REACTIONS IN SOME NON-AQUEOUS IONISING SOLVENTS

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IONISING solvents are inherently polar and dissolve many ionic and covalent compounds to give conducting solutions. Water is undoubtedly the most important member in this group, but its usefulness as a medium for chemical reactions is limited by its chemical properties. Thus it reacts with the chlorides of non-metals and of many transition elements and cannot be used as a medium to facilitate their reactions in solution, whereas phosphorus oxychloride,[1] for example, has been found to be a suitable solvent for this group of compounds.

Non-aqueous solvents are found among widely different classes of chemical compound.[2–4] Thus, the ionising properties of liquid ammonia [5] and sulphur dioxide [3] are well known. Like water and ammonia, a number of hydrides, such as hydrazine, hydrogen fluoride, and hydrogen cyanide, behave as ionising solvents. Anhydrous acids, such as sulphuric, nitric, or acetic acid, are also ionising solvents, as are alcohols and acid amides. Further groups include a number of covalent halides, *e.g.*, bromine(III) fluoride, arsenic(III) chloride, oxides of non-metals, molten iodine, and certain organic compounds, such as pyridine or nitrobenzene.

Properties of Ionising Solvents.—Both the physical properties and the general chemical character determine the ionising power of a polar solvent. It is usually greater when the dielectric constant and the enthalpies of solvation are high and when the solvent molecules are associated, as shown by high heats of vaporisation, L (in kcal. mole^{-1}) in Table 1, which also shows *inter alia* the dielectric constant ε and the specific conductivity κ (in ohm^{-1} cm.$^{-1}$).

Ionising solvents dissolve certain compounds with the formation of conducting solutions and their tendency to solvate solutes or ions is frequently exhibited by the formation of crystalline compounds containing solvent molecules (solvates). Most ionising solvents possess a self-conductivity, which is usually small and is to be attributed to the presence of solvent ions (self-ionisation). It is usually possible to recognise substances which behave as acids or bases,[6] and ionic reactions may be carried out which may be either metathetical or acid–base in type.

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[1] Gutmann, *Österr. Chem. Ztg.*, 1955, **56**, 126.

[2] Audrieth and Kleinberg, " Non-Aqueous Solvents ", John Wiley and Sons Inc., New York, 1953.

[3] Jander, " Die Chemie in wasserähnlichen Lösungsmitteln ", Springer, Berlin, Göttingen, Heidelberg, 1949.

[4] Moeller, " Inorganic Chemistry ", John Wiley and Sons Inc., New York, 1952.

[5] Franklin, " The Nitrogen System of Compounds ", Reinhold Publ. Corp., New York, 1935.

[6] Cady and Elsey, *J. Chem. Educ.*, 1928, **5**, 1425.

TABLE 1. *Some physical properties of certain ionising solvents*

Solvent	Ions produced by self-ionisation	M.p.	B.p.	ε (temp.)	$\varkappa$ (temp.)	L
H_2O	H_3O^+, OH^-	0°	100°	81·1 (18°)	6×10^{-8} (25°)	9·72
NH_3	NH_4^+, NH_2^-	−78	−33·5	22·0 (−34°)	4×10^{-11} (−78°)	5·64
$NH_2{\cdot}NH_2$	$N_2H_5^+$, $N_2H_3^-$	2	113·5	51·7 (25°)	2×10^{-6} (25°)	10·7
HF	H_2F^+, HF_2^-	−85	19·5	83·6 (0°)	1×10^{-5} (−37°)	6·5
HCN	H_2CN^+, CN^-	−13·4	25	123·0 (16°)	5×10^{-7} (0°)	6·74
HNO_3	$H_2NO_3^+$, NO_3^-	−41·4	86	Unknown	9×10^{-3} (0°)	7·25
H_2SO_4	$H_3SO_4^+$, HSO_4^-	10·4	274	*ca.* 85 (20°)	2×10^{-2} (18°)	
$CH_3{\cdot}OH$	$CH_3{\cdot}OH_2^+$, $CH_3{\cdot}O^-$	−98	64·8	31·2 (20°)	2×10^{-9} (25°)	8·42
$H{\cdot}CO_2H$	$H{\cdot}CO_2H_2^+$, $H{\cdot}CO{\cdot}O^-$	8·4	100·8	57·0 (25°)	6×10^{-5} (25°)	5·38
AcOH	$AcOH_2^+$, AcO^-	16·6	118	9·7 (18°)	4×10^{-9} (25°)	5·81
$H{\cdot}CO{\cdot}NH_2$	$H{\cdot}CO{\cdot}NH_3^+$, $H{\cdot}CO{\cdot}NH^-$	2·5	193	115·5 (20°)	6×10^{-7} (20°)	
BrF_3	BrF_2^+, BrF_4^-	−9	127	Unknown	8×10^{-3} (25°)	10
IF_5	IF_4^+, IF_6^-	9·6	98	36·2 (25°)	2×10^{-5} (25°)	10·1
AsF_3	AsF_2^+, AsF_4^-	−8·5	57·8	Unknown	2×10^{-5} (25°)	8·57
$AsCl_3$	$AsCl_2^+$, $AsCl_4^-$	−18	130·2	12·8 (20°)	1×10^{-7} (20°)	12·64
ICl	I^+, ICl_2^-	27·2	97·4	Unknown	5×10^{-3} (35°)	9·95
$POCl_3$	$POCl_2^+$, Cl^-	1·2	105·8	13·9 (22°)	2×10^{-8} (20°)	8·06
NOCl	NO^+, Cl^-	−61·5	−6·5	18·2 (−12°)	3×10^{-6} (−20°)	6·14
$SeOCl_2$	$SeOCl^+$, $SeOCl_3^-$	9·8	178	46·2 (20°)	2×10^{-5} (20°)	7·60
$SOCl_2$	$SOCl^+$, Cl^-	−104·5	75·7	9·1 (20°)	3×10^{-9} (20°)	6·48
SO_2Cl_2	SO_2Cl^+, Cl^-	−54·1	69·5	9·2 (20°)	2×10^{-8} (20°)	6·68
$HgBr_2$	$HgBr^+$, $HgBr_3^-$	238	320	9·8 (240°)	2×10^{-4} (242°)	20·01
I_2	I^+, I_3^-	113·6	183	11·1 (118°)	9×10^{-6} (140°)	10·39
SO_2	SO^{++}, SO_3^{--}	−75·7	−10	13·8 (15°)	1×10^{-7} (0°)	5·96
N_2O_4	NO^+, NO_3^-	−11·3	21·1	2·4 (18°)	1×10^{-12} (17°)	9·11

