the oxide ions. This increases the solubilities of the oxides in such melts (see, for example, Refs 122 and 123).

IV. The reactions of melts with gaseous acid and basic reagents

The gases present in the atmosphere over the melt can react both with its principal components and with impurities. In reactions of the first kind, which include, in particular, hydrolysis, the gas (H_2O) behaves as a Lux – Flood base, supplying O^{2-} ions to the melt. In reactions of the second type (purification of melts by halogenating agents, dissociation of bases), the gaseous reagent is an acid.

1. High-temperature hydrolysis of melts

Reactions of this type have been investigated mainly in relation to individual alkali metal halides and their mixtures. The hydrolysis of the solid and fused sodium chloride in the temperature range 600 – 950 °C has been investigated by a 'dynamic method',[127] which consists in passing nitrogen, containing water vapour, through a layer of solid or fused sodium chloride:

$$NaCl_{solid,\ liquid} + H_2O_{gas} \rightleftharpoons NaOH_{solid,\ liquid} + HCl_{gas}. \quad (23)$$

The HCl evolved was determined titrimetrically.

The rate of evolution of HCl can be described by the following equation:

$$\frac{dn}{d\tau} = \frac{\upsilon p_{HCl}}{p}, \quad (24)$$

where p is the overall pressure, p_{HCl} the 'equilibrium' partial pressure of HCl, and υ the rate of supply of the moist gas.

The equilibrium constant of reaction (23) is

$$K = \frac{\gamma n p_{HCl}}{N p_{H_2O}}, \quad (25)$$

where γ is the activity coefficient of NaOH in NaCl. Integration of Eqn (24) taking into account Eqn (25) leads to the expression

$$n = \left[\frac{2\upsilon N p_{H_2O} K}{p\gamma}\right]^{1/2} \tau^{1/2},$$

which is linear in terms of the $n-\tau^{1/2}$ variables. Evidently this relation should pass through the origin of coordinates ($\tau = 0$, $n = 0$). However, it was found that reaction (23) is complicated by the diffusion of NaOH in NaCl and the authors[127] therefore improved the model by introducing into the latter a correction λ, which is in essence the time required to reduce the diffusional limitations to a minimum:

$$n = \left[\frac{2\upsilon N p_{H_2O} K}{p\gamma}\right]^{1/2} \left\{\tau + \lambda\left[\exp\left(-\frac{t}{\lambda}\right) - 1\right]\right\}^{1/2}.$$

The hydrolysis of sodium chloride occurs to a slight extent, although the rate of evolution of HCl exceeded the expected value as a result of hydrolysis on dissolution of NaOH in NaCl.

An evident disadvantage of the above method is the use in it of the hypothesis that the partial pressure of HCl in the gas phase is equal to the equilibrium partial pressure. Judging from the experimental method, it should in fact be much lower, because NaCl is hydrolysed albeit at a low rate.

The same method has been used to investigate the high-temperature hydrolytic and oxidation reactions of sodium iodide.[128,129] According to the estimates made, the heats of the reactions

$$NaI + H_2O \rightleftharpoons NaOH + HI, \quad (26)$$

$$NaI + \tfrac{1}{2}O_2 \rightleftharpoons \tfrac{1}{2}Na_2O_2 + \tfrac{1}{2}I_2 \quad (27)$$

are 32.8±2 and 13.9±1 kJ mol^{-1} for solid sodium iodide and 30.6±2 and 9.3±2 kJ mol^{-1} for fused sodium iodide. Hence it follows that the latter shows a greater tendency to oxidise than to hydrolyse. In contrast to NaOH, sodium peroxide is almost insoluble in crystalline sodium iodide. The conclusions reached cannot be adopted without stipulation, because they are based on the values of ΔH and not ΔG for the reactions indicated above.

A simple but unquestionable method has been used to investigate high-temperature hydrolysis in the KCl–NaCl melt.[101] A mixture of HCl and H_2O, obtained by passing an inert gas through aqueous HCl solutions at a definite concentration, was passed into the melt. Measurements of the equilibrium O^{2-} concentration by the potentiometric method made it possible to calculate the equilibrium constants for the process

$$H_2O + 2Cl^- \rightleftharpoons O^{2-} + 2HCl \quad (28)$$

(p$K = 55.3 \times 10^3 T^{-1} - 40.2$). At 1000 K, p$K \approx 15.1$ and equilibrium (28) is therefore displaced to the left.

A similar method has been used to investigate the hydrolysis of the KCl–LiCl melt at 500 °C (p$K = 9.77 \pm 0.4$).[130] The hydrolysis of the chloride melt is thermodynamically unfavourable and is fully suppressed in the presence of bases (at a concentration of $\sim 10^{-3}$ mol kg^{-1}).

The cells

$$(H_2O + H_2)Au|N\ MOH + (1 - N)MX(l)|MX(l)|C(X_2), \quad (29)$$

where the symbols M and X designate the alkali metal and the halogen respectively, have been used to investigate the hydrolysis of individual alkali metal halide melts (with the exception of lithium salts).[131]

The e.m.f. of cell (29) is related to the concentrations of the reactants by the expression

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

where P_{H_2} and P_{X_2} are the partial pressures of hydrogen and the halogen over the melt respectively.

