# RECENT ADVANCES IN MOLTEN SALTS AS REACTION MEDIA

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## ABSTRACT

The factors which distinguish molten salts from other non-aqueous solvents are described and the range of systems available outlined.

Some illustrative examples of the various classes of reactions carried out in molten salts are then given. These include the exchange of halides and pseudo-halides in organic and inorganic compounds, organic chlorinations, eliminations and rearrangements, a consideration of acid–base phenomena in tetra-chloroaluminate and in nitrate melts and the problems of distinguishing the acidic and basic species in the latter, the coordination geometries adopted by nickel(II) in a series of halide melts, the formation of lower oxidation state cations including some novel clusters, the stabilization of high oxidation states and the kinetics of some oxidations in molten nitrates and, finally, two industrially important processes in molten sulphates, the corrosion of steel surfaces and the catalytic oxidation of sulphur dioxide.

Molten salts differ from conventional non-aqueous solvents in two major respects. Firstly, their melting points are considerably higher, and secondly, they are much more ionic in character. The first difference is not necessarily a great disadvantage, especially if the lower melting eutectics are used (see *Table 1*), and indeed the higher temperatures available can be of positive advantage in certain reactions. The second difference enables a range of

*Table 1.* Melting points and compositions of some molten salt eutectics

|  | mole % | m.pt |
|---|---|---|
| LiCl/KCl | (59:41) | 352° |
| KCl/ZnCl$_2$ | (48:52) | 228° |
| NaCl/AlCl$_3$ | (50:50) | 175° |
| LiF/NaF/KF | (46.5:11.5:42) | 454° |
| LiBr/KBr | (60:40) | 348° |
| LiI/KI | (63:37) | 260° |
| KCN |  | 634° |
| KSCN |  | 177° |
| LiNO$_3$/KNO$_3$ | (43:57) | 132° |
| NaNO$_2$/KNO$_2$ | (65:35) | 220° |
| Li$_2$SO$_4$/Na$_2$SO$_4$/K$_2$SO$_4$ | (78:13.5:8.5) | 512° |
| LiClO$_4$/KClO$_4$ | (76:24) | 207° |

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chemical reactions to be approached more readily, the ionic nature conferring high electrical and thermal conductivities and promoting the solution of ionic solutes.

Solubility in molten salts is partly physical in that solutes can enter the 'holes' in the ionic structure created by the quite large increase in molar volume caused by melting (e.g. $(\Delta V_f/V_s) \times 100$ for LiCl is 26.2; for NaBr, 22.4; for KI, 15.9; for LiNO$_3$, 21.4; for KNO$_3$, 3.3; for KSCN, 10). Such solutions are typified by the rare gases in molten nitrates where the solubilities increase with temperature (as well as with pressure). For example, the Henry's Law Constant for helium in sodium nitrate is 1.86 and 2.80 and for argon 0.64 and 1.04 mol ml$^{-1}$ bar$^{-1}$ at 332 and 441°C, respectively[1].

However, many other solutions are the result of 'chemical' interactions, as, for example, hydrogen fluoride dissolving in molten fluorides (cf. HF in NaF/ZnF$_4$ (60:40 mole %), $K_H$ = 1.53, 1.03, 0.81 mol ml$^{-1}$ bar$^{-1}$ at 600, 700 and 800°C)[2], while the solution of transition metal cations in chloride and nitrate melts leads to coordination, as is clearly shown by their spectra. It is perhaps less expected that metals are generally soluble in their molten halides
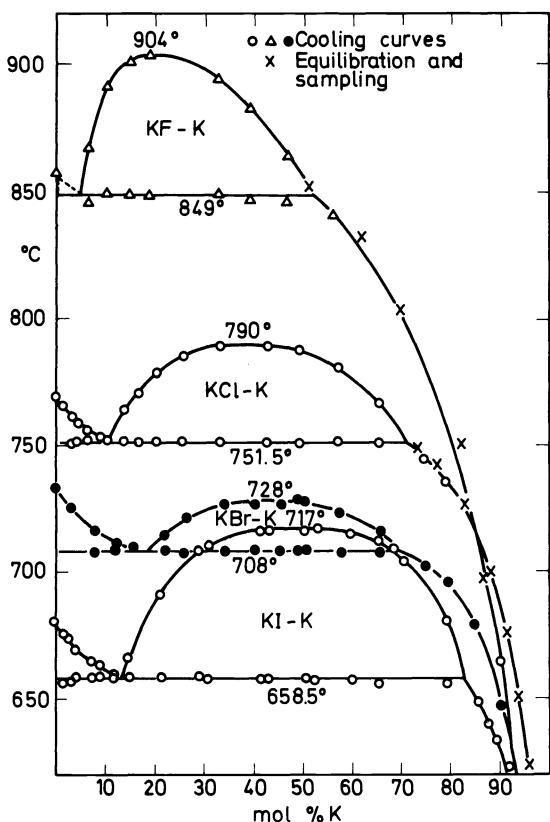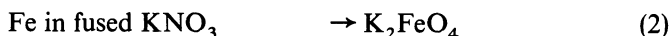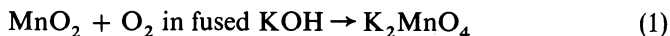


Figure 1. Temperature–composition phase diagrams of the potassium metal–potassium halide (ref. 3)
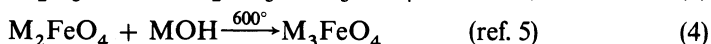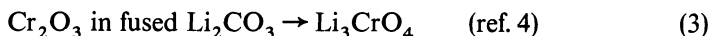
and that they are usually completely miscible at temperatures not far above the melting points of the molten salt (see *Figure 1*). Such solutions have frequently been interpreted in terms of the formation of lower oxidation states[3].

The study of reactions in molten salts is often facilitated not only by such solubilities and the higher temperatures but also by the fact that the solvent itself can act as a reactant and that it is at the highest possible concentration (e.g. for molten LiOH molality is 42 m). Earlier chemists (e.g. Scheele) took advantage of this to some extent, e.g.

$$MnO_2 + O_2 \text{ in fused } KOH \rightarrow K_2MnO_4 \qquad (1)$$

$$Fe \text{ in fused } KNO_3 \qquad \rightarrow K_2FeO_4 \qquad (2)$$

and the use of melts in preparative reactions has never completely ceased:

$$Cr_2O_3 \text{ in fused } Li_2CO_3 \rightarrow Li_3CrO_4 \qquad (ref. 4) \qquad (3)$$

$$M_2FeO_4 + MOH \xrightarrow{600°} M_3FeO_4 \qquad (ref. 5) \qquad (4)$$
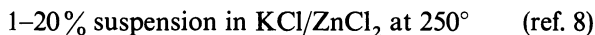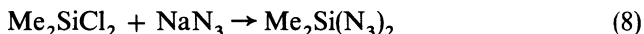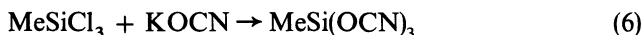
Finally, the point may be made that a really vast choice of potential solvents exists, since literally any salt which is thermally stable can be melted to provide a solvent with potentially interesting properties. The chemical characteristics vary widely from the alkali metal halides to more covalent halides, including transition metal halides, pseudo-halides, oxoanion salts such as nitrates, nitrites, sulphates, carbonates, to the higher melting complex polymeric borates and silicates.
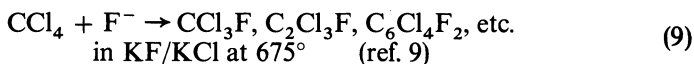
Some account of recent advances in the use of such non-aqueous solvents as reaction media will now be given. For convenience they are set out under five headings: 1. Exchange reactions; 2. Reactions of organic compounds; 3. Acid–base phenomena; 4. Coordination equilibria; 5. Oxidation–reduction reactions.