Classification of Ionising Solvents.—In considering, first, acid–base reactions, a distinction is usually made between *protonic* and *non-protonic solvents*. The former contain hydrogen in an ionisable form and the cations produced by auto-ionisation are considered to be solvated protons. Typical *protonic solvents* are: water, liquid ammonia,[2–5] hydrazine,[2, 7] hydrogen cyanide,[3] hydrogen sulphide,[3] sulphuric acid,[2] nitric acid,[3] formic and acetic acids,[8] alcohols,[9] and amides.[10] Liquid hydrogen fluoride [2, 3] is frequently also included.

Non-protonic solvents do not contain hydrogen.[11] The following are typical: certain oxides of non-metals (liquid sulphur dioxide [3] and liquid dinitrogen tetroxide [12]), some covalent fluorides [bromine(III) fluoride,[13] iodine(V) fluoride,[14] arsenic(III) fluoride,[15] and fluorosulphonic acid [16]], chlorides [iodine(I) chloride,[17] arsenic(III) chloride [18] and probably also antimony(III) chloride], oxychlorides (selenium oxychloride,[19] carbonyl

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[7] Audrieth and Ogg, "The Chemistry of Hydrazine", John Wiley and Sons Inc., New York, 1951.

[8] Maass and Jander, *Fortschr. chem. Forsch.*, 1953, **2**, 619.

[9] Williams, *Chem. Rev.*, 1931, **8**, 303.

[10] Walden, "Elektrochemie nicht-wässriger Lösungen", Barth, Leipzig, 1924.

[11] Spandau and Gutmann, *Angew. Chem.*, 1952, **64**, 93.

[12] Addison and Thompson, *J.*, 1950, S211, 218.

[13] Woolf and Emeléus, *J.*, 1949, 2865; for a review see Gutmann, *Angew. Chem.*, 1950, **62**, 312.

[14] Emeléus and Sharpe, *J.*, 1949, 2206; Woolf, *J.*, 1950, 3678.

[15] Woolf and Greenwood, *J.*, 1950, 2200.

[16] Woolf, *J.*, 1955, 433.

[17] Gutmann, *Z. anorg. Chem.*, 1951, **264**, 156.

[18] *Idem, ibid.*, 1951, **266**, 331.

[19] Smith, *Chem. Rev.*, 1938, **23**, 165.

chloride,[20] thionyl chloride,[21] sulphuryl chloride,[22] phosphorus oxychloride,[1] nitrosyl chloride [23]), bromides [mercury(II) bromide,[24] aluminium bromide,[25] iodine bromide [26]] and molten iodine.[27] Some organic compounds have been mentioned among protonic solvents, but others are non-protonic, such as acetic anhydride [28] or diethyl ether.[29] In addition, organic ionising solvents are known, which appear to have no self-ionisation in the pure liquids. Among these nitrobenzene, pyridine, ethylenediamine, acetone, and acetonitrile may be mentioned.

Acids and Bases.—Acids may be defined as solutes which increase the concentration of cations characteristic of the pure solvent, and bases as solutes which increase that of anions characteristic of the pure solvent.[6] Thus each solvent with self-ionisation may be regarded as a parent of acids and bases. According to the self-ionisations of water and liquid ammonia ($2H_2O \rightleftharpoons H_3O^+ + OH^-$ and $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$) the hydroxyl and amide ions are considered formally analogous with respect to the corresponding solvent systems, being characteristic for basic solutions. Similarly, hydroxonium and ammonium compounds are analogous, since they behave as acids in the respective solvents by increasing the concentration of solvent cations. In an analogous way each solvent with self-ionisation may be considered as a parent for a system of compounds.

An alternative description of acid–base behaviour is that due to Brønsted [30] and Lowry.[31] These definitions can be applied to protonic systems only, since proton-transfer reactions are considered as responsible for both the auto-ionisation of the amphoteric solvent molecules and for most acid–base reactions in their solutions. Acids and bases are defined as proton-donors and proton-acceptors respectively. Detailed discussions of the concept of acids and bases in non-aqueous systems have been given by various authors [2–6, 11, 30–39] and so need not be discussed further.

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[20] Germann, *J. Amer. Chem. Soc.*, 1925, **47**, 2461.

[21] Spandau and Brunneck, *Z. anorg. Chem.*, 1952, **270**, 201 ; 1955, **278**, 197.

[22] Gutmann, *Monatsh.*, 1954, **85**, 393, 404.

[23] Burg and McKenzie, *J. Amer. Chem. Soc.*, 1952, **74**, 3143.

[24] Jander and Brodersen, *Z. anorg. Chem.*, 1950, **261**, 261 ; 1950, **262**, 33.

[25] Jander and Zschaage, *ibid.*, 1953, **272**, 53.

[26] Gutmann, *Monatsh.*, 1951, **82**, 156.

