Chem. Soc. Rev., 1987, **16**, 1—43

Stabilization of Unusual Cationic Species in Protonic Superacids and Acidic Melts

By T. A. O'Donnell
DEPARTMENT OF INORGANIC CHEMISTRY, UNIVERSITY OF MELBOURNE, PARKVILLE, VICTORIA 3052, AUSTRALIA

1 Introduction

The essential aims of this review are threefold:

(i) to explain and systematize many diverse observations and measurements previously reported in a range of acidic protonic and non-protonic solvents including molten salts. Melts are often regarded as so different from those protonic or non-protonic solvents which are liquid at room temperature as to lie in a separate area of chemistry and many authors of text-books treat them accordingly. For simplicity, the molten salts considered here have been limited to chloroaluminate systems. Many of the generalizations made appear to apply equally validly to molten fluorides, nitrates, sulphates, *etc.*,

(ii) to assess critically past preparative procedures and to outline the experimental conditions for future synthetic or mechanistic inorganic chemistry. For example, it points the way to the most suitable reaction conditions, *e.g.* deliberate choice of the nature and stoicheiometry of oxidants or reductants as well as the level of acidity or basicity needed to stabilize known species in solution and then to isolate solid products containing these species from solution. It should assist in 'setting the conditions' to study new reactions and their mechanisms and to isolate new compounds.

(iii) to direct attention to the need to postulate, as a normal requirement, the existence of cationic species in the interpretation of observed reaction pathways in acidic systems. There has been far too little acceptance of the existence of solvated cationic species in many non-aqueous systems. This seems strange when we accept cations, however complex, as the expected species in acidic aqueous solutions and anions as the norm under basic aqueous conditions.

It is commonplace in considering the aqueous solution chemistry of inorganic systems to recognize that, for cations of metals in stable oxidation states in aqueous solution, the higher the charge on a cation the greater the interaction of the cation with the base or bases of the solvent or with any other bases present. $CrOH^{2+}$ and CrX^{2+} (for $X = $ a uninegative base other than OH^-) form to a greater extent than $CrOH^+$ and CrX^+ under similar solution conditions. Similarly Cr^{3+} (and Fe^{3+} *etc.*) form polymeric species such as $Cr_2(OH)_2^{4+}$ and $Cr_3(OH)_4^{5+}$ to a greater extent than Cr^{2+} and analogous systems. The formation of species of the general type $Cr_x(OH)_y^{(3x-y)+}$ by interaction of the cation with the base OH^- provides further opportunity for reducing the ratio of positive charge to metal. In moderately basic solutions Cr^{III} species are no longer cationic but anionic.

With higher formal charge on a *d*-transition metal, the discrete aquo-cation as such will not be observed for most elements. The ratio of charge-to-ionic volume is too great for the formal aquo-cation $Ti(OH_2)_6^{4+}$ to exist in aqueous solution, even under strongly acidic conditions. The aquo-cation can be considered to undergo deprotonation or to interact with OH^-, the base of the solvent system, to form $Ti(OH)_2(OH_2)_4^{2+}$ or even the trihydroxo species. These are the forms in which cationic titanium(IV) exists in acidic aqueous solution.[1a] The Zr^{IV} cation has been described in solution as $[Zr_4(OH)_8]^{8+}$. Similarly vanadium(IV) and vanadium(V) can be considered as being in solution as $V(OH)_2(OH_2)_4^{2+}$ and $V(OH)_4(OH_2)_2^+$ each of which can lose one or more water molecules from one of more pairs of OH^- ligands to form $VO(OH_2)_5^{2+}$ and $VO_2(OH_2)_4^+$, frequently represented simply as VO^{2+} and VO_2^+.[1b] For metals with larger cationic radii, *e.g.* for Th^{4+} and for actinides with atomic numbers greater than that of Th, the aquo-cation of charge +4 can be observed in aqueous solutions which are sufficiently acidic, *i.e.* have very low concentrations of OH^-, and are free from other bases which can form complexes. For *f*-transition metals with formal charges +5 and +6, cations in solution, and in the solids derived from aqueous solution, are based on the MO_2^+ and MO_2^{2+} entities. These dioxo cations are monomeric in aqueous solution only at low pH values.[1b] As the pH is gradually increased, they accept bridging base anions to form polymeric cations in which, with increasing pH, the charge-to-metal ratio is gradually decreased still further. Alternatively, the species containing metals with high formal charge may be anionic in basic aqueous solution, $CrO_4{}^{2-}$ and $MnO_4{}^-$ being commonplace examples.

As will be seen below, cations of the non-metallic elements of Groups VI and VII of the Periodic Classification, *e.g.* I_2^+, I_3^+, I_5^+, S_4^{2+}, S_8^{2+}, Se_{10}^{2+}, Te_6^{4+} *etc.*, can be generated in superacidic media—more particularly in the absence of bases; but these species are hydrolysed, *i.e.* react with the bases of the aquo-solvent system, and disproportionate to form oxo and hydroxo anions even in very strongly acidic aqueous solutions. These elements cannot be cationic in *aqueous* solution.

On the basic side of neutrality in aqueous solution, anions of high charge are readily protonated, *e.g.* PO_4^{3-} to HPO_4^{2-} and to $H_2PO_4^-$. For transition metals, monomeric anions which are stable in strongly basic solution become complex and polymeric on progressive acidification. This leads to a decrease in negative charge per metal atom, *e.g.* MoO_4^{2-} to $[Mo_7O_{24}]^{6-}$ and $[Mo_8O_{26}]^{4-}$. Even transition metals of the first row of the Periodic Classification, which might be expected to form cationic species more readily than elements of the second and third rows, form anions except in very strongly acidic aqueous solution when they are in high oxidation states. Species of vanadium(V) show a progressive decrease in charge per vanadium atom from pH 13 to 4.[2] VO_4^{3-}, the dominant species at pH values above pH 13, changes progressively through $V_2O_7^{4-}$ and $VO_3(OH)^{2-}$, at about pH 10, to $VO_2(OH)_2^-$, $V_3O_9^{3-}$, and $V_4O_{12}^{4-}$, about pH 7, to $V_{10}O_{28}^{6-}$, $V_{10}O_{27}OH^{5-}$, and

---

[1] J. Burgess, 'Metal Ions in Solution', Ellis Horwood, Chichester, 1978. (*a*) pp. 25—29 (*b*) 269—270.

[2] C. F. Baes and R. E. Mesmer, 'The Hydrolysis of Cations', John Wiley, New York, 1976, p. 210.

$V_{10}O_{26}(OH)_2^{4-}$ at pH values of 6 to 3. Cationic species are formed only around pH 2 to 3. The nature of the complex ions depends on the concentration of vanadium(v) as well as on the pH of the solution.

As the acidity of the medium increases from that attainable in aqueous solution—more particularly as the availability of the base needed to decrease the cationic charge decreases—the possibility of forming cationic species which are unstable in aqueous media increases.

For well over a century it had been known that elements of Group VI and Group VII of the Periodic Classification dissolved in sulphuric acid and in oleums to form highly coloured solutions, supposedly containing oxo compounds of the elements concerned. In 1938 Masson had postulated the existence in sulphuric acid of I_3^+ and I_5^+ in explaining iodination of aromatic compounds. Subsequently it was suggested that the characteristic deep blue colour resulting from dissolution of I_2 in oleum arose from the formation of I^+ in solution. This historical background has been covered by Gillespie and Passmore in reviews on the homopolyatomic cations of the Group VI and VII elements and of other elements.[3-5]

Since the mid-1960s Gillespie and co-workers have adduced conclusive evidence that the coloured species resulting from dissolving I_2 in H_2SO_4, oleums, and HSO_3F under oxidizing conditions are the cations I_2^+, I_4^{2+}, I_3^+, and I_5^+. They have generated some corresponding cations of bromine and of chlorine in superacidic or very weakly basic media. They have characterized homo- and heteropolyatomic cations of S, Se, and Te as well as polyatomic cations of Hg. Somewhat later in the same period, Corbett, Bjerrum, Mamantov and others demonstrated or postulated the existence in acidic molten salts, usually $AlCl_3$-rich melts, of polyatomic cations of the non-metals of Group VI and VII and of metallic elements such as Bi, Cd, Zn, Hg *etc.*

A less generally recognized property of very acidic media is their ability to stabilize monatomic cations of transition metals in unusually low oxidation states. In the early 1960s Gruen, McBeth, and Øye recorded spectra in molten $AlCl_3$ of transition metals in 'normal' oxidation states; but, more significantly from the point of view of this review, they also reported spectra of Cr^{II}, V^{II}, and Ti^{II}, oxidation states regarded as 'abnormal' in aqueous solution. Subsequently Mamantov adduced electrochemical evidence for Ti^{II}, Zr^{III}, and Zr^{II} in acidic melts. More recently O'Donnell and co-workers have recorded spectra at ambient temperatures of the HF-solvated cations U^{3+}, Cr^{2+}, V^{2+}, and Ti^{2+} in stable solutions where the medium is anhydrous HF, the acidity of which has been increased by use of appropriate Lewis acids. In the Melbourne work U^{3+}, stable in HF–BF_3 has been shown to disproportionate to UF_4 and U on increasing the basicity of the weakly acidic HF. Ti^{2+} also disproportionates as the basicity of an acidic HF solution is increased by addition of the base F^-. Also, we have shown that generation in HF of polyatomic cations, such as those of iodine and sulphur depends on the degree of

---

[3] R. J. Gillespie and J. Passmore, 'Advances in Inorganic Chemistry and Radiochemistry', ed. H. J. Emeléus and A. G. Sharpe, Vol. 17, Academic Press, 1975, pp. 49–87.

[4] R. J. Gillespie and J. Passmore, *Chem. Brit.*, 1972, **8**, 475

[5] R. J. Gillespie and J. Passmore, 'M.T.P. Int. Rev. Sci., Inorg. Chem., Ser. 2', Vol. 3, 1975, 121—36.

acidity of the HF and that the disproportionation reactions which occur when these solutions are made gradually more basic by addition of F^- are reversible. In this review disproportionation of cationic species will be shown to be a general phenomenon in other protonic solvents and in molten salts as the basicity of the medium is increased.

The overall purpose of this review is to show that a similar set of principles applies to stabilization of unusual cations, regardless of whether the medium is a protonic solvent, such as H_2SO_4, an oleum, HSO_3F or HF, or an acidic melt and that the temperature or chemical nature of the medium has little effect on the equilibria involved. Further, base-induced disproportionation leads to decomposition of these cations. It is a consequence of this that many of these cations can be generated as 'naked' cations from solvents such as SO_2 and SO_2ClF which are themselves very weakly basic and provided that the counter-anions used to isolate these cations as solids are also very weakly basic. In this way crystals have been grown for structural determination of compounds such as $I_2^+Sb_2F_{11}^-$, $Br_3^+Sb_3F_{16}^-$, and $S_8^{2+}(AsF_6^-)_2$.

As will be discussed briefly towards the end of the review, it is a corollary of what will be presented on stabilities of unusual cations that unusual anionic species, such as Zintl ions, *e.g.* Sn_9^{3-}, Pb_5^{2-}, Sb_7^{3-}, *etc.*, and alkali metal anions, are generated in strongly basic media or under 'naked' conditions, *e.g.* with a cryptated counter-cation to prevent electron transfer between the anion and cation. They are generated in the virtual absence of acidic species, particularly of protons.

References to the work presented in this Introduction will be given in the detailed sections of the body of this review. In the case of polyatomic cations, only homopolyatomic ions will be considered. Heterocations, such as $S_8Se_2^{2+}$ and fluorocations, *e.g.* those of the Group VII and Group VI elements, will not be included. This review is not intended as an exhaustive survey of the extant literature. In the interests of ease of accessibility, it draws as far as possible on earlier reviews. However, many individual papers have been cited when details relative to specific compounds need to be given and are not available in the reviews. Little detail is given on the structures of species discussed because the acid–base dependence of species *in solution* is of primary interest.

The intention in presenting the review is to establish some generalizations on the conditions of stabilization and the reactivity of unusual cationic species in strongly acidic media (or of unusual anions in bases) and to point the way to future work, using as a foundation the general principles established here.

2 Homopolyatomic Cations of Group VII Elements

No fluorine cations have been prepared. Homopolyatomic cations of iodine are easier to produce than those of, in turn, bromine and chlorine and were characterized before those of the two lighter halogens. Therefore cations of iodine will be discussed initially.

A. Iodine Cations.—Several homopolyatomic cations of iodine, I_2^+, I_4^{2+}, I_3^+, and I_5^+

have been generated in the solid state, in protonic superacidic media, and in molten salts.

(i) *In Protonic Solvents and in Solids.* Gillespie and Morton[6] have reviewed the formation and stability of polyatomic cations of iodine in HSO_3F, H_2SO_4, and oleum. They report the earlier work by Gillespie and Milne in which I_2 and the oxidant $S_2O_6F_2$ were reacted in the ratio 2:1 in HSO_3F. Conductance measurements indicating the number of moles of SO_3F^- produced from the oxidant $S_2O_6F_2$ per mole of I_2 were coupled with cryoscopic data to suggest that the resulting deep blue solution contained I_2^+. This solution had the same spectrum as that reported much earlier for solutions of I_2 in oleum, where it had been believed that the coloured species was I^+. Subsequently Kemmitt *et al.*[7] isolated blue solids from mixtures of I_2, IF_5, and SbF_5, or TaF_5, which they formulated as $I_2^+Sb_2F_{11}^-$ and $I_2^+Ta_2F_{11}^-$. Later Gillespie and co-workers obtained dark-blue crystals, suitable for structure determination, of $I_2^+Sb_2F_{11}^-$ by treating I_2 in liquid SO_2 with an approximate threefold excess of SbF_5.[8] The pentafluoride acted as an oxidant *and* as a Lewis acid and produced the very weakly basic anion $Sb_2F_{11}^-$. Neither the reduction product SbF_3 nor the solvent SO_2 is sufficiently basic to cause the disproportionation of the cation I_2^+ that is discussed below. The diatomic cation has a bond length (2.56 Å), shorter than that in I_2 (2.66 Å) and the frequency of the stretching vibration for I_2^+ (238 cm^{-1}) is greater than that for I_2 (213 cm^{-1}), consistent with the formation of a stronger bond as a result of removal of an electron from an antibonding π^* orbital in forming the cation.

Cooling of the deep-blue solution of I_2^+ in HSO_3F from room temperature to -70 or -80 °C caused a reversible colour change to red, explained on cryscopic and spectroscopic grounds as dimerization of I_2^+ to I_4^{2+}. Subsequently the structure of the rectangular cation I_4^{2+} has been reported.[9] Study of the 1:1 reaction mixture for $I_2{:}S_2O_6F_2$ gave no evidence for the previously postulated cationic species I^+, even though this redox stoicheiometry would have favoured the formation of the monatomic cation.

Gillespie and Peel[10] have reported a value for the Hammett acidity function (H_0) of -15.07 for pure HSO_3F. When the oxidant $S_2O_6F_2$ is reduced to SO_3F^- by I_2 in HSO_3F, the medium is made slightly more basic. Assuming $[SO_3F^-] \approx 0.05$ M, H_0 for the reaction medium would be about -14.1.[10] Gillespie and Morton[6] report that under these conditions I_2^+ is not completely stable, interacting with SO_3F^- (the base of the solvent system) and disproportionating partially to I_3^+ and $I(SO_3F)_3$. They state that in 100% H_2SO_4($H_0 \approx -11.9$)[11] this disproportionation is virtually complete. Resonance Raman spectroscopy, which is capable of detecting I_2^+ down to about 1 part in 10^6, shows only traces of I_2^+ in H_2SO_4. It is

---

[6] R. J. Gillespie and M. J. Morton, *Quart. Rev.*, 1971, **25**, 553.

[7] R. D. W. Kemmitt, M. Murray, V. M. McRae, R. D. Peacock, M. C. R. Symons, and T. A. O'Donnell, *J. Chem. Soc.* (*A*), 1968, 862.

[8] C. G. Davies, R. J. Gillespie, P. R. Ireland, and J. M. Sowa, *Can. J. Chem.*, 1974, **52**, 2048.

[9] R. J. Gillespie, R. Kapoor, R. Faggiano, C. J. L. Lock, M. Murchie, and J. Passmore, *J. Chem. Soc., Chem. Commun.*, 1983, 8.

[10] R. J. Gillespie and T. E. Peel, *J. Am. Chem. Soc.*, 1973, **95**, 5173.

[11] R. J. Gillespie, T. E. Peel, and E. A. Robinson, *J. Am. Chem. Soc.*, 1971, **93**, 5083.

highly significant that when the SO_3F^- concentration in the solvent HSO_3F is substantially reduced by addition of SbF_5, I_2^+ is quite stable in HSO_3F. Values of H_0 for such solutions would be likely to be -16 to -18 depending on the amount of SbF_5 added. I_2^+ is also reported to be stable[6] in 65% oleum for which H_0 is $-$ 14.84.[11]

By setting the stoicheiometric ratio of reactants I_2:S_2O_6F at 3:1 and 5:1 in HSO_3F, Gillespie and Milne[6] obtained evidence for the formation of I_3^+ and I_5^+. These had previously been postulated as the cationic species in 100% H_2SO_4. ($H_0 = -11.93$).

