On the Commonality of Speciation of Inorganic Solutes in Superacids, Strong Bases, Molten Salts, and Water

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Keywords: Inorganic solute speciation / Superacids / Molten salts / Unusual oxidation states / Disproportionation

When dealing with inorganic solutes in protic solvents such as superacids, ammonia, and water, and especially in the case of molten salts, the authors of most textbooks and specialised reviews treat solution processes in each solvent or class of solvent separately, and rarely, if ever, draw the separate sections together to indicate the commonality of the solution processes from a generalised acid-base viewpoint. Initially in this review three chemically-simple solution media, H_2O, anhydrous HF, and molten chloroaluminates, are used to illustrate the generality of the behaviour of Cr^{III} in the three solvents. In neutral media "$Cr(OH)_3$", CrF_3, and $CrCl_3$ are sparingly soluble, whereas in basic media the solvo-anions $Cr(OH)_4^-$, CrF_6^{3-}, and $CrCl_6^{3-}$ are the dominant species. In acidic media Cr^{3+} cations, solvated to a greater or less extent, are formed. In highly acidic media, transition metal cations in very low oxidation states can be generated, e.g. Ti^{2+}, U^{3+}, and Sm^{2+}, as well as homopolyatomic cations, such as I_2^+, Se_8^{2+}, Te_6^{4+}, N_5^+, and Hg_3^{2+}. Each of these cations would disproportionate in aqueous solutions and, indeed, they do so on addition of sufficient base, even in HF or chloroaluminates. Under oxidising conditions solvo-anions in high oxidation states, e.g. CrO_4^{2-}, AgF_4^- and NiF_6^{2-}, are stable in basic media. Solute speciation in sulfur acids and ammonia is dealt with briefly because most investigation of homopolyatomic cations and anions has been carried out in these solvents. The overall aim of this review is to demonstrate the generality of inorganic solute speciation in all ionising solvents. It is proposed here that the primary determinant of speciation in all media is the level of acidity or basicity of the solvent rather than its chemical composition or its temperature domain.

1. Introduction

Dissolution processes in ionising media for simple ionic solids, such as the halides, nitrates, sulfates, and other oxoanions of the elements of Groups I and II of the Periodic Table are relatively straightforward, yielding solvated cations and anions in aqueous and nonaqueous media unless the ions, usually the anions, undergo solvolysis. The vast majority of inorganic compounds, particularly those of the transition elements, do not follow this simple pattern. So the nature of solute-solvent interaction for these compounds assumes great importance in considering their solution processes.

All too frequently, in the presentation of the solution chemistry of inorganic compounds in a range of ionising media, textbooks, and even specialised monographs and book series deal in separate sections or chapters with ionisation, dissolution, and solvolysis processes in solvents such as water, basic solvents such as ammonia and amides, and in acidic media such as sulfuric acid, fluorosulfuric acid, and hydrogen fluoride. This is especially the case in the presentation of chemistry in molten salts which, being nonprotic and frequently in elevated temperature domains, are perceived as being very different from protic or even nonprotic solvents which are liquid at or near ambient temperature.

The six-volume series[1] which gives the most extensive coverage of chemistry in nonaqueous solvents is structured in this way. Furthermore, in most earlier presentations, solvents such as H_2SO_4 and liquid NH_3 have been referred to as being "acidic" or "basic" (relative to H_2O). It is im-

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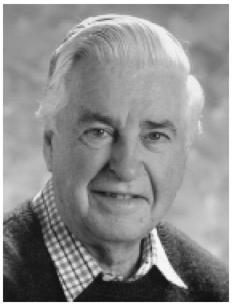

Tom O'Donnell was born at Ballarat, Australia, in 1923 and is a graduate of the University of Melbourne − Ph.D. (1954) and D.Sc. (1971). He was a member of the academic staff of the Melbourne School of Chemistry from 1949 to 1988 when he retired as Professor of Inorganic Chemistry. He spent a sabbatical year at Cambridge in 1955 with Professor H. J. Emeléus in order to commence research in inorganic fluorine chemistry. His earliest work was on systematisation of the chemical reactivity of the higher fluorides of d- and f-transition elements. Later he studied acid-base reactions and solute speciation in anhydrous HF and extended this to similar studies in other superacids. On retirement he joined the Melbourne Department of Chemical Engineering where he has worked collaboratively on fluoride-based chemistry directed towards development of novel commercial processes.

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portant to stress that, *as separate solvent systems*, 100% H_2SO_4 and anhydrous NH_3 are neutral media, each of which can be made more acidic by addition of appropriate Bronsted or Lewis acids (e.g. SO_3 or NH_4^+) or more basic by addition of suitable bases, such as HSO_4^- or NH_2^-.

Very rarely are the separate sections either presented or drawn together to indicate the commonality of the solution processes from a generalised acid-base viewpoint. This review sets out to demonstrate this commonality. Much of the material is drawn from a recent book[2] which was written, in part, to draw the attention of specialised researchers interested in chemistry in highly acidic media to these generalisations. The book also serves as a reference in the presentation and discussion of some superacid solution work carried out at the University of Melbourne which is not yet in readily available journals, as well as in the re-interpretation of some earlier published work from other groups. The present review extends the generalisation concept to include basic solvents such as ammonia and to describe recently reported chemistry in superacids, e.g. synthesis of the homopolyatomic cation N_5^+ and generation of AgF_4^- and NiF_6^{2-}, fluoro-anions of transition elements in very high oxidation states.

In the first two major sections of this review, solution speciation will be compared for three solvents only, namely water, anhydrous HF, and molten chloroaluminates. In most presentations of nonaqueous chemistry, water serves as the primary reference solvent. A vast amount of physical and inorganic chemistry has been studied in aqueous solution and a wide range of solvated cationic and anionic species has been characterised spectroscopically. These three solvent media have been chosen because comparison of spectra recorded in each of these media has allowed reliable postulations to be made about the extent of solvation of transition metal cations in these media. Additionally, HF and chloroaluminates were selected as the nonaqueous media because they have special properties concerned with their stability and self-ionisation, to be discussed below.

To those not familiar with solution chemistry in anhydrous HF, this solvent may seem to be an unlikely choice for a model solvent system, given its reactivity towards the usual materials of construction of scientific apparatus; but, with the availability of spectroscopic and electrochemical equipment constructed from fluorocarbons such as Teflon and KelF, synthetic sapphire and platinum, manipulation of and physico-chemical investigation of HF solutions in closed systems is now reasonably straightforward.

There are two main reasons why anhydrous HF is the superacid of choice for generation of highly-reducing stable monatomic transition metal cations in very low oxidation states, such as Ti^{2+} and Sm^{2+}, which reduce H_2O, and of highly oxidising transition metal solvo-anions with the metals in very high oxidation states, such as NiF_6^{2-} and AgF_4^- which oxidise water:

(i) it has a very large useable potential range of 4 to 4.5 volt between anodic and cathodic generation of F_2 and H_2. This compares with a range of about 2 volt, depending on pH, for H_2O.

(ii) it has the widest range of acidity-basicity of any of the superacids. HF exhibits this large acidity-basicity range because it undergoes a simple self-ionisation to about the same extent as H_2O, as discussed below.

Intrinsically, HF is so acidic that no compound is known to act as a Bronsted acid towards it. In the equations below, the self-ionisation equilibria [Equation (1)] are shown schematically as being shifted by the addition of the weak Lewis acid BF_3 [Equation (2)] and the strong Lewis acid SbF_5 [Equation (3)], to give the most acidic protic solutions yet generated:

$$3\,HF \rightleftharpoons H_2F^+ + HF_2^- \qquad (1)$$

$$2\,HF + BF_3 \rightleftharpoons H_2F^+ + BF_4^- \qquad (2)$$

$$2\,HF + SbF_5 \rightleftharpoons H_2F^+ + SbF_6^- \qquad (3)$$

By simple addition of a soluble fluoride, e.g. NaF, HF can be made more basic than any other superacid.

Levels of acidity and basicity in different superacidic media can be compared reliably using values of the Hammett Acidity Function, H_o. These were measured by Gillespie and co-workers for HSO_3F[3] and HF[4] solutions. Table 1 shows that, whereas pure HSO_3F and pure HF have identical value for H_o, additions of only 0.4 m base (F^-) and 0.4 m acid (SbF_5) to HF cause much greater changes in acidity and basicity than additions of 0.4 m base (SO_3F^-) and 0.4 m acid [$SbF_2(SO_3F)_3$] to HSO_3F. This is a reflection of the magnitudes of the autoprotolysis constants for the two superacids, as cited in Table 1.

The very high levels of acidity, or more specifically, the very low levels of basicity in HF containing Lewis acids are such that stable unusual cationic species such as Ti^{2+} and Sm^{2+} (Section 2.2.2) and I_2^+ and the recently characterised N_5^+ (Section 2.2.3) can be generated in HF. Enhanced basicity allows generation of stable anions such as NiF_6^{2-} and AgF_4^- (Section 2.3.2).