## 1. EXCHANGE REACTIONS
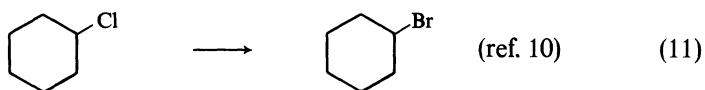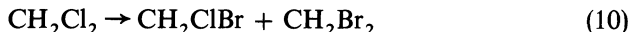
The ready exchange of halide and pseudo-halide ions for other combined halogens is an immediately useful feature of molten salt solutions. Many such reactions have been established (especially as the result of the researches of Professor W. Sundermeyer). Four examples out of the many reactions studied are as follows:

$$Me_3SiCl + KCN \rightarrow Me_3SiCN \qquad (5)$$

2.3 m soln in LiCl/KCl at 450°       (ref. 6)

$$MeSiCl_3 + KOCN \rightarrow MeSi(OCN)_3 \qquad (6)$$

1.9 m soln in LiCl/KCl at 400°       (ref. 6)

$$COCl_2 + KSCN \rightarrow CO(NCS)_2 \qquad (7)$$

0.7 m soln in LiCl/KCl at 400°       (ref. 7)

$$Me_2SiCl_2 + NaN_3 \rightarrow Me_2Si(N_3)_2 \qquad (8)$$

1–20% suspension in KCl/ZnCl_2 at 250°       (ref. 8)

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Such exchanges have now been extended to the preparation of fluorocarbon compounds and because of the industrial importance of these compounds a careful parametric study has been made of the influence of temperature, flow rates and concentration. For example,

$$CCl_4 + F^- \rightarrow CCl_3F, C_2Cl_3F, C_6Cl_4F_2, \text{etc.} \tag{9}$$
$$\text{in KF/KCl at } 675° \quad \text{(ref. 9)}$$
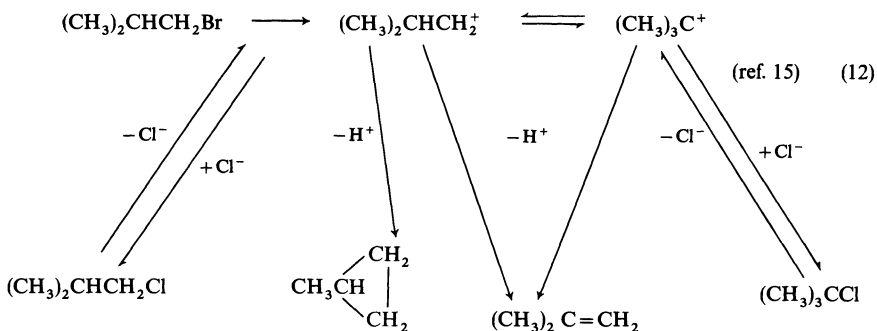
The formation of bromides has also been carried out in a low melting eutectic which is thus less thermally destructive towards organic compounds. Two examples are

$$CH_2Cl_2 \rightarrow CH_2ClBr + CH_2Br_2 \tag{10}$$

 (ref. 10) (11)

using $NaBr/AlBr_3$ at 170°.

## 2. REACTIONS OF ORGANIC COMPOUNDS
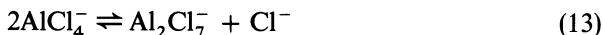
Many other reactions of organic substances can usefully be carried out in molten salts. For example, hydrogenations, dehydrogenations, chlorinations, eliminations and rearrangements take place efficiently in molten salt reactors and much of the pioneering work has been well summarised by Sundermeyer[11]. This type of work has been extended in particular by Kunugi and co-workers[12, 13] and Kikkawa et al.[14]. For example, on chlorination in KCl/CuCl at 320° propene was found to form 1- and 3-chloropropenes and 1,2-dichloro-propene, while in the same solvent at 300°C, 1,3-butadiene forms 3,4-dichloro-1-butene, cis- and trans-1,4 dichloro-2-butene, 1-chloro-1,3-butadiene, and at 350° 4-vinyl-1-cyclohexene and cyclo-octadiene are also formed[13, 14]. Rearrangement reactions including cyclizations have been found when haloalkanes were passed through KCl/SnCl₂ eutectic at 280°. For example, 1-bromo-2-methyl-propane undergoes a series of reactions, which may be set out schematically as
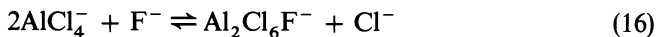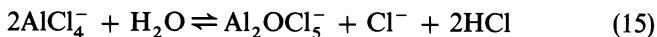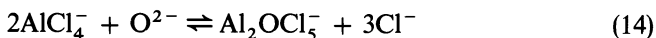


Altogether 15 haloalkanes were investigated in this way.

## 3. ACID–BASE PHENOMENA

Ionization schemes analogous to those found in non-aqueous solutions may, in some molten salts, also take on a specific acid–base character. For example, the chloride exchange reactions in sodium tetrachloroaluminate, which melts at 175°, can be represented by the equilibrium

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \tag{13}$$

This is displaced to the right-hand side with increasing temperature and also with substitution of lithium for sodium ions[16]. Chloride ions, defined here as the basic species, are produced by the addition of the strongly basic oxide ion, water and the weakly basic fluoride ion, e.g.

$$2AlCl_4^- + O^{2-} \rightleftharpoons Al_2OCl_5^- + 3Cl^- \tag{14}$$

$$2AlCl_4^- + H_2O \rightleftharpoons Al_2OCl_5^- + Cl^- + 2HCl \tag{15}$$

$$2AlCl_4^- + F^- \rightleftharpoons Al_2Cl_6F^- + Cl^- \tag{16}$$

On the other hand, the concentration of the polymeric acidic ion is increased by the addition of protons:

$$2AlCl_4^- + H^+ \rightleftharpoons Al_2Cl_7^- + HCl \tag{17}$$
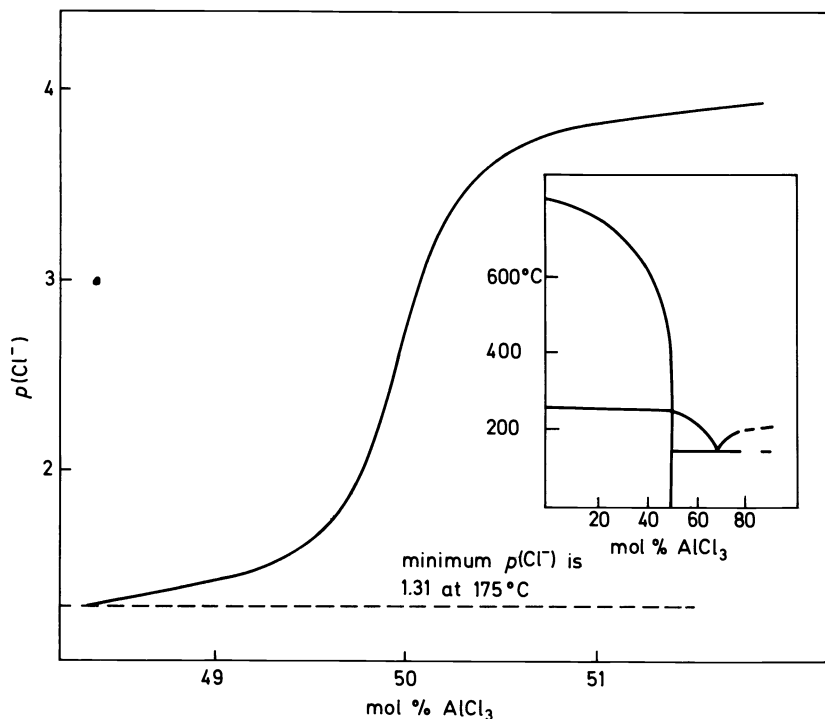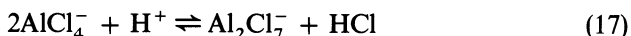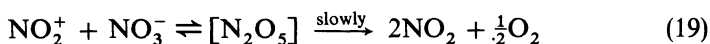


Figure 2. Changes in the chloride activity with composition for the solvent system NaCl–AlCl$_3$ at 175°C (adapted from B. Tremillon and G. Letisse, J. Electroanal. Chem. 17, 371, 1968). The insert shows the phase diagram for this system (W. Fischer and A. L. Simon, Z. Anorg. Chem. 306, 1, 1960)

or by the addition of aluminium trichloride itself. Evidence for the ethane-like binuclear complex has been obtained from Raman spectroscopy[17], while e.m.f. and vapour pressure studies have provided evidence for the binuclear and for the trinuclear $Al_3Cl_{10}^-$ anion in solutions containing additional aluminium trichloride[18]. The rapid variation in chloride ion concentration is illustrated in *Figure 2*.
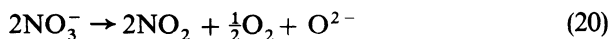
In contrast to this simple formulation, the acidic and basic species present in molten alkali metal nitrates have been the subject of considerable controversy. Duke and his co-workers[19] have proposed the ionization reaction

$$NO_3^- \rightleftharpoons NO_2^+ + O^{2-} \tag{18}$$

followed by

$$NO_2^+ + NO_3^- \rightleftharpoons [N_2O_5] \xrightarrow{\text{slowly}} 2NO_2 + \tfrac{1}{2}O_2 \tag{19}$$

However, Topol, Osteryoung and Christie[20] were not able to confirm the presence of the acidic nitryl ions and suggested nitrogen dioxide as the acidic species:

$$2NO_3^- \rightarrow 2NO_2 + \tfrac{1}{2}O_2 + O^{2-} \tag{20}$$
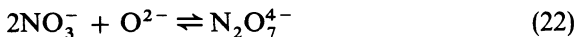
though without offering a mechanism for its formation. The controversy has since lain dormant, although increasingly other authors have postulated small concentrations of nitryl ions to explain aspects of reaction kinetics, and the hypothesis has been shown to be essential in explaining the results of certain electrochemical experiments[21].
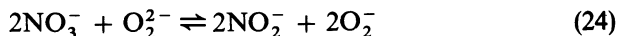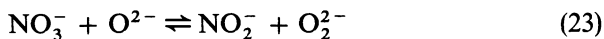
The assumption that oxide ions were the basic species was first challenged by Kohlmuller, who postulated the formation of orthonitrate:

$$NO_3^- + O^{2-} \rightarrow NO_4^{3-} \tag{21}$$

i.e. effectively a solvated oxide anion[22]. Shams El Din and El Hosary[23] suggested that in fact the pyronitrate species was formed:

$$2NO_3^- + O^{2-} \rightleftharpoons N_2O_7^{4-} \tag{22}$$

Most recently, Zambonin and Jordan[24] have postulated the oxidation reactions

$$NO_3^- + O^{2-} \rightleftharpoons NO_2^- + O_2^{2-} \tag{23}$$

$$2NO_3^- + O_2^{2-} \rightleftharpoons 2NO_2^- + 2O_2^- \tag{24}$$
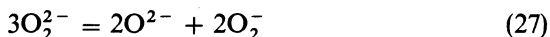
with equilibrium constants derived from their voltammetric studies of $K_{23} = 3$ and $K_{24} = 6.7 \times 10^{-11}$, although in the presence of oxygen the superoxide ion is also formed by the reaction

$$O_2^{2-} + O_2 \rightleftharpoons 2O_2^- \tag{25}$$

for which the equilibrium constant $K_{25}$ is $3.5 \times 10^5$. Although these observations were further considered and substantiated by several subsequent papers by Zambonin, until recently they had received no independent support. Now it has proved possible to calculate $K_{24}$ from a manometric study of the oxidation (25) using solid oxides[25] and from the equilibrium constant of the reaction[26]:

$$NO_3^- \rightleftharpoons NO_2^- + \tfrac{1}{2}O_2 \tag{26}$$

It may be noted that $K_{23}$ itself can only be calculated using the equilibrium constant of

$$3O_2^{2-} = 2O^{2-} + 2O_2^- \qquad (27)$$

derived from hydroxide melts, although a similar value was found for the solid state equilibrium.
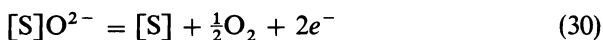
The conclusion that all basic melts contain peroxide and also superoxide if exposed to oxygen is not, however, in accordance with other chemical evidence. An explanation has been sought in terms of solvation reactions:

$$[S] + O^{2-} \rightleftharpoons [S]O^{2-} \qquad (28)$$
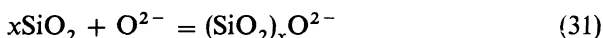
where $[S]$ could be one or two nitrate ions. This could explain the one-electron electrode reaction found by Zambonin and his co-workers and the two-electron reaction found by most other workers, in terms of the reactions

$$O_2^- \rightleftharpoons O_2 + e^- \qquad (29)$$

and

$$[S]O^{2-} = [S] + \tfrac{1}{2}O_2 + 2e^- \qquad (30)$$
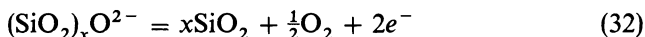
Calculation shows (*Figure 3*) that with the measured values of $K$ the concentration of oxide ions is $<0.001$ per cent even for the most favourable conditions where there is a high initial oxide concentration and where $K_{28} \to 0$, while the proportion of $O_2^{2-}$ reaches 1 per cent only if initial oxide is more than $10^{-3}$ m and $K_{28} < 10^7$. In fact, one-electron slopes have been found in electrochemical experiments using solutions as concentrated as $10^{-2}$ m and two-electron slopes with solutions as dilute as $10^{-6}$ m. However, an explanation for these anomalies was sought in the fact that the former solutions were contained in platinum or Teflon and the latter in glass or silica, suggesting that silicate formation may introduce an additional equilibrium reaction,