The logarithms of the equilibrium constants

$$\ln K = \frac{F}{RT}E - \frac{\Delta G^0_{HX}}{RT} + \ln\frac{P_{H_2}^{1/2} P_{X_2}^{1/2}}{P_{H_2O}} a_{MOH}$$

are negative, which indicates that the hydrolysis of alkali metal halide melts is thermodynamically unfavourable. The tendency towards hydrolysis of melts of individual alkali metal halides diminishes with increase in the radii of both the cation and the anion. According to the results of Smirnov *et al.*,[131] the solutions of alkali metal hydroxides in the corresponding individual chlorides are close to ideality.

2. Elimination of oxygen-containing impurities from alkali metal halides

The studies of the elimination of oxygen-containing impurities from melts are as a rule of an applied character and are performed in melts having industrial applications. Various halogenating agents, usually hydrogen halides or the halogens themselves, are used to eliminate the impurities:[132–138]

$$2HX\uparrow + O^{2-} \rightleftharpoons H_2O\uparrow + 2X^-, \quad (30)$$

$$X_2\uparrow + O^{2-} \rightleftharpoons \tfrac{1}{2}O_2\uparrow + 2X^-,$$

where X is the halogen. However, the water formed in reaction (30) exhibits the properties of a Lux–Flood acid, *i.e.*

$$H_2O + O^{2-} \rightleftharpoons 2OH^-,$$

and this retards the purification process. The cessation of the effect of XH may lead to partial hydrolysis, because, as can be seen from the previous section, the type (30) reactions are reversible. The shift of process (30) to the left is also promoted by the thermal instability of HBr and HI.

The effectiveness of the purification of melts based on lithium salts by hydrogen halides is much lower. Water dissolves in the KCl–LiCl melt in appreciable amounts and is firmly retained at temperatures up to 400 °C.[139] When dry HCl is passed for 1 h, H_2O is not fully removed.

The effectiveness of the purification by the halogens depends on their oxidation-reduction potentials and decreases from chlorine to iodine. In addition, the latter can disproportionate:

$$3I_2 + 3O^{2-} \rightleftharpoons 5I^- + IO_3^-.$$

The iodate ions formed are stable in the melts and oxygen-containing impurities are thus not removed from the iodide melt.

The effect of ammonium halides NH_4X involves the formation of the corresponding hydrogen halide as a result of thermal dissociation:[140–142]

$$NH_4X = NH_3\uparrow + HX\uparrow. \quad (31)$$

However, the addition of NH_4X is recommended only for the drying and heat treatment of the initial components and its use for

the industrial purification of the fused salts is undesirable because it is much easier to ensure the continuous supply of the corresponding hydrogen halide into the melt being purified. Ammonium halides constitute a very convenient means for the removal of oxygen-containing impurities from melts before the investigation: the addition of these crystalline salts lowers the equilibrium concentration of oxide ions to $10^{-5}-10^{-6}$ mol kg^{-1}.[109]

It is believed that the most convenient method for the elimination of oxygen-containing impurities from alkali metal halide melts is carbohalogenation.[143–150]

The effectiveness of CCl_4, $COCl_2$, Cl_2, and the $C + Cl_2$ mixture (C is acetylenic carbon black) can be explained by the occurrence of the reactions [143]

$$CCl_4\uparrow + 2O^{2-} \longrightarrow CO_2\uparrow + 4Cl^-, \quad (32)$$

$$COCl_2\uparrow + O^{2-} \longrightarrow CO_2\uparrow + 2Cl^-, \quad (33)$$

$$C + Cl_2 + O^{2-} \longrightarrow CO(CO_2)\uparrow + 2Cl^-. \quad (34)$$

Thermodynamic analysis of reactions (32)–(34) showed that the effectiveness of the purification is in all cases approximately the same,[144] but reaction (32) has the advantage that highly toxic reagents such as chlorine and phosgene are not used in it. For this reason, CCl_4 has been used in virtually all the subsequent studies involving the carbochlorination of melts.[145–149]

It has been suggested that $CHBr_3$, CBr_4,[150] C_2H_5Br, and CH_3I [142] be used for the removal of oxygen-containing impurities from bromide and iodide melts. A significant advantage of carbohalogenation is the fact that this process leads to an appreciable decrease in the concentration of transition metal cations in the melts being purified. However, in the purification of melts by halogen-substituted compounds with a low halogen content, carbon (carbon black) accumulates in the melt and is displaced by the crystallisation front when single crystals are grown.[143] The presence of a suspension of carbon in alkali metal halide melts is not always desirable and this method cannot therefore be recognised as universal.

The carbohalogenation of the melt leads to the formation of CO_2, which reacts with oxide ions and lowers the equilibrium concentration of O^{2-} and induces the accumulation of the fairly stable carbonate ions CO_3^{2-}. The latter are the main form in which oxygen-containing impurities exist in melts purified in this way.

The use of halo-derivatives of silicon for the purification of iodide melts [151] is based on the reaction

$$SiX_4 + 2O^{2-} \longrightarrow SiO_{2,\,solid}\downarrow + 4X^-,$$

the product of which is silicon dioxide, which is separated from the melt as a consequence of the differences between the densities. Thermodynamic analysis showed [152] that the effectiveness of the purification of iodide melts diminishes in the sequence $SiH_4 > HI > I_2$.

The use of silicon halides for the purification of the melts used in the growing of single crystals does not lead to the appearance of additional impurities, because the processes are carried out in quartz (*i.e.* containing silicon) containers.

Although the methods of purification described are fairly effective in most cases, some kind of oxygen-containing and cationic impurities characteristic of each method always remain in the melt. The method of purification must therefore be selected depending on the aims of the subsequent application of the melt.

