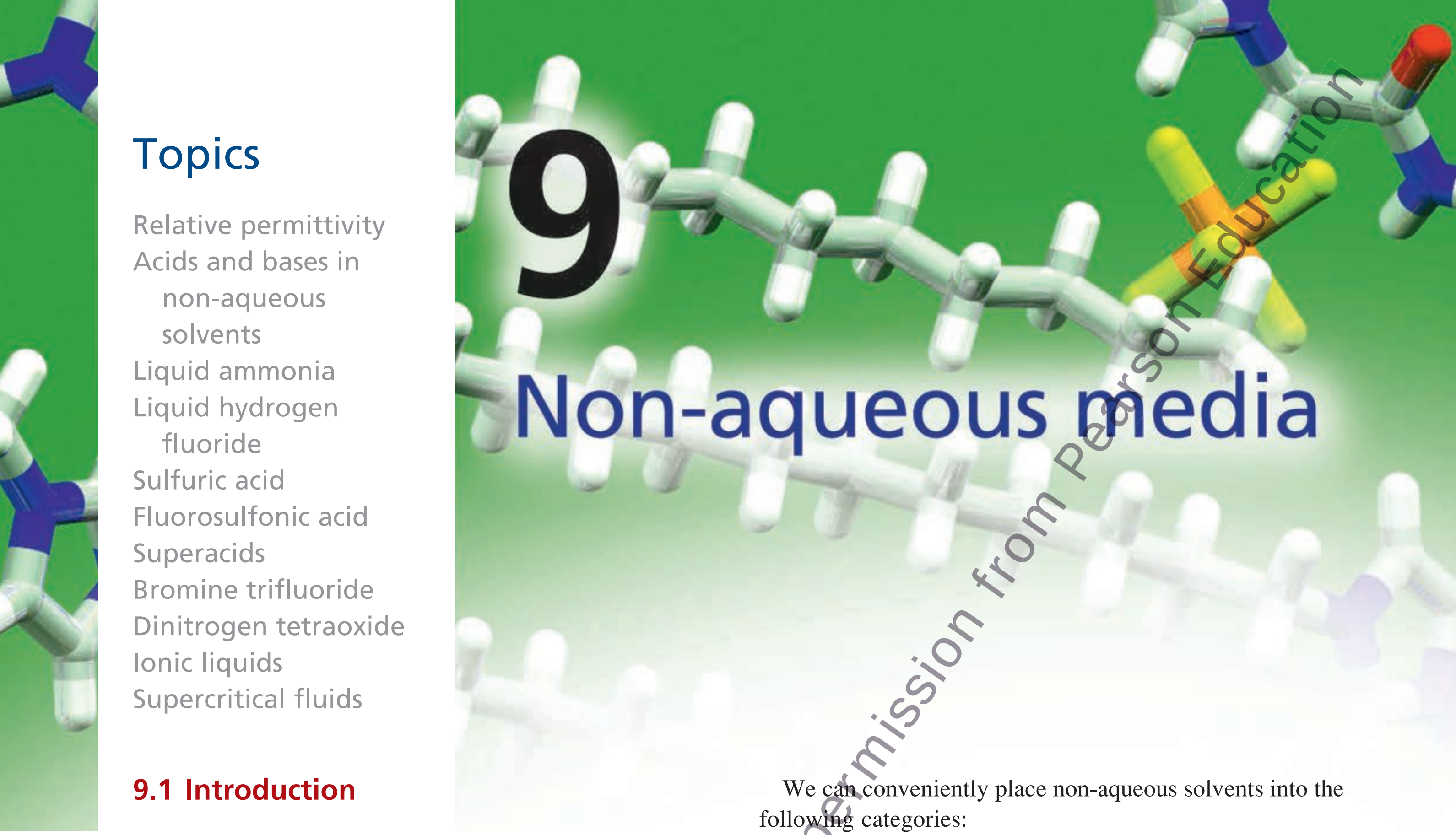


Topics

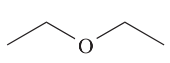
- Relative permittivity
- Acids and bases in non-aqueous solvents
- Liquid ammonia
- Liquid hydrogen fluoride
- Sulfuric acid
- Fluorosulfonic acid
- Superacids
- Bromine trifluoride
- Dinitrogen tetraoxide
- Ionic liquids
- Supercritical fluids

