

Stabilisation of high oxidation states in basic molten salts

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INTRODUCTION

Our understanding of molten salt chemistry has advanced considerably in recent years, but appreciation of general principles tends to be at a less developed stage. One such principle is the enhanced stability of high oxidation states conferred by basic solutions, whose validity extends from aqueous solutions to other non-aqueous solvents of which molten salts are higher melting and less well known representatives than the more commonly considered liquid ammonia, liquid hydrogen fluoride etc. An example in aqueous solution is permanganate, which is more stable in alkaline solutions and is a stronger oxidising agent in aqueous acids, as indicated by the different standard electrochemical potentials, i.e. 1.3 V for $\text{MnO}_4^- \rightarrow \text{MnO}_4^{2-}$ at pH 13 and 1.51 V for $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$ at pH 1.

In the case of molten salts the converse concept, that acidity stabilises lower oxidation state compounds, has been briefly noted by O'Donnell [1], although the major topic of interest in his review is the formation of cations in acidic solutions. Moreover, the only molten salts discussed are the chloroaluminates, although an aside notes that "many of the generalisations made appear to apply equally to molten fluorides, nitrates, sulphates, etc." In a further review [2] molten chlorides have been referred to "as basic melts of the chloroaluminate system", though in fact the alkali metal chloride melts are at the extreme of basicity (with molten aluminium trichloride being the extreme acid of the AlCl_4^- melt system). However, the main interest was in the anions formed in these systems.

Thus there is no extant review of the known examples of the general principle of stabilisation of high oxidation states in basic melts, particularly of oxyanion melts (nitrates, nitrites and sulphates) and simple halide melts (alkali metal fluorides and chlorides), a lack which will now be made good.

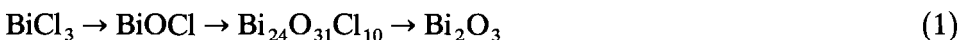
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FORMATION OF HIGH OXIDATION STATES IN BASIC MELTS

Molten nitrates and nitrites

Some of the most interesting examples of this general principle have been recently elucidated in molten alkali metal nitrates, though it should also be noted that the early chemists frequently extracted the rarer transition metals, in the form of their higher oxidation state species, from their ores by fusion with nitrates to which bases had been added, e.g. manganese(IV) ores with KNO_3/KOH to manganate(VI), rhenium to perrhenate(VII), ruthenium to ruthenate(VI), osmium to osmate(VI), iridium to iridium(VI) oxide, etc. all in the same mixed melt.

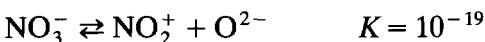
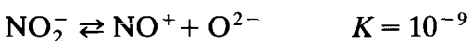
More recently, bismuth(III) has been found to be oxidised to bismuth(V) (as Li_3BiO_4) providing it has been made basic with hydroxide (e.g. $\text{BiCl}_3:\text{NaOH} = 1:14.5$) [3]. The oxidation with nitrate alone requires 48 h at 500°C , but milder conditions are possible, e.g. 4 h at 450°C , providing an additional oxidising agent is present ($\text{BiCl}_3:\text{Na}_2\text{O}_2 = 1:6$). Significantly, peroxide is a base as well as an oxidising agent. At lower temperatures, bismuth(III) is the only oxidation state formed, bismuth trichloride reacting as follows:



The temperature may well be significant because the nitrate thermal decomposition



becomes more important with increasing temperature and nitrite is more basic than nitrate and a greater source of oxide ions: for example



both at 300°C in $\text{NaNO}_3\text{--KNO}_3$.

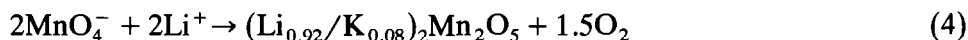
A similarly clear example has been found in iodine chemistry. Iodide anions are oxidised in a pure nitrate melt above 140°C :



but at higher temperatures (above 400°C) where the melt is more basic (see eqn. (2)) oxidation to iodine(VII) takes place, either to soluble paraperiodate anions (in $\text{NaNO}_3\text{--KNO}_3$ eutectic) or to precipitates of paraperiodates if suitable cations are present, e.g. Li_5IO_6 from $\text{LiNO}_3\text{--KNO}_3$, $\text{Ca}_5(\text{IO}_6)_2$ from $\text{NaNO}_3\text{--KNO}_3$ containing $\text{Ca}(\text{NO}_3)_2$, and LiCa_2IO_6 from $\text{LiNO}_3\text{--KNO}_3$ eutectic containing $\text{Ca}(\text{NO}_3)_2$ [4]. Oxidation also takes place at lower temperatures if alkali metal hydroxides are added and oxygen or

ozone are present, e.g. at 275°C in LiNO₃ to form Li₅IO₆, at 325°C in NaNO₃ to form Na₅IO₆ and at 360°C in KNO₃ to form K₅IO₆ [5].