[27] Jander and Bandlow, *Z. phys. Chem.*, 1943, *A*, **191**, 321.

[28] Jander, Rüsberg, and Schmidt, *Z. anorg. Chem.*, 1948, **255**, 238 ; Schmidt, Wittkopf, and Jander, *ibid.*, 1948, **256**, 113.

[29] Jander and Kraffczyk, *ibid.*, 1955, **282**, 121 ; 1956, **283**, 217.

[30] Brønsted, *Rec. Trav. chim.*, 1923, **42**, 718.

[31] Lowry, *J. Soc. Chem. Ind.*, 1923, **42**, 43.

[32] Ebert and Konopik, *Österr. Chem. Ztg.*, 1949, **50**, 184.

[33] Gutmann and Lindqvist, *Z. phys. Chem.*, 1953, **203**, 250.

[34] Gutmann, *Svensk Kem. Tidskr.*, 1955, **68**, 1.

[35] Lindqvist, *Acta Chem. Scand.*, 1955, **9**, 73.

[36] Bjerrum, *Angew. Chem.*, 1951, **63**, 527.

[37] Bell, *Quart. Rev.*, 1947, **1**, 113 ; *Ann. Reports*, 1934, **31**, 71.

[38] Luder and Zuffanti, " The Electronic Theory of Acids and Bases ", John Wiley and Sons Inc., New York, 1946.

[39] Bradley, *J. Chem. Educ.*, 1950, **27**, 208.

Some Reactions in Liquid Ammonia.—Liquid ammonia is one of the best-known non-aqueous ionising solvents and serves to illustrate some general points. Numerous compounds are soluble to give conducting solutions. According to its self-ionisation ($2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$) ammonium salts behave as acids and amides as bases. Solutions of protonic acids in liquid ammonia contain NH_4^+ ions and thus show acidic properties. Owing to the high proton affinity of the solvent they will be stronger acids than in water, *e.g.*, ammonium acetate is a strong acid in liquid ammonia, although acetic acid is rather weak in water; acetamide is a weak base in water, but shows acidic properties in liquid ammonia:

$$CH_3 \cdot CO \cdot NH_2 + NH_3 \rightleftharpoons NH_4^+ + CH_3 \cdot CO \cdot NH^-.$$

The two types of solvent ions may combine on mixing of acidic and basic solutions (neutralisation reaction). Solvent molecules are produced and the ions remaining in the solution may give a salt, *e.g.*, $NH_4^+Cl^- + K^+NH_2^- = K^+Cl^- + 2NH_3$. Solvolytic reactions occur very readily in liquid ammonia solution, *e.g.*, $SO_2Cl_2 + 4NH_3 \rightleftharpoons SO_2(NH_2)_2 + 2NH_4Cl$, or $TiCl_4 + 8NH_3 \rightleftharpoons Ti(NH_2)_4 + 4NH_4Cl$. Metathetical reactions are also possible. Thus, insoluble barium chloride is formed from mixtures of soluble silver chloride and barium nitrate. Many examples of complex formation are also known.[40]

Weak acids or bases may react both with strong bases and with acids and thus show amphoteric properties. This is illustrated by the behaviour of silver amide in liquid ammonia: $AgNH_2 \rightleftharpoons Ag^+ + NH_2^-$ (basic reaction) and $AgNH_2 + 2NH_3 \rightleftharpoons NH_4^+ + [Ag(NH_2)_2]^-$ (acid reaction). The reactions may be studied by preparative, conductometric, or potentiometric methods. The glass electrode may be used [41] and a number of polarographic investigations have also been reported.[42–44]

Liquid ammonia is unique in its ability to dissolve alkali and alkaline-earth metals without oxidation. The solutions show extremely high conductivities owing to the presence of electrons, which are more or less solvated.[45] These solutions are therefore very powerful reducing agents.[45–47] Zintl and his co-workers [48, 49] found that solutions of alkali metals in liquid ammonia were able to reduce many compounds to the free elements, to intermetallic compounds, or to homopolyatomic anionic complexes containing the reduced elements. For example, with lead iodide the compound $Na_4[Pb(Pb)_8]$ has been obtained.

The formation of compounds containing the elements with unfamiliar

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[40] Schmitz-Dumont, *Angew. Chem.*, 1950, **62**, 560.

[41] Heyn and Bergin, *J. Amer. Chem. Soc.*, 1953, **75**, 5120.

[42] Laitinen and Nyman, *ibid.*, 1948, **70**, 2241, 3002.

[43] Laitinen and Shoemaker, *ibid.*, 1950, **72**, 663, 4975.

[44] McElroy and Laitinen, *J. Phys. Chem.*, 1953, **57**, 564.

[45] Kraus, *J. Amer. Chem. Soc.*, 1908, **30**, 653, 1197, 1323; 1921, **43**, 749; *Chem. Rev.*, 1931, **8**, 251.

[46] Watt, *Chem. Rev.*, 1950, **46**, 289.

[47] Fernelius and Watt, *ibid.*, 1937, **20**, 195.

[48] Zintl, Goubeau, and Dullenkopf, *Z. phys. Chem.*, 1931, *A*, **154**, 1.