9

Non-aqueous media

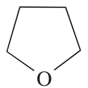
9.1 Introduction

Although many inorganic reactions take place in aqueous solution, it is not always suitable to use water as a solvent. Some reagents may react with H_2O (e.g. the alkali metals) and non-polar molecules are insoluble in water. This chapter discusses *non-aqueous solvents*. The use of solvents other than water is commonplace, and common organic solvents include dichloromethane, hexane, toluene and ethers such as diethyl ether, **9.1**, tetrahydrofuran, **9.2**, and diglyme, **9.3**.



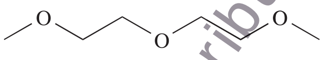
diethyl ether

(9.1)



tetrahydrofuran (THF)

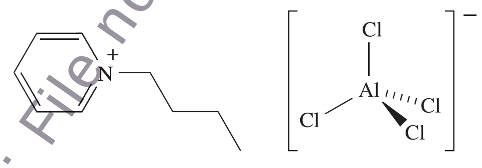
(9.2)



diglyme

(9.3)

These solvents are of significant use to the inorganic chemist, but more exotic solvents are also available. These include liquid NH_3, liquid SO_2, H_2SO_4, BrF_3 and ionic liquids such as $[pyBu][AlCl_4]$, **9.4** (see Section 9.12).



N-butylpyridinium ion tetrachloroaluminate ion

(9.4)

We can conveniently place non-aqueous solvents into the following categories:

- protic solvents (e.g. HF, H_2SO_4, MeOH);
- aprotic solvents (e.g. N_2O_4, BrF_3);
- coordinating solvents (e.g. MeCN, Et_2O, Me_2CO).

> A ***protic solvent*** undergoes ***self-ionization*** (see Section 7.2) to provide protons which are solvated. *If* it undergoes self-ionization, an ***aprotic solvent*** does so without the formation of protons.

As we discuss the properties and uses of some non-aqueous solvents, we must keep in mind that the extent to which non-aqueous solvents can be used is limited by the fact that many are highly reactive.

Quantitative data are scarce for non-aqueous media, and, in solvents of relative permittivity lower than that of water, data are difficult to interpret because of ion-association. Much of the discussion therefore centres on the properties and uses of selected solvents.

A number of non-aqueous solvents (e.g. NH_3, EtOH, H_2SO_4) exhibit *hydrogen bonding*. An $X{-}H{\cdots}Y$ interaction is called a *hydrogen bond* if it constitutes a local bond, and if X–H acts as a proton donor to Y. Whether or not solvent molecules form intermolecular hydrogen bonds affects properties such as boiling point, enthalpy of vaporization and viscosity, as well as the ability of the solvent to solvate particular ions or molecules. If you are unfamiliar with the concept of hydrogen bonding, you may wish to read Section 10.6 before studying Chapter 9.

9.2 Relative permittivity

Before beginning a discussion of non-aqueous solvents, we must define the *relative permittivity*, also referred to as the *dielectric constant*, of a substance. In a vacuum, the Coulombic potential energy of a system of two unit electronic charges is given by eq. 9.1 where ε_0 is the (absolute) permittivity of a vacuum ($8.854 \times 10^{-12}\,\mathrm{F\,m^{-1}}$), e is the charge on the electron ($1.602 \times 10^{-19}\,\mathrm{C}$) and r is the separation (in metres) between the point charges.

$$\text{Coulombic potential energy} = \frac{e^2}{4\pi\varepsilon_0 r} \qquad (9.1)$$

If a material is placed between the charges, the force is reduced by an amount that depends upon the *relative permittivity* of the material. The new Coulombic potential energy is given by eq. 9.2 where ε_r is the relative permittivity of the material. Since it is a *relative* quantity, ε_r is dimensionless.

$$\text{Coulombic potential energy} = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r} \qquad (9.2)$$

For example, at 298 K, ε_r of water (the dielectric constant) is 78.7, but as Fig. 9.1 shows, ε_r varies with temperature. A value of 78.7 can be considered to be a 'high' value and from eq. 9.2, we see that in aqueous solution, the force between two point charges (or two ions) is considerably reduced compared with that in a vacuum. Thus we can consider a dilute aqueous solution of a salt to contain well-separated, non-interacting ions.