Gillespie's work has shown that I^+ cannot be generated in HSO_3F, whereas I_2^+ is marginally stable. In the less acidic medium H_2SO_4, I_3^+ and I_5^+ are the iodine cations of highest formal charge to be stable. Of course, in the more acidic HSO_3F, I_3^+ and I_5^+ exist as stable entities, if the reactant stoicheiometry is such as to generate these species. The implicit strategy behind Gillespie's work in HSO_3F was to use a medium of sufficient acidity that the polyatomic cations sought would be stable in it and then to adjust the oxidant stoicheiometry to generate the cations I_5^+, I_3^+, or I_2^+.

Subsequently, Passmore and co-workers isolated and structurally characterized compounds containing the I_3^+ and I_5^+ cations under 'naked' (*i.e.* non-basic) conditions. I_2 and AsF_5 were reacted in stoicheiometric proportions in SO_2 solution to give crystalline I_3AsF_6.[12] Neither the solvent SO_2 nor AsF_3, the product of reduction of the oxidant AsF_5, is sufficiently basic to cause disproportionation of the cation I_3^+. For similar reasons, they were able to isolate I_5SbF_6 from a stoicheiometric mixture of I_2 and SbF_5 in liquid AsF_3.[13]

Some fairly recent Melbourne HF chemistry[14] is consistent with these generalizations. A controlled amount of elemental F_2, sufficient to form I_2^+, was added to a suspension of I_2 in anhydrous HF. The resulting brown solution however gave a spectrum indicating I_3^+ as the major product with I_5^+ also present. When the same experiment was repeated with the solvent HF saturated with GeF_4, a deep-blue solution with the characteristic spectrum of I_2^+ was obtained and this gave the red colour of I_4^{2+} on cooling.

These observations are easily explicable on the basis of unpublished Hammett acidity function measurements by Gillespie and Liang.[15] Applying the same methodology as had been used by Gillespie to determine H_0 for pure H_2SO_4 and HSO_3F, *i.e.* making H_0 measurements in the solvent with concentrations of base and of acid sufficient to 'swamp' any basicity resulting from adventitious presence of water or other base-producing impurities, Gillespie decided on the point of inflection in the plot of H_0 *vs.* concentration of base or acid as the Hammett function for the pure solvent.[10,11] On this basis, pure HF has a value of -15.1 for H_0.[15] Minute amounts of base or acid change H_0 by about 4 units, a reflection of the very small self-ionization of HF compared with that of HSO_3F or H_2SO_4. It must be assumed that HF stored in KelF will be basic because of protonation of

---

[12] J. Passmore, G. Sutherland, and P. S. White, *Inorg. Chem.*, 1981, **20**, 2169.

[13] J. Passmore, P. Taylor, T. Whidden, and P. S. White, *Can. J. Chem.*, 1979, **57**, 968.

[14] R. W. Cockman and T. A. O'Donnell, unpublished observations.

[15] J. J.-N. Liang, Ph.D. Thesis, McMaster University, 1976.

material (plasticizer or, alternatively, low molecular weight, and therefore partially unsaturated, polychlorotrifluoroethylene) leached from the solid polymer. Minute traces of H_2O remaining after purification of the HF by distillation will also be protonated and so enhance the concentration of F^-, the base of the solvent system. More importantly in the present context, F_2 acting as an oxidant in HF will produce F^-, the base of the solvent system. If it is assumed that the resulting $[F^-] \approx 0.05M$, H_0 for the reaction system will be about -10.3.[15] GeF_4 is an extremely weak Lewis acid in HF[16] but is capable of combining with free F^- ion to form GeF_6^{2-}. Therefore it is reasonable to assume that in HF–GeF_4 mixtures, H_0 is at least -15. The stabilization of I_2^+ in such a solution becomes consistent with that of its stability in media such as HSO_3F, oleum, and pure H_2SO_4. The relationship of the stability of I_2^+ and I_3^+ to values of H_0 for the protonic solvents H_2SO_4, oleum, HSO_3F, and HF has been summarized and tabulated in a recent review.[17]

In all of the above it is proposed that cations of 'high' formal positive charge per iodine atom, *e.g.* 0.5 for I_2^+, disproportionate as the availability of base increases into cations of lower formal charge and covalent compounds which contain iodine in a higher formal oxidation state than in the original cation. A disproportionation reaction leading to the formation of elemental I_2 is also possible, depending on the basicity of the medium. The following idealized equations represent these processes:

$$\begin{aligned} 8I_2^+ + 3X^- &\longrightarrow 5I_3^+ + IX_3 \\ 7I_3^+ + 3X^- &\longrightarrow 4I_5^+ + IX_3 \quad \text{where X} = HSO_4^-, SO_3F^-, \text{or } F^- \\ 3I_5^+ + 3X^- &\longrightarrow 7I_2 + IX_3 \end{aligned}$$

The possibility of species IX forming in solution cannot be excluded, particularly for X = HSO_4^- or SO_3F^-, although the known covalent compounds which have been isolated are $I(HSO_4)_3$ and $I(SO_3F)_3$. IF_3 is not as easy to prepare as IF_5. It probably could exist in HF solution, particularly in the presence of a Lewis acid such as SbF_5 since adducts such as $IF_2^+SbF_6^-$ and $IF_2^+AsF_6^-$ have been characterized, $IF_2^+SbF_6^-$ being stable to 45 °C. However, a postulated disproportionation to IF_5 would be equally effective in describing the dependence of the degree of stability of iodine cations on the extent of superacidity of the medium.

In summary, it has been proposed in this section on iodine cations that, as the availability of basic species decreases *i.e.*, considering the most general case, as the superacidity of the medium increases, polyatomic iodine cations of progressively higher formal charge per iodine atom are stabilized.

Recognizing that the above base-induced disproportionations should be reversible, we have recently generated homopolyatomic cations of iodine in acidic HF,[18] initially by adding SbF_5 in HF to a stoicheiometric mixture of I_2 and IO_3^- to generate I_2^+ as indicated by the spectrum of the resulting solution. Because the oxygen from the iodate is ultimately converted into protonated water in HF, a large

---

[16] P. Davies and T. A. O'Donnell, unpublished observations.

[17] T. A. O'Donnell, *J. Fluor. Chem.*, 1984, **25**, 75.

[18] J. Besida and T. A. O'Donnell, unpublished observations.

amount of unwanted base (F^-) is generated in the solution. Consequently we reacted I_2 and IF_5 in stoicheiometric proportions in HF made strongly acidic with SbF_5 and generated solutions and solids containing both I_2^+ and I_4^{2+}.[18] By carefully controlling the HF acidity by addition of appropriate Lewis acids or bases we have demonstrated that, at lower acidities, I_3^+ and I_5^+ are generated.

A highly significant feature of our most recent Melbourne work in HF is that for the I_2–F_2 reactions or for the I_2–IF_5 reactions it does not matter whether the oxidant or the reductant is in excess. The *level of acidity* of the HF is the principal determinant as to whether the cation formed is I_5^+, I_3^+, or I_2^+. This aspect will be developed in greater detail in the section 'Principles Governing Stabilization of Cations' presented towards the end of this review.

(ii) *In Chloride Melts.* Although, by comparison with the observations in protonic solvents at or near room temperature, studies of homopolyatomic cations of iodine in chloride melts at the necessarily elevated temperatures are few, the data reported for these media support the trends shown for superacids as developed here.

Corbett and co-workers[19] conducted studies of phase equilibria and used nuclear quadrupole resonance spectroscopy in systems that they described as 'neat' (*i.e.* stoicheiometric) mixtures of I_2, ICl, and $AlCl_3$. In the context of this review, these are best seen as neutral chloride melts. It is highly significant that the cations observed under these conditions were I_3^+ and I_5^+ in the isolated compounds $I_3^+AlCl_4^-$ and $I_5^+AlCl_4^-$, and that *in these neutral media* there was no evidence for formation of I_2^+.

However, Mamantov has reported the existence of I_2^+ in acidic melts.[20] Iodine was shown by u.v.–visible spectroscopy to be soluble both in an acidic eutectic (63 mole % $AlCl_3$–37 mole % NaCl) and in neutral melts (50% $AlCl_3$–50% NaCl). When each of these systems was oxidized either anodically or by elemental chlorine, the intense and characteristic resonance Raman spectrum for I_2^+ was observed in the acidic but not in the neutral melt. Since both oxidative paths generate I_2^+, it is unnecessary to regard Cl_2 as a specific chemical oxidant in these reactions. The generation of I_2^+ can be represented simply as:

$$I_2 - 1e \longrightarrow I_2^+$$

With decrease in acidity of the medium i.e. with increase in concentration of the base of the system Cl^-, I_2^+ would disproportionate according to the equation:

$$2I_2^+ + 2Cl^- \longrightarrow 2ICl + I_2$$

although it must be recognized that there could be intermediate species such as I_3^+ and I_2Cl^+.

Mamantov reported that extended anodic oxidation of I_2 beyond the formation of I_2^+ involved the formation of ICl. This is consistent with the fact that I_3^+ would not be observed even in this acidic medium. It would have been further oxidized.

---

[19] D. J. Merryman, J. D. Corbett, and P. A. Edwards, *Inorg. Chem.*, 1975, **14**, 428.

[20] K. Tanemoto, G. Mamantov, and R. Marassi, *J. Inorg. Nucl. Chem.*, 1981, **43**, 1779.

B. Bromine Cations.—By comparison with the investigation of iodine cations, relatively little work has been reported on corresponding homopolyatomic cations of bromine. Unlike the iodine case, there has been relatively little study of bromine cations in solution.

(i) *In Solid Compounds.* The first formation of Br_3^+ as such was postulated by McRae on the basis of a tensiometric study of the reaction of Br_2 and SbF_5.[21] She observed a rise in vapour pressure of bromine when the Br_2 content of the mixture exceeded 30 mole %. The brown colour of this system ($\lambda_{max.} = 375$ nm, later shown to be characteristic of Br_3^+) migrated to the cathode on electrolysis. No single compound was isolated from the reaction mixture because the desired product was contaminated with SbF_3; SbF_5 is both the oxidant and the source of the very weakly basic anion according to the following equation:

$$3Br_2 + 7SbF_5 \longrightarrow 2Br_3^+Sb_3F_{16}^- + SbF_3$$

Subsequently, and again significantly in the terms of this review, Edwards reacted Br_2 and SbF_5 in the *oxidizing* solvent BrF_5 and generated $Br_2^+Sb_3F_{16}^-$ under oxidizing, weakly basic conditions.[22]

$$9Br_2 + 2BrF_5 + 30SbF_5 \longrightarrow 10Br_2^+Sb_3F_{16}^-$$

His crystal structure showed a bond length of 2.15 Å in Br_2^+ compared with 2.27 Å in Br_2, a similar difference to that observed for I_2^+ and I_2.

(ii) *In Superacids.* Gillespie and Morton have done much of the experimental work and have reviewed the experimental data for the existence of Br_3^+ and Br_2^+ in superacids.[23] Br_3^-, unstable in 100% H_2SO_4, is not completely stable in basic HSO_3F, *i.e.* HSO_3F containing SO_3F^- from the oxidant $S_2O_6F_2$. Br_3^+ can be represented as disproportionating according to the equation:

$$Br_3^+ + SO_3F^- \longrightarrow Br_2 + BrSO_3F$$

In $SbF_5{\cdot}3SO_3{-}HSO_3F$ the appropriate amount of $S_2O_6F_2$ oxidizes Br_2 to brown Br_3^+ which is quite stable. Further oxidation with $S_2O_6F_2$ gives a cherry red solution for which there is the very sensitive resonance Raman spectroscopic evidence for Br_2^+. There is also some spectroscopic evidence[24] for a complex disproportionation of Br_2^+ into Br_3^+, $BrSO_3F$, and $Br(SO_3F)_3$. This disproportionation was rationalized by showing that dissolution of $BrSO_3F$ in $SbF_5{\cdot}3SO_3{-}HSO_3F$, itself an oxidizing solution gives a solution providing u.v.–visible spectroscopic evidence for Br_2^+ and Br_3^+ and resonance Raman spectroscopic evidence for Br_2^+. This solution also contains $Br(SO_3F)_3$. This complex system will be discussed later.

---

[21] V. McRae. Ph.D. Thesis, University of Melbourne, 1966.

[22] A. J. Edwards, G. R. Jones, and R. J. C. Sills, *J. Chem. Soc., Chem. Commun.*, 1968, 1527.

[23] Ref. 6. pp. 559 62.

[24] R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, 1972, 11, 586.

C. Chlorine Cations.—The progression from iodine, which has a rich cationic chemistry in superacids, through bromine is complete at chlorine, for which there does not appear to be any reliable evidence for the existence of any homopolyatomic cation, as such, in solution. Again Gillespie and Morton have summarized their own experimental observations.[25] Conductivity and Raman spectra of solutions of $ClOSO_2F$ and Cl_2 in $SbF_5{\cdot}3SO_3$–HSO_3F gave no evidence for the existence of polychlorine cations in solution at 25 °C. ClF and Cl_2 in SbF_5–HF gave a yellow solid at −76 °C identified from its Raman spectrum (see below) as containing Cl_3^+. This solid, on warming to room temperature, is reported to have given Cl_2 and salts containing $ClF_2{}^+$. In the presence of the strong Lewis acid SbF_5, which readily accepts F^- from ClF_3, this represents an overall disproportionation:

$$3Cl_3^+ + 3F^- \longrightarrow 4Cl_2 + ClF_3$$

the ClF_3 undergoing fluoride transfer to SbF_5 to form $ClF_2^+SbF_6^-$. The stepwise reaction probably involves a preliminary dissociation of Cl_3^+ into Cl_2 and Cl^+ followed by disproportionation of Cl^+ which, in the presence of the base F^- from the solvent, would be far too unstable to exist:

$$3Cl^+ + 3F^- \longrightarrow Cl_2 + ClF_3$$

The cation Cl_3^+ was characterized by the Raman spectrum of the solid isolated after direct reaction at −76 °C of a mixture of Cl_2, ClF, and AsF_5, no HF being used. In addition to the Raman-active bands for AsF_6^- there were three relatively intense bands at 490, 225, and 508 cm^{-1}, assigned to ν_1, ν_2, and ν_3 for the bent Cl_3^+ cation by comparison with the isoelectronic molecule SCl_2, which has a bond angle of 103° and vibrational frequencies of 514, 208, and 525 cm^{-1}.

The solid $Cl_3^+AsF_6^-$, stable at −76 °C, decomposed to Cl_2, ClF, and AsF_5 at room temperature. ClF is a thermally stable entity in the gas phase and so the complex disproportionations proposed above for reaction in HF solution would not occur. When Cl_2, ClF, and the weaker Lewis acid BF_3 were mixed at temperatures down to −130 °C there was no evidence of adduct formation.

(i) *In Solution.* No evidence has been adduced for the presence of stable discrete Cl_3^+ cations in any protonic solvent or molten salt. Considering the relative stabilities of the cations I_2^+ and I_3^+ and of Br_2^+ and Br_3^+ in solvents of differing acidities, it seems even less likely that Cl_2^+ will be observed in solution.

D. Relative Stability of Group VII Cations.—It is obvious from the preceding major section that the ease of formation of compounds of I_2^+ and I_3^+ and the stability of these cations in superacidic solutions is far greater than for the corresponding Br_2^+

---

[25] Ref. 6, pp. 562–64.

Table 1 *Homopolyatomic cations of halogens*

General Formula		X_2^+	X_3^+
Oxidation State		0.5	0.33
Iodine	Solids:	$I_2^+Sb_2F_{11}^-$ from stoicheiometric $I_2 + SbF_5$ in SO_2	$I_3^+AsF_6^-$ from stoicheiometric $I_2 + AsF_5$ in SO_2[a]
	Solutions: (i)	Stable in 60% oleum ($H_0 \approx -14.8$)[b]	Stable in H_2SO_4–HSO_4^- ($H_0 \approx -11.9$)
	(ii)	Marginally stable in HSO_3F–SO_3F^-($H_0 \approx -13.8$) Stable in HSO_3F–SbF_5($H_0 \approx -18$)	Stable in HSO_3F–SO_3F^- ($H_0 \approx -13.8$)
	(iii)	Stable in acidic HF ($H_0 \approx -15$ to -16)	Stable in HF–F^- ($H_0 \approx -11$ to -12[c])
	(iv)	Stable in acidic melt (63% $AlCl_3$–37% NaCl)	Stable in neutral $AlCl_3$ melt[d] (50% $AlCl_3$–50% NaCl)
Bromine	Solids:	$Br_2^+Sb_3F_{16}^-$ from $Br_2 + BrF_5 + SbF_5$	$Br_3^+Sb_3F_{16}^-$ from $Br_2 + SbF_5$
	Solutions:	Marginally stable in $SbF_5 \cdot 3SO_3$–HSO_3F($H_0 \approx -19$)	Marginally stable in HSO_3F–SO_3F^-($H_0 \approx -13.8$) Stable in $SbF_5 \cdot 3SO_3$–HSO_3F ($H_0 \approx -19$)
Chlorine	Solids:	Not isolated	$Cl_3^+AsF_6^-$ from $Cl_2 + ClF + AsF_5$ at -78 °C
	Solutions	No evidence	No evidence

[a] $I_5^+SbF_6^-$ was isolated from stoicheiometric reacting proportions of I_2 and SbF_5 in liquid AsF_3. [b] Numbers in parenthesis are values of Hammett acidity functions for the different media, adjusted to experimental conditions, *i.e.* containing appropriate concentrations of Lewis acids or deemed to be about 0.05M in base, where a base is produced in the synthesis, *e.g.* F^- from F_2 in HF, SO_3F^- from $S_2O_6F_2$ in HSO_3F, or HSO_4^- in H_2SO_4. The values have been calculated from references 10, 11, and 15. [c] Spectroscopic evidence for some I_5^+ as well as I_3^+ in this basic HF medium, at values of H_0 nearer to -11. [d] I_3AlCl_4 was crystallized from an equimolar mixture of I_2, ICl and $AlCl_3$, *i.e.* a neutral melt. An appropriate stoicheiometry yielded I_5AlCl_4 under neutral conditions. I_2^+ is not stable in neutral $AlCl_3$ melts.

and Br_3^+ and, in turn, for chlorine for which the only cation prepared to date is Cl_3^+, and that in solid compounds but not in solution.