3. Dissociation of Lux – Flood bases

The problems of the dissociation of oxide ion donors (Lux – Flood bases) in ionic melts is important both for experimental studies of oxo-acidity and for technological purposes.

Investigators have paid particular attention to strong bases: hydroxide, carbonate, and peroxide ions and barium oxide. The dissociation of the last two bases proceeds in accordance with the equations

$$O_2^{2-} \rightleftharpoons O^{2-} + \tfrac{1}{2}O_2\uparrow, \quad (35)$$

$$BaO \rightleftharpoons O^{2-} + Ba^{2+}.$$

The dissociation of barium oxide (see Section III) leads to the accumulation of 'foreign ions' Ba^{2+} in the melt. Furthermore, BaO exhibits a limited solubility in ionic melts. This imposes a series of limitations on the practical use of this compound. It should not be used for the investigation of the solubility of alkaline earth metal oxides with which BaO forms solid solutions, for the investigation of acid–base equilibria in solutions of anions in which Ba^{2+} forms insoluble compounds [$Ba_3(PO_4)_2$, $BaCrO_4$, *etc.*], and for the investigation of bromide and iodide melts, in which incomplete dissociation takes place.

As regards the remaining three bases mentioned above, their behaviour in ionic melts requires separate consideration. The point is that alkali metal hydroxides distill without decomposition at temperatures above 1300 °C, while sodium and potassium carbonates melt without decomposition at 854 and 890 °C respectively and the CO_2 pressure over their melts is low even at 1000 °C. The thermal dissociation of sodium peroxides begins at 460 °C, whilst K_2O_2 melts without decomposition at 490 °C.[51] Thus the above bases should be sufficiently stable under the conditions of the majority of investigations (200–800 °C).

On the other hand, their dissolution in melts in the absence of conjugate acid gases (H_2O, CO_2, O_2) in an inert atmosphere should lead, according to the Le Chatelier rule, to complete dissociation with formation of O^{2-}, which is bound by the melt cations. The degree of decomposition of the base is determined by the concentration and acidity of the cations,the association of the melt ions, temperature, the solubility in the melt of the conjugate acid gas, and its content in the form of impurities in the inert atmosphere. Owing to the diversity and complexity of these factors, the estimation of the strength of the bases from the results of thermodynamic calculations is frequently incorrect. It is therefore difficult to overestimate the contribution of experimental studies to the solution of this problem.

Potentiometric studies of the dissociation of O_2^{2-} in nitrate melts have shown [153–156] that at temperatures in the range 200–350 °C the main form in which oxygen ions exist in basic media is O_2^{2-}, because oxide ions are oxidised in accordance with the reaction

$$O^{2-} + NO_3^- \longrightarrow NO_2^- + O_2^{2-}.$$

Naturally, the use of a gaseous oxygen electrode in potentiometric studies leads to the appearance in the atmosphere above the melt of gaseous oxygen, which also oxidises the O^{2-} ions. The decrease in the basicity of the melt both owing to the enhancement of the acid properties of the cations constituting the melt [156] and as a result of the decrease in the concentration of oxygen ions [157, 158] lowers the stability of O_2^{2-}. Under these conditions, the main form in which oxygen anions exist in the melt becomes O^{2-}.

Studies of the stability of the O_2^{2-} ions in higher-temperature chloride and sulfate melts [69, 117, 118, 159] have shown that the peroxide ions may be formed in appreciable amounts only in the presence of gaseous oxygen, whilst in an inert atmosphere they are decomposed fully to O^{2-}. The constants of equilibrium (35) at 1100 K in NaCl and Na_2SO_4 melts are 0.05–0.07 and 0.03–0.05 respectively.

The behaviour of carbonate ions in nitrate melts has been investigated.[160, 161] The experimental results show that CO_3^{2-} dissociates fully in these melts and the oxide ions formed are stabilised as a result of the formation of pyronitrate. On the other hand, it has been shown [162] on the basis of potentiometric studies that carbonate ions are not fully dissociated in fused nitrates. In order to establish the truth, cooled specimens of carbonate solutions in nitrate melts were subjected to titrimetric analysis [163] by standard methods.[164] It was found that the consumption of the acid on each of the two titration steps is the same and carbonate ions are therefore fully stable in nitrate melts.

The temperature dependence of the dissociation constant for the carbonate ion in KCl–NaCl melts is given by the following equation:[165]

$$pK_{CO_3^{2-}} = 1.32 \times 10^4\, T^{-1} - 8.4.$$

At 1000 K, pK = 4.8. According to Combes *et al.*,[165] the carbonate ion can be used as the reference base at temperatures above 1000 K, because it should be fully dissociated at low partial pressures of CO_2.

The use of sodium carbonate as a strong base and in the determination of the solubility products of CaO and MgO in the $BaCl_2$–$CaCl_2$–NaCl eutectic melt at 600 °C has been described.[122] The study was performed on the assumption that the base employed is fully dissociated without testing it. The correctness of the results obtained is therefore doubtful.