The small value of the autoprotolysis constant for HF means that large increases in basicity of HF will occur as very small amounts of base added. A practical consequence is that "neat" HF, as obtained by repeated distillation, will contain sufficient of the most likely impurity, H_2O which acts as a strong Bronsted base, that such a liquid will have a value for H_o much less than that of -15.1 determined for pure HF. Gillespie and Liang[4] showed experimentally that addition to HF of as little as 0.1 mol% of water reduced the observed H_o to -10.66. Extrapolation of their plot of H_o vs. concentration of H_2O in HF suggests strongly that even minute concentrations of water and other impurities that can be protonated will produce a medium with values of H_o for "neat" HF of around -11, an observation that has been made experimentally.

The first transition metal cations generated in HF solutions acidified with the weak Lewis acid BF_3 were Ni^{2+}, Co^{2+}, Pr^{3+}, and Nd^{3+} [5] – all cations in "normal" oxidation states. These cations were characterised by comparison of their HF spectra with previously reported aqueous spec-

Table 1. Dependence of acidity/basicity levels of superacids on the magnitude of autoprotolysis constants

Superacid	Autoprotolysis constant [mol^2 kg^{-2}]	Values of Hammett Acidity Function, H_o Lewis base added (0.4 m)	Pure acid	Lewis acid added (0.4 m)
HF	3×10^{-13}	-9.63	-15.1	-20.64
HSO_3F	3.8×10^{-8}	-13.24	-15.1	-17.71

tra and were so similar that the same level of solvation was postulated for the cations in both solvents.[5]

The term "normal" oxidation state is used here where an ion in that oxidation state is stable in aqueous solution. The terms "unusually low" or "unusually high" are used for ions which would be unstable in aqueous solution, e.g. Ti^{2+} or $NiF_6{}^{2-}$.

Another rich source of spectra available for comparative purposes with those for cations in HF was the work of Gruen and colleagues who recorded spectra of a range of dipositive transition metal cations in molten $AlCl_3$,[6] which is the pure acid of the chloroaluminate system, and in chloroaluminates at elevated temperatures.[7] Later workers carried out voltammetric investigations[8] in chloroaluminates which are liquid at room temperature and these also provided insights into the interpretation of ionic spectra in HF and other solvents.

Frequently ionisation in molten salt media is extremely complex, showing a multiplicity of interdependent ionic equilibria. This is particularly the case for melts of metallurgical or geological interest. Chloroaluminate melts are mixtures of $AlCl_3$ and an ionic chloride such as NaCl or, in the case of media which are liquid at or near ambient temperature, a salt such as *N*-butylpyridinium chloride ($BuPy^+Cl^-$). These exhibit relatively simple *solvent* speciation and so can be viewed as model systems for molten salt investigations. More importantly in the present context, they provide a nonprotic medium in which acidity and basicity can be controlled accurately. A 1:1 mixture of $AlCl_3$, the acid of the system, and NaCl (or BuPyCl) provides the neutral medium $Na^+AlCl_4{}^-$ (or $BuPy^+AlCl_4{}^-$), Cl^- being the base of the chloroaluminate solvent system. So any excess of NaCl over $AlCl_3$ constitutes a basic medium and, conversely, excess of $AlCl_3$ provides an acidic medium, as indicated in Figure 1. Consequently acid-base dependent *solute* speciation can be studied under controlled conditions and, as with HF, unusual ionic species which are unstable in H_2O can be generated, presenting a potentially rich area for new synthetic work.

High temperature chloroaluminates have a large useable potential range − from cathodic deposition of Al to anodic release of Cl_2. Room temperature chloroaluminates have a more restricted range because of oxidation or reduction of the organic cation.

2. Acid-base Dependence of Speciation of Transition Metals in H_2O, HF and Chloroaluminates

Figure 2 gives a brief summary of solution behaviour in the ionising media H_2O, HF, and chloroaluminates and provides the basis for a discussion of the general nature of the dependence of solute speciation on acidity or basicity of the medium. The solution behaviour of chromium(III), which is characteristic of many transition metals, is discussed first to illustrate typical solute speciation in each solvent in the absence of applied reduction or oxidation. Superimposed on this framework are several of the currently known species that can be generated when oxidants or reductants are added to the basic or acidic medium in each case.

2.1 Neutral Media

There is general acceptance of the insolubility of the so-called hydroxides of the transition metals in neutral water. The precipitates obtained when an aqueous solution is neutralised are not the simple hydroxides [idealised as $Cr(OH)_3$ in Figure 2] but are complex mixtures of metal centres with which are associated H_2O, OH^-, and even O^{2-} as bridging or terminal ligands. The key characteristic is that these aggregates carry no overall charge and so polymerise to form sparingly soluble nonstoichiometric compounds.

CrF_3 is typical of the neutral binary fluorides of First Row Transition Elements in "normal" oxidation states, each of which, along with some Main Group fluorides such as AlF_3, has very low solubility in anhydrous HF.

A survey of a large body of published work shows that neutral binary chlorides show similar behaviour in chloroaluminates. $CoCl_2$, $NiCl_2$, $FeCl_2$, $NpCl_3$, $NpCl_4$, and lanthanide trichlorides have all been reported as precipitating from neutral chloroaluminates. A specific reference is found in the work of Osteryoung and colleagues.[8] Cyclic voltammo-

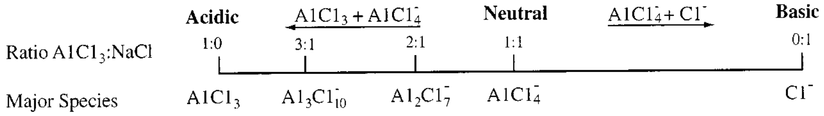

Figure 1. Acid-base dependence of solvent speciation in chloroaluminates (from *Superacids and Acidic Melts as Inorganic Chemical Reaction Media*, VCH, New York, **1993**)

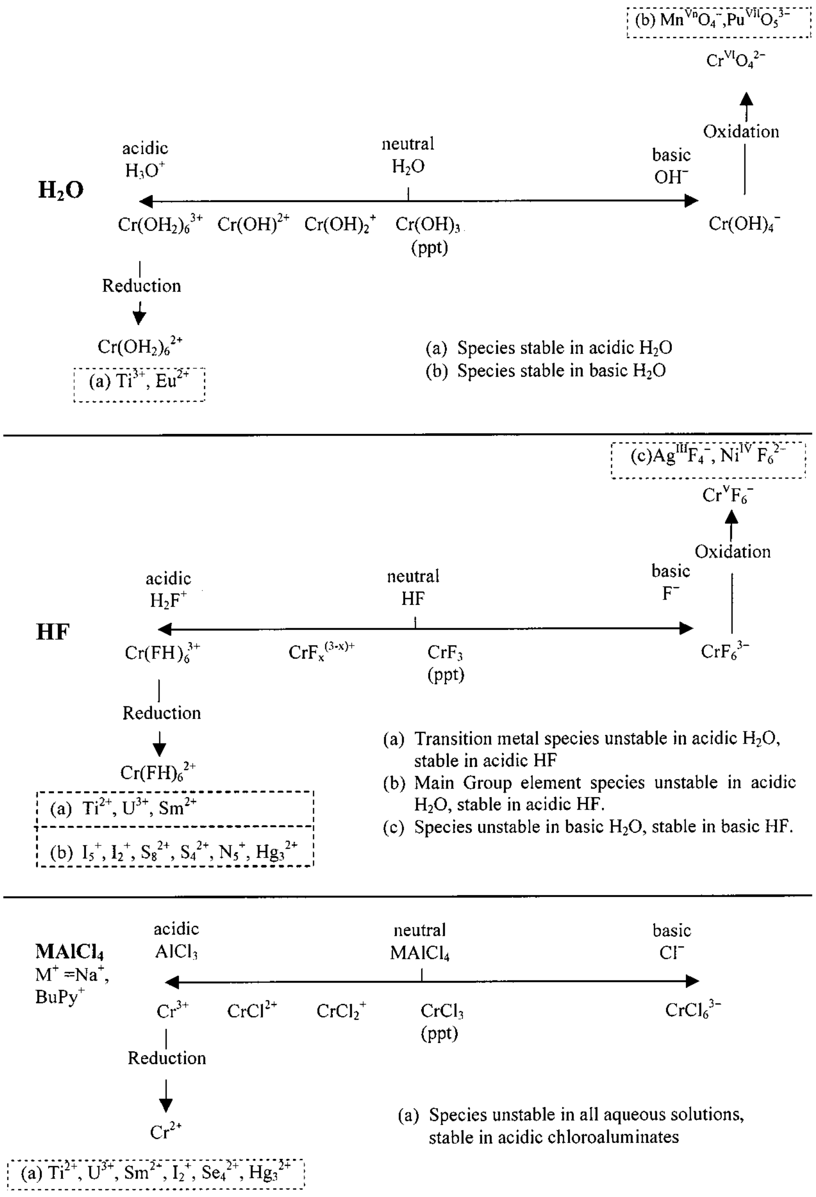

Figure 2. Generalised scheme for dependence of solute speciation on acidity and basicity in ionising solvents

grams were recorded in $AlCl_3-BuPyCl$ for the $Fe^{III}-Fe^{II}$ system from a basic medium ($AlCl_3/Cl^-$, 0.75:1) to acidic ($AlCl_3/Cl^-$, 2:1). This work will be discussed in greater detail in the section below; but in the present context, it is relevant to quote this report which shows that precipitation of $FeCl_2$ occurs near neutrality, commencing near a melt ratio of $AlCl_3/Cl^-$, 0.99:1 with redissolution occurring in the 1.1:1 acidic melt.