[49] Zintl and Harder, *ibid.*, p. 47.

oxidation states is one of the lesser known features of chemistry in liquid ammonia solution.[50] For example, tetracyanonickelate(II) is reduced by potassium in liquid ammonia at − 33° to the red cyanonickelate(I),[51] which is slowly reduced further at 0° to the yellow cyanonickelate(0), $K_4[Ni(CN)_4]$.[52] No cyanonickelate(I) is observed when cyanonickelate(II) is reduced by excess of potassium.[52] Similarly the compounds $K_4[Co(CN)_4]$[53] and $K_4[Pd(CN)_4]$[54] are produced, which contain the transition metal in the zero oxidation state. On the other hand, the reduction of the cyano-complex of chromium(III) gives a product containing chromium(I), and that of the corresponding compound of manganese yields a mixture of complex cyanides containing Mn(I) and Mn(0).[55] The reduction of bromopentamminoiridium(III) bromide leads to the interesting compound $Ir(NH_3)_4$,[56] which is insoluble in liquid ammonia. There is also evidence for a less stable ammine of platinum(0).[57]

Carbonyl compounds of the transition metals with an oxidation number of zero [58] may be further reduced to carbonyl metallates. These are salt-like compounds containing the metals with negative oxidation numbers in the complex anions, *e.g.*, $Na[Co^{1-}(CO)_4]$ or $Na_2[Fe^{2-}(CO)_4]$.[59] Other types of reduction reactions in liquid ammonia have been reviewed elsewhere.[46, 47, 60]

Reactions in Glacial Acetic Acid.—Although acetic acid is a poorer ionising solvent [8] than formic acid, it has found many applications in analytical chemistry, mostly for acid–base titrations. These are carried out with great ease, accuracy, and elegance. The pH scale of acetic acid covers 12 units [61] against only 6 for formic acid, which is furthermore less easily accessible in the pure state.[62] Compounds which are very weak bases in water and thus cannot be titrated in this medium become strong bases in glacial acetic acid.[8, 63, 64] Although the strength of perchloric acid in acetic acid is smaller than in water, accurate titrations with organic bases are readily carried out.[65] Absolute perchloric acid solutions in glacial acetic acid are easily prepared by mixing aqueous perchloric acid with the calculated quantity of acetic anhydride in glacial acetic acid. The solutions can be standardised against sodium carbonate or sodium phthalate. The end-point may be found potentiometrically or, preferably, by the use of

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[50] Colton, *J. Chem. Educ.*, 1954, **31**, 527.

[51] Eastes and Burgess, *J. Amer. Chem. Soc.*, 1942, **64**, 1187.

[52] Watt, Hall, Choppin, and Gentile, *ibid.*, 1954, **76**, 373.

[53] Hieber and Bartenstein, *Naturwiss.*, 1952, **13**, 300.

[54] Burbage and Fernelius, *J. Amer. Chem. Soc.*, 1943, **65**, 1484.

[55] Davidson and Kleinberg, *J. Phys. Chem.*, 1953, **57**, 571.

[56] Watt and Mayfield, *J. Amer. Chem. Soc.*, 1953, **75**, 6178.

[57] Watt, Walling, and Mayfield, *ibid.*, 6175.

[58] Hieber, *Angew. Chem.*, 1942, **55**, 1 ; Emeléus and Andersson, " Modern Aspects of Inorganic Chemistry ", Routledge, London, 1952.

[59] Behrens and Weber, *Z. anorg. Chem.*, 1955, **281**, 190.

[60] Birch, *Quart. Rev.*, 1950, **4**, 69.

[61] Jander and Klaus, *J. Inorg. Nucl. Chem.*, 1955, **1**, 334.

[62] Lange, *Z. phys. Chem.*, 1940, *A*, **187**, 27.

[63] Hall, *Chem. Rev.*, 1931, **8**, 191. [64] Hammett, *ibid.*, 1933, **13**, 61.

[65] Auerbach, *Drug Standards*, 1951, **19**, 127.

colour indicators, such as crystal-violet, which gives a sharp colour change from blue to green. The sharpness of the colour change is suppressed by the presence of water, which therefore should be excluded.

Among the compounds which can be titrated with an accuracy of ± 0·2% are aniline, pyridine, and other nitrogenous bases.[66] Tertiary aliphatic amines can be estimated in the presence of primary and secondary amines,[67] since the latter can be converted into neutral amides by addition of acetic anhydride.[68] It seems of particular interest that amino-acids can also be determined with great ease in glacial acetic acid.[69–71] Amino-sulphamides have been estimated by potentiometric methods.[72, 73] Alkali salts of weak acids, such as picrates, citrates, or tartrates yield the respective acetates in acetic acid and thus may be easily titrated with perchloric acid in this medium.[67] Furthermore, derivatives of pyrrole and chlorophyll[74] may be determined as well as polypeptides.[75]

Apart from acid–base titrations, various addition, substitution, and redox reactions have been found of analytical interest. Iodine numbers of fats and essential oils may be determined[76] and bromine may be used to titrate organic compounds, which can form bromo-derivatives.[76] For the titration of phenol with bromine the addition of sodium acetate has been recommended. Redox reagents are chromium(VI) oxide, sodium permanganate, bromine, titanium(III) chloride, and chromium(II) salts.[77, 78] The titrations are usually carried out in perchloric acid solutions and in an inert atmosphere, but traces of water are tolerable.

Reactions in Bromine(III) Fluoride.—Bromine(III) fluoride dissolves a number of fluorides and is a powerful fluorinating agent. Many elements, oxides, halides, or salts of oxy-acids are converted into fluorides, in which the highest valency states are often found.[79] It is an ionising solvent for fluorides and has a self-ionisation in the pure liquid state,[13, 80] which may be explained in terms of fluoride-ion transfer processes between solvent molecules (autofluoridolysis) :[33, 34]

$$\underset{\text{base 2}}{\mathrm{BrF_3}} \overset{\mathrm{F^-}}{\longrightarrow} \underset{\text{acid 1}}{\mathrm{BrF_3}} \qquad \underset{\text{base 2}}{\mathrm{BrF_3}} + \underset{\text{acid 1}}{\mathrm{BrF_3}} \rightleftharpoons \underset{\text{acid 2}}{\mathrm{BrF_2^+}} + \underset{\text{base 1}}{\mathrm{BrF_4^-}}$$

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[66] Blumrich and Bandel, *Angew. Chem.*, 1941, **54**, 373.