Potentiometric study of the dissociation of the carbonate ion in the KCl–NaCl melt at 700 °C showed[66] that the carbonate does not dissociate fully even in the absence of CO_2 in the atmosphere over the melt. The 'formal' stability constant of CO_3^{2-}, which was understood as the ratio $[CO_3^{2-}]/[O^{2-}]$, was 2.5±0.5 (the concentrations were expressed in mol.%). It was postulated that the partial pressure of CO_2 over the melt is constant. It was found that, even at concentrations of the order of 10^{-3} mol kg^{-1}, the degree of dissociation of CO_3^{2-} in the KCl–LiCl melts at 500 °C and in KCl–NaCl at 700 °C does not exceed 70%.[130] Thus the hypothesis[165] of the complete dissociation of the carbonate ion at temperatures of ~1000 K has not been confirmed.

Only a few quantitative studies on the dissociation of OH^- in melts are known. It has been established potentiometrically[166,167] that the constant for equilibrium (9) in the KNO_3–$NaNO_3$ melt at 500 K is 10^{-18}. This indicates the stability of OH^- ions. There are no data in the studies quoted on the stability of the hydroxide under a dry atmosphere.

The hydroxide ions do not decompose fully in the KCl–LiCl melt at 400 °C.[168] It may be that this is associated with the fact that the above melt retains water fairly strongly.[139] According to polarographic[91,92] and potentiometric[130] data, an increase in temperature to 500 °C leads to the complete decomposition of the hydroxide.

In order to investigate equilibrium (9), an O^{2-} donor was added to the KCl–NaCl melt, after which the equilibrium e.m.f.'s were measured at water vapour pressures from 1 to 8 mm Hg.[101,169] The calculation of the constant for equilibrium (9), based on the e.m.f.'s obtained, showed that the temperature dependence of the pK in the range 737–817 °C is expressed by the equation

$$pK = 8.15 \times 10^3\, T^{-1} - 6.75.$$

It has been shown[130,170] that the dissociation of hydroxide ions in alkali metal halides does not correspond to Eqn (9) and that the decomposition of OH^- proceeds in accordance with the scheme

$$(OH)_2^{2-} \rightleftharpoons O^{2-} + H_2O. \qquad (36)$$

The pK values for reaction (36) in the KCl–LiCl melt at 500 °C and the KCl–NaCl melt at 700 °C are 2.76±0.15 and 2.22±0.06 respectively. In the absence of water vapour in the atmosphere over the melt, equilibrium (36) is fully displaced to the right in both systems. The main form of the existence of hydroxide ions in the melts is dimers, while OH^- ions may be present only in trace amounts and do not exert an appreciable influence on the equilibria investigated. A possible cause of the formation of the dimers $(OH)_2^{2-}$ in the melts is the formation of a hydrogen bond. The existence of such bonds in the OH^-–containing NaCl melt has been indicated.[102,171]

Thus, among the bases examined, only Na_2O_2 and NaOH dissociate fully at temperatures above 500 °C and may be recommended for investigation. The application of BaO and CO_3^{2-} is less desirable, because their solubility is limited and they do not dissociate fully even in high-temperature melts.

V. Conclusion

The above analysis of literature data made it possible to discover a series of causes which prevent the development of studies on oxo-acidity in ionic melts. Evidently the existing view that the properties of ionic and molecular liquids are fundamentally different precludes the application of the approaches and rules developed for molecular solvents to the study and treatment of data on oxo-acidity in ionic melts. This state of affairs led to the isolation of studies on oxo-acidity in melts from the investigation of acid–base equilibria in other media. This resulted not only in a low scientific level of the studies carried out (for example, in nitrate melts) but also in the absence of any qualitative development of the field under consideration. Ultimately, studies on homogeneous equilibria virtually ceased completely and the rate of accumulation of data on the solubilities of oxides diminished sharply.

The results of the investigation of acid–base reactions in nitrate melts require a significant revision. It is essential to alter the very approach to further studies on oxo-acidity: the acid–base solubility products should be determined in oxygen-containing melts, while the acid–base equilibrium constants should be determined in oxygen-free melts, having made sure beforehand that the proposed mechanism of the acid–base process corresponds to reality.

The lack of an explanation of the scatter of data on the solubilities of oxides has still remained the main reason retarding the development of this field of study. Such an explanation has now been given on the basis of the Ostwald–Freundlich equation. In order to establish the general rules governing the solubility of oxides in ionic melts, it has been suggested that a single technique be used for the measurements (the same electrodes, identical initial concentrations of reactants). However, the solubilities obtained should nevertheless be treated with a certain degree of caution because the method of preparation of the initial oxide may exert a fairly considerable influence on them (Fig. 2). Studies on the interaction of melts with gaseous reagents have begun to develop, which may be accounted for by the great applied importance of the results.

Overall, the study of the acid–base interactions in melts is far from being completed. After the boom in the development of this field observed in the 1960s–1970s, which did not, however, yield significant results, the time has come to proceed to serious systematic investigations.

References

1. H Lux *Z. Elektrochem.* **45** 303 (1939)
2. H Flood, T Förland *Acta Chem. Scand.* **1** 592 (1947)
3. H Flood, T Förland *Acta Chem. Scand.* 781 (1947)
4. H Flood, T Förland, B Roald *Acta Chem. Scand.* 790 (1947)
5. V L Cherginets *Preprint of the All-Union Single Crystals Research Institute, Kharkov, 1989* No. 6
6. Yu F Rybkin, A S Seredenko *Ukr. Khim. Zh.* **36** 133 (1970)
7. Yu F Rybkin, A S Seredenko *Ukr. Khim. Zh.* **40** 137 (1974)
8. Yu F Rybkin, V V Banik, in *Monokristally i Tekhnika* (Single Crystals and Engineering) (Kharkov: The All-Union Single Crystals Research Institute, 1973) No. 2 (9), p. 153
9. N N Ovsyannikova, F F Rybkin *Ukr. Khim. Zh.* **42** 151 (1976)
10. J E Huheey *Inorganic Chemistry. Structure and Reactivity* (Translated into Russian; Moscow: Khimiya, 1987)
11. M Dratovsky, D Havlichek *Electrochim. Acta* **28** 1761 (1983)
12. A M Shams El Din, A A El Hosary *J. Electroanal. Chem.* **9** 349 (1965)
13. B J Brough, D H Kerridge, M Mosley *J. Chem. Soc. (A)* 1556 (1966)
14. J A Duffy, M D Ingram, I D Sommerville *J. Chem. Soc., Faraday Trans.* **74** 1410 (1978)