2.2 Acidified Media

2.2.1 Cations in "Normal" Oxidation States

First Row transition elements and metallic Main Group elements occur as aquo-cations, e.g. $Cr(OH_2)_6^{3+}$, $Fe(OH_2)_6^{3+}$ $Al(OH_2)_6^{3+}$, etc., in strongly acid, noncomplexing aqueous solution (e.g. in aqueous $HClO_4$). As indicated in Figure 2, hydroxo-complexation occurs progressively as the solution approaches neutrality, together with more complex species such as $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$, etc., the ratio of charge to metal decreasing as neutrality is approached. In addition to hydroxo-complexation, there is the possibility of a vast range of complexed cations, depending on the availability in the acidic aqueous solutions of other potential ligands. As the simplest of examples, species such as $[Cr(H_2O)_5Cl]^{2+}$ and $[Cr(H_2O)_4Cl_2]^+$ can be formed if the solution contains Cl^-.

As stated above, binary fluorides of transition metals are sparingly soluble in "neat" HF. The equilibrium [Equation (4)]

$$MF_n + (n + m)\,HF \rightleftharpoons M(HF)_m^{n+} + nHF_2^- \qquad (4)$$

lies overwhelmingly to the left. The weak Lewis acid BF_3 and the strong Lewis acid SbF_5 react as in Equation (5) and Equation (6),

$$BF_3 + HF_2^- \rightleftharpoons BF_4^- + HF \quad (5)$$

$$SbF_5 + HF_2^- \rightleftharpoons SbF_6^- + HF \quad (6)$$

displacing the equilibrium in Equation (4) to markedly increase the concentration of solvated M^{n+} cations. The weak acid BF_3 produces solutions in HF of dispositive *d*-transition metal cations. The strong acid SbF_5 was required to dissolve *d*-transition metal trifluorides.

CrF_3 dissolves in HF−SbF_5 to give the lowest of the spectra in Figure 3.[9]

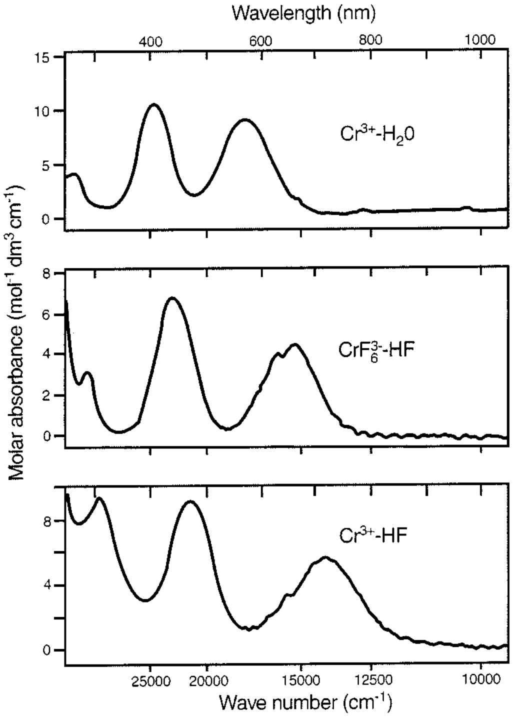

Figure 3. UV/Visible spectra of chromium(III) as $Cr(OH_2)_6^{3+}$ in H_2O, CrF_6^{3-} in HF, and $Cr(FH)_6^{3+}$ in HF (from *Superacids and Acidic Melts as Inorganic Chemical Reaction Media*, VCH, New York, **1993**)

Evidence for the existence of the six-coordinate cation $Cr(FH)_6^{3+}$ is provided by a comparison of the HF−SbF_5 spectrum with the known spectrum for $Cr(OH_2)_6^{3+}$ and with the experimentally observed spectra, which are virtually identical, for CrF_6^{3-} dissolved in both H_2O and HF. CoF_2 dissolved in HF−BF_3[5] gives a broad, shouldered peak very similar to that for $Co(H_2O)_6^{2+}$ in water and to that in Figure 4(b), indicating octahedral coordination, i.e. $Co(FH)_6^{2+}$, rather than tetrahedral coordination which would give a more intense and complex spectrum like that in Figure 4(a).

In the Melbourne research program, cations in acidified anhydrous HF were shown to have the same solvent coordination as in H_2O for Cr^{3+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Cu^{2+}, Pr^{3+}, Nd^{3+}, and many others. Some degree of spectral band broadening with reduction in acidity was ascribed to formation of fluorocations in solutions nearer to neutrality. There was no spectroscopic evidence for coordination to the cations in HF solution of solvo-anions of the Lewis acids, eg. BF_4^-, SbF_6^-, etc.

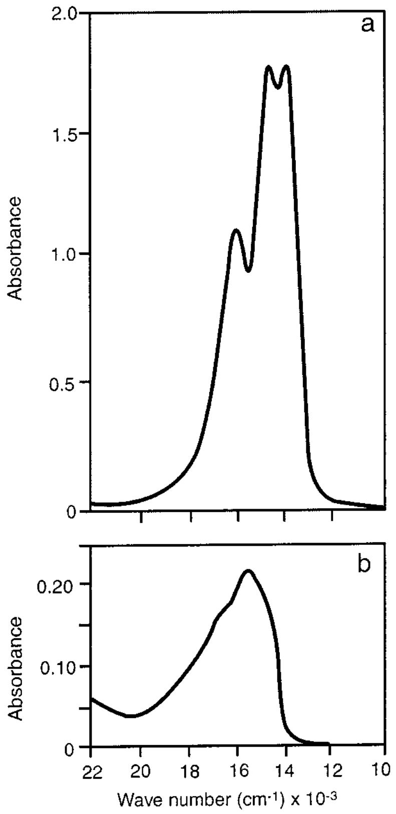

Figure 4. UV/Vis spectra of cobalt(II) (a) as $CoCl_4^{2-}$ in basic chloride melt and (b) as Co^2+ in acidic chloroaluminate melt (from *Superacids and Acidic Melts as Inorganic Chemical Reaction Media*, VCH, New York, **1993**)

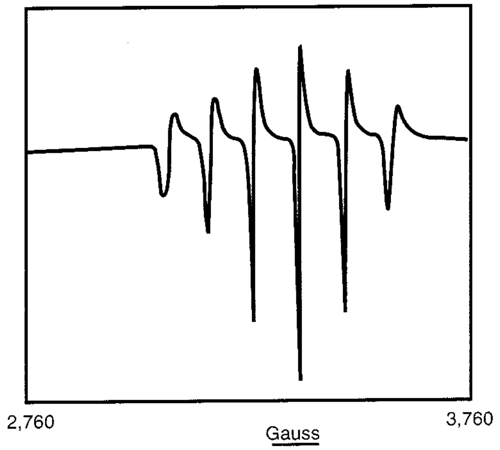

Figure 5. ESR spectrum of manganese(II) in AsF_5/HF (from *Superacids and Acidic Melts as Inorganic Chemical Reaction Media*, VCH, New York, **1993**)

The ESR spectrum of a solution of MnF_2 in HF−AsF_5 (Figure 5)[9] provided excellent evidence for existence of the cation $Mn(FH)_6^{2+}$. The ESR spectrum of the HF solution is very similar to that for $Mn(OH_2)_6^{2+}$ in H_2O, showing the characteristic six lines due to the interaction of the unpaired electrons with the nuclear spin of 5/2 on the manganese.

Øye and Gruen[6] recorded spectra of the dichlorides of the *3d* transition elements from Ti to Cu in $AlCl_3$, the pure acid of the chloroaluminate system, at 227°C. Their evidence points to cation formation in all cases. Their Co^{II} spectrum was the broad band of Figure 4(b), similar to that for $Co(OH_2)_6{}^{2+}$, whereas in earlier work in a basic chloride melt (the eutectic LiCl−KCl) Gruen and McBeth[7] had observed the spectrum in Figure 4(a), which is virtually identical to that for $CoCl_4{}^{2-}$ in an aqueous solution containing excess Cl^-.

Few researchers studying solutions of compounds of transition elements in chloroaluminates have been prepared to postulate directly the existence of solvated cations, as such, in acidic media whereas there is general agreement that the species in basic media are chloro-anions, as will be presented below.