[67] Wagner, Brown, and Peters, *J. Amer. Chem. Soc.*, 1947, **69**, 2609.

[68] Haslam and Hearn, *Analyst*, 1944, **69**, 141.

[69] Harris, *Biochem. J.*, 1935, **29**, 2820.

[70] Nadeau and Branchen, *J. Amer. Chem. Soc.*, 1935, **57**, 1363.

[71] Toennis and Callan, *J. Biol. Chem.*, 1938, **125**, 259.

[72] Markunas and Riddick, *Analyt. Chem.*, 1951, **23**, 337.

[73] Tomiček, *Coll. Czech. Chem. Comm.*, 1948, **13**, 116.

[74] Conant, Chow, and Dietz, *J. Amer. Chem. Soc.*, 1934, **56**, 2185.

[75] Harris, *J. Biol. Chem.*, 1929, **84**, 296.

[76] Tomiček and Dolezal, *Acta Pharm. Int.*, 1950, **1**, 31.

[77] Tomiček and Heyrovsky, *Coll. Czech. Chem. Comm.*, 1950, **15**, 997.

[78] Tomiček and Valcha, *ibid.*, 1951, **16**, 113.

[79] Sharpe and Emeléus, *J.*, 1948, 2135.

[80] Banks, Emeléus, and Woolf, *J.*, 1949, 2861.

Fluorides of the alkali and alkaline-earth metals, as well as silver, nitrosyl, and nitryl fluorides, act as bases by donating fluoride ions to the solvent : $KF + BrF_3 = K^+ + BrF_4^-$. Fluorides of other elements may accept fluoride ions from the solvent and thus show acidic properties : $BrF_3 + SbF_5 = BrF_2^+ + SbF_6^-$. Other acids are the fluorides of boron, gold(III), silicon, germanium(IV), tin(IV), titanium(IV), phosphorus(V), arsenic(V), vanadium(V), niobium(V), tantalum(V), bismuth(V), ruthenium(V), and platinum(IV), as well as hydrogen fluoride [81] and sulphur trioxide. Thus a fluoride-ion donor may be regarded as a base and a fluoride-ion acceptor as an acid. Compounds have been found which appear to contain solvent ions, *e.g.*, $K^+BrF_4^-$ or $BrF_2^+SbF_6^-$.

Complex fluorides are formed by neutralisation reactions, *e.g.*, $KBrF_4 + BrF_2SbF_6 \rightleftharpoons KSbF_6 + 2BrF_3$, which may simply be written : $K^+ + SbF_6^- \rightleftharpoons KSbF_6$. Such compounds are easily prepared by making use of both the fluorinating and ionising properties of bromine(III) fluoride : compounds which will yield the acidic and basic fluorides by fluorination are mixed in the desired proportions and allowed to react with excess of bromine(III) fluoride. A mixture of potassium chloride and antimony(III) oxide, for example, may be used to obtain potassium hexafluoroantimonate, while a mixture of gold and silver in equimolar proportions will yield the insoluble silver tetrafluoroaurate, $AgAuF_4$, by treatment with bromine(III) fluoride.[82] Hexafluorovanadates,[83] hexafluororuthenates(V),[84] pentafluoromanganates(IV),[85] complex oxyfluorides of rhenium,[86] and a number of nitrosonium and nitronium compounds [87, 88] have been prepared for the first time by analogous reactions and many other complex fluorides may easily be obtained by this method [86–91] (see Table 2).

TABLE 2. *Examples of complex formation in bromine trifluoride*

Reactants for :		Product	Ref.	Reactants for :		Product	Ref.
acid solution	basic solution			acid solution	basic solution		
Au	Ag	$AgAuF_4$	82	B_2O_3	NaCl	$NaBF_4$	89
VCl_3	$BaCl_2$	$Ba(VF_6)_2$	83	As_2O_3	NO_2	NO_2AsF_6	88
VCl_3	AgCl	$AgVF_6$	83	SO_3	NO_2	NO_2SO_3F	89
V_2O_5	NOCl	$NOVF_6$	85	Ru	KBr	$KRuF_6$	84
Nb	$CaCl_2$	$Ca(NbF_6)_2$	90	$Mn(IO_3)_2$	KCl	$KMnF_5$	85
GeO_2	NOCl	$(NO)_2GeF_6$	87	Cr_2O_3	AgCl	$AgCrOF_4$	85

[81] Rogers and Katz, *J. Amer. Chem. Soc.*, 1952, **74**, 1375.

[82] Sharpe, *J.*, 1950, 2901.

[83] Emeléus and Gutmann, *J.*, 1949, 2979.

[84] Hepworth, Peacock, and Robinson, *J.*, 1954, 1197.

[85] Sharpe and Woolf, *J.*, 1951, 798.

[86] Peacock, *J.*, 1955, 602.

[87] Woolf, *J.*, 1950, 1053.

[88] Woolf and Emeléus, *ibid.*, p. 1050.

[89] Emeléus and Woolf, *ibid.*, p. 164.

[90] Gutmann and Emeléus, *ibid.*, p. 1046.

[91] Sharpe, *ibid.*, p. 3444.