For each element, there is a greater attenuation of the single positive charge over X_3^+ than over X_2^+. X_3^+ is less electrophilic than X_2^+, *i.e.* X_3^+ can exist with a greater availability of base, either in solid compounds or in solution than can X_2^+. Within the Group, X_n^+, for a particular value of n, is more electrophilic for X = Cl than for X = Br and I, in turn. That is, Cl_n^+ reacts more readily than Br_n^+ and I_n^+ with bases such as HSO_4^-, SO_3F^-, and F^- (or with the base of any other medium, such as that of a molten salt).

These trends are summarized in Table 1 from which it can be seen that stabilization of I_3^+ requires a medium for which H_0 can be -10 to -12. Br_3^+

requires much higher acidity, $H_0 \approx -19$, and Cl_3^+ can only be prepared at low temperature in the solid state, *i.e.* with no basic species available from a solvent. The natural extension of this is that I_2^+, more electrophilic than I_3^+, requires a medium with $H_0 \approx -15$ for stability. Br_2^+ is only marginally stable at $H_0 \approx -19$, and Cl_2^+ has not been formed.

E. Factors Governing Synthesis and Stability of Polyatomic Halogen Cations.—The most generally accepted postulation is that the formation of a particular cation X_n^+ will depend on (a) the ratio of oxidant to halogen (or other compound oxidized) and (b) the degree of acidity of the medium—more significantly, the extent of availability of basic species. In this review it is postulated that the level of acidity of the medium is far more important in determining cation stability than the oxidant–reductant stoicheiometry.

If a polyatomic cation of a particular element is stable above a certain level of acidity and the basicity of the system is then increased progressively by adding the anion which is the base of the solvent system, or by adding any compound which will increase the concentration of the base, that cation will disproportionate into a cation of lower formal charge per atom of the element and a compound, *essentially covalent*, formed between one or more of the basic anionic entities and an atom of the element concerned in a higher formal positive oxidation state than in the original cation. Ultimately there may be disproportionation to the element itself and an essentially covalent compound of the element and the base, depending on the nature of the element itself and on the degree of acidity of the medium *i.e.* the availability and strength of the basic species in the medium. In sufficiently basic media, anionic species may be formed.

Some reaction pathways for halogen cations in protonic and non-protonic media have been proposed which can be rationalized somewhat more easily within the framework outlined in this review. Gillespie and Morton[24] have given details for the oxidation of Br_2 by $S_2O_6F_2$ in differing stoicheiometries in HSO_3F and in $SbF_5{\cdot}3SO_3$–HSO_3F and for the observed products resulting from the dissolution of $BrSO_3F$ in $SbF_5{\cdot}3SO_3$–HSO_3F. They report that Br_3^+ is produced as a stable entity in HSO_3F itself but Br_2^+ is not stable, whereas the diatomic cation can be observed in $SbF_5{\cdot}3SO_3$–HSO_3F, but is only marginally stable. Of course, Br_3^+ could be generated in this more acidic medium by reacting appropriate ratios of Br_2 and $S_2O_6F_2$. They report further that when $BrSO_3F$ is dissolved in $SbF_5{\cdot}3SO_3$–HSO_3F, the species Br_2^+, Br_3^+, and $Br(SO_3F)_3$ are all observed in solution. They postulate that $BrSO_3F$ disproportionates in the most acidic medium to form Br_2^+ and $Br(SO_3F)_3$. This probably is a reasonable summary of the overall position; but it seems somewhat more systematic to say that as the basicity of the medium is increased from that of $SbF_5{\cdot}3SO_3$–HSO_3F to HSO_3F and ultimately to basic HSO_3F, *i.e.* HSO_3F containing significant amounts of SO_3F^- from the reduction of $S_2O_6F_2$, Br_2^+ disproportionates to $BrSO_3F$ and Br_3^+ and ultimately to $BrSO_3F$ and Br_2. However, this scheme as proposed would require that $BrSO_3F$ is a stable compound which undergoes no further reaction.

Gillespie and Morton point to the non-existence of ISO_3F as suggesting probable instability of $BrSO_3F$, involving disproportionation. The situation with the analogous fluorides is similar. ClF, like $ClSO_3F$, is thermally stable at room temperature. BrF disproportionates to Br_2 and BrF_3 and IF cannot be isolated. It seems reasonable then to postulate that $BrSO_3F$, the acidity-dependent product of disproportionation of Br_2^+ and Br_3^+, disproportionates thermally to Br_2 and $Br(SO_3F)_3$. The solvent $SbF_5{\cdot}3SO_3$–HSO_3F is a strongly oxidizing system and it would oxidize Br_2 to Br_3^+ and Br_2^+ depending on the net acidity of the medium.

The modification suggested above of the Gillespie and Morton reaction scheme for bromine cations might seem unnecessarily detailed were it not for the observed disproportionation of Cl_3^+, also reported by Gillespie and Morton. The solid Cl_3^+-AsF_6^-, in isolation, dissociates to Cl_2, ClF, and AsF_5. However, $Cl_3^+SbF_6^-$ in SbF_5–HF gives Cl_2 and ClF_2^+ adducts as products[25] implying formation of ClF_3. Earlier in this review, it has been proposed that Cl_3^+ *in HF solution* would dissociate initially into Cl_2 and Cl^+ and that the highly unstable Cl^+ would then interact with the minute amount of F^- in SbF_5–HF solution to disproportionate to Cl_2 and ClF_3. The ClF_3 would then undergo fluoride exchange with the Lewis acid SbF_5.

An even clearer case for postulating disproportionation of halogen cations with increasing base concentration, rather than disproportionation of covalent halogen compounds with decreasing availability of base, arises in the observation by resonance Raman spectroscopy of I_2^+ in acidic $AlCl_3$ and the quenching of the I_2^+ resonance Raman signal with increasing basicity of the melt. Mamantov and co-workers[20] report u.v.–visible spectroscopic evidence for molecular iodine when iodine is added to $AlCl_3$–NaCl melts. When these solutions are oxidized anodically or by elemental chlorine in $AlCl_3$-rich melts, there is definitive resonance Raman spectroscopic evidence for I_2^+; but in chloride-rich melts the Raman signal for I_2^+, is not observed.

This suggests that regardless of whether the oxidation is anodic or chemical, I_2^+ is formed:

$$I_2 - 1e \longrightarrow I_2^+ \quad \text{and}$$
$$2I_2 + Cl_2 \longrightarrow 2I_2^+ + 2Cl^-$$

In $AlCl_3$-rich melts, the chloride formed would be converted into chloroaluminate predominantly. However as the ratio of $Cl^-:AlCl_3$ in the melt is increased to and beyond the point of neutrality, disproportionation occurs by reaction with the base chloride which is now available;

$$2I_2^+ + 2Cl^- \longrightarrow I_2 + 2ICl$$

In the experiment as reported, Cl_2 was added to I_2 in the melt in the ratio 1:1, whereas the ratio in the oxidation reaction written above is 0.5:1. So, depending on the acidity of basicity of the melt, Cl_2 in excess of the amount required for initial production or I_2^+ could further oxidize I_2 produced by disproportionation or present in the basic melt to I_2^+ or to ICl.

The schemes proposed above for redox reactions of I_2 and Cl_2 in chloroaluminates are more consistent with the interaction of cationic species and bases in protonic solvents than the suggestion by the authors that the species undergoing disproportionation is ICl, which would require the unlikely formation of ICl_3 in order to generate I_2^+. Their other proposal that Cl_2 oxidizes I_2 to form ICl, which then reacts with more I_2 to form I_2^+ and Cl^-, is not consistent with the stoicheiometry of the I_2–Cl_2 reaction or with the electrolytic production of I_2^+ in $AlCl_3$-rich (*i.e.* chloride-deficient) melts.

Overall, it seems fair to comment that in many systems the necessary *concomitant* and *complementary* roles of oxidation and of acidity have been overlooked in discussion of the formation of unusual cationic species in a wide range of solvents and reaction media. It is true that the oxidant $S_2O_6F_2$ has been used deliberately and imaginatively in the solvent HSO_3F; but frequently there has been too little recognition of the strongly oxidizing properties of SO_3 in oleums or of SbF_5 in HF or in HSO_3F when these have been added as Lewis acids and they have then been recognized only as increasing the acidity of the medium.

Some apparent anomalies in the above rationalizations are easily explained. For example a cation of low formal oxidation state can be generated in a medium of an acidity which can maintain a higher formal oxidation state for the element concerned, providing a limited amount of oxidant is used. Thus Gillespie generated stable I_5^+ and I_3^+ in HSO_3F in which I_2^+ is marginally stable by limiting the amount of the oxidant $S_2O_6F_2$.[6] Conversely many of the investigations in molten salts involving non-metal cations have involved electrolytic oxidation and obviously such a technique can 'override' oxidation states, which are marginally stable in the medium, under the forcing condition of electrolysis—particularly under voltammetric conditions where the applied potential is being changed continuously and where the absolute amount of product being produced by oxidation (or reduction) and sensed in the region of the working electrode is very small. Under these conditions, a cation could be produced which has a higher formal charge than that expected for the bulk acidity of the medium.

It must be stressed that the conditions put forward to relate charge to acidity and basicity apply to *cationic* species. Thus a bromine(III) compound $Br(SO_3F)_3$, which is essentially covalent, is stable under superacidic conditions where Br_3^+ (formal oxidation state 0.33) and Br_2^+ (0.5) are in equilibrium. Indeed the whole postulation about disproportionation of cationic species involves the formation of non-ionic species containing the element concerned in a higher formal oxidation state than that of the cation from which it was derived.

3 Homopolyatomic Cations of Group VI Elements

Historically, as was the case for iodine in Group VII, sulphur was the first of the Group VI elements to be subjected to systematic investigation for formation of cationic species. In Group VII stability of cations was seen to decrease in passing from iodine to bromine to chlorine. Not surprisingly, the same trend holds in Group VI—the attainability of a higher ratio of charge-to-element in polyatomic cations becomes greater with increase in atomic number of the element.

The chemistry of Group VI elements differs from that of group VII in that the first member, oxygen, can form the diatomic cation O_2^+. It was first characterized definitively in a solid compound by the oxidation of O_2 by PtF_6, the resultant cation being stabilized in the compound $O_2^+PtF_6^-$ in association with weakly basic PtF_6^-.[26] Subsequently it has been isolated as a solid with many weakly basic anions in compounds such as $O_2^+Sb_2F_{11}^-$, $O_2^+SbF_6^-$, $O_2^+AsF_6^-$ *etc.*[3,4] As this is the only oxygen cation characterized to date and is always isolated *as a solid* in association with a weakly basic anion, it will not be discussed further in this review.

A. Sulphur Cations.—(i) *In Protonic Solvents.* Early in the 19th century, it was reported that treatment of elemental sulphur with oleums gave coloured solutions, the colour depending on the strength of the oleum, *i.e.* the SO_3 content.[3–5] The nature of these coloured species began to be resolved when Gillespie and co-workers reacted stoicheiometric amounts of S_8 and either AsF_5 or SbF_5 in HF.[27] They reported that S_8 and AsF_5 (or SbF_5) in the reacting proportions 2:3 gave $S_{16}(AsF_6)_2$ and AsF_3. They found that by reacting S_8 with excess SbF_5 directly or in SO_2 they produced S_4^{2+} and ascribed this to the greater oxidant strength of SbF_5 than AsF_5. It seems more likely that with a suitable excess of oxidant present, the lower basicity of the medium containing SbF_5 allowed stabilization of the cation with higher charge per sulphur atom.

Subsequently Gillespie's group used $S_2O_6F_2$ as an oxidant for S_8 in HSO_3F[27] and reported reaction patterns based on cryoscopic observations and on monitoring by conductance methods the number of moles of SO_3F^- produced in a reaction and thence the extent of oxidation of S_8. SO_3F^- is both the reduction product of the oxidant $S_2O_6F_2$ and the highly conducting base of the solvent HSO_3F. They reported that a 2:1 ratio of S_8 to $S_2O_6F_2$ produced S_{16}^{2+} and $2SO_3F^-$ and that the 1:1 mixture gave S_8^{2+} and $2SO_3F^-$, but that the S_8^{2+} was somewhat unstable in HSO_3F (basic because of the SO_3F^- present) and that sulphur slowly precipitated as a result of disproportionation to S_8 and SO_2. Excess $S_2O_6F_2$ with S_8 in liquid SO_2 at low temperature gave solid $S_4^{2+}(SO_3F^-)_2$, *i.e.* S_4^{2+} was formed in the absence of excess base. However, in HSO_3F, with the base SO_3F^- available, colourless S_4^{2+} gradually changed to blue S_8^{2+}. It is significant that S_4^{2+} is stable in the less basic protonic medium SbF_5–HSO_3F.

In their review[3] Gillespie and Passmore delineate the limits of existence in the H_2O–H_2SO_4–SO_3 solvent system of the cations S_4^{2+}, S_8^{2+}, and the cation described by them at that stage as S_{16}^{2+}. It will be shown below that later work from Gillespie's group indicates that this very large cation of small charge per S atom is probably S_{19}^{2+}. They say that S_8 dissolves slowly as such in 95—100% H_2SO_4 but that in 5% oleum oxidation, presumably by SO_3, to 'S_{16}^{2+}' is observed. In 10—15% oleum there is rapid oxidation to a mixture of 'S_{16}^{2+}' and S_8^{2+} which is then slowly oxidized to SO_2. The 'S_{16}^{2+}' and S_8^{2+} produced initially in 30% oleum are oxidized to S_4^{2+} and finally to SO_2, whereas in 45% and 65% oleum S_4^{2+}, following initial generation of 'S_{16}^{2+}' and S_8^{2+} is rather stable and subsequent oxidation to SO_2 is very slow. This

---

[26] N. Bartlett and D. H. Lohman, *Proc. Chem. Soc.*, 1962, 115.

[27] (*a*) Ref. 3, pp. 63—5. (*b*) Ref. 4, p. 476.

scheme seems to set the limits of acidity below which S_8^{2+} and S_4^{2+} will not be stable; but the system is very complex because SO_2 can be the end product of ultimate oxidation or can be the higher oxidation state form of sulphur after disproportionation of cations in media which are not sufficiently acidic. Gillespie and Passmore[3] state that S_8^{2+} disproportionates to S_{16}^{2+} and SO_2 in oleum containing less than 15% SO_3, and that S_4^{2+} disproportionates to S_8^{2+} and SO_2 below 40% SO_3. Even though SO_3 is a strong oxidant, S_4^{2+} is more stable in 45% and 65% oleum than in 30% oleum. The higher acidity prevents disproportionation to SO_2 and outweighs the oxidant effect.

The data in Table 2 (p. 19) suggest that in the oleum system S_4^{2+} is stable for H_0 values more negative than -14, S_8^{2+} at about -13 and 'S_{16}^{2+}' for H_0 less negative than -13. The same order of stabilities with change in H_0 values is observed in the chemically simpler solvent system HSO_3F in which the oxidant $S_2O_6F_2$ is reduced to the base of the solvent and in which there is a clearer differentiation between sulphur-containing oxidation products (cations) and products of disproportionation. Even though a smaller amount of the base SO_3F^- will be available in the solvent HSO_3F than of the base HSO_4^- in the solvent H_2SO_4 because of the great difference in the self-ionization processes for the two solvents, the more electronegative SO_3F^- would be expected to interact with cations more readily than the less electronegative HSO_4^-. On this basis, the absolute acidities in which different cations will be stabilized would be expected to differ from solvent to solvent.