Osteryoung's voltammetric investigation of the $Fe^{III}-Fe^{II}$ system in $AlCl_3$−BuPyCl[8] provides spectacular evidence for change in speciation as acidity and basicity of the medium are varied. Using potentiometry, they demonstrated the existence of $FeCl_4{}^-$ and $FeCl_4{}^{2-}$ in basic solution and they showed, as in Figure 6, that as the medium was made acidic the redox potential for $Fe^{III}-Fe^{II}$ changed by about 1.8 volt. Obviously there is a drastic change in solute speciation and it has been proposed[2a] that, on acidification, the electroactive species change from being anionic to being cationic.

In cyclic voltammetry, a value of 62 mV for ΔE_p, the difference between the cathodic and the anodic peak potentials, is observed for a system that is perfectly electrochemically reversible; but this value increases with decrease in reversibility. Reference to Figure 6 shows that, not only is there a vast and rapid change in peak positions in passing through neutrality, but electrochemical reversibility decreases as indicated by increase in values of ΔE_p.

A major criterion for electrochemical reversibility is that the stereochemistries of reduced and oxidised species are identical, as in basic melts. The present author has postulated[2a] that this would also be the case if, in strongly acidic chloroaluminate media, the electroactive species were the cations, Fe^{3+} and Fe^{2+}, each weakly but identically solvated. Some proposed intermediate equilibria, which are pCl dependent, are shown in Figure 6 and are based on the fact that Fe^{III} is known to form complexes with Cl^- and other ligands more strongly than does Fe^{II}, i.e. in weakly acidic medium $FeCl_2{}^+$ and $FeCl^+$ could be the dominant chloro complexes of Fe^{III} and Fe^{II}. Such nonidentical coordination geometry would contribute to nonreversibility leading to

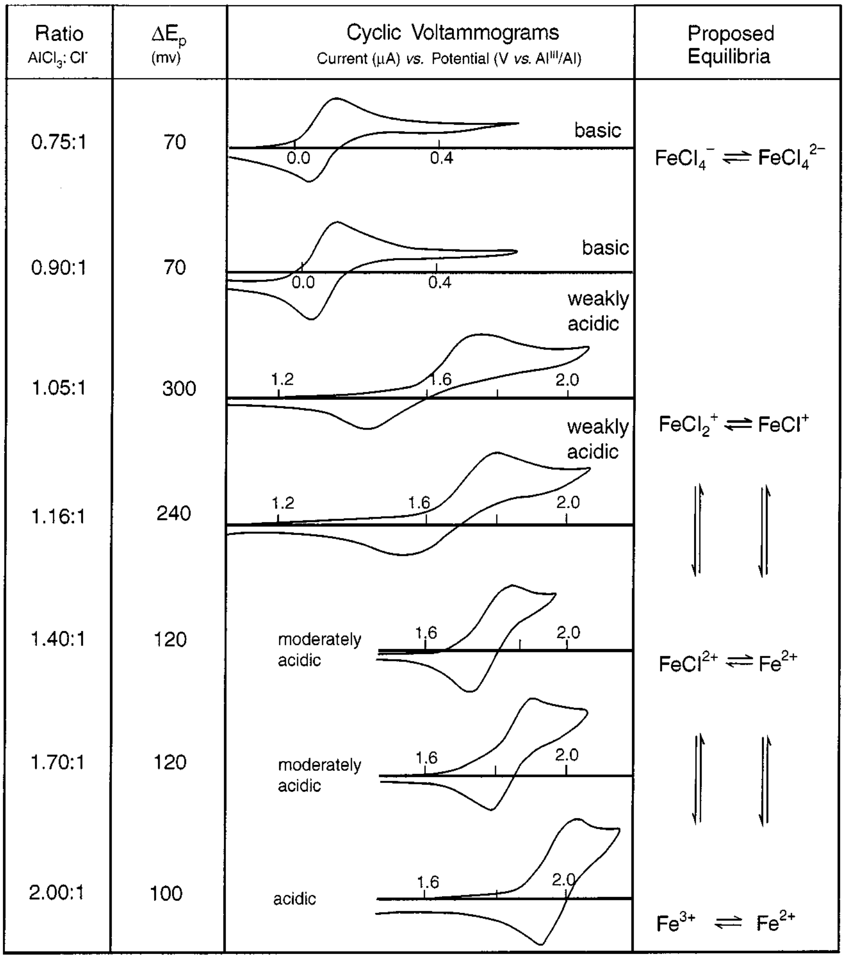

Figure 6. Cyclic voltammograms for $Fe^{III}-Fe^{II}$ in chloroaluminates of varying acidity and basicity (from *Superacids and Acidic Melts as Inorganic Chemical Reaction Media*, VCH, New York, **1993**)

greater values of ΔE_p. The present author has discussed the re-interpretation of this work and other evidence for simple cation formation in chloroaluminates in more detail elsewhere.[2b]

2.2.2 Transition Metal Cations in Unusually Low Oxidation States

Earlier, those cationic oxidation states which are stable in water were classified as "normal". There are certain low oxidation states which can be generated in aqueous solution only under strongly acidic conditions. It is possible to produce stable aqueous solutions of Cr^{2+} by reduction of Cr^{III} under acidic conditions in the absence of air. Similarly a few other low oxidation state cations can be generated in acidic aqueous solution, e.g., V^{2+}, Eu^{2+}, and Ti^{3+}. Ions such as Ti^{2+}, Yb^{2+}, Sm^{2+}, and Zr^{3+}, which can be generated in nonaqueous media, would reduce water, even when strongly acidified.

After being generated electrolytically or by chemical reduction in H_2O, U^{III} is known to be oxidised over relatively short time periods to U^{IV}, reducing H_2O. In 1976, O'Donnell treated metallic U with HF saturated with the weak nonoxidising Lewis acid BF_3 and generated lilac-coloured solutions containing U^{3+} which were stable indefinitely.[10] The acidified HF was reduced to H_2. Spectrum (b) in Figure 7 is that for U^{3+} in $HF-BF_3$ and can be compared with Spectrum 7(a) which was recorded while U was maintained in oxidation state III in acidic aqueous solution, using continuous electrolysis.[11]

Subsequently, treatment of metallic Ti with strongly acidic $HF-SbF_5$ yielded a solution containing Ti^{2+} [12] characterised initially by comparison of the HF spectrum (Figure 8a) with that previously reported[6] for that of $TiCl_2$ in molten $AlCl_3$ (Figure 8b), which has been interpreted[2c] as being the spectrum for weakly solvated Ti^{2+}.

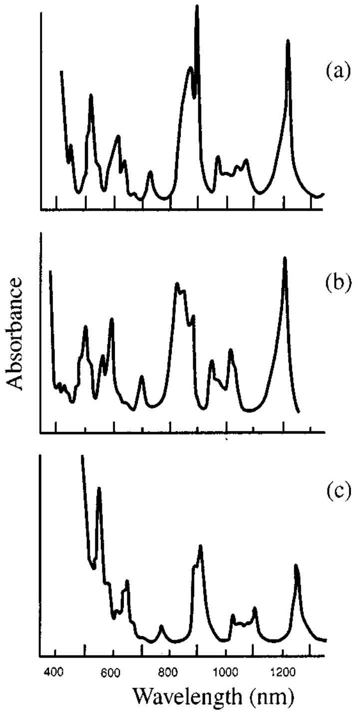

Figure 7. Spectra of uranium(III) in (a) 1 M $DClO_4$ (b) BF_3/HF, and (c) $AlCl_3/BuPyCl$, 2:1 (from *Superacids and Acidic Melts as Inorganic Chemical Reaction Media*, VCH, New York **1993**)

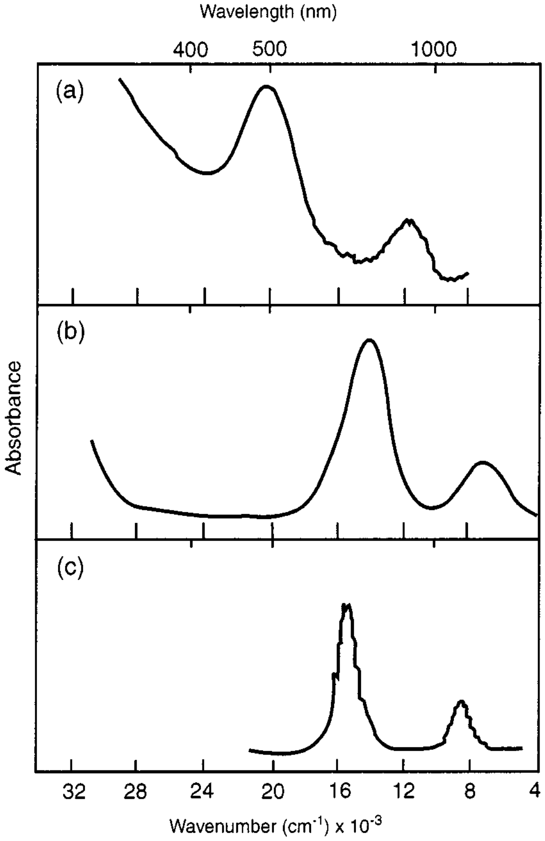

Figure 8. Spectra of titanium(II) in (a) SbF_5/HF, (b) molten $AlCl_3$ (c) crystalline NaCl at 10 K (doped at 1% level) (from *Superacids and Acidic Melts as Inorganic Chemical Reaction Media*, VCH, New York **1993**)