Reactions in Solutions of Some Chlorides and Oxychlorides.—Self-ionisation of the pure liquid seems to occur in iodine(I) chloride,[17] arsenic(III) chloride,[18] carbonyl chloride,[20] nitrosyl chloride,[23, 92] phosphorus oxychloride,[1, 93] selenium oxychloride,[19] thionyl chloride,[21] sulphuryl chloride,[22] and possibly also in antimony(III) chloride. The equilibria may be regarded as due to chloride-ion-transfer reactions between solvent molecules,[33–35], *e.g.*:

$$\begin{array}{lcl}
\multicolumn{3}{l}{\overset{\mathrm{Cl}^-}{\curvearrowright}} \\
\mathrm{ICl} & + \ \mathrm{ICl} & \rightleftharpoons & \mathrm{I}^+ & + \ \mathrm{ICl_2}^- \\
\mathrm{AsCl_3} & + \ \mathrm{AsCl_3} & \rightleftharpoons & \mathrm{AsCl_2}^+ & + \ \mathrm{AsCl_4}^- \\
\text{base 2} & \text{acid 1} & & \text{acid 2} & \text{base 1}
\end{array}$$

Accordingly, an acid may be defined as a chloride-ion acceptor and a base as a chloride-ion donor. These solvents give conducting solutions with various solutes, from which compounds between solute and solvent may be isolated (solvates). Examples are the compounds $\mathrm{KCl,ICl}$, $\mathrm{(CH_3)_4NCl,3AsCl_3}$,[94] $\mathrm{Ca(AlCl_4)_2,2COCl_2}$,[95] $\mathrm{FeCl_3,2NOCl}$,[96] $\mathrm{SbCl_5,POCl_3}$,[97] $\mathrm{ZrCl_4,2POCl_3}$,[98] and $\mathrm{FeCl_3,2SeOCl_2}$.[99] Some of them may contain the solvent molecules bound in complex ions,[34] *e.g.*, $\mathrm{K^+ICl_2^-}$,[100] $\mathrm{POCl_2^+SbCl_6^-}$,[101] or possibly $\mathrm{[(CH_3)_4N]^+[As_3Cl_{10}]^-}$, $\mathrm{[N_2O_2Cl]^+[FeCl_4]^-}$.[96]

Chlorides may behave as acids or bases (Table 3) and neutralisation reactions lead to the formation of chloro-complexes. Thus chloroantimonates,[102] chlorostannates,[103] chloroaluminates,[104] and chlorozirconates [98] have been isolated from the solutions. Other complex compounds such as chlorovanadates(IV) [105] seem to be formed in the solutions, but cannot be obtained free from acidic and basic components. It is interesting that usual colour indicators can be used to follow neutralisations between anhydrous chlorides in thionyl chloride [21] or phosphorus oxychloride.[105a] Table 3 gives examples investigated by conductimetric titrations or preparative investigations; the relative basicities for chlorides in phosphorus oxychloride, determined potentiometrically,[105a] increase in the order $\mathrm{SbCl_5}$, $\mathrm{FeCl_3}$, $\mathrm{ZrCl_4}$, $\mathrm{SbCl_3}$, $\mathrm{POCl_3}$, $\mathrm{SnCl_4}$, $\mathrm{TaCl_5}$, $\mathrm{NbCl_5}$, $\mathrm{AlCl_3}$, $\mathrm{PCl_5}$, $\mathrm{TiCl_4}$, $\mathrm{Me_4NCl}$, pyridinium chloride, $\mathrm{Et_4NCl}$.

[92] Lewis and Wilkins, *J.*, 1955, 56.

[93] Gutmann, *Monatsh.*, 1952, **83**, 164.

[94] Lindqvist and Andersson, *Acta Chem. Scand.*, 1954, **8**, 128.

[95] Germann and Gagos, *J. Phys. Chem.*, 1924, **28**, 965; Germann and Timpany, *J. Amer. Chem. Soc.*, 1925, **47**, 2275.

[96] Addison and Lewis, *Quart. Rev.*, 1955, **9**, 124.

[97] Gutmann, *Z. anorg. Chem.*, 1952, **269**, 279.

[98] Gutmann and Himml, unpublished results.

[99] Wise, *J. Amer. Chem. Soc.*, 1923, **45**, 1233.

[100] Wyckoff, *ibid.*, 1920, **42**, 1100.

[101] Maschka, Gutmann, and Sponer, *Monatsh.*, 1955, **86**, 52.

[102] Gutmann, *Research*, 1950, **4**, 336.

[103] *Idem, Z. anorg. Chem.*, 1952, **270**, 179.

[104] Germann and Birosel, *J. Phys. Chem.*, 1925, **29**, 1469.

[105] Gutmann, *Monatsh.*, 1951, **82**, 473.

[105a] Gutmann and Marringer, *Z. anorg. Chem.*, in the press.

TABLE 3. *Examples of acids and bases in chlorides and oxychlorides*

(A = acid, B = base, Am = amphoteric, i = insoluble or sparingly soluble.)

Solvent / Solute	ICl	$AsCl_3$	$SbCl_3$	$COCl_2$	NOCl	$POCl_3$	$SOCl_2$	SO_2Cl_2	$SeOCl_2$
Pyridine	B	B	B	B	B	B	B	B	B
KCl	B	i (?)	B	B	i	B	B		B
R_4NCl	B	B	B	B	B	B	B	B	B
AgCl		i		i		i	i		i
$BaCl_2$	i			B				i	B
$AlCl_3$	Am (?)	A	i	A	A	Am	A	A	A
$FeCl_3$		A			A	A	A		A
$SnCl_4$	A	A			A	Am	A	A	A
$TiCl_4$	A	A				Am	Am	A	A
$ZrCl_4$		i			Am	Am	Am	i	Am
VCl_4	A	A				A	A	A	
$TeCl_4$		Am				Am	B		
PCl_5	Am	B				Am	Am	B	
$SbCl_5$	A	A			A	A	A	A	A