Table 9.1 lists dielectric constants for water and a range of common organic solvents. The *absolute* permittivity of a solvent is found using eq. 9.3, but it is usual to discuss solvent properties in terms of the relative values.

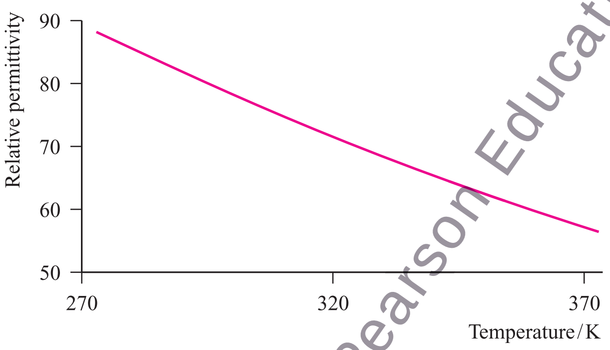


Fig. 9.1 Variation in the relative permittivity (dielectric constant) of water as a function of temperature.

$$\text{Absolute permittivity of a material} = \varepsilon_0\varepsilon_r \qquad (9.3)$$

Table 9.1 also gives the dipole moment (μ) of each solvent. In general, the trend in values of dipole moments follows that in values of the relative permittivities for solvents having related structures. Ion–solvent interactions are favoured (e.g. to facilitate the dissolution of an ionic salt) by using a solvent with a large dipole moment, but for maximum effect, the solvent molecule should also be small, and both ends of it should be able to interact with the ions in the same way that water interacts with cations through the oxygen atoms (see Fig. 7.5) and with anions through the hydrogen atoms. Thus, ammonia ($\varepsilon_r = 25.0$, $\mu = 1.47\,\mathrm{D}$) is a better solvent (see Section 9.6) for ionic salts than dimethylsulfoxide or nitromethane, even though these have ε_r values of 46.7 and 35.9, and dipole moments of 3.96 and 3.46 D, respectively.

Table 9.1 Relative permittivity (dielectric constant) values at 298 K (unless otherwise stated) for water and selected organic solvents.

Solvent	Formula[†]	Relative permittivity, ε_r	Dipole moment, μ / debye
Formamide	$HC(O)NH_2$	109 (293 K)	3.73
Water	H_2O	78.7	1.85
Acetonitrile	MeCN	37.5 (293 K)	3.92
N,*N*-Dimethylformamide (DMF)	$HC(O)NMe_2$	36.7	3.86
Nitromethane	$MeNO_2$	35.9 (303 K)	3.46
Methanol	MeOH	32.7	1.70
Ethanol	EtOH	24.3	1.69
Dichloromethane	CH_2Cl_2	9.1 (293 K)	1.60
Tetrahydrofuran	C_4H_8O (structure **9.2**)	7.6	1.75
Diethyl ether	Et_2O	4.3 (293 K)	1.15
Benzene	C_6H_6	2.3	0

[†] Me = methyl; Et = ethyl.

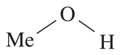
Self-study exercises

In the text, we state that *in general, the trend in dipole moments follows that in values of the relative permittivities for solvents having related structures*. Carry out the following two exercises, and then critically assess this statement.

1. **Produce a scatter plot (i.e. no line or curve fitted to the points) for values of μ against ε_r for all the solvents listed in Table 9.1.**
2. **Produce a scatter plot for values of μ against ε_r for H_2O, MeOH, EtOH and Et_2O using data listed in Table 9.1.**

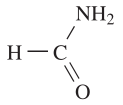
9.3 Energetics of ionic salt transfer from water to an organic solvent

In this section, we consider the changes in enthalpy and Gibbs energy that accompany the transfer of simple ions from water to some organic solvents of high relative permittivity. These data provide us with an idea of the *relative* abilities of water and these organic liquids to act as solvents with regard to the ions considered. Since most organic liquids are soluble in water to some extent, or are completely miscible with water, thermodynamic data for the dissolution of salts are usually obtained by considering the two solvents separately. Data for the transfer of ions ($\Delta_{transfer}G^o$ and $\Delta_{transfer}H^o$) can be derived from the differences between the values corresponding to the dissolution processes in the two solvents. Our discussion centres on four organic solvents: methanol (**9.5**), formamide (**9.6**), *N,N*-dimethylformamide (DMF, **9.7**) and acetonitrile (**9.8**), relative permittivities and dipole moments for which are listed in Table 9.1.