15. T Maekawa, T Yokokawa *Nippon Kagaku* (6) 900 (1982)
16. A Kato, R Nishibashi, M Nagano, I Mochida *J. Am. Ceram. Soc.* **55** 183 (1972)
17. N Iwamoto *Youen* **21** 287 (1978)
18. F R Duke, S Yamamoto *J. Am. Chem. Soc.* **80** 5061 (1958)
19. F R Duke, S Yamamoto *J. Am. Chem. Soc.* **81** 6378 (1959)
20. J M Shlegel *J. Phys. Chem.* **69** 3638 (1965)
21. J M Shlegel *J. Phys. Chem.* **71** 1520 (1967)
22. F R Duke, J M Shlegel *J. Phys. Chem.* **67** 2487 (1963)
23. I Slama *Collect. Czech. Chem. Commun.* **28** 985 (1963)
24. I Slama *Collect. Czech. Chem. Commun.* **28** 1069 (1963)
25. A M Shams El Din, A A El Hosary *J. Electroanal. Chem.* **8** 312 (1964)
26. A M Shams El Din, A A A Gerges *J. Inorg. Nucl. Chem.* **26** 1537 (1963)
27. A M Shams El Din, A A A Gerges *Electrochim. Acta.* **9** 123 (1964)
28. A M Shams El Din, A A El Hosary *J. Electroanal. Chem.* **7** 464 (1964)
29. A M Shams El Din, A A El Hosary *J. Electroanal. Chem.* **17** 238 (1968)
30. A M Shams El Din, A A El Hosary, A A A Gerges *J. Electroanal. Chem.* **6** 131 (1963)
31. A M Shams El Din *Electrochim. Acta* **7** 285 (1962)
32. A M Shams El Din, A A A Gerges *J. Electroanal. Chem.* **4** 309 (1962)
33. A M Shams El Din, A A El Hosary *J. Electroanal. Chem.* **16** 551 (1968)
34. A M Shams El Din, A A El Hosary, H D Taki El Din *Electrochim. Acta* **13** 407 (1968)
35. A A El Hosary, M E Ibrahim, A M Shams El Din *Electrochim. Acta* **24** 645 (1979)
36. A M Shams El Din, A A El Hosary *Electrochim. Acta* **13** 135 (1968)
37. A M Shams El Din, A A El Hosary *Electrochim. Acta* **12** 1665 (1967)
38. J D Burke, D H Kerridge *Electrochim. Acta* **19** 251 (1974)
39. A M Shams El Din, A A A Gerges, in *Proceedings of the First Australian Conference on Electrochemistry* (Oxford: Pergamon Press, 1964) p. 562
40. A M Shams El Din, A A A Gerges *Electrochim. Acta* **9** 613 (1964)
41. N Coumert, M Porthault, J-C Merlin *Bull. Soc. Chim. Fr.* **33** 910 (1965)
42. N Coumert, M Porthault, J-C Merlin *Bull. Soc. Chim. Fr.* **35** 332 (1967)
43. M Hassanein, N S Youssep *Indian J. Chem. A, Inorg. Phys. Theor. Anal.* **21** 72 (1982)
44. C Liteanu, E Cordos, L Margineanu *Rev. Roum. Chim.* **15** 583 (1970)
45. J M Schlegel *J. Chem. Educ.* **43** 362 (1966)
46. Y Hoshino, T Utsunomiya, O Abe *Bull. Chem. Soc. Jpn.* **54** 135 (1981)
47. A Baraka, A Abdel-Razik, A J Abdel-Rohman *Surf. Technol.* **25** 31 (1985)
48. A Baraka, A J Abdel-Rohman, E A El-Taher *Mater. Chem. Phys.* **9** 447 (1983)
49. A Baraka, A J Abdel-Rohman, E A El-Taher *Mater. Chem. Phys.* **9** 583 (1983)
50. A I Efimov et al. (Eds) *Svoistva Neorganicheskikh Soedinenii. Spravochnik* (Properties of Inorganic Compounds. Handbook) (Leningrad: Khimiya, 1983)
51. I T Goronovskii, Yu P Nazarenko, E F Nekryach *Kratkii Spravochnik po Khimii* (A Short Handbook of Chemistry) (Kiev: Naukova Dumka, 1987)
52. G J Janz *Molten Salts Handbook* (New York: Academic Press, 1967)
53. Y Kaneko, H Kojima, in *Proceedings of the First International Symposium on Molten Salts Chemical Technology, 1983* p. 441
54. Y Kaneko, H Kojima *Youen* **28** 109 (1985)
55. A Rahmel *J. Electroanal. Chem.* **61** 333 (1975)
56. H Flood, W Knapp *J. Am. Ceram. Soc.* **46** 61 (1963)
57. T Förland, M Tashiro *Glass Ind.* **37** 381 (1956)
58. T Förland *Glastekn. Tidskr.* **17** 35 (1962)
59. V I Minenko, S M Petrov, N S Ivanova *Izv. Vyssh. Uchebn. Zaved., Cher. Metall.* (7) 10 (1960)
60. US P. 4 313 799; *Chem. Abstr.* **96** 115 179g (1982)
61. H Itoh, T Yokokawa *Trans. Jpn. Inst. Met.* **25** 879 (1984)
62. T T Bobrova, V V Moiseev, T V Permyakova, G E Sheshukova *Izv. Akad. Nauk SSSR, Neorg. Mater.* **9** 1416 (1973) [a]
63. R Didtschenko, E G Rochow *J. Am. Chem. Soc.* **76** 3291 (1954)
64. V I Shapoval, O G Tsiklauri, in *Fizicheskaya Khimiya i Elektrokhimiya Rasplavlennykh Solei i Tverdykh Elektrolitov* (Physical Chemistry and Electrochemistry of Molten Salts and Solid Electrolytes) (Sverdlovsk, 1973) Vol. 2, p. 32