$$xSiO_2 + O^{2-} = (SiO_2)_xO^{2-} \qquad (31)$$
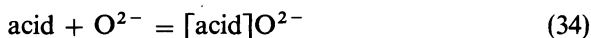
leading to the electrode reaction

$$(SiO_2)_xO^{2-} = xSiO_2 + \tfrac{1}{2}O_2 + 2e^- \qquad (32)$$

Now the reaction of a Lux–Flood acid in melts contained in glass vessels would be represented by

$$[acid] + (SiO_2)_xO^{2-} = [acid]O^{2-} + xSiO_2 \qquad (33)$$

and in a silica-free nitrate melt by

$$acid + O^{2-} = [acid]O^{2-} \qquad (34)$$

Fortunately, the equilibria

$$H_2O + O^{2-} \rightleftharpoons 2OH^- \qquad (35)$$

and

$$NO_2^+ + O^{2-} \rightleftharpoons NO_3^- \qquad (36)$$

have been studied in both types of melt and the value of $K_{31}$ found to be reassuringly similar, $2 \times 10^{15}$ and $10^{16}$ from reactions (35) and (36), respectively. The species $[acid]O^{2-}$ is then $>95$ per cent of the basic species present.
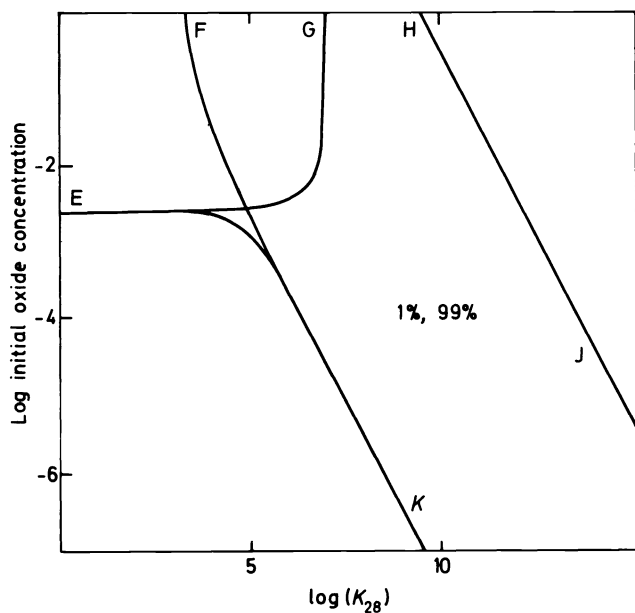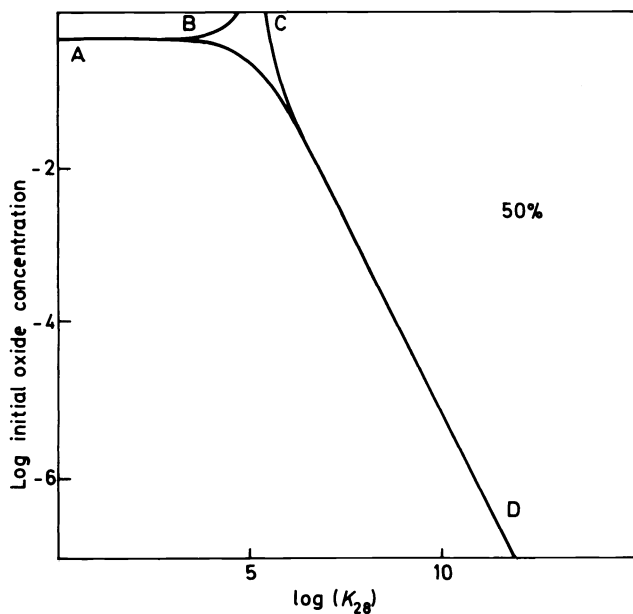
*Figure 3.* Calculated concentrations of peroxide, superoxide and $[\text{acid}]O^{2-}$ ions. (Above and to the left of lines AB and EG the $O_2^{2-}$ ion will represent, respectively, more than 50 and 1% of the initial oxide concentration. Below and to the left of lines EK, AD, and HJ the $O_2^-$ ion will represent, respectively, more than 99, 50 and 1% of initial oxide. Above and to the right of lines HJ, CD, and FK the $[\text{acid}]O^{2-}$ ion will represent more than 99, 50 and 1% of initial oxide.)

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This is of relevance largely for the low concentrations used in electrochemical measurements, since it has been found that with higher concentrations ( > 0.1 m) equilibrium is approached only slowly and glass is considerably less acidic than silica. Thus to refer to solutions of oxide, peroxide and hydroxide ions in nitrate melts is still meaningful provided the time scale is measured in hours[27].

## 4. COORDINATION EQUILIBRIA

There is a long-established interest in the coordination stereochemistries adopted by transition metal cations dissolved in and thus possibly solvated in molten salt solutions, and many such cations have been used as probes in the investigations of melt structures. Nickel(II) cations, which historically gave the first evidence for the tetrahedral $NiCl_4^{2-}$ complex when dissolved in lithium chloride–potassium chloride, have also been used with other chloride melts. An increase in the concentration of lithium ions or a decrease in temperature is found to encourage the alternative octahedral geometry[28]. Increasing concentrations of nickel chloride in caesium chloride melts produce a new species, also possibly of tetrahedral coordination[29], whereas introduction of magnesium chloride into potassium chloride melts containing nickel(II) results in a conversion to octahedral coordination[30], probably because chloride ions bonded to magnesium cations contribute less charge to the nickel cations.

When zinc chloride is added to potassium chloride, a more complex series of equilibria are found[31]. *Figure 4* shows clearly the change of coordination from tetrahedral to octahedral symmetry and then back to tetrahedral symmetry as the zinc chloride concentration is increased. Increasing temperature again produces a change to tetrahedral, though both two-species equilibria and continuous distortion mechanisms have been suggested to operate at different concentrations (see *Table 2*).