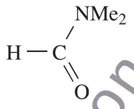
methanol

(9.5)



formamide

(9.6)



DMF

(9.7)

$Me-C\equiv N$

acetonitrile

(9.8)

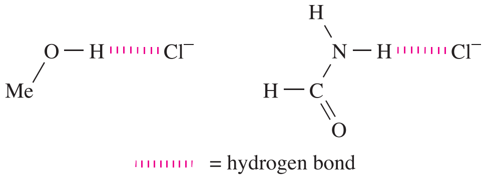
In an analogous approach to that discussed in Section 7.9, we can make the assumption that very large ions such as $[Ph_4As]^+$ and $[BPh_4]^-$ have the same values of $\Delta_{transfer}G^o$ and the same values of $\Delta_{transfer}H^o$. By considering a series of $[Ph_4As]X$ and $M[BPh_4]$ salts (in conjunction with $[Ph_4As][BPh_4]$), it is possible to obtain the thermodynamic data given in Table 9.2, where $\Delta_{transfer}H^o$ and $\Delta_{transfer}G^o$ refer to the transfer of the specified ion from water to the organic solvent. A positive value of $\Delta_{transfer}G^o$ indicates an unfavourable transfer, while a negative value corresponds to a favourable process.

The data in Table 9.2 show that the large, non-polar $[Ph_4As]^+$ and $[BPh_4]^-$ ions are more solvated in each organic solvent than in water; enthalpy and entropy effects both contribute in the same direction. Alkali metal ions exhibit no simple pattern of behaviour, although in each solvent, values of $\Delta_{transfer}H^o$ and $\Delta_{transfer}G^o$ are less positive for the alkali metal ions than for the halide ions. For the halide ions, transfer from water to the organic media is thermodynamically unfavourable, but we can go further than this generalization. Methanol and formamide are

Table 9.2 Values of $\Delta_{transfer}H^o$ and $\Delta_{transfer}G^o$ for the transfer of ions from water to an organic solvent at 298 K.

Ion	Methanol		Formamide		*N,N*-Dimethylformamide		Acetonitrile	
	$\Delta_{transfer}H^o$ / kJ mol^{-1}	$\Delta_{transfer}G^o$ / kJ mol^{-1}	$\Delta_{transfer}H^o$ / kJ mol^{-1}	$\Delta_{transfer}G^o$ / kJ mol^{-1}	$\Delta_{transfer}H^o$ / kJ mol^{-1}	$\Delta_{transfer}G^o$ / kJ mol^{-1}	$\Delta_{transfer}H^o$ / kJ mol^{-1}	$\Delta_{transfer}G^o$ / kJ mol^{-1}
F^-	12	20	20	25	–	≈60	–	71
Cl^-	8	13	4	14	18	48	19	42
Br^-	4	11	−1	11	1	36	8	31
I^-	−2	7	−7	7	−15	20	−8	17
Li^+	−22	4	−6	−10	−25	−10	–	25
Na^+	−20	8	−16	−8	−32	−10	−13	15
K^+	−19	10	−18	−4	−36	−10	−23	8
$[Ph_4As]^+$, $[BPh_4]^-$	−2	−23	−1	−24	−17	−38	−10	−33

capable of forming hydrogen bonds (see Section 10.6) between the H atoms of the OH or NH_2 groups and the halide ions in solution; MeCN and DMF do not possess this capability.