65. V I Shapoval, A Sh Avaliani, O G Tsiklauri *Soobshch. Akad. Nauk Gr. SSR* **72** 585 (1973)
66. Yu K Delimarskii, V I Shapoval, O G Tsiklauri, V A Vasilenko, *Ukr. Khim. Zh.* **40** 8 (1974)
67. V I Shapoval, A Sh Avaliani, N A Gasviani *Soobshch. Akad. Nauk Gr. SSR* **72** 105 (1973)
68. V I Shapoval, V F Grishchenko, L I Zarubitskaya *Ukr. Khim. Zh.* **39** 867 (1973)
69. V I Shapoval, V F Grishchenko, L I Zarubitskaya *Ukr. Khim. Zh.* **38** 1088 (1972)
70. V I Shapoval, Yu K Delimarskii, V F Grishchenko, in *Ionnye Rasplavy* (Ionic Melts) (Kiev: Naukova Dumka, 1974) No. 1, p. 222
71. O G Tsiklauri, N A Gasviani, in *Materialy Konf. Molodykh Nauchnykh Sotrudnikov* (Proceedings of the Conference of Young Researchers) (Tbilisi: Institute of Chemistry and Electrochemistry, Academy of Sciences of Gr. SSR, 1976) p. 63
72. V I Shapoval, O G Tsiklauri, N A Gasviani *Soobshch. Akad. Nauk Gr. SSR* **88** 609 (1977)
73. Kh B Kushkhov, V I Shapoval, in *X Vsesoyuz. Konf. po Fizkhimii i Elektrokhimii Ionnykh Rasplavov i Tverdykh Elektrolitov, Ekaterinburg, 1992* (The Xth All-Union Conference on the Physical Chemistry and Electrochemistry of Molten Salts and Solid Electrolytes, Ekaterinburg, 1992) Vol. 2, p. 3
74. R Combes, B Tremillon *J. Electroanal. Chem.* **83** 297 (1977)
75. M Tazika, S Mizoe, M Nagano, A Kato *Denki Kagaku* **46** 37 (1978)
76. R Combes, F De Andrade, L Carvalho *C. R. Hebd. Sciences Acad. Sci., Ser. C* **285** 137 (1977)
77. V L Cherginets, V V Banik *Rasplavy* (6) 92 (1990)
78. V L Cherginets, V V Banik *Rasplavy* (2) 118 (1991)
79. T P Boyarchuk, E G Khailova, V L Cherginets *Ukr. Khim. Zh.* **58** 758 (1992)
80. V L Cherginets, V V Banik *Zh. Fiz. Khim.* **68**145 (1994) [b]
81. V L Cherginets *Potentsiometricheskoe Issledovanie Kislotnykh Svoistv Oksidov Niobiya(V) i Germaniya(IV) v Khloridnom Rasplave, Khar'kov, 1991* [Potentiometric Study of the Acid Properties of Niobium(V) and Germanium(IV) Oxides in a Chloride Melt, Kharkov, 1991] Article deposited at the ONIITEKhIM, Cherkassy, 1991, No 241-khp91
82. Yu F Rybkin, V V Banik, in *Metody Polucheniya i Issledovaniya Monokristallov i Stsintillyatorov* (Methods for the Synthesis and Investigation of Single Crystals and Scintillators) (Kharkov: The All-Union Single Crystals Research Institute, 1980) p. 121
83. Yu F Rybkin, V V Banik, in *Monokristally i Tekhnika* (Single Crystals and Engineering) (Kharkov: The All-Union Single Crystals Research Institute, 1974) p. 111
84. V L Cherginets *Funct. Mater.* **3** 233 (1996)
85. F De Andrade, R Combes, B Tremillon *C. R. Hebd. Seances Acad. Sci., Ser. C* **280** 945 (1975)
86. Yu K Delimarskii, V N Andreeva *Zh. Neorg. Khim.* **5**1123 (1960) [c]
87. A V Volkovich *Rasplavy* (4) 24 (1991)
88. M V Smirnov *Elektrodnye Potentsialy v Rasplavlennykh Khloridakh* (Electrode Potentials in Molten Chlorides) (Moscow: Nauka, 1973)
89. J Picard, F Seon, B Tremillon *Electrochim. Acta* **22** 1291 (1978)
90. F Seon, J Picard, B Tremillon *J. Electroanalyt. Chem.* **138** 315 (1982)
91. G Delarue *Bull. Soc. Chim. Fr.* 1654 (1960)
92. G Delarue *J. Electroanal. Chem.* **1** 13 (1959)
93. V I Shapoval, V F Makogon *Ukr. Khim. Zh.* **45** 201 (1979)
94. V I Shapoval, O F Perchik *Elektrokhimiya* **10** 1241 (1974)
95. H A Laitinen, B B Bhatia *J. Electrochem. Soc.* **107** 705 (1960)
96. D Naumann, G Reinhardt *Z. Anorg. Allgem. Chem.* **343** 165 (1966)
97. V I Shapoval, O G Tsiklauri *Soobshch. Akad. Nauk Gr. SSR* **89** 101 (1978)
98. Yu K Delimarskii, V I Shapoval, N N Ovsyannikova *Ukr. Khim. Zh.* **43** 115 (1977)
99. R Combes, F De Andrade, A De Barros, H Ferreira *Electrochim. Acta* **25** 371 (1980)
100. R Combes, J Vedel, B Tremillon *Anal. Lett.* **3** 523 (1970)
101. R Combes, J Vedel, B Tremillon *Electrochim. Acta* **20** 191 (1975)