The properties of nickel ions dissolved in caesium chloride–zinc chloride melts show even more complex behaviour, as is evidenced in a particularly careful study by another group of American workers[32] (see *Table 3*). Here octahedral$_N$ and tetrahedral$_N$ indicate nickel at sites in a network of zinc chloride sharing six and four chlorides, respectively, and octahedral$_p$ and

*Table 2.* Coordination of nickel(II) in $KCl/ZnCl_2$ melts

| Melt composition, mole per cent of $ZnCl_2$ | Temperature | | |
|---|---|---|---|
| | 320° | | 700° |
| 0 } 42 } | mainly tetrahedral | | mainly tetrahedral |
| 47.5 | octahedral | ← 2-species equilibria → | tetrahedral |
| 54.7 | octahedral | ← continuous distortion → | tetrahedral |
| 93.5 | mainly octahedral | | |
| 100 | tetrahedral | | octahedral + tetrahedral |

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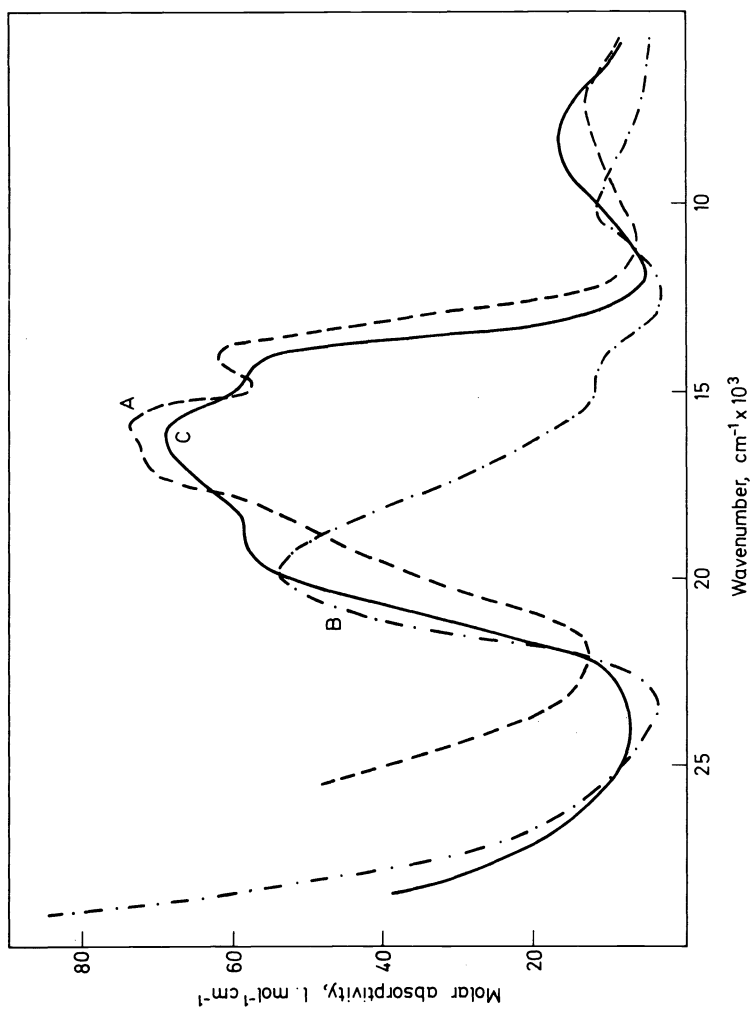
*Figure 4.* Spectra of nickel(II) in KCl–ZnCl$_2$ melts at 320° (ref. 31). Curve A, 58% KCl, 42% ZnCl$_2$; Curve B, 45% KCl, 55% ZnCl$_2$; Curve C, 0% KCl, 100% ZnCl$_2$.

tetrahedral$_p$ indicate nickel associated with the smaller but probably still polymeric entities formed as the zinc chloride network is broken up by the addition of caesium chloride. Equilibria indicated by straight lines have been shown by computor calculation to be internally linear. Those not internally linear are indicated by wavy lines.

*Table 3.* Coordination of nickel(II) in CsCl/ZnCl$_2$ melts

| Melt composition, mole per cent of ZnCl$_2$ | Temperature | |
|---|---|---|
| | 350° | 600° |
| 0 | tetrahedral NiCl$_4^{2-}$ | |
| 50 | tetrahedral$_p$ | |
| | ↑↓ | |
| 72 | octahedral$_p$ ⟷ | more tetrahedral |
| 92 | octahedral$_N$ + little tetrahedral$_N$ | |
| | ↑↓ | |
| 100 | tetrahedral$_N$ + little octahedral$_N$ ⟷ | new tetrahedral and octahedral geometry |

In pure molten aluminium chloride, dissolved nickel(II) has been found to have octahedral symmetry[33] possibly by sharing two Al$_2$Cl$_7^-$ triangular faces, However, in CsAlCl$_4$ a new coordination neither octahedral nor tetrahedral has been reported[34].

Correlation of tetrahedral or octahedral coordination with the size and polarizability of the available ligands is evident from the octahedral coordination in fluoride melts (LiF/NaF/KF and LiF/BeF$_2$ at 550°C)[35], from the mainly tetrahedral coordination in LiBr/KBr at 335° (though with an absorption shoulder at $19\,000\ cm^{-1}$ thought to be due to octahedral coordination) and from the entirely tetrahedral coordination in LiI/KI even at 295° [36].
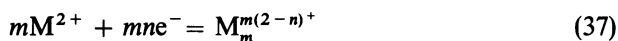
## 5. OXIDATION–REDUCTION REACTIONS

(*a*) *Lower oxidation states*—The aspect of most general interest is probably the formation of novel cationic species of low oxidation state which are clusters of various geometries. Lower oxidation states are easily formed when a metal is allowed to come to equilibrium with its own molten halide, and indeed most metal–metal halide reactions are now understood in terms of such compounds.

These compounds are stabilized, however, in the presence of Lewis acids such as aluminium trichloride and are frequently more easily obtained pure by crystallization from alkali metal tetrachloroaluminate melts. The most studied element in this field is undoubtedly bismuth, which has been found to form Bi$^+$, Bi$_5^{3+}$ and Bi$_8^{2+}$ cations in molten NaCl/AlCl$_3$, the last two being shown to have trigonal bipyramidal and square antiprismatic structures,

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respectively. $Bi_5^{3+}$ is isoelectronic with the polyborane $B_5H_5^{2-}$ (see *Figure 5*), the cage being bonded in each case by 12 electrons in molecular orbitals embracing nine equal M–M distances[37].

Earlier e.m.f. studies had indicated that in the reduction

$$mM^{2+} + mne^- = M_m^{m(2-n)+} \tag{37}$$

$mn = 3$ for tin(II), $mn = 1$ for lead(II) and $mn = 2$ for cadmium(II), dissolved in $NaCl/AlCl_3$ which correspond to the probable species $Sn_2^+$, $Pb^+$ or $Pb_2^{3+}$ and $Cd_2^{2+}$[38]. With selenium and tellurium the cations produced are $Se_4^{2+}$, $Se_8^{2+}$, $Te^{2+}$, $Te_2^{2+}$, $Te_3^+$, $Te_4^{2+}$ and possibly $Te_6^{2+}$ and $Te_8^{2+}$. The $M_4^{2+}$ species have been shown to adopt a square geometry[39, 40].