(9.9)

Not only are the values of $\Delta_{\text{transfer}}G^{\text{o}}$ for the halide ion significantly more positive for MeCN and DMF than for MeOH and formamide, but the variation in values among the halide ions is much greater. We may conclude that halide ions (and F^- and Cl^- in particular) are much less strongly solvated in solvents in which hydrogen bonding is not possible than in those in which hydrogen-bonded interactions can form (these, of course, include water). This difference is the origin of the solvent dependence of reactions involving halide ions. An example is the bimolecular reaction 9.4, for which the rate increases from X = F to I in aqueous solution, but decreases in DMFe.

$$CH_3Br + X^- \longrightarrow CH_3X + Br^- \qquad (X = F, Cl \text{ or } I) \tag{9.4}$$

Fluoride ion in solvents with which it is not able to form hydrogen bonds is sometimes described as 'naked', but this term is misleading. In DMF, it still has a Gibbs energy of solvation of about $-400\,\text{kJ mol}^{-1}$ ($\approx 60\,\text{kJ mol}^{-1}$ less negative than in water) and so is still very much less reactive than in the gas phase.

Self-study exercises

You may need to refer to the first part of Section 10.6 before attempting the following exercises.

1. Why can EtOH form hydrogen bonds with chloride ion, whereas Et_2O cannot?

2. Which of the following solvents are capable of forming hydrogen bonds with Br^-: MeOH; THF; DMF; $MeNO_2$; H_2O?

[*Ans.* MeOH, H_2O]

3. Figure 7.5 shows H_2O molecules coordinating to Na^+. Explain how THF and MeCN may act as coordinating solvents.

9.4 Acid–base behaviour in non-aqueous solvents

Strengths of acids and bases

When we dealt with acid–base behaviour in aqueous solution in Chapter 7, we saw that the strength of an acid HX (eq. 9.5) depended upon the relative proton donor abilities of HX and $[H_3O]^+$.

$$HX(aq) + H_2O(l) \rightleftharpoons [H_3O]^+(aq) + X^-(aq) \tag{9.5}$$

Similarly, the strength of a base, B, in aqueous solution depends upon the relative proton accepting abilities of B and $[OH]^-$ (eq. 9.6).

$$B(aq) + H_2O(l) \rightleftharpoons [BH]^+(aq) + [OH]^-(aq) \tag{9.6}$$

Tabulated values of K_a (or K_b) generally refer to the ionizations of acids in *aqueous solution*, and in stating that 'HCl is a strong acid', we assume an aqueous medium. However, if HCl is dissolved in acetic acid, the extent of ionization is far less than in water and HCl behaves as a weak acid.

Levelling and differentiating effects

Non-aqueous solvents that are good proton acceptors (e.g. NH_3) encourage acids to ionize in them. Thus, in a *basic solvent*, all acids are strong. The solvent is said to exhibit a *levelling effect* on the acid, since the strength of the dissolved acid cannot exceed that of the protonated solvent. For example, in aqueous solution, no acidic species can exist that is a stronger acid than $[H_3O]^+$. In an acidic solvent (e.g. $MeCO_2H$, H_2SO_4), ionization of bases is facilitated. Most acids are relatively weak under these conditions, and some even ionize as bases.

We noted above that HCl, when dissolved in acetic acid, behaves as a weak acid. Hydrogen bromide and hydrogen iodide behave similarly but the *extent of ionization* of the three hydrogen halides varies along the series: HI > HBr > HCl. This contrasts with the fact that all three compounds are classed as strong acids (i.e. fully ionized) in aqueous solution. Thus, acetic acid exerts a *differentiating effect* on the acidic behaviour of HCl, HBr and HI, whereas water does not.

'Acids' in acidic solvents

The effects of dissolving 'acids' in acidic non-aqueous solvents can be dramatic. When dissolved in H_2SO_4, $HClO_4$ (for which pK_a in aqueous solution is −8) is practically non-ionized and HNO_3 ionizes according to eq. 9.7.

$$HNO_3 + 2H_2SO_4 \rightleftharpoons [NO_2]^+ + [H_3O]^+ + 2[HSO_4]^- \tag{9.7}$$

Reaction 9.7 can be regarded as the summation of equilibria 9.8–9.10, and it is the presence of $[NO_2]^+$ that is responsible for the use of an HNO_3/H_2SO_4 mixture in the nitration of aromatic compounds.

$$HNO_3 + H_2SO_4 \rightleftharpoons [H_2NO_3]^+ + [HSO_4]^- \qquad (9.8)$$

$$[H_2NO_3]^+ \rightleftharpoons [NO_2]^+ + H_2O \qquad (9.9)$$

$$H_2O + H_2SO_4 \rightleftharpoons [H_3O]^+ + [HSO_4]^- \qquad (9.10)$$

These examples signify caution: *just because we name a compound an 'acid', it may not behave as one in non-aqueous media*. Later we consider superacid media in which even hydrocarbons may be protonated (see Section 9.9).