102. V E Komarov, V E Krotov, in *Tr. In-ta Elektrokhimii UNTs AN SSSR, Sverdlovsk, 1978* (Transactions of the Institute of Electrochemistry of the Ural Scientific Centre, Academy of Sciences of the USSR, Sverdlovsk, 1978) No 27, p. 61
103. V L Cherginets, E G Khailova *Zh. Neorg. Khim.* **35** 1277 (1991) [c]
104. V L Cherginets, V V Banik *Rasplavy* (1) 69 (1991)
105. G A Laitinen, U E Kharris *Khimicheskii Analiz* (Chemical Analysis) (Moscow: Khimiya, 1966)
106. V L Cherginets, E G Khailova *Zh. Neorg. Khim.* **35** 3205 (1991) [c]
107. V L Cherginets, E G Khailova *Zh. Fiz. Khim.* **66** 1654 (1992) [b]
108. T A Lysenko, V L Cherginets, E G Khailova *Zh. Neorg. Khim.* **38** 175 (1993) [c]
109. T P Boyarchuk, E G Khailova, V L Cherginets *Electrochim. Acta* **39** 1481 (1993)
110. V L Cherginets, E G Khailova *Zh. Neorg. Khim.* **38** 1281 (1993) [c]
111. V L Cherginets, E G Khailova *Electrochim. Acta* **39** 823 (1994)
112. O V Demirskaya, E G Khailova, V L Cherginets *Zh. Fiz. Khim.* **69** 1658 (1995) [b]
113. V L Cherginets, E G Khailova, O V Demirskaya *Electrochim. Acta* **41** 463 (1996)
114. V L Cherginets, E G Khailova *Ukr. Khim. Zh.* **62** 90 (1996)
115. V L Cherginets, E G Khailova, O V Demirskaya *Zh. Fiz. Khim.* **71** 371 (1997) [b]
116. F F Grigorenko, V Molodkina, V M Solomakha, M S Slobodyanik *Vestn. Kievsk. Univ., Ser. Khim.* (14) 38 (1973)
117. Y Ito, H Hayashi, Y Itoh, S Yoshizawa *Bull. Chem. Soc. Jpn.* **58** 3172 (1985)
118. Y Ito *Proc. Electrochem. Soc.* **86** 445 (1986)
119. M L Deanhardt, K H Stern *J. Electrochem. Soc.* **128** 2577 (1981)
120. M L Deanhardt, K H Stern *J. Electrochem. Soc.* **129** 2228 (1982)
121. R F Watson and G S Perry *J. Chem. Soc., Faraday Trans.* **87** 2955 (1991)
122. P Bocage, D Ferry, J Picard *Electrochim. Acta* **36** 155 (1991)
123. G T Kosnyrev, V N Desyatnik, N A Kern, E N Nosonova *Rasplavy* (2) 121 (1990)
124. R Combes, M N Levelut, B Tremillon *Electrochim. Acta* **23** 1291 (1978)
125. D Ferry, Y Castrillejo and G Picard *Electrochim. Acta* **34** 313 (1989)
126. G N Kucera, M-L Saboungi *Metall. Trans. B, Process Metall.,* **7** 213 (1976)
127. N W Hanf, M J Sole *Trans. Faraday Soc.* **66** 3065 (1970)
128. Yu F Rybkin, Yu A Nesterenko, in *Ionnye Rasplavy* (Ionic Melts) (Kiev: Naukova Dumka, 1974) No. 2, p. 184
129. Yu F Rybkin, Yu A Nesterenko *Zh. Fiz. Khim.* **50** 781 (1976) [b]
130. V L Cherginets, V V Banik *Rasplavy* (4) 98 (1991)
131. M V Smirnov, I V Korzun, V A Oleynikova *Electrochim. Acta* **33** 781 (1988)
132. C Butler, J R Russel, R B Quincy *J. Chem. Phys.* **45** 968 (1966)
133. F Rosenberger *Mater. Res. Bull.* **1** 123 (1966)
134. D Ecklin. *Helv. Chim. Acta* **50** 1107 (1967)
135. J M Peech, D A Bower, R O Rohl *J. Appl. Phys.* **38** 2166 (1967)
136. U Gross *Mater. Res. Bull.* **5** 117 (1970)
137. L A Ploom, in *Tr. In-ta Fiziki i Astronomii Akad. Nauk Est. SSR, Tartu, 1975* (Transactions of the Institute of Physics and Astronomy, Academy of Sciences of Est. SSR, Tartu, 1975) Vol. 43, p. 81
138. V V Banik, O V Demirskaya, L N Chervonnaya, in *Monokristallicheskie Materialy* (Single Crystal Materials) (Kharkov: The All--Union Single Crystals Research Institute, 1983) No. 11, p. 90
139. W J Burkhardt, J D Corbett *J. Am. Chem. Soc.* **79** 6361 (1957)
140. R Taylor *Chem. Rev.* **62** 503 (1962)