Among the lower oxidation states of transition metals found in such melts are

Ti(III), Ti(II); Fung and Mamantov[41]
Zr(III), Zr(II); Larson et al.[42]
Hf(III) and possibly $Hf_2Cl_5$; Struss and Corbett[43]
V(II); Oye and Gruen[33]
Ta(III); Gut[44]
Cr(II); Oye and Gruen[33]
Cu(I), Ag(I) probably in the polymeric form $Ag_q^{p+}$[45]

while mercury forms the polymeric cation $Hg_3^{2+}$[46].
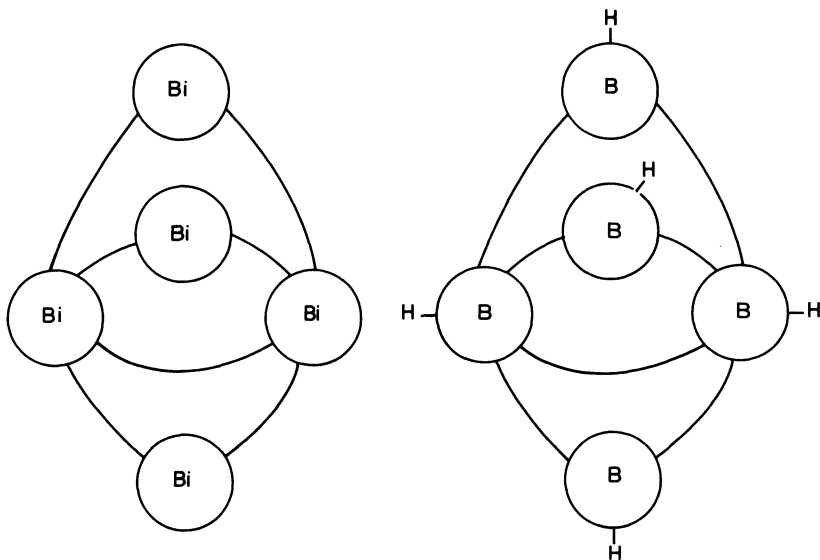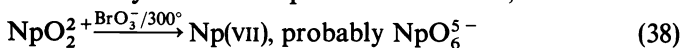


*Figure 5*. The similarity of the structures of polyatomic bismuth species $Bi_5^{3+}$ and the corresponding polyborane $B_5H_5^{2-}$

(b) *Higher oxidation states*—While no completely new high oxidation states have so far been observed in molten salts, the highest oxidation state can frequently be readily obtained in this type of solvent. For example, neptu-

nium(VII) is rapidly formed in sodium nitrate–potassium nitrate eutectic containing added sodium hydroxide and potassium bromate, i.e.
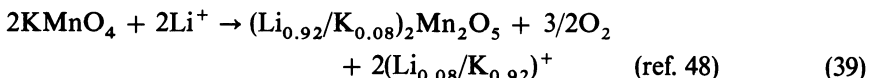
$$NpO_2^{2+} \xrightarrow{BrO_3^-/300°} Np(VII), \text{ probably } NpO_6^{5-} \tag{38}$$
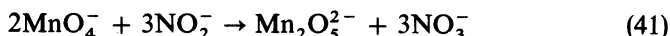
$$\text{in NaNO}_3/\text{KNO}_3/\text{NaOH} \qquad \text{(ref. 47)}$$

Even high oxidation states normally unstable in melts can be stabilized under suitable conditions. For example, potassium permanganate is decomposed within 5 min in lithium nitrate/potassium nitrate at 210° according to the reaction

$$2KMnO_4 + 2Li^+ \rightarrow (Li_{0.92}/K_{0.08})_2Mn_2O_5 + 3/2O_2$$
$$+ 2(Li_{0.08}/K_{0.92})^+ \qquad \text{(ref. 48)} \tag{39}$$

However, in the presence of 0.05 m $KBrO_3$ or $KIO_4$, the permanganate ion persists for more than 2 months (*Figures 6* and *7*). The decomposition is thought to proceed via the nitrite ion produced by thermal decomposition[49]:

$$NO_3^- \rightarrow NO_2^- + \tfrac{1}{2}O_2 \tag{40}$$

$$2MnO_4^- + 3NO_2^- \rightarrow Mn_2O_5^{2-} + 3NO_3^- \tag{41}$$

and that the nitrite reacts preferentially with halate or perhalate:

$$IO_4^- + NO_2^- \rightarrow IO_3^- + NO_3^- \tag{42}$$
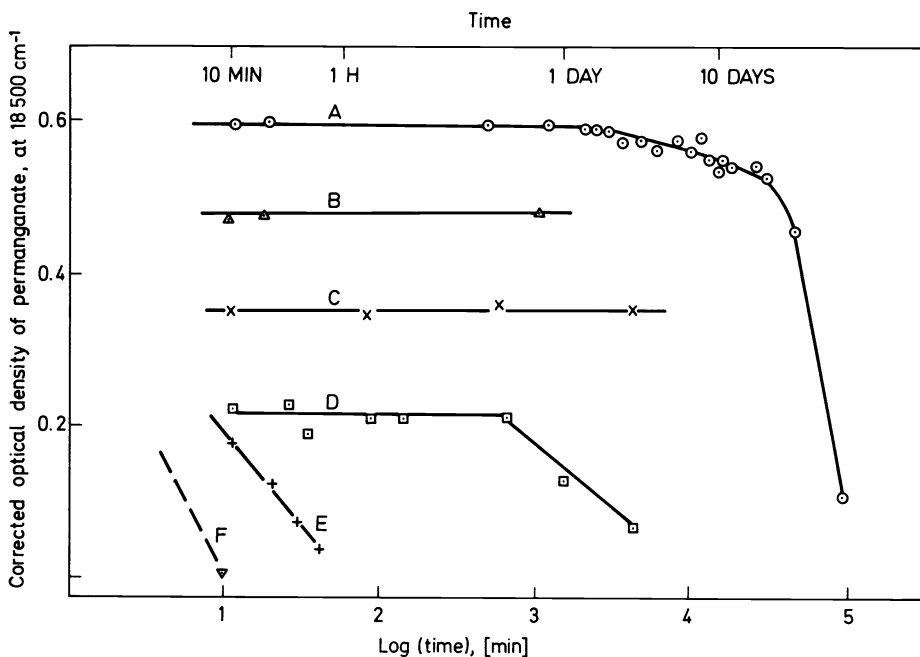