These solvents can be used as chlorinating agents ; *e.g.*, iodine(I) chloride converts various elements into the chlorides,[106] and vanadium(III) chloride may be obtained either from finely divided vanadium powder and iodine(I) chloride [107] or from vanadium(III) oxide and thionyl chloride.[108] Thionyl chloride reacts less readily with metals, but the rate is considerably increased by addition of acids, such as aluminium or ferric chlorides.[109] Thionyl chloride converts vanadium pentoxide into the oxytrichloride, and zirconium(IV) oxide into the compound $ZrCl_4,SOCl_2$.[108] Aluminium chloride has been removed from Friedel–Crafts mixtures by the use of phosphorus oxychloride.[110] Derivatives of the unknown arsenic(V) chloride, *e.g.*, $PCl_5,AsCl_5$ and $AsCl_5,SbCl_5$, have been obtained by passing chlorine through the solutions of phosphorus(V) or antimony(V) chloride in arsenic(III) chloride.[111] These may contain the $[AsCl_4]^+$ ion, which is known to exist in the compound $[AsCl_4]^+[AsF_4]^-$.[112] This interesting compound is formed [112] when chlorine is passed through liquid arsenic(III) fluoride at 0°.

It has recently been discovered that thionyl and carbonyl chloride are excellent dehydrating agents, since with water they give exclusively volatile products,[113] *e.g.*, $SOCl_2 + H_2O \rightleftharpoons SO_2 + 2HCl$. By this method the commercially available " anhydrous " hydrogen fluoride can be freed from the last traces of water.[2] Since water of crystallisation may also react, anhydrous chlorides can be produced from the corresponding hydrates. This method is particularly useful for preparing anhydrous chlorides from hydrates which are decomposed by heat.

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[106] Gutmann, *Z. anorg. Chem.*, 1951, **264**, 169.
[107] *Idem*, *Monatsh.*, 1950, **81**, 1155.
[108] Hecht, Jander, and Schlapmann, *Z. anorg. Chem.*, 1947, **254**, 255.
[109] Hubbard and Luder, *J. Amer. Chem. Soc.*, 1951, **73**, 1373.
[110] Dye, *ibid.*, 1948, **70**, 2595.
[111] Gutmann, *Monatsh.*, 1951, **82**, 473.
[112] Kolditz, *Z. anorg. Chem.*, 1955, **280**, 313.
[113] Hecht, *ibid.*, 1947, **254**, 37.

Reactions in Molten Mercury(II) **Bromide.**—Anhydrous mercury(II) bromide when molten is an excellent solvent for various classes of compound.[24] Its self-conductivity is attributed [24] to ionisation according to the equation $2HgBr_2 = HgBr^+ + HgBr_3^-$, which may be considered as due to bromide-ion transfer between solvent molecules.[33, 34]

Mercuric salts of perchloric, sulphuric, nitric, and phosphoric acids show acidic properties in this solvent, *e.g.*, $Hg(ClO_4)_2 + HgBr_2 \rightleftharpoons HgBr^+ + 2ClO_4^-$, while bromides of the electropositive metals are typical bases. Halides of mercury also behave as bases in molten mercury(II) bromide,[114] since they produce bromide ions by reaction with solvent molecules, *e.g.*, $HgO + HgBr_2 \rightleftharpoons Hg_2OBr^+ + Br^-$. Ionic reactions between acids and bases may lead to insoluble products ; *e.g.*, thallium(I) sulphate is formed from mercury(II) sulphate and thallium(I) bromide. Similarly, anhydrous copper(II) sulphate can be prepared by using a copper(II) halide. Perchlorates, nitrates, and phosphates of many other elements can be prepared in a similar manner. By allowing mercury(II) oxide to react with the sulphate in mercury(II) bromide solution a red, insoluble product of composition $(HgO)_2HgSO_4$ is formed.[114] Analogous compounds are formed from the sulphide, selenide, and telluride of mercury.

Mercury(II) bromide acts as a good dehydrating agent for compounds containing water of crystallisation, which is volatile at temperatures corresponding with the liquid range of mercury(II) bromide ; [24] *e.g.*, anhydrous salts have been prepared from the hexahydrate of mercury(II) perchlorate and the dihydrate of mercury(II) nitrate. Many conductometric titrations have been carried out in this medium.[115] For potentiometric work the gold electrode has been found to give reproducible potential values.[116] It has been suggested that conductometric and potentiometric methods could be used for the estimation of electrolytes in molten mercury(II) bromide ; [116] *e.g.*, mercury(II) oxide may be readily titrated with mercury(II) perchlorate.

Some Reactions in Liquid Sulphur Dioxide.—The ionising properties of liquid sulphur dioxide were first observed by Walden.[117] Jander and his school [3, 118] have based the interpretation of their results on the self-ionisation of liquid sulphur dioxide according to the equation : $2SO_2 \rightleftharpoons SO^{++} + SO_3^{--}$ Although it is well established that sulphites behave as bases in its solutions,[119] no typical acid is known with certainty. Thionyl compounds are very poor electrolytes [120] and do not exchange with solvent cations.[121] It seems therefore more likely that $SOCl^+$ and Cl^- ions, but only negligibly small concentrations of SO^{++} ions, are produced in these solutions. In the presence of aluminium chloride, however, slow exchange is observed,[122] which might be explained by the formation of $SO(AlCl_4)_2$.

[114] Jander and Brodersen, *Z. anorg. Chem.*, 1950, **262**, 33.

[115] *Idem, ibid.*, 1951, **264**, 92.

[116] *Idem, Z. analyt. Chem.*, 1951, **133**, 146.

[117] Walden, *Ber.*, 1899, **32**, 2862.

[118] Jander and Ullmann, *Z. anorg. Chem.*, 1937, **230**, 405.