Six-coordination in $Ti(HF)_6{}^{2+}$ was supported by similarity of the HF spectrum to that for $TiCl_2$ doped at 1% level into a host crystal of NaCl in which the coordination number is six (Figure 8c).[13] Not unexpectedly solvated V^{2+} and Cr^{2+}, generated in similar fashion, were observed in acidified HF.[12] The lanthanide metals Eu, Yb, and Sm reacted with neat anhydrous HF to give Eu^{2+}, Yb^{2+}, and Sm^{2+} and H_2.[14]

Belgian researchers[15] conducted potentiometric and spectroscopic studies of U^{III} and U^{IV} in the low temperature (40°C) melt $BuPyCl-AlCl_3$. The similarity of their spectrum (Figure 7c) in the acidic melt ($AlCl_3/BuPyCl$, 2:1) to the spectra for U^{3+} in H_2O and in HF (Figure 7a and 7b) strongly suggest the existence of cationic U^{III} in this melt. The spectrum for U^{III} in basic chloride melts,[16] where the absorbing species is postulated to be an anionic chloro-complex of U^{III}, is very different from that in the acidic melt, showing a broad very intense absorption in the region 400−700 nm and no sign of the sharp peak above 1200 nm observed in the acidic melt spectrum.

As indicated above, the spectrum (Figure 8b) recorded by Øye and Gruen[6] for a solution of $TiCl_2$ in the pure acid, $AlCl_3$, indicates the presence of Ti^{2+}.

Gilbert and co-workers[17] conducted electrochemical and spectroscopic studies for lanthanide(III)−lanthanide(II) systems in 40°C melts ranging from acidic ($AlCl_3$/BuPyCl, >60:<40), through weakly acidic ($AlCl_3$, 60 to 50.1 mol%) to neutral and basic. Over this acidity-basicity range, values of $E_{1/2}$ for the $Ln^{III}-Ln^{II}$ systems shifted to more cathodic potentials. They postulated formation of anionic chlorocomplexes in basic media and they reported low solubilities of lanthanide dichlorides and trichlorides near neutrality. They proposed cationic species such as Sm^{3+} and Sm^{2+} in acidic melts, with $SmCl^{2+}$ nearer to neutrality and anionic species such as $SmCl_6{}^{3-}$ in basic media.

It will be demonstrated in Section 2.2.4 that addition of the base F^- to acidified HF or of the base Cl^- to acidic chloroaluminates containing cations such as U^{3+} and Ti^{2+} causes disproportionation of the cations to form the metal and a higher oxidation state fluoride or chloride in each case. Stability of these low oxidation state cations in these acidic media demonstrates the low basicity of these media, i.e. there is not sufficient of the base F^- or Cl^- to cause instability of the cations.

2.2.3 Homopolyatomic Cations of Non-metallic Elements

The pioneering work on generation of homopolyatomic cations such as $I_2{}^+$, $I_3{}^+$, $Br_3{}^+$, $S_4{}^{2+}$, $Se_8{}^{2+}$, and $Te_6{}^{4+}$ *in solution* was initiated by Gillespie and the bulk of the experimental work was carried out by his co-workers who prepared them in oleums and in HSO_3F and characterised them spectroscopically. Their existence and stability in sulfur acids will be discussed in Section 3.1.1. These cations cannot exist even in acidified aqueous solution because the medium is too basic. They would disproportionate on contact with water, as will be discussed in Section 2.2.4.

A relatively small amount of work has been done on generation and stability of homopolyatomic cations in HF and in chloroaluminates − the two solvent systems other than H_2O being discussed in the major part of this review. Gillespie and Passmore[18] reported isolation of solid $S_8{}^{2+}(AsF_6{}^-)_2$ from addition of sulfur to an AsF_5−HF solution [Equation (7)]:

$$S_8 + 3\,AsF_5 \xrightarrow{HF} S_8{}^{2+} + 2\,AsF_6{}^- + AsF_3 \qquad (7)$$

AsF_5 acts as oxidant, Lewis acid, and source of $AsF_6{}^-$ to provide both a superacidic reaction medium and a counter-ion of sufficiently weak basicity to prevent disproportionation of the cation. *Electrophilic cations which are stable in strongly acidic solutions require very weakly nucleophilic counter-ions to be stabilised in the solid state.*

Using Gillespie's spectral data to identify iodine cations in HF solutions, Besida and O'Donnell[19] determined the acidity thresholds at which polyiodine cations were formed in HF solutions. They treated excess of iodine with controlled amounts of elemental F_2 in HF solutions ranging from basic to strongly acidic. In separate solutions, decreasing concentrations of NaF were used to reduce the basicity of the medium and known concentrations of the Lewis acids of increasing strength, NbF_5, TaF_5, and SbF_5, were used to increase the acidity in controlled fashion. They demonstrated that the only species detected in basic solutions were I_2 and IF_5, shown in Section 2.2.4 to be the final disproportionation products for polyiodine cations in basic media. $I_5{}^+$, the iodine cation with the smallest charge-to-atom ratio, was not formed until a threshold H_o value of −10.95 was reached, the value for neutral HF being −15.1, as stated earlier. $I_5{}^+$ and $I_3{}^+$ were in co-existence until an H_o value of about −15. Then, $I_3{}^+$ and $I_2{}^+$ co-existed, with $I_2{}^+$ becoming the dominant species. $I_2{}^+$ was the only species detectable for H_o values more negative than −16.20. These reactions were shown to be reversible in the manner shown in Section 2.2.4, i.e. cations of high charge-to-atom ratio disproportionate on addition of base.

Recently, Christe and colleagues[20] have reported a spectacular example of a stable homopolyatomic cation in $N_5{}^+$, the third known all-nitrogen entity after N_2 itself and $N_3{}^-$. The potentially unstable cation — its enthalpy of formation has been calculated as being about 1470 kJ mol^{-1} — was generated in superacidic medium at low temperature and isolated as a solid compound with the weakly basic anion $AsF_6{}^-$. They treated $N_2F^+AsF_6{}^-$, formed by direct reaction of *cis*-N_2F_2 and AsF_5, with HN_3 in anhydrous HF at −78°C and isolated the solid product $N_5{}^+AsF_6{}^-$, which is marginally stable at ambient temperature but stable indefinitely at −78°C. There is indirect chemical evidence that the acidity of the HF reaction medium may have been enhanced by availability of some free AsF_5 formed during the reaction.

While several nonmetal homopolyatomic cations have been reported in chloroaluminates, very little definitive work has been reported on relating the stability of these cations to acidity-basicity levels in molten chloroaluminates. Initially $I_5{}^+$ and $I_3{}^+$ were synthesised by reacting fused stoichiometric amounts of I_2, ICl, and $AlCl_3$ to form I_5AlCl_4 and I_3AlCl_4 i.e. under neutral conditions, Cl^- reacting with $AlCl_3$ to form the neutral $AlCl_4{}^-$.[21] Increased acidity was required to stabilise $I_2{}^+$ in the melt 63 mol% $AlCl_3$/37 mol% NaCl.[22]

2.2.4 Base-induced Disproportionation of Cations

It has been seen that generation of stable solutions of monatomic cations of transition metals in unusually low oxidation states and of homopolyatomic nonmetal cations is possible in highly acidic media, i.e. in media of very low basicity. Addition of an appropriate base to such solutions renders the cations unstable due to disproportionation.

The necessity for an acidic medium for these cation is indicated by the observation that gradual addition of a basic solution of NaF to a solution of U^{3+} in HF/BF_3[2d] led to the formation of metallic U and solid UF_4 according to the Equation (8):

$$4\,U^{3+} + 12\,F^- \rightarrow U + 3\,UF_4 \qquad (8)$$

A more complex disproportionation was observed when F^- was added to a solution of Ti^{2+} in HF−SbF_5 where the formation of metallic Ti was accompanied by formation of fluorides of Ti in oxidation states III and IV.[2e]

Homopolyatomic nonmetal cations are susceptible to step-wise disproportionation reactions on gradual addition of base to solutions of the cations in superacids. Quantitative investigation[19] has shown that with increasing basicity, the cation I_2^+ in HF−SbF_5 disproportionates firstly to I_3^+ and IF_5, Equation (9), then to I_5^+ and IF_5, Equation (10), and finally to I_2 and IF_5, Equation (11):

$$14\,I_2^+ + 5\,F^- \rightleftharpoons 9\,I_3^+ + IF_5 \quad (9)$$

$$12\,I_3^+ + 5\,F^- \rightleftharpoons 7\,I_5^+ + IF_5 \quad (10)$$

$$5\,I_5^+ + 5\,F^- \rightleftharpoons 12\,I_2 + IF_5 \quad (11)$$

These lead to the overall reaction, Equation (12):

$$10\,I_2^+ + 10\,F^- \rightleftharpoons 9\,I_2 + 2\,IF_5 \quad (12)$$

(IF_3 was shown spectroscopically to be a minor component of the products of disproportionation of polyiodine cations in HF solutions).