*Figure 6.* The stabilization of dissolved permanganate in $LiNO_3/KNO_3$ melt solutions at 210° by the addition of halates and perhalates. A, 0.1 M $KBrO_3$; B, 0.4 M $KBrO_3$; C, 0.4 M $KIO_4$; D, 0.1 M $KIO_4$; E, 0.4 M $KClO_3$; F, 0.4 M $KIO_3$; 0.4 M $KClO_4$
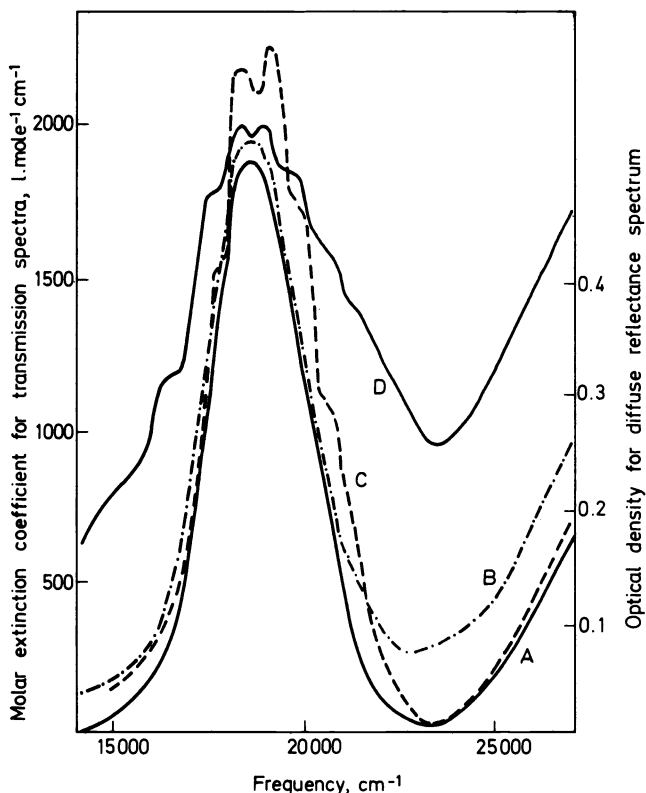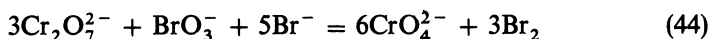
*Figure 7.* The spectra of permanganate solutions. A, 0.1 M $KBrO_3$ in $LiNO_3/KNO_3$ at 210°; B, 0.1 M $KIO_4$ in $Li/KNO_3$ at 210°; C, aqueous solution; D, reflectance spectrum (0.1 M $KIO_4$ in $LiNO_3/KNO_3$)

In a manner somewhat analogous to aqueous solutions, manganate(VI) which normally decomposes rapidly, is found to be stabilized by solutions of alkali metal hydroxides ($m > 0.1$) in sodium nitrate–potassium nitrate; manganate(V) is stabilized by solutions of monoxide or peroxide ($m > 0.1$)[50].

(c) *Kinetics*—Kinetic studies have shown that reactions in molten salts do not necessarily follow a simple mechanism. Thus even the apparently simple reaction of oxalate ions in a nitrate melt,

$$C_2O_4^{2-} + NO_3^- = NO_2^- + CO_3^{2-} + CO_2 \qquad (43)$$

can only be understood if the further reaction of oxalate with nitrite is allowed for and if the presence of nitryl cations is assumed[51, 52]. Oxidations involving halogens continue to show more complexity. The reaction of bromate with bromide and dichromate in sodium nitrate–potassium nitrate containing little chromate follow a stoichiometry analogous to that found in aqueous solution, i.e.

$$3Cr_2O_7^{2-} + BrO_3^- + 5Br^- = 6CrO_4^{2-} + 3Br_2 \qquad (44)$$

When bromate, bromide and chromate are in excess compared with dichromate, the reaction follows a different course:

$$Cr_2O_7^{2-} + BrO_3^- + Br^- = 2CrO_4^{2-} + Br_2 + O_2 \tag{45}$$

and two intermediates were invoked to explain the observed kinetics:

$$Cr_2O_7^{2-} + BrO_3^- \rightleftharpoons BrO_2^+ + 2CrO_4^{2-} \quad \text{rapid equilibrium} \tag{46}$$

$$BrO_2^+ + 2Br^- \rightleftharpoons BrO_2^- + Br_2 \quad \text{rapid equilibrium} \tag{47}$$

$$BrO_2^- \rightarrow Br^- + O_2 \quad \text{slow equilibrium} \tag{48}$$
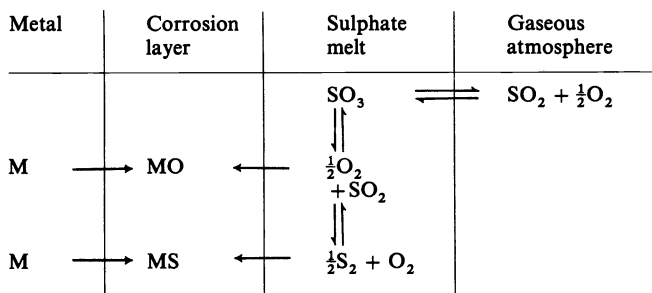
(ref. 53)

Several other halogen intermediates have since been postulated by Slama[54–58] in his recent series of papers on the kinetics of oxidation of iodide with iodate and hexoxoperiodate, chlorate with perchlorate and bromide with bromate.

(d) *Reactions of industrial importance*—Although much of the above chemistry may be judged at present to be of purely academic interest, it should not be forgotten that reactions in molten salts are of very considerable industrial importance. One need only mention the electrolytic reduction of aluminium metal from molten cryolite currently running at more than 10 million tonnes per annum for this to be appreciated.
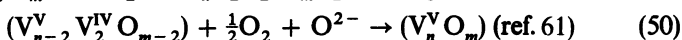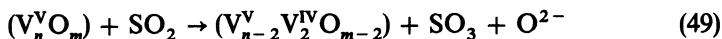
However, other important utilizations of molten salt chemistry are under-appreciated. As illustration, reference will be made to two instances in molten sulphate chemistry. Firstly, it may be noted that thin layers of molten sulphates formed in the course of the combustion reactions occurring in modern high-temperature power stations subsequently collect on the superheater and other heat exchange surfaces. Corrosion of the steel surfaces results following the generalized reaction scheme[59]:

| Metal | Corrosion layer | Sulphate melt | Gaseous atmosphere |
|---|---|---|---|
| | | $SO_3 \rightleftharpoons$ | $SO_2 + \frac{1}{2}O_2$ |
| | | $\Updownarrow$ | |
| M $\rightarrow$ MO | $\leftarrow$ | $\frac{1}{2}O_2 + SO_2$ | |
| | | $\Updownarrow$ | |
| M $\rightarrow$ MS | $\leftarrow$ | $\frac{1}{2}S_2 + O_2$ | |

This can be even more serious if the melt layer contains acidic oxides such as $V_2O_5$ or $WO_3$ which also give rise to partial electronic conductivity[60]. It may be noted that vanadium is a frequent impurity in fuel oils.

Vanadium solutions in molten sulphate have, however, been of great usefulness to industry for the last 45 years, as they catalytically oxidize sulphur dioxide to sulphur trioxide, which forms the vast quantities of sulphuric acid our modern economy needs to function. Despite their long use, our present

understanding of the inorganic chemistry of such melts is still rudimentary. The reaction has been expressed schematically as

$$(V_n^V O_m) + SO_2 \rightarrow (V_{n-2}^V V_2^{IV} O_{m-2}) + SO_3 + O^{2-} \tag{49}$$

$$(V_{n-2}^V V_2^{IV} O_{m-2}) + \tfrac{1}{2}O_2 + O^{2-} \rightarrow (V_n^V O_m) \text{ (ref. 61)} \tag{50}$$

but when it is realized that the nature of the vanadium(v) compound is in doubt and that even the oxidation state of the lower vanadium species has been challenged, it becomes clear that much remains to be understood here as well as in most other areas of molten salt chemistry.