141. L A Ploom, R I Gindina, N A Yaanson, in *Tr. In-ta Fiziki i Astronomii Akad. Nauk Est. SSR, Tartu, 1969* (Transactions of the Institute of Physics and Astronomy, Academy of Sciences of Est. SSR, Tartu, 1969) Vol. 37, p. 38
142. V V Banik, N I Davidenko, Yu A Nesterenko, in *Fizika i Khimiya Tverdogo Tela* (The Physics and Chemistry of Solids) (Kharkov: The All-Union Single Crystals Research Institute, 1983) No. 10, p. 139
143. M Lebl, J Trnka *Z. Phys.* **186** 128 (1965)
144. O V Demirskaya, Yu A Nesterenko, in *Fizika i Khimiya Kristallov* (The Physics and Chemistry of Crystals) (Kharkov: The All-Union Single Crystals Research Institute, 1977) p. 155
145. Yu F Rybkin, O V Demirskaya, in *Monokristally i Tekhnika* (Single Crystals and Engineering) (Khar'kov: The All-Union Research Institute for Single Crystals, 1974) No. 1 (10), p. 115
146. R C Pastor, A C Pastor *Mater. Res. Bull.* **10** 117 (1975)
147. R C Pastor, A C Pastor *Mater. Res. Bull.* **11** 1043 (1976)
148. A I Agulyanskii, P T Stangrit *Zh. Prikl. Khim.* **10** 1201 (1977) [d]
149. V V Banik, V L Cherginets, in *VII Vsesoyuz. Konf. po Khimii i Tekhnologii Redkikh Shchelochnykh Elementov (Tez. Dokl.) Apatity, 1988* [The Seventh All-Union Conference on the Technology of Rare Alkali Elements (Abstracts of Reports) Apatity, 1988] p. 116
150. US P. 3 969 491; *Ref. Zh. Khim.* 7 L 56P (1977)
151. J Eckstein, U Gross, G Rubinova *Krist. Tech.* **3** 583 (1968)
152. N N Smirnov, V R Lyubinskii, in *Monokristally i Tekhnika* (Single Crystals and Engineering) (Kharkov: The All-Union Single Crystals Research Institute, 1971) No. 5, p. 95
153. J Jordan, P G Zambonin *J. Am. Chem. Soc.* **91** 2225 (1969)
154. P G Zambonin *J. Electroanal. Chem.* **24** 365 (1970)
155. D A Tkalenko, S A Kudrya *Elektrokhimiya* **14** 1579 (1978)
156. D A Tkalenko, S A Kudrya, in *Fiziko-Khimicheskie Svoistva Rasplavlennykh i Tverdykh Elektrolitov* (Phisicochemical Properties of Molten and Solid Electrolytes) (Kiev: Naukova Dumka, 1979) p. 96
157. J D Burke, D H Kerridge *Electrochim. Acta* **19** 251 (1974)
158. J M Schlegel, D Uhr *Inorg. Chem.* **12** 595 (1973)
159. N S Wrench, D Inman *J. Electroanal. Chem.* **17** 319 (1968)
160. R N Kust *J. Phys. Chem.* **69** 3662 (1965)
161. M Frederics, R B Temple, G W Trickett *J. Electroanal. Chem.* **38** App. 5-8 (1972)
162. E Desimoni, L Sabbatini, P G Zambonin *J. Electroanal. Chem.* **71** 73 (1976)
163. P G Zambonin *Anal. Chem.* **44** 763 (1972)
164. A P Kreshkov *Osnovy Analiticheskoi Khimii. Teoreticheskie Osnovy. Kolichestvennyi Analiz* (Foundations of Analytical Chemistry. Theoretical Foundations. Quantitative Analysis) Moscow: Khimiya, 1976) Vol. 2, p. 185
165. R Combes, R Feys, B Tremillon *J. Electroanal. Chem.* **83** 383 (1977)
166. P G Zambonin *J. Electroanal. Chem.* **32** App. 1 (1971)
167. P G Zambonin, G Signorile *J. Electroanal. Chem.* **35** 251 (1972)
168. N S Wrench, PhD Thesis, University of London, London, 1967
169. R Combes, J Vedel, B Tremillon *C. R. Hebd. Seances Acad. Sci., Ser. C* **273** 1740 (1971)
170. V L Cherginets, E G Khailova *Zh. Neorg. Khim.* **41** 734 (1996) [c]
171. A I Novozhilov, E I Pchelina *Zh. Neorg. Khim.* **22** 2057 (1977) [c]

[a] — *Inorg. Mater. (Engl. Transl.)*
[b] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[c] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[d] — *Russ. J. Appl. Chem. (Engl. Transl.)*