Small increases in available base cause disproportionation of I_2^+ to I_3^+ and I_5^+. When available F^- is comparable with or somewhat greater than the concentration of I_2^+, total disproportionation occurs to elemental I_2 and an essentially covalent compound of iodine in a higher oxidation state than in the parent cation. These reactions were shown to be reversible. When the disproportionation products I_2 and IF_5 were added to HF solutions of varying acidity, mutual oxidation and reduction, i.e., conproportionation, yielded the products I_5^+, I_3^+, and I_2^+ as the acidity was increased even when each reactant was in ten-fold excess. It is apparent that, *unless a very powerful oxidant or reductant is present*, the level of acidity of the medium is the principal determinant of cationic speciation, regardless of whether oxidant or reductant is in excess i.e. regardless of reaction stoichiometry.

This pattern of stabilization of cations in unusual oxidation states in media of low basicity and their disproportionation on addition of base, which has now been well established quantitatively for iodine cations, appears to be quite general for homopolyatomic cations and for cations of transition metals in low oxidation states. It applies, regardless of the nature of the cations or of the media, to all the cations listed in Section 3.1.1. Even though many of the experimental observations are fragmentary, reports on synthesis and stability of cations in superacids other than HF and in chloroaluminates are all consistent with the scheme outlined above.

It is interesting to note that Hg_2^{2+}, the only homopolyatomic cation which has been shown to be stable in aqueous solution, disproportionates to metallic Hg and a Hg^{II} compound on addition of base. Furthermore the less stable Hg_3^{2+}, prepared in both chloroaluminate and in HSO_3F, disproportionates to Hg and a compound of Hg^{II} on contact with water.[23]

There is indirect but highly plausible evidence for disproportionation of U^{III} in nearly-neutral chloroaluminates in the work of Morrey and colleagues,[24,25] who prepared UCl_3 in situ in a series of sealed tubes by heating small amounts of U with very much larger comparable volumes of metallic Al and of chloroaluminate melts which ranged from acidic ($AlCl_3$/KCl, 2:1) through neutral (1:1) to basic (0.4:1). After prolonged heating, followed by quenching, each of the immiscible layers, metallic Al and chloroaluminates, was analysed for U. The uranium content of the metallic Al phase was very low when the chloroaluminate phase was strongly acidic or strongly basic but very much higher when the salt layer was nearly neutral. They reported different spectra for the U^{III} species in acidic and in basic melts. The present author has reinterpreted[2f] their work by postulating that U^{III} is present as stable cationic and anionic species in acidic and in basic melts but that near neutrality, U^{III} disproportionates to U^0 and U^{IV} in similar fashion as in Equation 8. Metallic U dissolves preferentially in the Al^0 phase and U^{IV}, present as a chlorouranate(IV) in the melt layer, is reduced to U^{III} by Al providing a cyclic disproportionation reaction leading to continually increasing concentrations of U^0 in the Al^0 layer.

Sø/rlie and Øye[26] dissolved $TiCl_2$ in $AlCl_3$ and reproduced the earlier spectrum (Figure 8b) recorded by Øye and Gruen.[6] They then recorded spectra for $TiCl_2$ dissolved in chloroaluminates of increasing basicity by progressive addition of KCl until the molar ratio was KCl/$AlCl_3$, 51:49. As neutrality was approached a large new band, possibly for $TiCl^+$, was observed with the original two bands characteristic of Ti^{2+} still present. In the basic melt (51:49) the spectrum changed dramatically to that observed by them for $TiCl_3$ in a basic melt. They reported that metallic Ti deposited on the walls of the spectroscopic cell in this slightly basic melt. Their observations are consistent with an idealised disproportionation reaction, Equation (13):

$$3\,Ti^{2+} + 12\,Cl^- \rightarrow Ti + 2\,TiCl_6^{3-} \quad (13)$$

2.2.5 Anions in Acidified Media

While several cations in unusually low oxidation states can be generated in highly acidic aqueous media, there does not appear to be anything particularly unusual about anion speciation in these media. A wide range of simple, familiar anions, e.g. halides, oxo-anions, carboxylates etc. can exist in acidified aqueous solutions as stable species, free or protonated to molecular species.

A much more limited range of anions can exist in the extremely acidic solvent HF. These are F^- itself, anions formed by Lewis acid-base interaction in HF e.g. BF_4^-, SbF_6^- and anions of superacids of comparable strength with HF, e.g. SO_3F^-. Other anions are fully protonated or solvolysed. Cl^- is protonated to HCl which is expelled from solution because of its insolubility and volatility. Carboxylates are doubly protonated to cationic species. Most oxo-anions undergo solvolysis, e.g. NO_3^- gives NO_2^+ and SO_4^{2-} forms SO_3F^-. The nonavailability of those simple anions which act as strong ligands in aqueous solution, e.g. Cl^-, means that metal cations undergo simple solvation in HF with no further complexation of the type exemplified for chlorochromium (III) cations in Section 2.2.1.

Little information is available on possible anionic species in chloroaluminates other than those derived from the medium or from solutes which are usually added as anhydrous chlorides. So the only anions reported in acidic media are Cl^- and those derived from the Lewis acid, namely $AlCl_4^-$, $Al_2Cl_7^-$ etc.

2.3 Base-enhanced Media

This section deals with H_2O, HF, and chloroaluminates to which the conjugate base of the solvent has been added. The anhydrous NH_3 solvent system, where the *neutral* medium is more basic than H_2O, will be discussed in section 3.2.

2.3.1 Anions in Normal Oxidation States

To an extent even greater than in acidic aqueous media, basic aqueous solutions can support a wide range of simple anions such as halides, oxo-anions, carboxylates, etc. In basic H_2O, solvo-anions of transition metals in normal oxidation states whose hydroxides are amphoteric can form e.g. $Cr(OH)_4^-$, $Zn(OH)_4^{2-}$, $Al(OH)_4^-$ etc.

The situation in basic HF is not very different from that in acidic HF. Most simple anions are protonated or solvolysed. In addition to F^-, the stable anions are those derived from interaction between F^- and a Lewis acid. Very weak Lewis acids will form fluoro-anions in basic HF more extensively than in acidic HF e.g. MoF_6^-, TiF_6^{2-} etc.

A similar situation exists in chloroaluminates. Cl^- interacts with binary chlorides to produce chlorometallate anions[7] with the metal in the same oxidation state as in the parent chloride, e.g., $CrCl_3$, $CoCl_2$, $NiCl_2$, $ZnCl_2$, etc. form $CrCl_6^{3-}$, $CoCl_4^{2-}$, $NiCl_4^{2-}$, $ZnCl_4^{2-}$, etc.

2.3.2 Solvo-anions of Metals in High Oxidation States

Reference to Figure 2 shows that, to the extent that information is available, a general property of solvents made strongly basic is the ability to allow preparation of stable anions based on metals in high oxidation states coordinated by ligands derived from the solvent. Thus, oxidation of chromate(III), $Cr(OH)_4^-$, in basic water yields chromate(VI), CrO_4^{2-}, Examples of other oxo-anions prepared by oxidation in strongly basic aqueous solution are MnO_4^- and PuO_5^{3-}, for which the metals are in oxidation state VII, the latter being very unusual for Pu.

The spectra in Figure 3 show that chromium(III) is soluble in basic HF as CrF_6^{3-}. Fluorochromate(V), CrF_6^- (see Figure 2) has been shown to be stable in basic anhydrous HF.[27] Solid CrF_5, prepared by fluorination of CrF_3, was added to an HF solution containing $NF_4^+HF_2^-$ – i.e. a basic solution – to yield $NF_4^+CrF_6^-$, a very powerful oxidant.

There have been several reported preparations of fluoronickelate(IV), NiF_6^{2-}, which is stable in HF. Stein and coworkers electrolysed strongly basic HF (0.5 to 1.5 M in KF) using a nickel anode and generated red NiF_6^{2-}, in solution.[28]

Žemva and colleagues used the very powerful oxidant KrF_2 to react with AgF_2 and NiF_2 in HF in the presence of XeF_6 at −60°C and produced the solids $[XeF_5^+Ag^{III}F_4^-]$[29] and $[(Xe_2F_{II}^+)_2Ni^{IV}F_6^{2-}]$.[30] XeF_6 ionises extensively in HF to form XeF_5^+ and F^-, providing both the basic HF solution necessary for the formation of the high oxidation state anions in solution and the counterions XeF_5^+ and $Xe_2F_{II}^+$ for isolation of the solid products.

More recently Bartlett has reported quantitative oxidation of NiF_2 and AgF_2 to $[Ni^{IV}F_6^{2-}]$[31] and $[Ag^{III}F_4^-]$[32] at room temperature using ultra violet – or sunlight – irradiated F_2 in very strongly basic HF (KF/HF $\approx$ 1:4). The anions were isolated as the stable solids K_2NiF_6 and $KAgF_4$.