In more recent work Gillespie and his colleagues set out to determine the crystal structure of the large sulphur cation postulated as S_{16}^{2+} from the cryoscopic and conductance data from solution studies. Much earlier they had determined the structure of $S_8^{2+}(AsF_6^-)_2$ in crystals isolated from SO_2. They used the appropriate reacting proportions of S_8 and AsF_5 to obtain crystals from the solvent SO_2–SO_2ClF at -25 °C and found that the cation was S_{19}^{2+}—two seven-membered rings of sulphur atoms joined by a chain of five sulphur atoms.[28]

In recent Melbourne work,[18] sulphur cations have been produced in acidic HF by reacting elemental sulphur with compounds containing sulphur in higher oxidation states such as SO_3^{2-} and SF_4. When the stoicheiometries required to produce S_8^{2+} were used in HF solutions 4—5M in SbF_5, blue solutions were produced within minutes, the absorption peak at about 587 nm indicating the presence of that cation. On standing for periods of one week or more the 587 nm peak decreased in intensity with concomitant growth of an intense peak at 321 nm, characteristic of S_4^{2+}. From these observations it can be deduced that S_8^{2+} stable in 4—5M SbF_5 in HF, was gradually oxidized to S_4^{2+} by SbF_5. This was confirmed by reacting S_8 and SF_4 in 0.5M SbF_5 in HF in the appropriate proportions to generate S_8^{2+}. No significant amount of S_4^{2+} was produced on standing. Here the Sb^V is present essentially as SbF_6^-, a much weaker oxidant than the free SbF_5 which would be present in 4—5M SbF_5 in HF.

When S_8 was reacted in SbF_5–HF with SF_4, present in excess of the amount required to produce S_4^{2+}, a blue solution developed within 5 minutes. Addition

---

[28] R. C. Burns, R. J. Gillespie, and J. F. Sawyer, *Inorg. Chem.*, 1980, **19**, 1423.

of more SF_4 caused the formation of a pale yellow-green solution and a colourless crystalline solid. The solution gave an intense absorption peak at 322 nm (S_4^{2+}) and a very weak broad peak at approximately 580 nm, indicating a small amount of S_8^{2+}. The crystalline solid was washed twice with SbF_5–HF and then partially dissolved in SbF_5–HF. The only species in solution for which there was spectroscopic evidence was S_4^{2+}.

(ii) *In Melts.* There is very little definitive work on isolation of polyatomic cations of sulphur from molten salts or on characterization of these cations in melts. With their various co-workers Bjerrum[29,30] and Mamantov[31] have adduced spectroscopic and electrochemical evidence in systems that they describe as very complex for the formation in the acidic eutectic melt (63% $AlCl_3$—37% NaCl) of sulphur cations S_2^{2+}, S_4^{2+}, S_8^{2+}, and S_{16}^{2+}—the latter probably postulated on the basis of the earlier report of this species in HSO_3F from the Gillespie group. Towards the end of this review it will be pointed out that, whereas unusual cationic species are stabilized in highly acidic media, anionic species are stabilized in basic media. In this context, the report[32] that the stable sulphur-containing species in basic melts are anionic (S^{2-}) is significant.

B. Selenium Cations.—(i) *In Protonic Solvents.* Stable selenium cations can be generated at much lower acidities than the corresponding sulphur cations. Gillespie and Passmore have set out the conditions governing the stability of selenium cations in protonic superacidic media.[33] Cryoscopic and conductometric evidence has been used to show that the appropriate stoicheiometries of Se and $S_2O_6F_2$ will produce Se_8^{2+} and Se_4^{2+} in HSO_3F, which is basic to the extent that it contains SO_3F^- as the reduction product of $S_2O_6F_2$. Obviously Se_4^{2+} which is stable in slightly basic HSO_3F can give, on reduction with Se, a cation Se_8^{2+} with a lower ratio of charge-to-element in the same medium, although, of course, it would be stable in a medium which was even more basic. Further, they report that Se can be oxidized by H_2SO_4 at 50—60 °C to Se_8^{2+}. This cation, stable in H_2SO_4 which is basic because of HSO_4^- produced in the redox reaction, can be oxidized by SeO_2 in that medium to Se_4^{2+}. In summary Se_8^{2+} and Se_4^{2+} are both stable in slightly basic HSO_3F and in the much more basic medium H_2SO_4.

(ii) *In Melts and other Non-protonic Media.* Investigation of selenium-containing species dissolved in melts is even more sketchy than for the corresponding sulphur case. Mamantov and Osteryoung[34] report that oxidation of selenium in acidic melts occurs at a potential ~0.1V less positive than that of sulphur and that, in basic melts, the species are anionic.

$Se_8(AlCl_4)_2$ and $Se_4(AlCl_4)_2$ have been prepared in neutral melts (*i.e.* those in

---

[29] N. J. Bjerrum, 'Characterization of Solutes in Non Aqueous Solvents', ed. G. Mamantov, Plenum Press, New York, 1978, pp. 251–71.

[30] R. Fehrmann, N. J. Bjerrum, and F. W. Poulsen, *Inorg. Chem.*, 1978, **17**, 1195.

[31] R. Marassi, G. Mamantov, M. Matsunaga, S. E. Springer, and J. P. Wiaux, *J. Electrochem. Soc.*, 1979, **126**, 231.

[32] G. Mamantov and R. A. Osteryoung, Ref. 29, p. 230.

[33] (*a*) Ref. 3, pp. 68–69. (*b*) Ref. 4, p. 477.

[34] G. Mamantov and R. A. Osteryoung, Ref. 29, p. 231.

which the ratio $Cl^-:AlCl_3$ is unity) by fusing appropriate stoicheiometric proportions of Se, $SeCl_4$, and $AlCl_3$ and the structures of the compounds have been determined.[35] $Se_8(AlCl_4)_2$ is reported[36] to disproportionate in SO_2 to $Se_{10}(AlCl_4)_2$ and compounds such as Se_2Cl_2. Both $Se_{10}(AsF_6)_2$ and $Se_{10}(SbF_6)_2$ were prepared[36] in SO_2 by oxidizing Se with AsF_5 or SbF_5, the pentafluorides forming the weakly basic AsF_6^- and SbF_6^- anions. Also Se and $Se_8(AsF_6)_2$ in SO_2 in the ratio 2:1 gave $Se_{10}(AsF_6)_2$. In this work the crystal structure of Se_{10}^{2+} was determined. The stability of $Se_8(AsF_6)_2$ in SO_2 and the disproportionation of $Se_8(AlCl_4)_2$ in the same solvent suggest that AsF_6^- is more weakly basic than $AlCl_4^-$, at least in liquid SO_2.

Another significant point from the acid–base aspect is that these authors[36] reported that the Se_{10}^{2+} which they had produced was stable in 95.5% H_2SO_4 but was oxidized fairly rapidly to Se_8^{2+} in the more acidic medium 100% H_2SO_4.

C. Tellurium Cations.—(i) *In Protonic Solvents.* Treatment of Te with H_2SO_4, weak oleums, and HSO_3F gave rise to red solutions and the evolution of SO_2, suggesting reduction of the solvent with corresponding oxidation of Te to Te_4^{2+}.[5] The u.v.–visible spectra of the red solutions were identical with those in $AlCl_3$ melts where reaction stoicheiometry indicated the presence of Te_4^{2+} (see below) and gave similar spectra to the previously recorded Raman spectra for Se_4^{2+}. In stronger oleums (*ca.* 45%), the solution changed colour from red to yellow-orange. Increase in SO_3 concentration was both increasing the acidity of the medium and providing stronger oxidizing conditions to produce Te_6^{4+}. This same colour change occurred when $S_2O_6F_2$ and $S_2O_8^{2-}$ were used to oxidize Te_4^{2+} in the acidic solvents HSO_3F and H_2SO_4. $S_2O_8^{2-}$ as an oxidant in H_2SO_4 is reduced initially to SO_4^{2-}, an entity too basic to exist in H_2SO_4. It is protonated to HSO_4^-, *i.e.* one mole of $S_2O_8^{2-}$ as oxidant in H_2SO_4 would produce four moles of the base HSO_4^-. Te_6^{4+}, formed by oxidation, was observed to disproportionate with increasing time and temperature in 100% H_2SO_4.

(ii) *In Non-protonic Media.* From the solvent SO_2, Te oxidized with $S_2O_6F_2$, SbF_5, or AsF_5 gave Te_4^{2+} associated with the very weakly basic anions SO_3F^-, $Sb_2F_{11}^-$, and AsF_6^-.[5] In appropriate reacting proportions, Te was reported[5] to react with AsF_5 in SO_2 to produce a residue 'Te_3AsF_6', considered more likely to be $Te_6^{2+}(AsF_6^-)_2$. Later Gillespie and co-workers demonstrated through structural determination the existence of a trigonal prismatic cation Te_6^{4+} in the compounds $Te_6(AsF_6)_4{\cdot}2AsF_3$ and $Te_6(AsF_6)_4{\cdot}2SO_2$ which were isolated from the solvents AsF_3 and SO_3.[37] Their observations on the relative stabilities of Te_6^{4+} and Te_4^{2+} in SO_2, AsF_3, and in oleums are discussed in more detail in the next section.

Bjerrum and Smith[38] reported purple melts resulting from dissolving Te and $TeCl_4$ in the 63%–37% $AlCl_3$–NaCl eutectic melt and obtained a dark purple solid

---

[35] R. K. McMullan, D. J. Prince, and J. D. Corbett, *Inorg. Chem.*, 1971, **10**, 1749.

[36] R. C. Burns, W.-L. Chan, R. J. Gillespie, W.-C. Luk, J. F. Sawyer, and D. R. Slim, *Inorg. Chem.*, 1980, **19**, 1432.

[37] R. C. Burns, R. J. Gillespie, W.-C. Luk, and D. R. Slim, *Inorg. Chem.*, 1979, **18**, 3086.

[38] N. J. Bjerrum and G. P. Smith, *J. Am. Chem. Soc.*, 1968, **90**, 4472.

Table 2 *Stability of homopolyatomic cations of chalcogens in protonic solvents*

General Formula	X_6^{4+}	X_4^{2+}	X_8^{2+}	$X_n^{2+}(n > 8)$
Oxidation State	0.67	0.5	0.25	<0.25
Tellurium	Te_6^{4+} Stable in oleums $>30\%$ in SO_3 $(H_0 \approx -13.76)^a$	Te_4^{2+} Stable in H_2SO_4–HSO_4^- $(H_0 \approx -11)$	—	—
Selenium	—	Se_4^{2+} Stable in 100% H_2SO_4 $(H_0 \approx -11.9)$	Se_8^{2+} Stable in 100% H_2SO_4 $(H_0 \approx -11.9)$	Se_{10}^{2+} Stable in 95.5% H_2SO_4 $(H_0 \approx -10)$
Sulphur	—	(i) S_4^{2+} Stable in oleums $>40\%$ in SO_3 $(H_0 \approx -14.1)$ (ii) Stable in HSO_3F–$SbF_5{}^b$ $(H_0 \approx -18)$	S_8^{2+} Stable in oleums $>15\%$ in SO_3 $(H_0 \approx -13.2)$ Marginally stable in HSO_3F–SO_3F^- $(H_0 \approx -13.8)$	S_{19}^{2+} Stable in oleums $>5\%$ in SO_3 $(H_0 \approx -12.7)$ Stable in HSO_3F–SO_3F^- $(H_0 \approx -13.8)$

[a] Approximate values of Hammett acidity functions calculated on basis of footnote (*b*) of Table 1. [b] For validity of comparisons, most media cited in Table 2 are H_2SO_4 containing either excess SO_3 (oleums) or the base HSO_4^- as a product of reaction, or H_2O in the case of 95.5% H_2SO_4. In a different medium, as for sulphur cations in HSO_3F, the general trends are the same, but absolute H_0 values may vary depending on chemical interaction with the base of the solvent system (see text).

by reacting Te, $TeCl_4$, and $AlCl_3$ in the mole ratio 7:1:4. They proposed formation of a cation Te_{2n}^{n+}, considered most likely to be Te_4^{2+}. By reacting appropriate proportions of Te, $TeCl_4$, and $AlCl_3$, Corbett and co-workers[39] isolated the solids $Te_4(AlCl_4)_2$ and $Te_4(Al_2Cl_7)_2$ and determined their structures. Te_4^{2+} is square planar with $Al_2Cl_7^-$ bidentate to the square cation.

Te_4^{2+} is stabilized by the acid $AlCl_3$ which reacts with the base Cl^- to form the anions. In the presence of excess of the base Cl^-, Te_4^{2+} disproportionates to Te and the covalent $TeCl_4$:

$$7Te + TeCl_4 \underset{Cl^-}{\overset{AlCl_3}{\rightleftharpoons}} 2Te_4^{2+} + 4Cl^-$$

D. Relative Stabilities of Group VI Cations.—Table 2 shows that the cation Te_6^{4+} with a relatively high charge per tellurium atom has no counterpart in selenium or sulphur chemistry. Cations of low formal charge (*i.e.* below 0.5) per tellurium atom have not been isolated. In proceeding through Se to S, cations of progressively lower charge per atom can be prepared relatively easily, the lowest reported being in Se_{10}^{2+} and S_{19}^{2+} respectively.

These same trends are observed in the acidities of the protonic media necessary to provide stable solutions of cations of S, Se, and Te. For all three elements data in

---

[39] T. W. Couch, D. A. Lokken, and J. D. Corbett, *Inorg. Chem.*, 1972, **11**, 357.

Table 2 are given for H_2SO_4-based solvent systems, *i.e.* pure H_2SO_4 itself or the solvent made acidic with SO_3, or made slightly basic with HSO_4^- produced during oxidation of an element to its cation or made more basic with H_2O which disturbs the self-ionization equilibria of the solvent to generate large concentrations of HSO_4^-. Table 2 shows an obvious correlation between the formal oxidation state of an element in its cations and the acidity of the H_2SO_4-based medium in which those cations are stable.

Additionally, for sulphur cations, H_0 values are given for stable species in HSO_3F-based media. The correlation between charge-per-sulphur atom and acidity follows the same trend, but the absolute values of H_0 at which particular cations are stabilized differ for each solvent system. It should be recalled that a cation is destabilized by a disproportionation reaction which, in its final and simplest form, will lead to formation of both the element itself and of a *covalent* compound formed between the base of the solvent system and the element concerned, with the element now in a higher oxidation state than in the original cation. In comparing the two solvent systems, it should be noted that SO_3F^- is more electronegative than HSO_4^- and will form covalent fluorosulphato compounds more readily than bisulphato compounds are formed. Therefore a higher acidity, *i.e.* a lower availability of base, is required to stabilize a sulphur cation in the presence of SO_3F^- than with HSO_4^- present.

Preliminary work in HF at Melbourne[18] shows that the H_0 values required for stabilization of S_8^{2+} and S_4^{2+} in HF are much more negative than those required, in turn, in media based on HSO_3F and on H_2SO_4. A critical evaluation of the stability of chalcogen cations in superacid media based on the solvents H_2SO_4, HSO_3F, and HF provides a sharp warning against adoption of a simple-minded rationalization based only on values of H_0 for the different media. Differing chemical interactions during disproportionations—*i.e.* bond energies for the chalcogen concerned bound to the different bases of each system—must also be taken into account.

In summary, no polyatomic cation of sulphur is stable in 100% H_2SO_4. Cations of 'high' charge disproportionate through S_8^{2+} and larger cations S_n^{2+} to S_8 and SO_2 ultimately. S_8^{2+} is stable in HSO_3F and S_4^{2+} can be produced in HF–SbF_5. By comparison, even Se_4^{2+}, with a 'high' charge-to-element ratio, is stable to disproportionation in 100% H_2SO_4 as is Se_8^{2+} and therefore, of course, both are stable in the more acidic HSO_3F. Se_{10}^{2+}, with a smaller charge-to-selenium ratio is stable in 95.5% H_2SO_4. Te_4^{2+} with a high charge-to-atom ratio has been reported as capable of existence in 98% H_2SO_4, a fairly basic medium in terms of superacidity studies. In their paper on the structure of the Te_6^{4+} cation[37] the Gillespie group report that Te_4^{2+} is 'oxidized' to Te_6^{4+} by increasing the SO_3 content of oleums. The role of SO_3 in increasing the acidity of the medium is probably much more important than its role as an oxidant—even in relatively dilute oleums there should be sufficient SO_3 to act solely as an oxidant. This matter, and much of what follows in this section, will be dealt with in detail in the concluding section of this review. They say that Te_4^{2+} and Te_6^{4+} can exist in 100% H_2SO_4 but that a precipitate of TeO_2 is formed on prolonged standing, a process that is accelerated by heating. This observed reaction scheme probably begins with a disproportionation of the cations to Te and TeO_2 in this medium which is not strongly acidic. The Te, as formed, would be progressively re-oxidized by the solvent to cations of fractional formal charge. Elemental Te, its cations, and TeO_2 are probably in equilibrium at this acidity, the position of equilibrium being disturbed as TeO_2 is formed. They report that in the solvents SO_2 and AsF_3, Te is oxidized initially to Te_4^{2+} by SbF_5 and AsF_5. They say that further oxidation to Te_6^{4+} occurs but that Te_6^{4+} is in equilibrium with Te_4^{2+} 'even if a very large excess of oxidant is used'. Both sets of observations are consistent with an interpretation that Te_6^{4+} can be stabilized as the predominant cationic species in strong oleums but disproportionates, in part at least, to Te_4^{2+} in the weakly basic solvents SO_2 and AsF_3.

Much of the electrochemical work on oxidation of sulphur, selenium, and tellurium in acidic melts[29] is difficult to interpret, partly because of the intrinsic difficulty of the experimental procedures in melts, but also because the effect of an increasing voltage ramp is to produce in turn species like 'S_{16}^{2+}', S_8^{2+}, S_4^{2+}, (S_2^{2+}), S^{II}, probably as SCl_2, and S^{IV}, probably as SCl_3^+. Similar species have been proposed tentatively for Se and Te, although oxidation occurs at lower potentials. Under these conditions the applied potential can produce at the sensing electrode small quantities of species which would not necessarily be stable at the acidity or basicity of the bulk of the melt.