Acids and bases: a solvent-oriented definition

A Brønsted acid is a proton donor, and a Brønsted base accepts protons. In aqueous solution, $[H_3O]^+$ is formed and in bulk water, self-ionization corresponds to the transfer of a proton from one solvent molecule to another (eq. 9.11) illustrating amphoteric behaviour (see Section 7.8).

$$2H_2O \rightleftharpoons [H_3O]^+ + [OH]^- \qquad (9.11)$$

In liquid NH_3 (see Section 9.6), proton transfer leads to the formation of $[NH_4]^+$ (eq. 9.12), and, in a liquid ammonia solution, an acid may be described as a substance that produces $[NH_4]^+$ ions, while a base produces $[NH_2]^-$ ions.

$$2NH_3 \rightleftharpoons \underset{\text{ammonium ion}}{[NH_4]^+} + \underset{\text{amide ion}}{[NH_2]^-} \qquad (9.12)$$

This solvent-oriented definition can be widened to include behaviour in any solvent which undergoes self-ionization.

In a ***self-ionizing solvent***, an acid is a substance that produces the cation characteristic of the solvent, and a base is a substance that produces the anion characteristic of the solvent.

Liquid dinitrogen tetraoxide, N_2O_4, undergoes the self-ionization shown in eq. 9.13. In this medium, nitrosyl salts such as $[NO][ClO_4]$ behave as acids, and metal nitrates (e.g. $NaNO_3$) behave as bases.

$$N_2O_4 \rightleftharpoons [NO]^+ + [NO_3]^- \qquad (9.13)$$

In some ways, this acid–base terminology is unfortunate, since there are other, more common descriptors (e.g. Brønsted, Lewis, hard and soft). However, the terminology has been helpful in suggesting lines of research for the study of non-aqueous systems, and its use will probably continue.

Self-study exercises

1. **Why does KOH behave as a base in aqueous solution?**
2. **Why does NH_4Cl behave as an acid in liquid ammonia?**
3. **CH_3CO_2H behaves as a weak acid in aqueous solution, but is levelled to a strong acid in liquid ammonia. What does this tell you about the extent of ionization of CH_3CO_2H in each medium?**
4. **Explain why $NaNH_2$ behaves as a base in liquid NH_3.**

Proton-containing and aprotic solvents

In Sections 9.5–9.11, we consider selected inorganic non-aqueous solvents. Most of these solvents are self-ionizing. They can be divided into two categories:

- proton containing (NH_3, HF, H_2SO_4, $HOSO_2F$);
- aprotic (SO_2, BrF_3, N_2O_4).

9.5 Liquid sulfur dioxide

Liquid SO_2 is an important non-aqueous solvent. It is polar and aprotic, and readily solvates anions.[†] Selected properties of SO_2 are listed in Table 9.3, and its liquid range is compared with other solvents in Fig. 9.2.

Table 9.3 Selected physical properties of sulfur dioxide, SO_2.

Property / units	Value
Melting point / K	197.5
Boiling point / K	263.0
Density of liquid / $g\,cm^{-3}$	1.43
Dipole moment / D	1.63
Relative permittivity	17.6 (at boiling point)

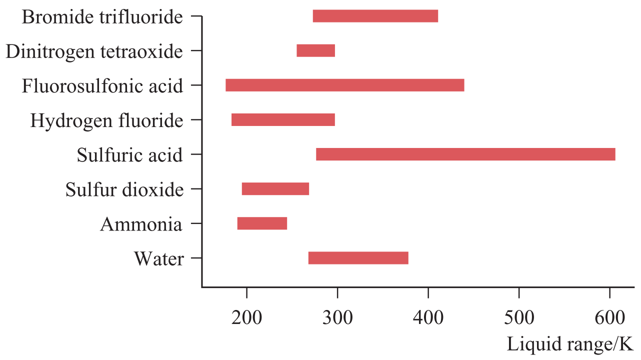


Fig. 9.2 Liquid ranges for water and selected non-aqueous solvents.