There does not appear to have been any work done on generation in basic chloroaluminates of chloro-anions of metals in very high oxidation states. This would appear to be a potentially fruitful synthetic route to new chlorides and chloro-anions, particularly as the very reliable voltammetric procedures developed for investigations in room temperature chloroaluminates could be used to indicate attainability of high oxidation states.

3. Other Ionising Media

In order to demonstrate in some depth the general nature of the dependence of formation and stability of cationic and of anionic species on acidity and basicity of the medium, the content of this article, to date, has been limited to speciation in H_2O, HF, and chloroaluminates, media for which a reasonably broad range of experimental information is available.

There is good reason to believe that the generalities propounded for these three solvents hold good for all ionising acid-base media. Two other types of media will now be considered briefly, the anhydrous sulfur acids (oleums and fluorosulfuric acid) and strongly basic media, particularly anhydrous ammonia. The principal reasons for adding these are that homopolyatomic cations, which were discussed briefly for HF and chloroaluminates, were first identified systematically in sulfur acids. Further, it is a corollary of the fact that homopolyatomic cations are stable in highly acidic media that homopolyatomic anions, e.g., the Zintl ions, are generated in strongly basic media such as NH_3. To the extent that information is available, it can be shown that transition metal ionisation in these solvents follows the same trends as in the three solvents discussed to date.

3.1 Sulfur Acids

3.1.1 Homopolyatomic Non-metal Cations

Earlier, in Sections 2.2.3 and 2.2.4 there was an account of a quantitative Melbourne study of the dependence of stability of iodine cations on acidity and basicity levels in HF.[19] This is the only such study in HF that has been reported. However, virtually all of the pioneering work on generation in solution of cations of iodine, bromine, sulfur, selenium, and tellurium had emanated earlier from Gillespie's group at McMaster University, Ontario. He and Passmore published an early review of that work which is relatively short and very readable.[33] More recently Passmore and colleagues have reviewed the field exhaustively.[34]

From nearly 200 years ago there had been reports of highly coloured solutions of I_2, S_8, Se_8, and Te in oleums (H_2SO_4 containing excess SO_3). Formation of oxo-cations or oxo-anions was proposed to account for these colours. Gillespie showed conclusively that the coloured species in oleums and in HSO_3F were the homopolyatomic cations I_2^+, I_4^{2+}, I_3^+, I_5^+, Br_3^+, Te_6^{4+}, Te_4^{2+}, Se_4^{2+}, Se_8^{2+}, Se_{10}^{2+}, S_4^{2+}, S_8^{2+}, and S_{19}^{2+}.

The basis for Gillespie's very elegant methodology in this area is illustrated below in the generation of Se_8^{2+} and Se_4^{2+}. He used the powerful oxidant peroxydisulfuryldifluoride ($S_2O_6F_2$) in appropriately varying stoichiometric amounts in the solvent HSO_3F to oxidise the elements, in this case Se. $S_2O_6F_2$, on reduction, yields two SO_3F^- anions. SO_3F^- is the base of the solvent and has a greatly enhanced ionic mobility in the solvent and so can be monitored conductometrically. After reaction, he and his coworkers determined the number of ionic particles in solution by cryoscopy and the number of SO_3F^- ions by an original specialised conductance method. For the oxidation of Se_8 by $S_2O_6F_2$ in the stoichiometric ratio 1:1 in HSO_3F, they demonstrated cryoscopically that there were three particles per mol of Se_8, two of which were shown to be SO_3F^- ions by conductance measurements, indicating that the third particle was doubly positively charged, Equation (14):

$$Se_8 + S_2O_6F_2 \rightarrow Se_8^{2+} + 2\,SO_3F^- \qquad (14)$$

If 1:2 stoichiometry were to be used, six particles would be observed, four of which would be SO_3F^- ions, so that Se_4^{2+} would be the reaction product, Equation (15):

$$Se_8 + 2\,S_2O_6F_2 \rightarrow 2\,Se_4^{2+} + 4\,SO_3F^- \qquad (15)$$

In the oleum experiments, SO_3 acted both as the Lewis acid and as a less specific oxidant.

The McMaster group recorded UV/Visible spectra to characterise each of the cations in oleums or HSO_3F and in many cases isolated solid products containing the cations, necessarily associated with weakly basic anions, and determined their structures by X-ray diffraction techniques.

On addition of base, SO_3F^- or HSO_4^-, all of these cations disproportionate to a cation of lower charge-to-atom ratio and a covalent compound in a higher oxidation state, in similar fashion to the disproportionation of iodine cations as discussed in Section 2.2.4. Ultimately, on addition of sufficient base, they disproportionate to the element and a covalent compound.

Table 2 shows two general trends for the dependence of the stability of polyatomic cations of S, Se and Te on the level of acidity of the medium. The media are all based on 100% H_2SO_4, made either acidic with SO_3 or, in one case, weakly basic with HSO_4^-. Values of H_o listed in Table 2 are taken from the work of Gillespie, Robinson, and Peel[35] and are based on the experimental conditions, such as addition of SO_3 or of HSO_4^- to H_2SO_4, cited in the reports of the preparation of each of the cations. Consideration of the threshold acidities for stabilisation of the sulfur cations shows that the higher the ratio of charge-to-atom, the higher is the required acidity, i.e., the lower the basicity of the medium. Less base is required to cause disproportionation of S_4^{2+} than for S_8^{2+} and S_{19}^{2+} in turn. For the cations of the same structure and charge S_4^{2+}, Se_4^{2+}, and Te_4^{2+}, the smaller the atomic number of the element the higher is the acidity required for stabilisation, i.e., the lower the basicity of the medium. There is greater attenuation of charge over Te_4^{2+} than for Se_4^{2+} and S_4^{2+}, in turn, i.e., Te_4^{2+} is the least electrophilic of the three cations and can exist with a greater availability of base without disproportionating. *These stability trends for chalcogen cations hold for all homopolyatomic cations of metals and nonmetals in other acidic solvents*, but less comprehensive data are available to allow similar quantitative comparisons for these other solvents.

3.1.2 Transition Metal Cations

Little work has been reported in the open literature on generation of cations or solvo-anions of transition metals in the sulfur acids. In Melbourne work the spectra of solvated Co^{2+}, Ni^{2+}, and Cr^{3+} were recorded after adding appropriate Lewis acids to oleums, HSO_3F, and CF_3SO_3H.[2g] $Co(HSO_4)_2$ was shown to be sparing soluble in 100% H_2SO_4. Addition of SO_3 caused marked increase in the Co^{II} concentration and the spectrum was that for six-coordinate Co^{II} (Figure 4b). Electrolysis was conducted in a three-compartment cell with Co^{II} in 20% $SO_3-H_2SO_4$ in the central compartment. Spectrometric analysis showed that Co^{II} moved quantitatively to the cathode compartment, with no detectable Co^{II} in the anode compartment, indicating the existence of solvated Co^{2+} in the oleum solution.

For most of these Melbourne studies,[2g] Co^{II} was chosen as a model solute because of the major differences in spectra for four-coordinate and six-coordinate Co^{II} (Figure 4a and 4b). $Co(SO_3F)_2$ and $Co(CF_3SO_3)_2$ were both found to be sparingly soluble in "neat" HSO_3F and CF_3SO_3H but dissolved when the Lewis acids SbF_5 and $B(OSO_2CF_3)_3$ were added to the two superacids. In each case spectra were very similar to that in Figure 4b indicating, as with $Co(H_2O)_6^{2+}$ and $Co(HF)_6^{2+}$, six-coordinate solvated cation formation in each case. Table 3 shows the similarity of the spectra in H_2O, the four superacids and $AlCl_3$. For spectra of all the *d*-transition metal cations studied, small shifts of peak positions relative to aqueous solutions were observed for all the superacids with larger shifts in chloroaluminates.

Table 2. Dependence of charge on chalcogen cations on acidity of the medium

Cation	S_4^{2+}	S_8^{2+}	S_{19}^{2+}
Medium	>40% $SO_3-H_2SO_4$	>15% $SO_3-H_2SO_4$	>5% $SO_3-H_2SO_4$
Hammett Function	-14.1	-13.2	-12.7
Cation	S_4^{2+}	Se_4^{2+}	Te_4^{2+}
Medium	>40% $SO_3-H_2SO_4$	100% H_2SO_4	$HSO_4^- - H_2SO_4$
Hammett Function	-14.1	-11.9	-11

Table 3. Peak positions for cobalt (II) in acidified water, superacids, and in acidic melts; sh = shoulder

Solvent	H_2O	HF	HSO_3F
Peak positions [nm]	458 sh	471 sh	477 sh
	510	532	545
Solvent	CF_3SO_3H	$SO_3-H_2SO_4$	$AlCl_3$
Peak positions [nm]	482 sh	483 sh	590 sh
	555	540	633

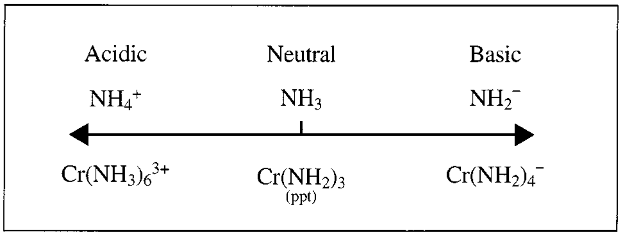

Figure 9. Dependence of Cr^{III} speciation in liquid NH_3 on acidity and basicity of the medium

3.2 Strongly Basic Media

3.2.1 Homopolyatomic Anions

The converse of stabilisation of homopolyatomic cations containing elements of fractional positive charge in strongly acidic (i.e. weakly basic) media is the formation of homopolyatomic anions containing elements of fractional negative charge in media which in the "neat" state are much more basic than H_2O.