Comparison of the elements of Groups VI and VII shows that, in a general sense, the polychalcogen cations are easier to isolate at lower acidities than polyhalogen cations. Comparing the cations of the lightest elements of the two groups (other than O_2 and F_2) all the known S_n^{m+} cations can be synthesized in protonic solvents, whereas Cl_2^+ has not been prepared and Cl_3^+ exists only at low temperatures in the absence of solvent, which would provide a source of base. All the known cations of selenium can be isolated in 100% H_2SO_4, whereas Br_3^+ and Br_2^+ need, respectively, as solvents HSO_3F and HSO_3F–SO_3–SbF_5. While tellurium cations are stable in media more basic than 100% H_2SO_4, I_2^+, and I_4^{2+} require oleums, HSO_3F, or HF to prevent disproportionation.

4 Homopolyatomic Cations of Metallic Elements

For metallic elements, homopolyatomic anions, frequently referred to as Zintl ions are much better known and structurally characterized than cluster cations and will be discussed briefly in an appropriate context towards the end of this review. The evidence for discrete polyatomic cations of metals is rather fragmentary. With the exception of reliable characterization in the solvents SO_2 and AsF_3 of cations of mercury and some work in the same solvents on cations of bismuth, the existence of most of the polyatomic cations of metals has been inferred from phase studies of melts or on the basis of species isolated from melts.

There will be no attempt in this review to give an exhaustive account of all the polyatomic metallic cations reported. As in earlier sections, reviews will be used as source material rather than original individual papers. It will be considered sufficient to demonstrate with several representative examples that the cationic species are produced and are stable under conditions similar to those which have been shown to be required for stabilization of polyatomic cations of elements of

Groups VI and VII—namely highly acidic media or the virtual absence of bases with which they can react. Only Hg_2^{2+} can exist in aqueous solution and it disproportionates as the basicity of the medium is increased, as shown below.

In one very important way, the polyatomic cations of metals differ from those of non-metals in that *lower* formal oxidation states are stabilized with increasing acidity of the medium whereas, with the non-metallic elements of Groups VI and VII, *higher* formal oxidation states, *i.e.* higher charge-to-element ratios, were shown to be stabilized by oxidation in progressively more acidic media. Thus increase in acidity allowed formation of I_2^+ at the expense of I_3^+ and of Br_2^+ rather than Br_3^+. S_{19}^{2+}, S_8^{2+}, and S_4^+ could be formed by oxidation in increasingly acidic solvents. We shall see that Hg_2^{2+}, stable in the basic solvent water, can be reduced to Hg_3^{2+}, which is marginally stable in HSO_3F, and that Hg_4^{2+} can be formed only in equilibrium with Hg_3^{2+} in this medium.

This is consistent with the general chemistry of non-metals and metals. Charged entities containing non-metals are usually anionic even, in some cases, when existing as complex species, *e.g.* I_3^-. They occur in a wide range of compounds in formal, high positive oxidation states, but as complexes, *e.g.* IF_6^- and IO_4^-. This review has shown that 'forcing' conditions—very high acidity or virtual absence of basic species—are necessary to form cationic species of non-metals, and the more acidic the medium the higher the charge-to-element ratio. On the other hand, non-complexed metal cations are in 'normal' oxidation states +1 and more frequently +2 and +3. For stable ions of metals in high oxidation states complexation must occur, as in UO_2^{2+}, MnO_4^-, or AuF_6^-. Metals can exist in very low formal oxidation states in complexes such as the carbonyls; but special conditions are required to stabilize metals in low oxidation states *as simple solvated cations*. This concept will be developed further in the last major section of this review on monatomic cations of transition metals in very low oxidation states.

A. Mercury Cations.—The familiar cation Hg_2^{2+} has been known since 1898; its Raman spectrum was observed in aqueous $Hg_2(NO_3)_2$ solution in 1934. Justifiably, expecially in the context of this review, its stability in the basic solvent H_2O has always been regarded as anomalous. However, it is consistent with the principles established in this review that rendering of the aqueous medium basic with NH_3 or OH^- leads to disproportionation of Hg_2^{2+} to Hg and non-ionic compounds of Hg^{II}.

In their review[40] Cutforth, Gillespie, and Ummat record that the first definite evidence for the cation Hg_3^{2+} was obtained in the absence of base when Mamantov and co-workers dissolved Hg in a melt of $HgCl_2$ and $AlCl_3$ to give a yellow solution with an absorption band at 325 nm. Polarographic reduction of Hg^{2+} in acidic $AlCl_3$–NaCl gave three waves consistent with reduction in turn to Hg_2^{2+}, Hg_3^{2+}, and Hg. By heating a mixture of Hg, $HgCl_2$, and $AlCl_3$, and removing excess Hg and $AlCl_3$ by evaporation, they obtained a yellow residue $Hg_3(AlCl_4)_2$ and determined the structure of the almost linear cation Hg_3^{2+}.

Gillespie and co-workers[40] oxidized Hg with AsF_5 and with SbF_5 in solution

---

[40] B. D. Cutforth, R. J. Gillespie, and P. K. Ummat, *Rev. Chim. Minérale*, 1976, **13**, 119.

in SO_2 and obtained yellow solids $Hg_3(AsF_6)_2$ and $Hg_3(Sb_2F_{11})_2$, stable in the presence of the solvent and of AsF_3 and SbF_3 (the products of reduction of AsF_5 and SbF_5), all three compounds SO_2, AsF_3, and SbF_3 being very weakly basic. Solutions of these solids in HSO_3F gave the characteristic absorption at 325 nm. It is highly significant in the context of this present review that, in HSO_3F, the compounds were reported to form Hg^{II} slowly. Hg would presumably have been formed in the disproportionation; but it had been reported as early as 1932 that Hg dissolves very slowly in HSO_3F, presumably by oxidation. Therefore Hg from the disproportionation would be oxidized to polyatomic cations which would in turn disproportionate. These authors also report that Hg_3^{2+} disproportionates rapidly and completely to Hg and Hg^{II} in the presence of 'water and other basic substances'.

Oxidative reaction of Hg with AsF_5 in the ratio 4:3, designed to yield $Hg_4(AsF_6)_2$ and the reduction product AsF_3, gave a mixture of yellow crystals of $Hg_3(AsF_6)_2$ and red-black $Hg_4(AsF_6)_2$, the crystal structure of which was determined.[40] Hg_4^{2+} is unstable in the weakly basic solvent SO_2, disproportionating to Hg_3^{2+} and the formal species $Hg^{0.35+}$ in the compound $Hg_{2.86}AsF_6$. In their review[40] Gillespie and colleagues discuss their preparation and structural determination of this very unusual and interesting compound which is based on discrete close-packed AsF_6^- anions with infinite cationic chains of Hg atoms running through channels in the solid, the average charge per Hg atom being 0.35.

In summary, the dimeric cation Hg_2^{2+} is unique in being stable in aqueous solution, although it disproportionates to Hg and non-ionic Hg^{II} compounds when bases of the aqueous system are added. Hg_3^{2+} can be prepared relatively easily but disproportionates slowly even in the very acidic solvent HSO_3F. Hg_4^{2+} disproportionates to Hg_3^{2+} and $Hg^{0.35+}$ under the attempted conditions of preparation, *i.e.* the presence of the weak base AsF_3 or in solution in the weakly basic solvent SO_2. It is interesting to speculate that Hg_4^{2+} may be isolable from very acidic media such as the solvents HSO_3F or HF to which appropriate Lewis acids are added.

B. Cadmium Cations.—Cutforth, Gillespie, and Ummat[40] quote the well-established fact that, in many experiments, metallic cadmium has been shown to dissolve in molten $CdCl_2$ to produce intensely coloured, even black, solutions. Explanations of this coloration have been based on the effect of charge-transfer bands associated with species containing both Cd^I and Cd^{II} joined by halogen bridges. They report that Corbett and co-workers showed that this intense coloration was discharged by the addition of $AlCl_3$. Corbett reported[41] that reduction of $CdCl_2$ by Cd to Cd_2^{2+} was at a maximum when the ratio $AlCl_3:CdCl_2$ in the melt was approximately 3:1 *i.e.* as the melt is made sufficiently acidic. Corbett was able to isolate $Cd_2(AlCl_4)_2$ from such melts. Cutforth *et al.* say that 'it seems that the charge-transfer complexes between Cd^I and Cd^{II}, which are held together by a chlorine bridge, are destroyed when chloride is replaced by the much less basic $AlCl_4^-$ ion'. It seems much simpler to state, as Corbett implied, that

---

[41] J. D. Corbett, W. J. Burkhard, and L. F. Druding, *J. Am. Chem. Soc.*, 1961, **83**, 76.

discrete Cd_2^{2+} ions are formed at the expense of all other formally positively charged species when the system is made sufficiently acidic with $AlCl_3$ under reducing conditions.

Corbett postulated weak Cd–Cd bonding in Cd_2^{2+} on the basis of a strong, Raman band for the melt at 183 cm^{-1} which can be related to a similar Raman band at 173 cm^{-1} in the solid compound with the formula $CdAlCl_4$. Corbett himself[41] reports absorptions at 289 and 218 nm in the electronic spectrum for Cd_2^{2+} in $NaAlCl_4$. He says that, when these melts are made 60% or more in Cl^-, the spectra are characteristic of those of Cd^{2+}–Cl^- systems. All of these observations are consistent with the reversible equilibrium:

$$Cd + CdCl_2 \underset{Cl^-}{\overset{AlCl_3}{\rightleftharpoons}} Cd_2^{2+} + 2Cl^-$$

It is not surprising that '$CdAlCl_4$' gave a dark precipitate of metallic Cd on contact with basic solvents such as water, dioxane, and ethanol.

In this reviewer's opinion, Corbett complicates the discussion of stable compounds containing polyatomic cations by concerning himself too much with lattice energies of Cd_2^{2+} or other polyatomic cations in conjunction with $AlCl_4^-$ or other anions as the counter-ions[41,42] It seems to be sufficient to postulate the stabilization in acidic melts of polyatomic cations and, additionally, their base-induced disproportionation. Their isolation is a separate issue. In the conclusion of this review it will be suggested that there are anionic types which are probably superior to $AlCl_4^-$ for producing stable solids containing polyatomic cations such as Cd_2^{2+}.

Cutforth, Gillespie, and Ummat[40] recount attempts to isolate Cd_2^{2+} and more complex homopolyatomic cations of Cd in media other than conventional melts. They report that Cd, interacting with AsF_5 or SbF_5 dissolved in AsF_3, does not form $Cd_2(AsF_6)_2$ but yields $Cd(AsF_6)_2$ and a grey compound. Presumably Cd_2^{2+} disproportionates in the weakly basic solvent. They say that the grey compound was formed by reaction of equimolar amounts of Cd and AsF_5 in AsF_3 at room temperature and had the formula $Cd_3(AsF_6)_2$. Not surprisingly it gave a white product and metallic Cd on reaction with atmospheric moisture. Excess Cd and AsF_5 in AsF_3 gave $Cd_4(AsF_6)_2$. They state that relatively sharp Raman bands at 75 cm^{-1} and 112 cm^{-1} may reasonably be assigned to the two symmetrical stretching modes of a symmetrical linear Cd_4^{2+} cation. Understandably, they point out the oddity of Cd_2^{2+} disproportionating in AsF_3 whereas $Cd_3(AsF_6)_2$ [and $Cd_4(AsF_6)_2$] can be isolated and suggest that this might be due to the insolubility of $Cd_3(AsF_6)_2$ in AsF_3.

C. Bismuth Cations.—The most systematically characterized polyatomic cations of metals appear to be those of Hg and Cd, discussed above. Earliest identifications were from work in acidic melts. Later Gillespie and his colleagues extended the range of known cations for each element by synthesis of compounds in the weakly

---

[42] J. D. Corbett, 'Progress in Inorganic Chemistry', Vol. 21, ed. S. J. Lippard, John Wiley, New York, 1976, pp. 129 158.

basic solvents SO_2 and AsF_3 and demonstrated some limits of stability of the complex cations in protonic acids.

Virtually all of the work on polyatomic cations of bismuth has been done in melts, initially simply by studying the dissolution of metallic Bi in $BiCl_3$. Later Bjerrum and Smith[43,44] adopted a procedure which might well have been expected to prove more profitable than was the case—they dissolved stoicheiometric amounts of Bi and $BiCl_3$ in excess of the acidic eutectics $AlCl_3$–NaCl and $ZnCl_2$–NaCl and obtained evidence for the cations Bi^+, Bi_5^{3+}, and Bi_8^{2+}.

Corbett worked from stoicheiometric mixtures, *e.g.* Bi added to $BiCl_3{\cdot}3AlCl_3$. These neutral melts gave crystalline compounds reported as $Bi_5(AlCl_4)_3$ and Bi_4AlCl_4.[45] In a general review on homopolyatomic cations of metals[42] Corbett reports isolation from Bi–$BiCl_3$ melts of the compound believed from earlier studies to have been BiCl. This in fact was $Bi_{12}Cl_{14}$ and was shown by *X*-ray structural analysis to be the ionic aggregate $Bi_9^{5+}(Bi^{III}Cl_5^{2-})_2(Bi_2^{III}Cl_8^{2-})_{0.5}$. He states, very significantly, in this review that, while small additions of KCl to the melt increased the yield—an effect that he puts down to effective production of chlorobismuthate(III) anions—larger additions caused 'the amount of reduction possible with excess metal to diminish rapidly because an excess of the $BiCl_3$ is converted into complex anions'. It seems much more likely that polybismuth cations of fractional charge disproportionated with increasing basicity of the medium. Later Corbett isolated the compound $Bi^+Bi_9^{5+}(HfCl_6^{2-})_3$, which contains the tricapped trigonal prismatic cluster cation, by reducing a 3:2 mixture of $HfCl_4$ and $BiCl_3$ with Bi.[46] This is an acidic melt which is provided with a good precipitating anion, the octahedral $HfCl_6^{2-}$—a favourable combination of reactants which will be discussed in more detail towards the conclusion of this review.

There is little work other than in melts. Burns, Gillespie, and Luk investigated the possible oxidation of Bi by PF_5, AsF_5, SbF_5, $SbCl_5$, HSO_3F, and HSO_3Cl in the solvent SO_2.[47] Only the pentafluorides oxidized Bi, firstly to Bi_8^{2+}, then to Bi_5^{3+}. AsF_5, quite strong as both oxidant and Lewis acid, yielded the compound $Bi_5(AsF_6)_3{\cdot}2SO_2$.

D. Polyatomic Cations of Other Metals.—While many metallic polyatomic cations other than those given above have been reported, the evidence for their existence is sketchy and fragmentary. It usually arises from simple studies of solubilities of metals in their halides or other salts with resultant mutual oxidation and reduction—much less frequently from electrochemical or spectroscopic (including e.s.r.) studies. Corbett[42] reports that the reduction of $SbCl_3$ by Sb is increased dramatically on addition of $AlCl_3$. Gillespie and Passmore make brief reference in a review on polycations of Group VI elements[48] to Zn_2^{2+}, Pb_2^{2+}, Mg_2^{2+}, Ca_2^{2+}, Sr_2^{2+},

---

[43] N. J. Bjerrum, C. R. Boston, and G. P. Smith, *Inorg. Chem.*, 1967, **6**, 1162.
[44] N. J. Bjerrum and G. P. Smith, *Inorg. Chem.*, 1967, **6**, 1968.
[45] J. D. Corbett, *Inorg. Chem.*, 1968, **7**, 198.
[46] R. M. Friedman and J. D. Corbett, *Inorg. Chem.*, 1973, **12**, 1134.
[47] R. C. Burns, R. J. Gillespie, and W.-C. Luk, *Inorg. Chem.*, 1978, **17**, 3596.
[48] R. J. Gillespie and J. Passmore, *Acc. Chem. Res.*, 1971, **4**, 413.

Ba_2^{2+}, Ag_2^+, Ag_4^+, and Ag_4^{3+}. Many of these are proposed on the basis of reduction of salts of metals by the metals themselves. Again it is significant that often a Lewis acid is reported as markedly increasing the reduction, *e.g.* that of $ZnCl_2$ by Zn when $CeCl_3$ is added.[49]

E. Summary.—Regardless of the limited evidence that is available for the existence of individual homopolyatomic cations of metallic elements, there are some common general features, well illustrated for Hg, Cd, and Bi but less so for many others. In melts, the existence of these cations is favoured as the melt is made more acidic and, where the evidence exists, inhibited as the melt is made more basic. The Gillespie group have used their experimental approach effectively to produce cations, in the case of Hg and Cd, which have not been postulated from melt studies. They used an oxidant, *e.g.* a pentafluoride, which also produces a very weakly basic fluoro anion. The medium for their studies was usually a very weakly basic solvent such as AsF_3 or SO_2.