[119] Johnson, Norris, and Huston, *J. Amer. Chem. Soc.*, 1951, **73**, 3052.

[120] Jander and Wickert, *Z. phys. Chem.*, 1936, *A*, **178**, 57.

[121] Herber, Norris, and Huston, *J. Amer. Chem. Soc.*, 1954, **76**, 2015.

[122] Masters and Norris, *ibid.*, 1955, **77**, 1346.

This might behave as a weak acid in liquid sulphur dioxide, but its reaction with sulphites has not yet been studied.

Sulphur dioxide is a very useful solvent for the preparation of various compounds. Niobium and phosphorus oxytrichlorides are formed from the pentachlorides,[3] while tungsten(VI) chloride yields the insoluble oxytetrachloride: $WCl_6 + SO_2 \rightleftharpoons WOCl_4 + SOCl_2$. The reaction $2KBr + SOCl_2 \rightleftharpoons SOBr_2 + 2KCl$ in liquid sulphur dioxide offers a useful way to produce thionyl bromide.[3] Solutions of other thionyl compounds, such as the thiocyanate or the acetate have been obtained, but it is not possible to isolate these compounds in the solid state.[118]

Sulphur dioxide is an excellent medium for complex formation. Tetramethylammonium hexachloroantimonate is easily prepared.[123] By the reaction of acetyl chloride with antimony(V) chloride [124] acetyl hexachloroantimonate is formed, while acetyl tetrafluoroborate is produced from acetyl fluoride and boron(III) fluoride.[125] It reacts with potassium acetate to give insoluble potassium tetrafluoroborate. When antimony(V) chloride is added to a solution of nitrosyl chloride in liquid sulphur dioxide, a bright yellow, conducting solution is formed, from which nitrosonium hexachloroantimonate can be obtained by evaporation of the solvent. The solution can be used to prepare a number of other nitrosonium compounds by metathetical reactions. For example, nitrosonium hexafluorophosphate, $NOPF_6$, is precipitated on addition of tetramethylammonium hexafluorophosphate,[126] and in an analogous manner nitrosonium nitroprusside, $(NO)_2[Fe(NO)(CN)_5]$, can also be obtained.[127, 128]

The solution of nitrosyl fluoride in sulphur dioxide contains the compound SO_2,NOF, which can be isolated.[129] It reacts with fluorides to form the respective nitrosonium fluoro-complexes, such as the fluoroborate or the fluorosilicate.[130] Boron(III) chloride is converted into the fluoride, *e.g.*, $BCl_3 + 3SO_2,NOF = BF_3 + 3NOCl + 3SO_2$, and the chlorides of phosphorus, arsenic, and antimony yield nitrosonium salts of the hexafluoro-acids, *e.g.*, $AsCl_3 + 6SO_2,NOF = NOAsF_6 + 2NO + 3NOCl + 6SO_2$. With sulphur trioxide nitrosonium fluorosulphonate, $NO(SO_3F)$, is formed.[130]

Nitronium hexachloroantimonate gives a conducting solution in liquid sulphur dioxide.[131] Metathetical reactions with tetramethylammonium salts may lead to the soluble tetramethylammonium hexachloroantimonate and insoluble nitronium compounds, such as the perchlorate or the tetrafluoroborate,[131] *e.g.*, $NO_2SbCl_6 + R_4NClO_4 \rightleftharpoons NO_2ClO_4 + R_4NSbCl_6$. It should be noted that solutions of nitryl chloride in sulphur dioxide do not give these reactions.

Another interesting group of compounds, the alkali fluorosulphinates,

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[123] Jander and Hecht, *Z. anorg. Chem.*, 1943, **250,** 308.

[124] Seel and Bauer, *Z. Naturforsch.*, 1947, **2,b,** 397 ; Seel, *Z. anorg. Chem.*, 1943, **252,** 24.

[125] *Idem, ibid.*, 1943, **250,** 331.

[126] Seel and Gössl, *ibid.*, 1950, **263,** 253.

[127] Seel, *ibid.*, 1950, **261,** 81.

[128] Seel and Walassis, *ibid.*, p. 85.

[129] Seel and Meier, *ibid.*, 1953, **274,** 196.

[130] Seel and Massat, *ibid.*, 1955, **280,** 185.

[131] Seel, Nógrádi, and Posse, *ibid.*, 1952, **269,** 197.

$F{\cdot}SO_2M$, has been obtained from solutions of alkali fluorides in sulphur dioxide,[132, 133] These are isomorphous with the corresponding isosteric chlorates[134] and have been shown to fluorinate complex compounds or oxychlorides; *e.g.*, thionyl chloride or arsenic(III) chloride is converted into the respective fluoride.[134]

Many other reactions in liquid sulphur dioxide, such as the occurrence of redox reactions, the sulphonation of aromatic compounds, and the possibility of carrying out Friedel–Crafts reactions[135] have been reviewed elsewhere.[2, 3, 11]

Conclusion.—Although only a few examples of recent advances of the chemistry in non-aqueous ionising solvents have been reviewed here, it is quite apparent that many new applications in preparative and analytical chemistry are opening up. It may well prove more difficult to obtain a detailed picture of the nature of these solutions. Hardly any precise physicochemical investigations have been carried out, and indeed these are usually more difficult than in aqueous solutions, and it is this aspect of the subject which merits special attention.

[132] Seel and Meier, *Z. anorg. Chem.*, 1953, **274**, 202.

[133] Seel and Riehl, *ibid.*, 1955, **282**, 293.

[134] Seel, Jonas, Riehl, and Langer, *Angew. Chem.*, 1955, **67**, 32.

[135] Ross, Percy, Brandt, Gebhart, Mitchell, and Yolles, *Ind. Eng. Chem.*, 1942, **34**, 924.