Historically, this class of anion dates back to the work of Zintl in Germany about 1930. He reduced PbI_2, dissolved in NH_3, with strongly basic solutions of Na in NH_3 to produce the ions Pb_7^{4-} and Pb_9^{4-} in solution. Zintl also generated Sn_9^{4-} and a range of anions A_n^{3-} (for A = As, Sb, Bi and $n = 3, 5, 7$) as well as dinegative polyatomic anions of Se and Te. Some four decades later ethylenediamine, more basic than NH_3 and, unlike NH_3, a liquid at room temperature, was used as a medium to produce many more polyatomic anions. This field has been reviewed by Corbett.[36]

Much work has been done on isolation of solid products containing the polyatomic anions for structure determination; but that lies outside the scope of this very brief survey of these anions *in solution*. However very little systematic work has been done on deliberate variation of the acidity or basicity of NH_3 by adding NH_4^+ or NH_2^- to study anion stability. There are some incidental observations[2h] that suggest strongly that these anions are more stable when the base NH_2^- is added and that they decompose on addition of the acid NH_4^+ − the opposite of the behaviour of polyatomic cations in acidic media, as expected.

3.2.2 Solute Speciation of Transition Metals

Figure 2 was used to indicate the generality of solute speciation in H_2O, superacids and molten salts i.e. solvated cations exist in acidified medium, sparingly soluble "binary" uncharged polymeric compounds in neutral medium and solvo-anions in the medium to which excess base has been added. A survey of solute speciation[37] shows that a similar situation holds in liquid NH_3, as indicated in Figure 9.

$CrCl_3$ dissolves in "neat" NH_3 to give $Cr(NH_3)_6^{3+}$ as well as $Cr(NH_3)_5Cl^{2+}$ (c.f. $Cr(H_2O)_5Cl^{2+}$ in water).[37] At first sight, it might seem surprising that solvated cations, rather than polymeric amides, are formed in "neat" NH_3 which undergoes the self-ionisation, Equation (16):

$$2\,NH_3 \rightleftharpoons NH_4^+ + NH_2^- \tag{16}$$

The self-ionisation constant, K_i, for this equilibrium is extremely small, being about 10^{-33} mol^2L^{-2} at -50 C.[37] The dependence of the acidity − basicity range in a protic solvent on its autoprotolysis constant was discussed in Section 1, where it was shown that minute traces of H_2O, acting as a Bronsted base in HF, could reduce the H_o value for HF by as much as four units. The most likely impurity in NH_3 is reported as being H_2O[37] which acts as a Bronsted acid to produce NH_4^+ and OH^-, the latter being an "innocent" ion in NH_3 in the acid-base sense. Because of the very small autoprotolysis constant for NH_3, traces of H_2O will greatly increase the acidity of the medium, favouring formation of cationic species.

Solute speciation in NH_3 parallels that in other solvents.[37] Thus addition of NH_2^- to $Cr(NH_3)_6^{3+}$ in NH_3 gives insoluble, polymeric chromium amide, $[Cr(NH_2)_3]_n$, which is amphoteric and forms soluble $Cr(NH_2)_4^-$ on further addition of NH_2^-. VCl_3 dissolves in "neat" NH_3 to form $V(NH_3)_6^{3+}$ as well as $[V(NH_3)_5NH_2]^{2+}$ which is the counterpart of $[V(H_2O)_5OH]^{2+}$ in water. Addition of NH_2^- gives $[V(NH_2)_3]_n$ and then $V(NH_2)_4^-$. The divalent metals Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} all form $M(NH_3)_6^{2+}$ in solution and give the amides $[M(NH_2)_2]_n$ on addition of NH_2^-.

Transition metals in higher "normal" oxidation states undergo more complex solvolysis[37] giving species like $TiCl(NH_2)_3$. Deprotonation of NH_3 to NH_2^- can proceed further to formation of imide, NH^{2-}, and nitride, N^{3-}, and many anionic species for metals in relatively high oxidation states are reported to be more complex through coordination of these latter two species, as in $[TiNH_2(NH)_2]^-$ and $[Zr(NH_3)_2(N)_2]^{2-}$. These are somewhat akin to Ti and Zr species containing OH^- and O^{2-} ligands in aqueous solution and in solids derived from aqueous solutions.

3.2.3 Anions of Transition Metals in Unusually Low Oxidation States

Unlike the situation in superacids where solvo-anions can be generated which contain transition metals in unusually high oxidation states (Section 2.3.2), anions based on transition metals in unusually low oxidation states have been generated in NH_3. Reduction by metallic K in NH_3 at −33°C of the entities $[Ni(CN)_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$, $Mn_2(CO)_{10}$, and $Fe(CO)_5$ led to formation of $[Ni(CN)_4]^{4-}$, $Pt(NH_3)_4$, $[Mn(CO)_5]^-$, and $[Fe(CO_4]^{2-}$ with the metals in formal oxidation states Ni^0, Pt^0, Mn^{-1}, and Fe^{-II}.

Conclusion

In Figure 2 and Figure 9, chromium(III) has been used to show that there is a common pattern of acid-base dependent solute speciation in the solvents H_2O, HF, NH_3, and chloroaluminates. Uncharged binary polymeric precipitates form in neutral medium.

Moderate increase in acidity leads to formation of cations, solvated to greater or less degree, particularly when considering transition elements of the First Row of the Periodic Classification. (Transition elements of the Second and Third Rows normally occur in high oxidation states and rarely occur as discrete monatomic cations in aqueous solutions. For example Mo and W normally exist in aqueous solution as molybdates and tungstates which, in some instances, are polymeric).

Elements other than chromium have been used to demonstrate that provision of a *highly acidic* medium can allow generation and stabilisation of cations of metals in unusually low oxidation state or, except for H_2O, homopolyatomic cations of metallic and nonmetallic elements. More specifically, a highly acidic medium is one of very low basicity − sufficiently low to prevent disproportionation of the cations. Superacidic conditions happen to be a convenient way of providing media of very low basicity. H_2O is too basic to allow existence of the homopolyatomic cations or of many of the low-oxidation-state transition metal cations generated in superacids.

When the uncharged precipitate is amphoteric, moderate increase in basicity of the medium will lead to formation of solvo-anions − complexes of the metal and the base of each solvent, e.g. $Cr(OH)_4^-$, CrF_6^{3-}, and $CrCl_6^{3-}$. It appears that many more binary chlorides are amphoteric in molten chloride media than is the case for precipitates in H_2O, HF, and most solvents. When each of the media is made *very strongly basic*, generation of very high oxidation states is possible for chromium and other metals in the solvo-anions.

For most solvent systems there is less information available on solute speciation across a wide range of acidity and basicity than is the case for the three solvents presented in Figure 2. Sulfur acids and ammonia have been included to show that the available information on solute speciation is consistent with the patterns outlined in this review. Thus the solvated cation $Cr(NH_3)_6^{3+}$, the neutral polymer $[Cr(NH_2)_3]_n$ and the solvo-anion $Cr(NH_2)_4^-$ are generated in acidic, neutral and basic NH_3. Further, inclusion of these two solvent systems indicates that some converse relationships exist between highly acidic and highly basic media. Thus homopolyatomic cations are stable in superacidic media while homopolyatomic anions are stable in NH_3 and ethylenediamine. Solvo-anions of transition metals in very high oxidation states can be generated in superacidic media, such as HF, while anions of transition metals in very low oxidation states are formed in basic media such as NH_3.

The only class of molten salt system presented here has been the chloroaluminates because of the ease of adjusting the acidity or basicity of the medium and because of the relative simplicity of ionic speciation in the molten salt itself. By comparison, molten silicates for example, where the acid of the system is SiO_2, the base is O^{2-} and the species in a neutral silicate is SiO_4^{4-}, are extremely complex. However it is to be expected that extremely complex silicate systems, like geological magma or metallurgical slags, would lend themselves to similar investigation and interpretation of solute species.

There are good reasons to believe that the systematisation demonstrated in this review for a limited number of solvents holds generally for acid-base interaction of inorganic solutes with all ionising solvents. What emerges from this overview is that, as a generalisation, the levels of acidity or basicity of solvent systems, rather than their chemical composition or temperature domain, are the principal determinants of charge and oxidation state of ionic species in solution.

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Received March 27, 2000
[I00119]