5 Monatomic Cations of Transition Metals in Unusually Low Oxidation States

Transition metals can exist in extremely low formal oxidation states in compounds such as the carbonyls and their derivatives. However in this review we are concerned only with discrete solvated cations, in solution, and containing only the metal (or non-metal) regardless of whether the cation is polyatomic or monatomic. 'Normal' monatomic cations are considered as those which are stable in aqueous solution, even though the solution conditions may need to be adjusted in rather specific ways, *e.g.* the pH may need to be quite low and all but the weakest complexing ligands may need to be absent. Cations in oxidation states which would reduce water or would disproportionate in aqueous solution are to be regarded as being in unusually low oxidation states. U^{3+} and Ti^{2+} will be considered in detail and others such as V^{2+}, Cr^{2+}, Zr^{3+}, and Sm^{2+} will be referred to briefly.

A. The Uranium(III) Cation.—(i) *In Acidic Hydrogen Fluoride.* Uranium(III) compounds reduce water to hydrogen, being oxidized to uranium(IV) species. The spectrum of ${U_{aq}}^{3+}$ has been recorded in a solution which contained UO_2^{2+} initially and in which U^{3+} was being produced by continuous cathodic reduction. When the reducing potential was no longer being applied, ${U_{aq}}^{3+}$ would have reduced H_2O and been oxidized to U^{IV}.

The first stable solution containing U^{3+} in a simple protonic solvent was produced by treating metallic U, washed free of all surface oxide by preliminary treatment with acidic HF, with anhydrous HF saturated with BF_3, a weak but non-oxidizing Lewis acid of the HF solvent system.[50] Protons, represented somewhat ideally as H_2F^+, were reduced by U to H_2. The clear lilac-coloured solution resulting from this reaction was shown to contain U^{3+} by comparison of the u.v.–visible spectrum of the solution with that for the aqueous solution produced cathodically as above.

[49] D. H. Kerridge and S. A. Tariq, *J. Chem. Soc. (A)*, 1967, 1122.

[50] M. Baluka, N. Edelstein, and T. A. O'Donnell, *Inorg. Chem.*, 1981, **20**, 3279.

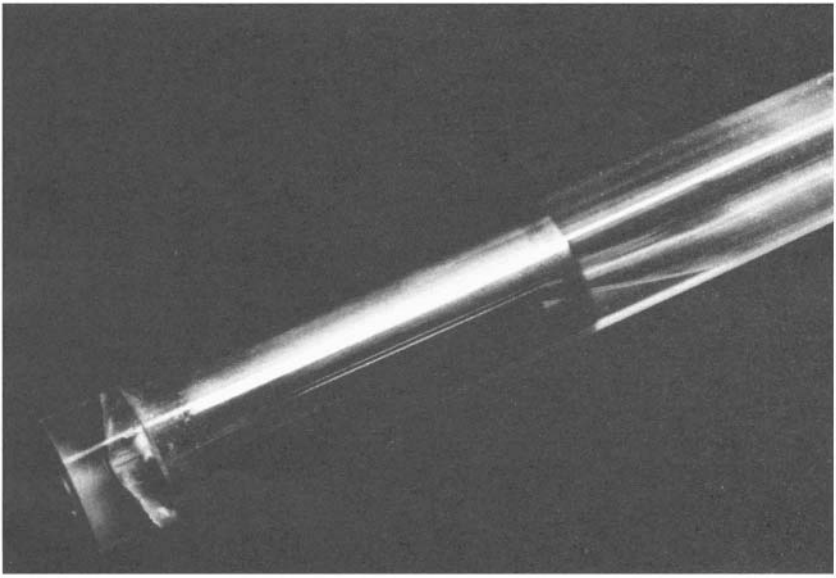


Figure 1 *Mirror of metallic uranium on the walls of a 'synthetic sapphire' reaction tube. This resulted from the disproportionation occurring when a solution of* U^{III} *in* HF, *the acidity of which had been increased by* BF_3, *was made basic with excess fluoride*

Subsequently, when excess of a solution of NaF in HF was added to the solution of U^{3+} in $HF-BF_3$, a green precipitate of UF_4 was formed and the supernatant solution was colourless, *i.e.* contained no U species. The green UF_4 was heavily 'flecked' with black particles, believed to be metallic uranium. Under favourable experimental conditions some of the metallic uranium was deposited as a reasonably uniform bronze-coloured mirror on the walls of the reaction vessel, which was constructed from so-called 'synthetic sapphire', *i.e.* crystalline alumina.[51] This mirror formation can be seen in Figure 1. The reaction is a simple base-induced disproportionation:

$$4U^{3+} + 12F^- \longrightarrow U + 3UF_4$$

Although somewhat simpler, this disproportionation is similar to those set out earlier in this review for the polyatomic non-metal cations of elements of Group VI and VII and for the polyatomic cations of metals such as Hg and Cd.

The disproportionation as the U^{3+} solution is made more basic demonstrates the necessity for superacidic medium conditions for the generation and stabilization of U^{3+}. Lewis acids stronger than BF_3, *e.g.* SbF_5 and AsF_5, would produce even more favourable conditions from the stand-point of acidity for the

---

[51] L. Dawkins, B.Sc. (Honours) Report, University of Melbourne, 1984.

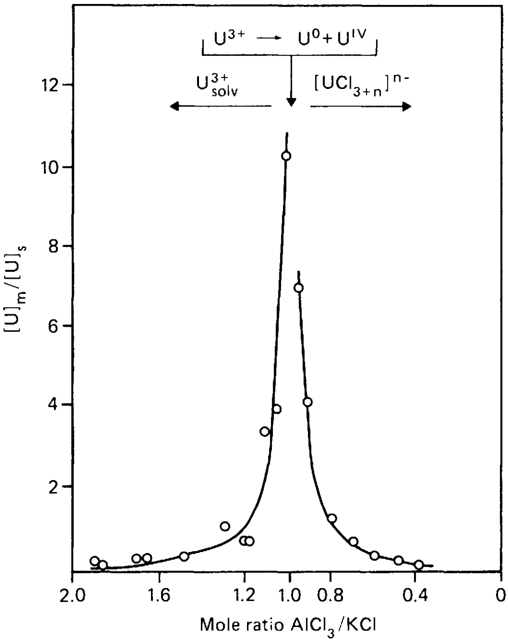


Figure 2 *Acid–base dependence of the formation of metallic uranium from uranium*(III) *in chloro-aluminate melts*

generation of U^{3+}, were it not for the possible oxidizing properties of these two Lewis acids. AsF_5–HF was used to wash the lumps of metallic U free of any surface oxide, as referred to above, because of the ease and speed with which U reacted with AsF_5–HF. After washing the metal with HF, a clean surface was available for reaction with BF_3–HF and the generation of U^{3+} under non-oxidizing conditions. (ii) *In Melts.* Two papers published in 1963 by J. R. Morrey and co-workers[52,53] set out to interpret the results of experiments in which, it was reported, UCl_3 was produced *in situ* in fused salts contained in sealed tubes and was then reduced by metallic aluminium using an amount of metallic Al comparable with that of the melt in each case. Analysis for uranium in each phase after quenching the immiscible metallic and salt phases was interpreted in terms of the supposed direct reduction by Al of UCl_3. Experiments were carried out over a range of melt basicity and acidity by having the ratio $AlCl_3/KCl$ differ from 0.39 through unity to 2.0 in individual experiments.

Formation of metallic uranium was dramatically greater in the region of the neutral melt (*i.e.* $AlCl_3$: KCl, 1 : 1), as shown in Figure 2 in which the variation in the ratio of concentration of uranium in the metallic phase to that in the salt phase

---

[52] R. H. Moore, J. R. Morrey, and E. E. Voiland, *J. Phys. Chem.*, 1963, **67**, 744.
[53] J. R. Morrey and R. H. Moore, *J. Phys. Chem.*, 1963, **67**, 748.

($[U]_m/[U]_s$) is plotted against melt acidity and basicity, expressed as the ratio $AlCl_3/KCl$. The second of these two papers was directed towards an elucidation of the mechanism of the observed reactions and was devoted to a computer-based analysis of the results using, as the species postulated as being present, chloro-anions of U^{III}, $Al_2Cl_7^-$, $AlCl_4^-$, and Cl^-.

It is much simpler to postulate that in an acidic melt uranium(III) would be present as solvated U^{3+}, that in a basic melt chloro anions of the general type $[UCl_{3+n}]^{n-}$ would predominate, and that each of these species is reasonably resistant to reduction, but that in a near-neutral melt U^{3+} would disproportionate according to the equation:

$$U^{3+} \longrightarrow U^0 + U^{IV}$$

The uranium(IV) formed would probably be present as a chloro-uranate(IV) species. This interpretation would suggest that the high yield of metallic uranium from neutral melts is at least as much a result of disproportionation as it is of direct reduction. The aluminium could reduce U^{IV} formed through disproportionation to U^{III} and cause a cyclic formation of metallic uranium through further disproportionation. This explanation is consistent with the observed disproportionation of U^{3+} in HF solution (above) and with the disproportionation of Ti^{2+} in HF and in melts described in the section below.

The proposal made here that uranium(III) exists in acidic melts as solvated U^{3+} appears very reasonable when another of Morrey's papers[54] is considered. In that work he recorded u.v.–visible spectra of uranium(IV) in many chloride environments. His systems included UCl_6^{2-} itself, UCl_6^{2-} and UCl_4 in chloride (basic) melts, and UCl_4 in the acidic melts $AlCl_3$ and $ZnCl_2$. The spectra in acidic melts were virtually identical with those for the hydrated cation U^{4+} in acidic aqueous solution, whereas in basic (chloride-rich) melts the U^{IV} spectra resembled those of UCl_6^{2-}. As generally accepted and as shown in a comparison of the spectra of actinide cations in H_2O and in HF,[50] the chemical environment has very little effect on the positions and relative intensities of spectral peaks for *f*-transition elements. Therefore it can be postulated that U^{IV} exists in acidic melts predominantly as solvated U^{4+}. It is then a considerably easier postulation that U^{III} would exist in acidic melts as solvated U^{3+}, a cation of lower positive charge. Unfortunately, no spectra for U^{III} in acidic melts appear to be available. Such spectra could be compared with those for the solvated U^{3+} cations in H_2O and in HF.

Considerable support for the mechanism proposed in this review is given by the observation reported by Morrey and co-workers that 'on moving to the $AlCl_3$-rich region the absorption spectrum, typical of UCl_6^{3-} is no longer observed'.[52]

B. The Titanium(II) Cation.—(i) *In Acidic Hydrogen Fluoride.* After it had been shown that U^{3+} could be stabilized in mildly acidic HF, O'Donnell and Schofield

---

[54] J. R. Morrey, *Inorg. Chem.*, 1963, **2**, 163.

set out to generate cations of *d*-transition metals in unusually low oxidation states. Not surprisingly, Cr^{2+} and V^{2+} were shown to exist in $HF–BF_3$, as will be discussed below, but the unexpected feature was that rigorously cleaned metallic Ti reacted with $HF–SbF_5$, not to give a bluish solution of Ti^{3+} as anticipated, but an orange-coloured solution containing Ti^{2+}.[55]

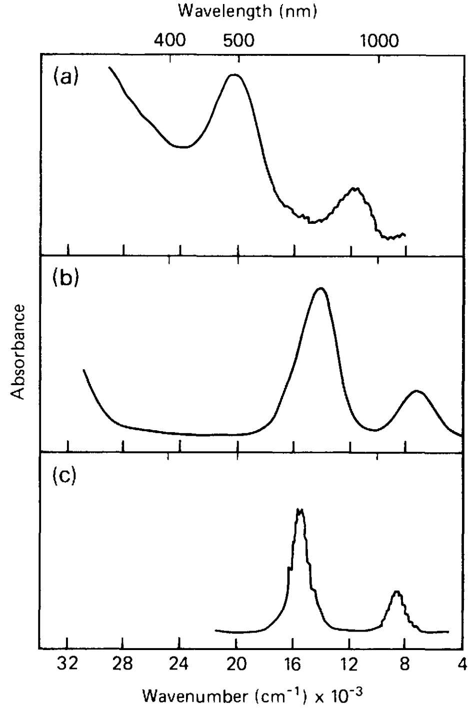


Figure 3 Ti^{II} *(a) in anhydrous* HF *(ref.* 55), *(b) in molten* $AlCl_3$ *at* 500 K *(ref.* 56), *(c) doped* (1%) *into crystalline* NaCl *at* 10 K *(ref.* 57)

Ti^{2+} was shown to be the absorbing species by comparison of its u.v.–visible spectrum reproduced in Figure 3(a) with two other sets of spectra. Øye and Gruen[56] had reported spectra for chlorides of dipositive first row transition metals dissolved in molten $AlCl_3$ at 500 K. Their spectrum for a solution of $TiCl_2$ in $AlCl_3$ is reproduced in Figure 3(b). They postulated hexa-coordination of the Ti^{II}. The presence of Ti^{2+} in anhydrous HF at room temperature as the six-coordinate species $Ti(FH)_6^{2+}$ is supported even more strongly by the comparison of its spectrum with that of Ti^{2+} in a host crystal of NaCl. W. E. Smith and co-workers[57] added stoicheiometric amounts of metallic Ti and $CdCl_2$ at the 1% level to molten

---

[55] C. G. Barraclough, R. W. Cockman, T. A. O'Donnell, and W. S. J. Schofield, *Inorg. Chem.*, 1982, **21**, 2519.

[56] H. A. Øye and D. M. Gruen, *Inorg. Chem.*, 1964, **3**, 836.

[57] D. H. Brown, A. Hunter, and W. E. Smith, *J. Chem. Soc., Dalton Trans.*, 1979, 79.

NaCl. After halogen-exchange, volatile Cd was dispelled from solution and, after crystallization of the NaCl, Ti^{2+} remained 'doped' into the host crystal in which the coordination number for ions is six. The spectrum for this system is given in Figure 3(c).

In preliminary work,[58] Schofield experienced some difficulty in reproducing the conditions for preparation of stable solutions of Ti^{2+}. Frequently she found evidence for oxidation of the Ti^{2+}. Subsequently, Cockman explored the system in detail and determined a narrow 'window' of acidity in which Ti^{2+} was stable in HF–SbF_5 solution.[55] At concentrations of SbF_5 in HF above 3M, Ti^{2+} is oxidized, presumably by free SbF_5, a stronger oxidant in HF solution than SbF_6^-. Below 2M SbF_5, oxidation products of Ti^{2+} were also observed. Very recent work[18] has shown that as an acidic solution containing Ti^{2+} is made basic, Ti^{2+} disproportionates to metallic Ti and Ti^{IV} compounds.

(ii) *In Melts.* Some early electrochemistry of Ti^{II} in $AlCl_3$–NaCl melts[59] had given some general indications that lower oxidation states were more stable in more acidic melts, *i.e.* those with high $AlCl_3$ contents; but the most valuable study in melts for comparison with the observed behaviour of Ti^{II} in acidic HF used spectroscopic methods to investigate melts which were initially 100% $AlCl_3$. Sørlie and Øye[60] added KCl progressively until the melts were ultimately basic. These basic melts had the composition 49 mole % $AlCl_3$–51 mole % KCl, *i.e.* they contained a slight excess of the base Cl^-. Spectra were recorded and were reproduced, separately in the original paper, for $TiCl_3$ and for $TiCl_2$ in this series of melts of increasing basicity.

In Figure 4 of this review the spectra for the solutes that were shown separately for $TiCl_2$(A) and $TiCl_3$(B) in the original paper are superimposed for four representative melt compositions: (a) 100 mole % $AlCl_3$, (b) 67% $AlCl_3$–33% KCl, (c) 51% $AlCl_3$–49% KCl, and (d) 49% $AlCl_3$–51% KCl. The spectrum for Ti^{III} is little changed from (a) to (b), but at (c), with a 1% excess of $AlCl_3$, the spectrum is essentially that of the tetrahedral anionic entity $TiCl_4^-$. Gruen and McBeth had previously recorded melt spectra for the tetrahedral $TiCl_4^-$ and for the octahedral $TiCl_6^{3-}$.[61] The relevant spectra are reproduced in Figure 5. The value of pCl for the system changes by about 2.5 units as the melt changes from one containing 51 mole % $AlCl_3$ to one containing 49% $AlCl_3$.[62] Over the same interval the spectrum changes from that characteristic of $TiCl_4^-$ to one more consistent with Ti^{III} in the octahedral environment in $TiCl_6^{3-}$.[61]

Sørlie and Øye's spectrum for Ti^{II} in 100% $AlCl_3$ is virtually identical with that recorded earlier by Øye and Gruen[56] in the same solvent and similar, but shifted to longer wavelengths, to that recorded in anhydrous HF.[55] Solvated U^{3+} has been postulated in HF[50] by comparison with the previously recorded spectrum for aquo-U^{3+} and this reviewer has postulated above that U^{III} is present in $AlCl_3$-rich melts as solvated U^{3+}. There is stronger case here for proposing that the spectrum for Ti^{II}

---

[58] W. S. J. Schofield, B.Sc. (Honours) Report, University of Melbourne, 1977.

[59] K. W. Fung and G. Mamantov, *J. Electroanal. Chem.*, 1972, **35**, 27.

[60] M. Sørlie and H. A. Øye, *Inorg. Chem.*, 1981, **20**, 1384.

[61] D. Gruen and R. L. McBeth, *Pure Appl. Chem.*, 1963, **6**, 23.

[62] D. H. Kerridge, 'The Chemistry of Non Aqueous Solvents'. Vol. VB. ed. J. J. Lagowski, Academic Press, New York, 1978, p. 287.