[†] See: W. Eisfeld and M. Regitz (1996) *J. Am. Chem. Soc.*, vol. 118, p. 11918—'Energetic and structural aspects of the solvation of anions in liquid SO2'.

Initially, it was proposed that SO_2 underwent self-ionization according to eq. 9.14. However, this equilibrium requires the separation of doubly charged ions, in contrast to the singly charged ions involved in other self-ionization equilibria described in Sections 9.6–9.11. Two observables suggest that no self-ionization occurs: (i) conductance data are not consistent with the presence of ions in liquid SO_2; (ii) when labelled $SOCl_2$ is dissolved in liquid SO_2, neither ^{35}S nor ^{18}O exchanges with the solvent.

$$2SO_2 \rightleftharpoons [SO]^{2+} + [SO_3]^{2-} \qquad (9.14)$$

Liquid SO_2 is an effective, inert solvent for both organic compounds (e.g. amines, alcohols, carboxylic acids, esters) and covalent inorganic substances (e.g. Br_2, CS_2, PCl_3, $SOCl_2$, $POCl_3$) and is quite a good ionizing medium for such compounds as Ph_3CCl (giving $[Ph_3C]^+$). It is also used for the syntheses of some group 16 and 17 cationic species. For example, $[I_3]^+$ and $[I_5]^+$ (eq. 9.15) have been isolated as the $[AsF_6]^-$ salts from the reactions of AsF_5 and I_2 in liquid SO_2, the product depending on the molar ratio of the reactants. Reactions of selenium with AsF_5 (at 350 K) or SbF_5 (at 250 K) in liquid SO_2 have yielded the salts $[Se_4][AsF_6]_2$ and $[Se_8][SbF_6]_2$ respectively.

$$3AsF_5 + 5I_2 \xrightarrow{\text{liquid } SO_2} 2[I_5][AsF_6] + AsF_3 \qquad (9.15)$$

9.6 Liquid ammonia

Liquid ammonia has been widely studied, and in this section we discuss its properties and the types of reactions that occur in it, making comparisons between liquid ammonia and water.

Physical properties

Selected properties of NH_3 are listed in Table 9.4 and are compared with those of water. The liquid range of NH_3 is less than that of H_2O (Fig. 9.2). The lower boiling point of NH_3 compared of H_2O suggests that hydrogen bonding (see Section 10.6) in liquid NH_3 is less extensive than in liquid H_2O, and this is further illustrated by the values of $\Delta_{vap}H^o$ (23.3 and 40.7 kJ mol^{-1} for NH_3 and H_2O respectively). This is in line with what is expected from the fact that in NH_3, there is one lone pair to accept a hydrogen bond, whereas in H_2O, there are two. In fact, one has to be cautious in rationalizing the degree of hydrogen bonding simply in terms of the number of lone pairs. Neutron diffraction studies using hydrogen/deuterium isotopic substitution have shown the presence of two hydrogen bonds per N atom in liquid NH_3. Structural data from X-ray and neutron diffraction and computational methods lead to the conclusion that the hydrogen bonding is relatively weak and, unlike liquid H_2O, liquid NH_3 does not exhibit an extended hydrogen-bonded network.

The relative permittivity of NH_3 is considerably less than that of H_2O and, as a consequence, the ability of liquid NH_3 to dissolve ionic compounds is generally less than that of water. Exceptions include $[NH_4]^+$ salts, iodides and nitrates which are usually readily soluble. For example, AgI, which is sparingly soluble in water, dissolves easily in liquid NH_3 (solubility = 206.8 g per 100 g of NH_3), a fact that indicates that both the Ag^+ and I^- ions interact strongly with the solvent; Ag^+ forms an ammine complex (see Section 22.12). Changes in solubility patterns in going from water to liquid NH_3 lead to some interesting precipitation reactions in NH_3. Whereas in aqueous solution, $BaCl_2$ reacts with $AgNO_3$ to precipitate AgCl, in liquid NH_3, AgCl and $Ba(NO_3)_2$ react to precipitate $BaCl_2$. The solubility of AgCl is 0.29 g per 100 g of liquid NH_3 compared with 1.91×10^{-4} g per 100 g of H_2O. Molecular organic compounds are generally more soluble in NH_3 than in H_2O.