Manganese(VII) (permanganate) is quite unstable in molten nitrates, being reduced in seconds to a black manganese(IV) precipitate in LiNO₃–KNO₃ eutectic above 210°C [6].

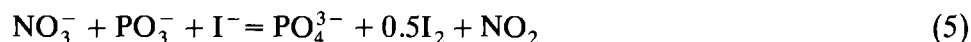


However, manganate(VI) can be stabilised in nitrate melts with additions of hydroxide (e.g. > 0.4 M NaOH or KOH in NaNO₃–KNO₃ at 260°C), while manganate(V) can be stabilised by peroxide (> 1 M Na₂O₂ in NaNO₃–KNO₃ at 260°C, or by 2 M NaOH, or KOH, in LiNO₃–KNO₃ at 260°C) [7].

At the lower end of the oxidation state scale, manganese(II) sulphate solutions in molten nitrate are oxidised to manganese(IV) (to 98.5% as MnO₂ in LiNO₃–KNO₃ at 160°C) but less so in acidic nitrate (62.5% in 1.4 M K₂S₂O₇) [8]. Similarly manganese metal is oxidised to manganese(IV) in pure nitrate (to MnO₂ in LiNO₃–KNO₃ at 300°C) though it forms manganese(II) in acidic melts (e.g. Mn²⁺ in 0.2 M K₂S₂O₇ at 160°C) [9].

Finally, perhaps the most surprising example of this principle has been found in actinide chemistry. Neptunium(V) is oxidised by nitrate solutions of bromate to neptunium(VI) (as (Na_{0.96}Li_{0.04})₂ Np₂O₇ in LiNO₃–NaNO₃ eutectic at 215°C) but bromate in basic nitrate melts (KBrO₃:NaOH = 1:2 in NaNO₃–KNO₃ at 300°C) oxidises neptunium(V) to the very rare highest oxidation state, neptunium(VII) [10].

Another example, known for much longer, is taken here out of strict order since it leads to a more precise definition of the general principle. It concerns the oxidation of iodide by nitrate in LiCl–KCl eutectic at 400°C. Iodine is only formed if an acid is present (Van Norman and Osteryoung [11] used metaphosphates or metavanadates) since iodide and nitrate are stable in a neutral melt. The stoichiometry may perhaps be



Expressed in this way the general principle argued above appears to be violated. However, it should be noted that while nitrate is reduced iodide is oxidised. Hence there is a need to define which of the two non-metals in this reaction is analogous to the transition metals and p-block metals in the above examples. A consistent rule is that the central atom (in the two possible anions) with the lowest group number, or of the highest atomic weight if of the same group number, is that which is oxidised in basic melts, and reduced in acidic melts.

This problem of definition does not arise with the oxidation of iodide by paraperiodate, which requires the presence of acidic carbon dioxide, or phosphorus pentoxide [12]:

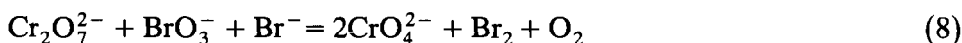


However, another example which is in accord with the more precisely defined rule is found in the kinetic study of the oxidation of iodide by bromate to iodate [13] in NaNO₃–KNO₃ eutectic:

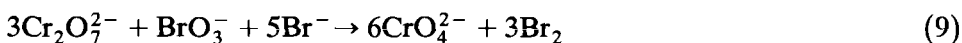


where consistent results were not obtained unless sodium carbonate was present, i.e. in basic solution. Significantly no oxygen was formed.

In contrast, bromate oxidised bromide only to bromine in acidic solutions containing potassium dichromate [14], though the stoichiometry varied. With low concentrations of K₂Cr₂O₇ the following reaction occurs:



and the oxygen is postulated to arise from the thermal decomposition of bromate(III), i.e. $\text{BrO}_2^- \rightarrow \text{Br}^- + \text{O}_2$. With relatively higher concentrations of potassium dichromate the reaction is

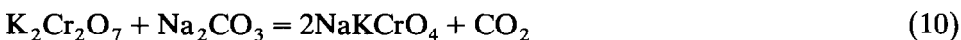


Without acid [15], bromate(V) thermally decomposes at 400°C to bromide and oxygen, but with other Lux–Flood acids, reaction of bromate(V) with bromide occurs at much lower temperatures (e.g. 170–210°C) to bromide and oxide (i.e. once again the lower oxidation state has been stabilised by acidic solutions) and the relative reactivity of various transition and p-block metal cations has been the subject of extensive early measurements [16].