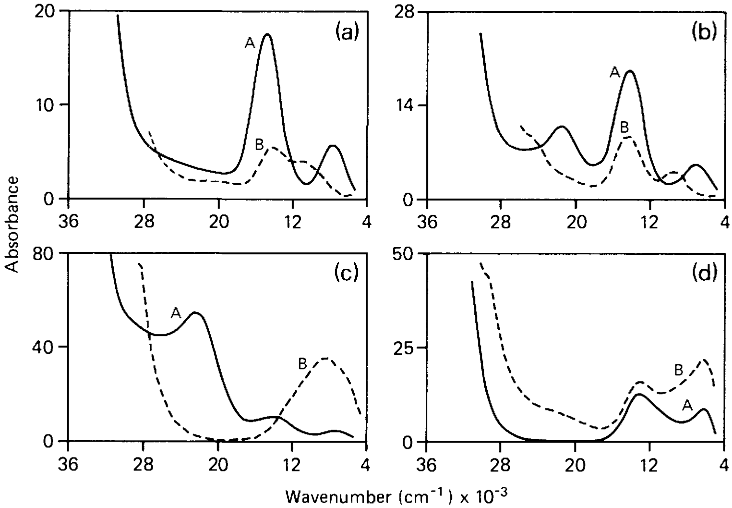


Figure 4 *Absorbance* (l mol^{-1} cm^{-1}) *vs. wave number* (cm^{-1} × 10^{-3}) *for* $TiCl_2$(A) *and* $TiCl_3$(B) *dissolved in molten salts at approximate temperatures given below:*

(*a*) 100 mole% $AlCl_3$: 500 K (*b*) 67% $AlCl_3$–33% KCl: 600 K

(*c*) 51% $AlCl_3$–49% KCl: 700 K (*d*) 49% $AlCl_3$–51% KCl: 750 K

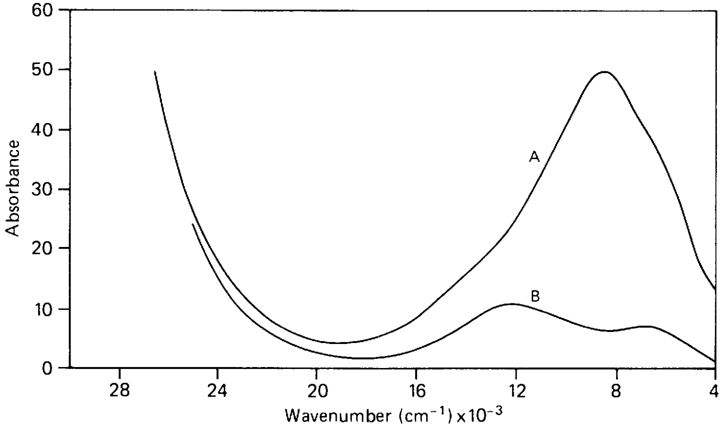


Figure 5 *Acid–base dependence of the equilibrium* $TiCl_4^- + 2Cl^- \rightleftharpoons TiCl_6^{3-}$
Spectrum A: Tetrahedral $TiCl_4^-$ *in* $CsGaCl_4$ (*neutral*) *at* 900 °C
Spectrum B: Octahedral $TiCl_6^{3-}$ *in* LiCl–KCl (*basic*) *at* 1000 °C
(Adapted from Ref. 61)

in acidic $AlCl_3$ is that of Ti^{2+} solvated by molecules of the melt, probably bidentate Al_2Cl_6. Øye and Gruen[56] and Sørlie and Øye[60] had previously proposed an octahedral environment for Ti^{II} in acidic melts. The peaks at about 14 000 and 7000

cm^{-1} are retained at 67% $AlCl_3$ and even at 51% $AlCl_3$, although a new strong peak grows in at about 22 000 cm^{-1}, possibly as a result of change of environment and symmetry as the anions $Al_2Cl_7^-$, $AlCl_4^-$, and Cl^- become progressively more important with continued addition of KCl to $AlCl_3$. Initially, at least, a solvating Al_2Cl_6 molecule could be replaced by a bidentate $Al_2Cl_7^-$. This anion has been shown crystallographically to coordinate in bidentate fashion in $Te_4(Al_2Cl_7)_2$.[39] Formation of a solvated $TiCl^+$ species could also account for the new high energy band resulting from a charge-transfer process.

As the melt becomes basic (at 51 mole % KCl), the spectrum for the system to which $TiCl_2$ has been added changes dramatically to that for octahedral Ti^{III} in the basic melt. Sørlie and Øye report that metallic titanium deposits on the cell walls at this stage. All of these observations fit an idealized disproportionation reaction:

$$3Ti^{2+} + 12Cl^- \longrightarrow Ti + 2TiCl_6^{3-}$$

Sørlie and Øye report only slight instability of Ti^{II} in basic melts, *e.g.* in the LiCl–KCl eutectic. This is not surprising since the Ti^{II} would now be anionic, *e.g.* $TiCl_6^{4-}$, and not subject to the base-induced disproportionation proposed throughout this review for *cationic* species.

C. Cations of Other Metals in Low Oxidation States.—Prior to the preparation of Ti^{2+} in the strongly acidic medium HF–SbF_5, O'Donnell and Schofield[55] had shown that when chemically cleaned metallic Cr and V were treated with the less acidic HF–BF_3, stable solutions of $Cr(FH)^{2+}{}_6$ and $V(FH)^{2+}{}_6$ were produced. Cr^{II} was identified by comparison of the spectrum for the species in solution in HF with those for Cr^{II} in aqueous solution and in molten $AlCl_3$.[56] The $V(FH)^{2+}{}_6$ spectrum was similar to that for crystalline alums containing $V(H_2O)^{2+}{}_6$, for VCl_2 in molten $AlCl_3$[56] and for V^{2+} in a host crystal of NaCl.[57] Again, the acidity of the medium, either HF or $AlCl_3$, was providing stabilizing conditions for production of the low oxidation state cations.

Metallic Zr, treated with HF–SbF_5, yielded a pale yellow solution with a major absorption band at 300 nm and a shoulder at approximately 370 nm.[63] Treatment of this solution with successive minute amounts of F_2 caused reductions in the intensities of these bands until they were eliminated. This indicates a low oxidation state compound in solution and the peak positions ascribed to Zr^{3+} fit into a sensible series with those for Zr^{III} in molten $AlCl_3$, $AlBr_3$, and AlI_3[64] in an analogous fashion to the correspondence between spectra for Ti^{II} and V^{II} in HF and in molten $AlCl_3$, *i.e.* there was a shift of 200—300 nm in the higher energy bands as the medium was changed from HF at room temperature to molten $AlCl_3$ at 500 K.

Spectra of solutions of Eu^{2+}, Yb^{2+}, and Sm^{2+} have been recorded in anhydrous HF.[65] Eu^{II} solutions are stable in acidified aqueous solutions. Yb^{II} and Sm^{II} both reduce aqueous solutions readily—the redox potentials for the Yb^{3+}/Yb^{2+} and

---

[63] K. Male, B.Sc. (Honours) Report, University of Melbourne, 1979.

[64] E. M. Larsen, J. W. Moyer, F. Gil-Arnao, and M. J. Camp, *Inorg. Chem.*, 1974, **13**, 574.

[65] R. W. Cockman, Ph.D. Thesis, University of Melbourne, 1983.

Sm^{3+}/Sm^{2+} couples in aqueous solution are -1.15 and -1.55 volts respectively. Spectra for the aquo cations of Yb^{II} and Sm^{II} have been recorded in solutions which were being cathodically reduced continuously. Reaction of the pure, cleaned metals Eu, Yb, and Sm with anhydrous HF gave stable solutions of Eu^{2+}, Yb^{2+}, and Sm^{2+} with evolution of H_2, without the necessity of addition of a Lewis acid. There would have been a stoicheiometric build-up of F^- in this reaction. So these dipositive cations are stable even in basic HF. Hammett acidity function measurements[15] have shown that such a solution would have an acidity comparable with that of 95% H_2SO_4.

When the solution of Sm^{2+} in HF was exposed to an excess of the gas GeF_4, a very weak Lewis acid which can interact with the F^- present, a bright yellow precipitate of insoluble $SmGeF_6$ formed immediately.[65] In much work at Melbourne GeF_6^{2-} has proved a very effective counter-ion for precipitating dipositive cations from HF solution.

D. Summary.—The very unusual solvated cations Ti^{2+} and Zr^{3+} require extremely acidic conditions for generation and stability—namely HF containing the strong Lewis acid SbF_5, solutions for which values of the Hammett function would be about -20 to -22.[15] The more familiar *d*-transition metal ions V^{2+} and Cr^{2+} can be formed in HF containing the weak Lewis acid BF_3, where the Hammett function would probably be about -16 or -17. The more highly charged *f*-transition metal cation U^{3+} is stable in HF–BF_3. The dipositive lanthanide cations Yb^{2+} and Sm^{2+}, unstable in acidified water, can be generated in HF even though it is rendered basic because of the F^- formed in the reaction. The Hammett function would be about -10 or -11.

This behaviour in HF of the cations of *f*-transition metals relative to *d*-transition metal cations of similar charge is consistent with the known solvolysis reactions for tripositive cations of *f*- and *d*-transition metals. Tripositive lanthanide cations are not hydrolysed until the pH of an aqueous solution reaches about 6. Cations such as Cr^{3+} and Fe^{3+} are extensively hydrolysed in the pH region 2 to 3.[66]

It can be seen as a corollary of the observed stabilization in acidic media of monatomic cations in unusually low oxidation states that the stabilization of *d*- and *f*-transition metals in high oxidation states will be favoured in basic media. Thus the familiar MnO_4^- is prepared by strong oxidation of basic solutions as are the more recently observed anions of Np^{VII} and Pu^{VII} *viz.* NpO_6^{5-} and PuO_6^{5-}. Fluorination of Ag^I and Co^{II} in the presence of basic CsF yields AgF_6^{3-} and CoF_6^{2-} and a similar procedure gives NdF_7^{3-}.

6 Stabilization of Unusual Anionic Species in Strongly Basic Media

Although the theme will not be developed at any length or in detail in this review, it is a further corollary of all that has gone before that, if unusual cationic species are formed as stable entities in highly acidic media (or in the absence of any significant amounts of base), unusual anionic species will be generated and have existence in

---

[66] Ref. 2, pp. 129, 219, and 237.

strongly basic media (or in the absence of any significant amounts of acidic species).

A. Homopolyatomic Anions.—The best known homopolyatomic anions are the so-called Zintl ions, such as Sn_9^{4-}, Pb_7^{4-}, Pb_9^{4-}, Sb_5^{3-}, Sb_7^{3-}, Bi_3^{3-}, Bi_5^{3-}, and Bi_7^{3-}. Many of these were originally postulated as being formed when alloys of Na and the heavier metal were dissolved in liquid anhydrous ammonia. There would have been mutual oxidation and reduction of Na and the other metal. Some were isolated as compounds such as $[Na(NH_3)_n^+]_3Sb_7^{3-}$. Subjecting these compounds to vacuum pumping removed NH_3 and yielded products such as NaSb, $NaSb_3$, and Sb. More recently several of them have been produced in the basic medium ethylenediamine.

Corbett has reviewed this field[67] and has drawn the distinction between formation of the polyanions in strongly basic media and their ultimate isolation as solids. He records his successful isolation and subsequent structural determination of many of these Zintl ions when Na or K cations are complexed with the octadentate ligand known as 2,2,2-crypt in compounds such as $[Na(crypt)^+]_3$-Sb_7^{3-}, isolated from ethylenediamine. He points out that such a macrocyclic ligand sequesters the cation and prevents electron transfer and formation of the types of products listed in the preceding paragraph. The macrocyclic ligand is sequestering the cation very much more efficiently than does the sheath of solvating ammonia molecules in some of the solids isolated in earlier work.

Subsequently, Corbett and his co-workers have generated new cage polyanions in ethylenediamine and characterized them structurally after isolation with cryptated K^+. Ge_9^{2-} and Ge_9^{4-} were identified in a single crystalline deposit[68] and the very unusual As_{11}^{3-} was analysed structurally after isolation from the same basic medium.[69]

The classic Zintl ion Sn_9^{4-} was recently precipitated in quantitative yield from dimethylformamide without use of cryptate ligands, the counter-ion being Me_4N^+.[70] However, the solid is not stable above −78 °C. The same workers isolated the polychalcogenide chain anions from extremely basic *aqueous* solution using Bu_4N^+ as the cation. The extreme basicity of the aqueous medium results from the fact that the chalcogenide is introduced into a small volume of water as an alloy with Na or K and subsequent redox reactions yield caustic solutions. These do not appear to require a medium as basic as the ring- or cage-like Zintl ions.

Highly coloured polysulphides S_x^{2-} have been known for a long time to exist in basic media such as amides.[71] The blue radical anion S^{3-}, characterized by Raman spectroscopy in dimethylformamide[72] has been identified by the same techniques in the *basic* melt, 55 mole % CsCl–45 mole % $AlCl_3$.[73]

---

[67] J. D. Corbett, *Chem. Rev.*, 1985, **85**, 383.

[68] C. H. E. Belin, J. D. Corbett, and A. Cisar, *J. Am. Chem. Soc.*, 1977, **99**, 7163.

[69] C. H. E. Belin, *J. Am. Chem. Soc.*, 1980, **102**, 6036.

[70] R. G. Teller, L. J. Krause, and R. C. Haushalter, *Inorg. Chem.*, 1983, **22**, 1809.

[71] F. Seel, H.-J. Güttler, G. Simon, and A. Wieckowski, *Pure Appl. Chem.*, 1977, **49**, 45.

[72] R. J. H. Clark and D. G. Cobbold, *Inorg. Chem.*, 1978, **17**, 3169.

[73] R. W. Berg, N. J. Bjerrum, G. N. Papatheodorou, and S. Von Winbush, *Inorg. Nucl. Chem.. Lett.*, 1980, **16**, 201.

B. The Monatomic Anions of the Alkali Metals.—Dye, who first isolated Na^- in a solid compound, has reviewed the spectroscopic and other evidence for the existence of alkali metal anions in solution in ammonia and amines.[74] He crystallized $[Na^+\cdot crypt]Na^-$ from ethylamine and characterized the compound by structural and other methods.

C. Summary.—It can be seen that the classic Zintl ions of metallic elements require strongly basic conditions for their formation and highly complexed cations for their isolation. Sn_9^{4-}, with a low charge-to-metal ratio, has been isolated from basic non-aqueous solution with the relatively simple counter-ion $(CH_3)_4N^+$.[70] Obviously, the polychalcogenide anions *can* be formed in such media, but they can also be isolated with a suitable cation from extremely basic aqueous solution. The natural extension of this is the well-known formation of polyhalide anions, *e.g.* I_3^-, in non-basic aqueous solution without any restriction on the counter-cation.

It is acknowledged that this short section on 'unusual' anions is far from complete. It is included to stress the quite generally well-known point that basic conditions favour the formation of such anions; and, as stated earlier, this is effectively a corollary of the proposition which forms the basis of this review, namely that the 'unusual' cations presented earlier must be generated in the virtual absence of basic species; otherwise they disproportionate. A convenient way of ensuring these conditions is to carry out syntheses of these cations in superacidic media. Control of the level of acidity allows control of speciation of cations, as will be discussed further in the concluding section which follows.

7 Principles Governing Stabilization, Isolation, and Reactivity of Cationic Species

Experimental approaches to inorganic syntheses are often limited by conventional ideas based on the limits imposed by hydrolysis occurring in the narrow window of acidities and basicities available in the common solvent water, or by the redox limits of that solvent. Attempts to avoid these limitations frequently go no further than seeking 'inert' or, at worst, coordinating solvents, such as halogenocarbons, ketones, DMSO, or MeCN.

Venturing into extremely acidic or basic media provides the opportunity to prepare unusual cations or anions, the stability of which depends on the availability or, more importantly, the non-availability of basic or acidic species in the solvent. These latter species can lead to decomposition, often through disproportionation of the desired products. To a first approximation, stabilization of particular cations or anions depends on the level of acidity or basicity of the solvent, *i.e.* to the low level of basic or acidic species in the media.

Considerable care must be taken in the choice of a superacidic medium. For example, in anhydrous H_2SO_4, for which the Hammett acidity function, H_0, is about -12,[11] there is extensive self-ionization and therefore the base of the system, HSO_4^-, is available to a large extent for solvolysis of the sought cation. Addition of SO_3 makes H_0 much more negative,[11] but self-ionization is still great and there is a

---

[74] J. L. Dye, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 587.

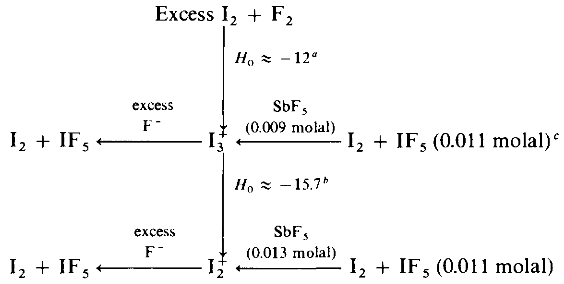
high degree of buffering. Pure HSO_3F ($H_0 \approx -15$)[10] is much more acidic than pure H_2SO_4 and the self-ionization is much smaller. So the base SO_3F^- is much less available than HSO_4^-. Pure HF, with a value of H_0[15] almost identical with that of HSO_3F, self-ionizes to about the same extent as H_2O. Therefore the availability of the base F^- is very small, particularly in solutions of SbF_5 in HF where $H_0 \approx 21$;[15] but the small self-ionization means that minute amounts of base, adventitiously present in the solvent or as formed in most chemical interactions between solutes and the solvent, can lead to values of $H_0 \approx -10$,[15] if supposedly pure HF is used as the synthetic medium.