# REFERENCES

[1] B. Cleaver and D. E. Mather, *Trans. Faraday Soc.* **64**. 2469 (1970).
[2] G. J. Janz, *Molten Salts Handbook*. Academic Press; New York (1967).
[3] M. A. Bredig, in *Molten Salt Chemistry* (Ed. M. Blander). Interscience; New York (1964).
[4] K. A. Wilhelmi and O. Jonsson, *Acta Chem. Scand.* **19**, 177 (1956).
[5] R. Scholder, *Bull Soc. Chim. France,* 1112 (1965).
[6] W. Sundermeyer, *Z. Anorg. Allgem. Chem.* **313**, 290 (1961).
[7] C. Jackl and W. Sundermeyer, *Chem. Ber.* **106**, 1752 (1973).
[8] W. Sundermeyer, *Chem. Ber.* **96**, 1293 (1963).
[9] F. Peter, J. Hitzke and J. Guion, *Bull. Soc. Chim. France,* 742 (1972).
[10] R. Baker, D. H. Kerridge and A. Onions, private communication (1974).
[11] W. Sundermeyer, *Angew. Chem. Int. Ed.* **4**, 222 (1965).
[12] T. Kunugi, H. Tominaga, A. Sawanabari and M. Nushi, *Kogyo Kagaku Zasshi,* **72**, 2385 (1969).
[13] T. Kunugi, H. Tominaga and T. Nishimura, *Kogyo Kagaku Zasshi,* **73**. 170 (1970).
[14] S. Kikkawa, T. Hayashi, T. Tani and H. Oshima, *Kogyo Kagaku Zasshi,* **73**, 964 (1970).
[15] R. A. Bailey and S. F. Prest, *Canad. J. Chem.* **49**, 1 (1971).
[16] G. Torsi and G. Mamantov, *Inorg. Chem.* **11**, 1439 (1972).
[17] S. J. Cyvin, P. Klaboe, E. Rytter and H. A. Oye, *J. Chem. Phys.* **52**, 2776 (1970).
[18] A. A. Fannin, L. A. King and D. W. Seegmiller. *J. Electrochem. Soc.* **119**, 801 (1972).
[19] F. R. Duke and R. N. Kust, *J. Amer. Chem. Soc.* **85**, 3338 (1963).
[20] L. E. Topol, R. A. Osteryoung and J. H. Christie, *J. Phys. Chem.* **70**, 2857 (1966).
[21] A. F. J. Geoting, Doc. Nat. Thesis, University of Amsterdam, 1972.
[22] R. Kohlmuller, *Ann. Chim.* **4**, 1183 (1959).
[23] A. M. Shams El Din and A. A. El Hosary, *J. Inorg. Nucl. Chem.* **28**, 3043 (1966).
[24] P. G. Zambonin and J. J. Jordan, *J. Amer. Chem. Soc.* **89**, 6345 (1967).
[25] J. Schlegel and D. Priore, *J. Phys. Chem.* **76**, 2861 (1972).
[26] R. N. Kust and J. D. Burke, *Inorg. Nucl. Chem. Lett.* **6**, 333 (1970).
[27] J. D. Burke and D. H. Kerridge, *Electrochem. Acta,* **19**, 25 (1974).
[28] J. Brynestad, C. R. Boston and G. P. Smith, *J. Chem. Phys.* **47**, 3179 (1967).
[29] G. P. Smith, C. R. Boston and J. Brynestad, *J. Chem. Phys.* **45**, 829 (1965).
[30] J. Brynestad and G. P. Smith, *J. Chem. Phys.* **47**, 3190 (1967).
[31] C. A. Angell and D. M. Gruen, *J. Phys. Chem.* **70**, 1601 (1966).
[32] W. E. Smith, J. Brynestad and G. P. Smith, *J. Chem. Phys.* **52**, 3890 (1970).
[33] H. A. Oye and D. M. Gruen, *Inorg. Chem.* **3**, 836 (1964).
[34] G. P. Smith, J. Brynestad, C. R. Boston and W. E. Smith, in *Molten Salts* (Ed. G. Mamantov). New York: Dekker (1969).
[35] J. P. Young, *Inorg. Chem.* **8**, 825 (1969).
[36] C. R. Boston, C. H. Liu and G. P. Smith, *Inorg. Chem.* **7**, 1938 (1968).
[37] J. D. Corbett, *Inorg. Chem.* **7**, 198 (1968).
[38] T. C. F. Munday and J. D. Corbett, *Inorg. Chem.* **5**, 1263 (1966).
[39] D. J. Prince, J. D. Corbett and B. Garbisch, *Inorg. Chem.* **9**, 2731 (1970).
[40] N. J. Bjerrum, *Inorg. Chem.* **10**, 2578 (1971); **11**, 2648 (1972).
[41] K. W. Fung and L. Mamantov, *J. Electroanal. Chem.* **35**, 27 (1972).
[42] E. M. Larson, F. Gil-Arnao, J. W. Mayer and M. J. Camp, *J. Chem. Soc. D.* 281 (1970).

[43] A. W. Struss and J. D. Corbett, *Inorg. Chem.* **9**, 1373 (1970).

[44] R. Gut, *Helv. Chim. Acta*, 43, 830 (1960).

[45] U. Anders and J. A. Plambeck, *Canad. J. Chem.* **47**, 3055 (1969).

[46] G. Torsi and G. Mamantov, *Inorg. Nucl. Chem. Lett.* **6**, 843 (1970).

[47] N. N. Krot, M. P. Mefod'eva, C. P. Shilov and A. D. Gelman, *Radiokhimiya,* **12**, 471 (1970).

[48] D. H. Kerridge and S. A. Tariq, *Inorg. Chim. Acta,* **2**, 371 (1968).

[49] B. J. Brough, D. A. Habboush and D. H. Kerridge, *Inorg. Chim. Acta,* 6, 259 (1972).

[50] B. J. Brough, D. A. Habboush and D. H. Kerridge, *Inorg. Chim. Acta,* **6**, 366 (1972).

[51] J. M. Schelgel and C. A. Pitak, *J, Inorg. Nucl. Chem.* **32**, 2092 (1970).

[52] J. D. Burke, Ph.D. Thesis, University of Utah, 1972.

[53] J. M. Schlegel, *J. Phys. Chem.* **73**, 4152 (1969).

[54] P. Pacak, I. Slama and I. Horsak, *Coll. Czech. Chem. Commun.* **38**, 2347 (1973).

[55] P. Pacak and I. Slama, *Coll. Czech. Chem. Commun.,* **38**, 2355 (1973).

[56] I. Horsak and I. Slama, *Coll. Czech. Chem. Commum.,***38**, 2366 (1973).

[57] Z. Kodjes, I. Horsak and I. Slama, *Coll. Czech. Chem. Commun.,* **38**, 2839 (1973).

[58] P. Pacak and I Slama, *Coll. Czech. Chem. Commun.,* **38**, 3595 (1973).

[59] A. J. B. Cutler, private communication (1973).

[60] A. Rahmel, private communication (1973).

[61] A. Kato, K. Tomoda, I. Mochida and T. Seiyama, *Bull. Chem. Soc. Japan,* **45**, 690 (1972).

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