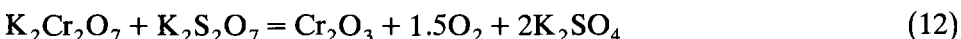
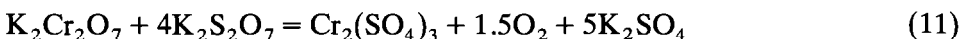
Molten nitrites currently show few examples of the general principle, but interestingly, despite the reducing power of nitrite, manganese(V) (as sky-blue MnO₄³⁻) can be stabilised by sodium peroxide dissolved in NaNO₃–KNO₃ eutectic, though in a neutral melt the product of the reaction of potassium permanganate is again manganese(IV) (brown insoluble (Na/K)₂Mn₂O₅) [17].

Molten sulphate

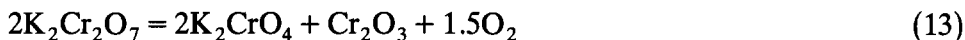
The general principle is exemplified by the observation that potassium dichromate dissolved in molten sulphate (Li₂SO₄–Na₂SO₄–K₂SO₄ eutectic at 580°C) forms chromate(VI) anions in basic solutions (of Na₂CO₃):



whereas reduction to chromium(III) occurs in acidic solutions (of K₂S₂O₇), to chromium(III) cations with excess acid and to chromium(III) oxide with equimolar quantities:



In a neutral melt, only half the chromium is reduced:



Potassium chromate behaves similarly [18].

Cobalt(II) sulphate undergoes a Lux–Flood acid–based reaction above 800°C in this ternary eutectic to form cobalt(II) oxide and some tricobalt tetraoxide, thus undergoing some oxidation. However, when potassium disulphate was added, only cobalt(II) cations were formed [19]:

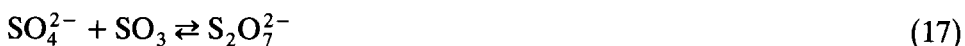


An apparently contrary example involves a change in the gaseous atmosphere above the melt. (This is a more important parameter for molten sulphate chemistry than for molten nitrates, or indeed for most other melts.) For molten sulphates, sulphur trioxide is the acid gas in the system (see eqn.(9)) which is also oxidising and related to the reducing agent, sulphur dioxide, by the equation



When sulphur dioxide and sulphur trioxide are both present, highly acid gas (> 90% SO_3) results in vanadium pentoxide solutions forming vanadyl(V) cations (VO_2^+), whereas less acidic atmospheres (< 30% SO_3) cause reduction to vanadyl(IV) (VO^{2+}) [20]. However, it is evident that there is a far higher partial pressure of the reducing sulphur dioxide in the latter case, and of the oxidising sulphur trioxide in the former. Thus oxidising/reducing characteristics have to be taken into account in addition to the acidic/basic effect.

In disulphate melts, related to the sulphates by the equilibrium



the relationship between vanadium(V) and vanadium(IV) is sensitive to basicity, i.e. to the disulphate concentration, as is shown by the Pourbaix diagram at 430°C [21]. Vanadium(V), as $\text{VO}_2(\text{SO}_4)_2^{3-}$, is the stable species at low pSO_4 values and vanadium(IV), as $\text{VO}(\text{SO}_4)_3^{4-}$, at higher values with the same equilibrium potential. Similarly in hydrogen sulphate melts at low pH values, vanadium(V) (e.g. as VO^{2+}) is stabilised, whereas at higher values, vanadium(V) (e.g. as VO_2^+ in NH_4HSO_4) is stabilised [22]. In molten potassium hydrogen sulphate at 220°C containing mercury [23], oxidation state I is stable at pH 0.5, as Hg_2^{2+} at 0.25 V potential, and oxidation state II, as $\text{Hg}(\text{SO}_4)^{2-}$, at pH 2.5.