Consideration of the stabilities of cations of sulphur as set out in Table 2 shows that the H_0 value for the pure solvent is not the sole determinant of cation stability. SO_3F^- is more electronegative than HSO_4^- and will form covalent products of disproportionation more readily than will HSO_4^-. To an even greater extent, F^- which is more electronegative than the oxo anions will form very strong bonds in disproportionation products. This matter of the electronegativity of the potential ligand F^-, coupled with the massive change in pF in passing from acidic through neutral to basic HF calls for—but also allows—very careful choice of experimental conditions when carrying out syntheses in HF.

Given the experimental difficulties involved in working with molten salts at elevated temperatures, it is not surprising that evidence for characterization of cationic species in melts is much more sketchy and fragmentary than parallel work in protonic superacids. A quantitative measure of the level of acidity or basicity of melts over a wide range is not available as is the case with Hammett function measurements for superacids. Therefore it is much more difficult to correlate cationic or anionic speciation with the level of acidity or basicity of the medium in molten salt chemistry than is the case for superacid work. Furthermore, the ionization processes are very complex, even in chloroaluminates, where species such as $Al_2Cl_7^-$, $AlCl_4^-$, and Cl^- can exist in equilibria determined by the melt composition and, presumably, by reactions occurring in the melt.

A. The Essential Role of Acidity Level in Stabilizing Cations.—Figure 6 summarizes much recent work, as yet unpublished, from the Melbourne group on formation and disproportionation reactions for polyatomic cations of iodine in the HF solvent system.[18] Gillespie[3–5] used stoicheiometric amounts of I_2 and the strong oxidant $S_2O_6F_2$ to generate iodine cations in HSO_3F, which was sufficiently acidic to provide stable solution conditions for each of the iodine cations produced, although I_2^+ did disproportionate slowly unless SbF_5 was used to increase the acidity of the HSO_3F.

In the Melbourne work we have concentrated on establishing the levels of acidity required to allow stabilization of the different iodine cations. F_2 reacts with excess I_2 to produce I_3^+ at H_0 values more negative than about -12. At less negative values the only species absorbing u.v.–visible radiation is I_2 and Raman spectroscopy shows the presence of IF_5. When the acidity is at about -15.5, I_2^+ is the predominant species. Each of these cations disproportionates to I_2 and a higher fluoride of iodine, probably IF_5, when the base F^- is added to the system.



[a,b] H_0 values for (*a*) PF_5–HF, (*b*) NbF_5–HF from R. J. Gillespie and J. J.-N. Liang: Ph.D. Thesis, McMaster University (1976). [c] The amount of solid elemental I_2 was such that IF_5 was in a tenfold excess relative to I_2 in the experimental volume of HF solution which was 0.011 molal in IF_5.

Figure 6 *Formation and disproportionation of homopolyatomic cations of iodine in the hydrogen fluoride solvent system*

We have shown that the disproportionation reactions of cations can be reversed by mixing the likely disproportionation products I_2 and IF_5 and fixing the acidity of the medium at a level at which each cation is stable. It is highly significant that it was unnecessary to fix stoicheiometric reacting proportions of I_2 and IF_5 in order to generate each cation—*acidity level alone dictated the nature of the cation.*

When F_2 was used to oxidize I_2, excess I_2 was used. In the reactions between the formal disproportionation products I_2 and IF_5, a tenfold excess of IF_5 was mixed with I_2, the molality of the IF_5 in HF being 0.011. IF_5 is a good fluoride donor, so that when the solution was made 0.009 molal in SbF_5, $IF_4^+SbF_6^-$ would have been formed, but the solution was still basic because it contained excess IF_5 at the level of 0.002 molal. In this slightly basic solution, u.v.–visible spectroscopy showed that I_3^+ was the dominant cation. When the solution was made 0.013 molal in SbF_5, the effective concentration of SbF_5, after formation of $IF_4^+SbF_6^-$, would have been 0.002 molal. Under these slightly acidic conditions, I_2^+ was the dominant cationic species. Regardless of whether excess reductant (I_2) or excess oxidant (IF_5) was used, the cation generated depended on the level of acidity of the HF.

Very complex systems such as those based on Te, Te_4^{2+}, Te_6^{4+}, TeO_2, H_2SO_4, and SO_3 can be rationalized similarly. Elemental Te is reported[37] to be oxidized to Te_4^{2+} in weak oleums. As the SO_3 concentration is increased, the Te_4^{2+} is said to be oxidized to Te_6^{4+}. SO_3 must also be increasing the acidity sufficiently to allow stabilization of Te_6^{4+} at the expense of Te_4^{2+}. Ultimately, on long standing or on heating, excess SO_3 is said to oxidize Te_6^{4+} to TeO_2. It seems equally probable that Te_6^{4+} disproportionates to Te_4^{2+} and Te. The element would then be reoxidized by the oleum to Te_4^{2+}. This, with the Te_4^{2+} initially present and that formed by disproportionation of Te_6^{4+}, could disproportionate, in small part at least, to Te and TeO_2. Thus on long standing a series of cycles of disproportionations and re-oxidations would ultimately favour the formation of a precipitate of TeO_2.

Of course, in a medium of acidity in which a non-metal cation A_n^{x+} would be stable, a polycation of the same non-metal, A_{n+m}^{x+}, with a lower charge-to-element ratio would also be stable. That is, the redox stoicheiometry can dictate formation of a species in an oxidation state lower than that which *could* be supported in the acidic medium. First the higher and then the lower oxidation state cation would disproportionate as the acidity of the medium was gradually reduced.

An effect often seen in melts is that electrolysis, particularly voltammetry, can force oxidation or reduction to an oxidation state in the region of the working electrode which would not be appropriate for the bulk acidity or basicity of the medium. However this review is concerned with the relationship between the acidity of the medium and the limits of stability of particular cationic species which are representative of the bulk acidity.

The key concept is that if the acidity of the medium is set at an appropriate level, oxidation of the element with a covalent compound of that same element in a higher oxidation state or with some other specific oxidant can result in the formation of a cationic species, often in an unusual oxidation state. If, however, the acidity of the medium is reduced, the cation will interact with the base of the solvent system to form either the element or another cation with a lower charge-to-element ratio together with an essentially covalent compound of the element in a higher formal oxidation state than in the original cation.

B. Acids, Oxidants, and Precipitants.—In much reported work, confusion about the interpretation of observed reactivity can occur because a single compound has been used as a Lewis acid, an oxidant, and a precipitant (or the source of the counter-anion used to isolate the generated cation). A particularly representative example of a compound with a multiple role is SbF_5 which has been used in many syntheses to increase the acidity of media and to act as an oxidant. In the latter role, it produces SbF_3 on reduction. Additionally it can accept F^- to form SbF_6^- or $Sb_2F_{11}^-$ as a counter-ion. In this context clean syntheses have frequently been made difficult or impossible by co-precipitation of the SbF_3 or by mixed oxidation state anion formation between SbF_5, SbF_3, and F^-. Reactions which lead to solid residues yield contaminated products because of the very low volatility of SbF_3.

AsF_5 is somewhat less troublesome, although a weaker Lewis acid than SbF_5, and has led to the successful isolation of compounds such as $Cl_3^+AsF_6^-$. The reduction product AsF_3 is volatile and is very weakly basic and therefore does not interact to any observable extent with the cationic species formed. In fact, liquid AsF_3 is sufficiently weakly basic to have been used as a solvent for the successful synthesis of some cationic species, *e.g.* Cd_3^{2+} and Cd_4^{2+}.

The dual role of SO_3 in acting as an oxidant of Te in oleum and in simultaneously increasing the acidity of the oleum has been discussed in the section immediately above.

In the chemistry of molten chloroaluminates, $AlCl_3$ frequently plays a dual role, about which there is much confusion. It both determines the acidity of the melt and provides an anion for isolation of the cation under investigation. In some work $BiCl_3$ acts similarly. In many papers and reviews Corbett recognized the vital role of the acid $AlCl_3$ in leading to the formation of Cd_2^{2+}, for example. He describes isolation of compounds such as $Cd_2(AlCl_4)_2$ in terms of coulombic interactions in

Born–Haber cycles for the cadmium-containing compounds Cd_2Y_2 and CdY_2 in the so-called 'decomposition' reaction:

$$Cd_2Y_2 \longrightarrow CdY_2 + Cd$$

Where Y can be both Cl^- and $AlCl_4^-$.[41] He implies that $Cd_2(AlCl_4)_2$ is formed at the expense of $CdCl_2$ or $Cd(AlCl_4)_2$ on the basis of favourable balances of lattice energies.

However, it is now apparent that, if $Cd_2(AlCl_4)_2$ were to be isolated and then treated with excess Cl^- in a melt, the ultimate product would be $CdCl_2$ or perhaps $Cd(AlCl_4)_2$. It seems necessary to postulate only an acid–base dependent formation–disproportionation equilibrium when Cd, $CdCl_2$, and $AlCl_3$ are in the molten state:

$$CdCl_2 + Cd \underset{Cl^-}{\overset{AlCl_3}{\rightleftharpoons}} Cd_2^{2+} + 2Cl^- \text{ or, more simply, } Cd^{2+} + Cd \underset{Cl^-}{\overset{AlCl_3}{\rightleftharpoons}} Cd_2^{2+}$$

Then the isolation of a chloroaluminate of Cd_2^{2+} is quite incidental. In coulombic terms, considering the interaction of a dipositive cation with a dinegative anion, Cd_2^{2+} would almost certainly be isolated more effectively with an anion MCl_6^{2-}, where M might be Sn, Ge, Hf, *etc.* This will be discussed further in the next section.

C. Strategies for Synthesis of Unusual Cations.—Because of the chemical simplicity of the solvent HF, of the oxidant of the system F_2, of the base F^-, and of Lewis acids such as SbF_5, AsF_5, and BF_3, this solvent system will be used to map out synthetic strategies for solvent systems which are much more complex, *e.g.* oleums, or for which there are great experimental difficulties associated with synthetic and characterization procedures, *e.g.* in melts.

Ideally the following steps should be followed to produce cations from a particular element: (i) adjustment of the acidity level, (ii) addition of an oxidant in the correct stoicheiometric proportions, and (iii) addition of a precipitant if isolation of the cation in a solid product is required.

HF can be made basic quantitatively by addition of an alkali metal or ammonium fluoride or by adding a proton acceptor. It is known that adventitious impurities, particularly traces of moisture, increase the basicity dramatically because of the low self ionization of HF. 'Neutral' HF can be produced by working with a Lewis acid of strength approaching zero, *e.g.* GeF_4. A range of Lewis acids is available, BF_3 being a commonly used weak acid. SbF_5 is very strong and acids such as TaF_5 and AsF_5 are intermediate. NbF_5 is very weak in producing 'near-neutral' HF solutions.

F_2 is the simplest oxidant of those that have been used for synthetic work in protonic superacids. It can be metred on to a weighed amount of material in HF using *p–V–T* relationships, or added quantitatively by even simpler techniques. Alternatively, cations such as I_3^+, I_2^+, S_8^{2+}, and S_4^{2+} have been produced by reacting stoicheiometric proportions, at the appropriate acidity, of I_2 with IF_5 or of S_8 with

SF_4.[18] The same cations are produced in reactions of I_2 with IO_3^- or of S_8 with SO_3^{2-};[18] but the former series is to be preferred because the oxo anions produce many moles of the base F^- per mole of oxo anion as a result of successive protonations of the oxygens.

Finally, ideally, a selective precipitant can be added. TaF_5, normally used as a Lewis acid, has proved an effective precipitant and SiF_4 and GeF_4 both combine with free F^- to give very insoluble compounds containing the fluoro anions SiF_6^{2-} and GeF_6^{2-} with cations of charge +2 ranging from the familiar Co^{2+} to the highly reducing Sm^{2+}.[14]

In the sulphur acids, which are less chemically-simple solvent systems than HF, SO_3, HSO_3F itself, and $S_2O_8^{2-}$ have been used as oxidants. For some of these, stoicheiometry control is not easy. Gillespie's use of $S_2O_6F_2$ in HSO_3F is an obvious exception to this objection. In fact $S_2O_6F_2$ in HSO_3F is the direct analogue of F_2 in HF—the oxidant is reduced to the species which is the base of the solvent system.

It seems that much work in molten salt systems could be made simpler and more definitive if procedures such as these were to be used. A metallic or non-metallic element in excess $AlCl_3$ to which an appropriate amount of KCl had been added could be oxidized electrolytically, or with stoicheiometric amounts of either Cl_2 or of a higher chloride of the element. Then a precipitant such as MCl_6^{2-} could be added. For a polyatomic cation of charge +2 this, on a lattice energy basis, would be the equivalent of adding SO_4^{2-} to Ba^{2+} in water. The postulated cation Ba_2^{2+},[48] for which there is little good evidence, could be investigated by dissolving equimolar Ba and $BaCl_2$ in $AlCl_3$ and adding a hexachlorometallate(IV). Corbett and colleagues considered this approach in attempts to isolate polyiodine cations.[19] They experienced little success in that instance but found $HfCl_6^{2-}$ effective in isolating Bi_9^{5+}.[46] The effectiveness of GeF_6^{2-} in precipitating many dipositive cations from HF suggests that this type of approach should be explored more fully in melt work.

The central theme of this review, namely that it is essentially the acidity of the medium which determines the nature of the cation produced, suggests that in preliminary investigations of syntheses in experimentally difficult systems, such as molten salts, there would be advantage in using protonic solvents, particularly HF, as model systems. Spectroscopic, electrochemical, and other properties of species produced at room temperature in HF or some other protonic solvent could be determined with a high degree of experimental control and then matched with those measured under less favourable conditions in melts.

D. Postulation of Existence of Cationic Species in Interpretation of Reactions in Acid–Base Systems.—While considerable effort has gone into the *generation* of unusual cationic species under highly acidic conditions, it appears a fair observation that there has been too little recognition of the existence and reactivity of solvated *cations* in many complex, acidic reaction systems, particularly in acidic melts. As one example, the reactivity of U^{III} equilibrated with metallic Al in molten chlorides, was interpreted exclusively in terms of reduction of anionic chlorouranate(III) species by Al in the presence of the *anions* $Al_2Cl_7^-$, $AlCl_4^-$, and Cl^-, even though it was observed that the U^{III} spectrum in acidic chloroaluminates was different from that in the basic melts.[52]

By direct analogy with U^{III} solutions in acidic H_2O and in HF, it can be postulated that the U^{III} species in acidic melts is solvated U^{3+}. As discussed earlier in this review, U^{3+} would disproportionate in the neutral melt to U^0 and U^{IV}. The latter could be reduced by Al to U^{III} which would then disproportionate. U^{III} would be expected to exist in the basic, *i.e.* chloride-rich, melt as a chloroanion. This explanation suits the reported facts better than that given in the original papers and is consistent with the observed stabilization of U^{3+} in acidic HF and its disproportionation when the base F^- is added to the HF solution.

Within this review there has been less drastic reinterpretation of some aspects of the speciation and disproportionation of Ti^{II} in acidic and basic chloroaluminates[60] as well as a reassessment of the original description of the generation and disproportionation of I_2^+ in similar melts.[20]

These examples serve to show that the major new theme brought out in this review—namely that cations, even very unusual ones, are the *expected* species in acidic media—can be used to reinterpret existing reaction pathways and to rationalize new work in highly acidic protonic or non-protonic media.

8 Conclusion

The basic propositions put forward in this review have been that, despite differences in the chemical nature and temperature domains of various solvent media, elements will be expected to exist as cations under sufficiently acidic conditions and as anions in strongly basic media. For non-metals, homopolyatomic cations of increasing charge per atom of the element are stabilized as the acidity of the medium increases. For metallic elements, the charge per metal on homopolyatomic cations decreases with increasing acidity. The charge on stable monatomic cations of metallic elements also decreases with increasing acidity.

In all of the above, increasing acidity of the medium implies decreasing availability of the base of the solvent system. For all of the cations above—metallic or non-metallic, polyatomic or monatomic—progressive additions of base lead ultimately to disproportionation of the cationic species to the element itself and to a non-ionic compound formed between the base and the particular element in an oxidation state higher than that in the cation which disproportionated. For polyatomic cations, disproportionation resulting from the addition of a relatively small amount of base may lead to the formation of a cationic species with a formal oxidation state intermediate between that of the parent cation and the zero oxidation state of the element. Typical generalized equations were given on page 7.

Although not dealt with in detail, the review suggests that the reverse situation holds for stabilization of unusual anionic species. Homopolyatomic anions of Groups VII, VI, V, and IV require progressively more basic media for their stabilization and special attention must be given to the nature of the counter-cation in isolation of solid compounds.

Acknowledgement. The author wishes to express deep gratitude to Professor R. J. Gillespie for very many helpful discussions and for permission to use data unpublished at the time of writing.