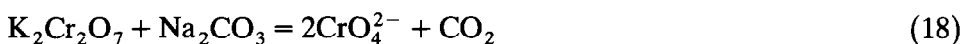
Molten fluorides and chlorides

In molten fluoride eutectic (LiF–NaF–KF) chromium(III) is slowly oxidised in the presence of an oxidant and a base to chromium(VI), e.g. with

Na_2O_2 , or NaO_2 , to CrO_4^{2-} . Without base and an oxidising agent, chromate is slowly reduced in graphite with formation of carbon dioxide [24].

Molten chlorides provide many examples of this general principle of a higher oxidation state being stabilised in basic solutions, partly, of course, because far more chemistry is known in molten chlorides.

An early, but complete, example can be seen with potassium dichromate where the addition of acids (HCl or NaPO_3 in LiCl-KCl eutectic at 400°C) causes reduction to chromium(III) and evolution of chlorine, whereas in the presence of base (e.g. Na_2CO_3), chromium(VI) is stable and the product is chromate [11]:



The Pourbaix diagram for LiCl-KCl eutectic at 470°C shows that at low pO^{2-} values, i.e. in basic media, the stable anion is chromate(VI) and as these values increase, chromium(III) and then chromium(II) become stable as Cr_2O_3 and Cr^{2+} respectively at -1.0 V [25].

A less obvious example is seen in the oxidation of tungsten metal, in NaCl-KCl chloride at $700-900^\circ\text{C}$, when tungsten(IV) is formed (as WCl_5^- etc.) but in the presence of 30% sodium fluoride (F^- acts as a base in molten chlorides) tungsten(V) is formed [26].

Similarly when hafnium metal is oxidised at 720°C in molten alkali metal chlorides, concentrations of hafnium(II) increase in the series $\text{Cs} > \text{K} > \text{Na} > \text{Li}$ (i.e. with the more acidic nature of the cations) and in contrast the concentration of hafnium(IV) increases in the reverse order, i.e. with increase in basicity [27].

The tetrachloroaluminate melts, of AlCl_4^- with alkali metal or organic cations, have been extensively studied and reviewed [1,2,28–30] in recent years, so an extended account here is unnecessary, although their chemistry will be summarised briefly. Acidic melts can be readily obtained by increasing the proportion of aluminium trichloride and, since the latter is miscible, extremely acidic melts, to pure AlCl_3 , can be obtained. However, the saturated solution of sodium chloride at 170°C just gives a 1:1 melt; therefore in many cases this is described as the “basic” solution and the basicity range can be extended very little further even at higher temperatures. However, O’Donnell [2] has extended the conceptual range by taking the molten alkali metal chlorides as examples of basic melts even though they contain no aluminium trichloride at all.

Since these pure chloride melts are not sufficiently basic to give rise to particularly high oxidation states and their chemistry has been considered above, the main interest here is in acidic melts (i.e. where $\text{NaCl}/\text{AlCl}_3$ is less than 1/2) in which many low oxidation states have been produced, some indeed not previously known and which have not subsequently been prepared by other methods. The list includes Ti(II) [31], Zr(II) , Zr(III) , V(II) [32], Nb_2^{8+} , Nb_2^{7+} , Nb_2^{6+} [33], Cr(II) [32], Cd_2^{2+} [34], Hg_3^{2+} [35], U(III)

[36], Sn_2^+ , Pb^+ [37], Bi_4^{4+} , Br_5^{3+} , Bi_8^{2+} [38], $\text{Bi}_{12}\text{Cl}_{14}$ (i.e. $\text{Bi}_9^{5+}(\text{BiCl}_5^{2-})_2-$ $(\text{Bi}_2\text{Cl}_8^{2-})_{0.5}$) [39], S_2^{2+} , S_4^{2+} , S_8^{2+} and S_{16}^{2+} [40], Se_4^{2+} , Se_8^{2+} [41], Te_4^{2+} [42] and I_2^+ [43].

However, in addition to these low oxidation states, the general principle discussed in this review can also be illustrated, for example, with the relatively little known work of Bermond [44] on mercury electrochemistry. He found that mercury(II) and mercury(I) are stabilised at $\text{pCl} < 2.8$ and at $\text{pCl} > 4$ respectively.

CONCLUSION

Although not exhaustive, sufficient examples are given above to show both the general applicability of this principle and its utility in deciding the conditions necessary for preparative work. Though simple, there is still considerable scope for further exploration, since basic salt melts have been used relatively seldom in the past, probably because of concerns over the corrosion of containers, particularly those of glass or quartz. For example, the possibility of forming copper(III) in a basic salt melt medium might be of great help in the efficient preparation of high temperature superconductors of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ type, by avoiding the slow high temperature oxygenation step.

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