Self-ionization

Liquid NH_3 undergoes self-ionization (eq. 9.12), and the small value of K_{self} (Table 9.4) indicates that the equilibrium lies far over to the left-hand side. The $[NH_4]^+$ and $[NH_2]^-$ ions have ionic mobilities approximately equal to those of alkali metal and halide ions. This contrasts with the situation in water, in which $[H_3O]^+$ and $[OH]^-$ are much more mobile than other singly charged ions.

Reactions in liquid NH_3

We described above some precipitations that differ in liquid NH_3 and H_2O. Equation 9.16 shows a further example; the solubility of KCl is 0.04 g per 100 g NH_3, compared with 34.4 g per 100 g H_2O.

$$KNO_3 + AgCl \longrightarrow \underset{\text{ppt}}{KCl} + AgNO_3 \quad \textit{in liquid } NH_3 \qquad (9.16)$$

Table 9.4 Selected physical properties of NH_3 and H_2O.

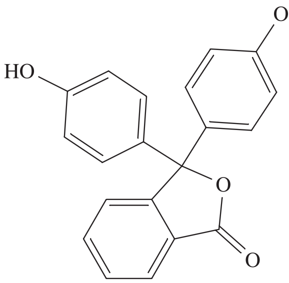
Property / units	NH_3	H_2O
Melting point / K	195.3	273.0
Boiling point / K	239.6	373.0
Density of liquid / g cm^{-3}	0.77	1.00
Dipole moment / D	1.47	1.85
Relative permittivity	25.0 (at melting point)	78.7 (at 298 K)
Self-ionization constant	5.1×10^{-27}	1.0×10^{-14}

In water, neutralization reactions follow the general reaction 9.17. The solvent-oriented definition of acids and bases allows us write an analogous reaction (eq. 9.18) for a neutralization process in liquid NH_3.

$$\text{Acid} + \text{Base} \longrightarrow \text{Salt} + \text{Water} \quad \textit{in aqueous solution} \qquad (9.17)$$

$$\text{Acid} + \text{Base} \longrightarrow \text{Salt} + \text{Ammonia} \quad \textit{in liquid } NH_3 \qquad (9.18)$$

Thus, in liquid NH_3, reaction 9.19 is a neutralization process which may be followed by conductivity or potentiometry, or by the use of an indicator such as phenolphthalein, **9.10**. This indicator is colourless but is deprotonated by a strong base such as $[NH_2]^-$ to give a red anion just as it is by $[OH]^-$ in aqueous solution.

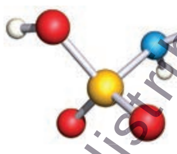


(9.10)

$$NH_4Br + KNH_2 \longrightarrow KBr + 2NH_3 \qquad (9.19)$$

Liquid NH_3 is an ideal solvent for reactions requiring a strong base, since the amide ion is strongly basic.

As discussed in Section 9.4, the behaviour of 'acids' is solvent-dependent. In aqueous solution, sulfamic acid, H_2NSO_2OH, **9.11**, behaves as a monobasic acid according to eq. 9.20, but in liquid NH_3 it can function as a dibasic acid (eq. 9.21).



(9.11)

$$H_2NSO_2OH(aq) + H_2O(l)$$
$$\rightleftharpoons [H_3O]^+(aq) + [H_2NSO_2O]^-(aq) \quad K_a = 1.01 \times 10^{-1} \qquad (9.20)$$

$$H_2NSO_2OH + 2KNH_2 \longrightarrow K_2[HNSO_2O] + 2NH_3 \qquad (9.21)$$

The levelling effect of liquid NH_3 means that the strongest acid possible in this medium is $[NH_4]^+$. Solutions of ammonium halides in NH_3 may be used as acids, for example in the preparation of silane or arsane (eqs. 9.22 and 9.23). Germane, GeH_4, can be prepared from Mg_2Ge in a reaction analogous to the preparation of SiH_4.

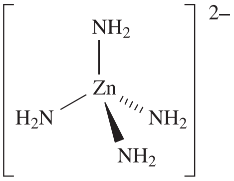
$$Mg_2Si + 4NH_4Br \longrightarrow SiH_4 + 2MgBr_2 + 4NH_3 \qquad (9.22)$$

$$Na_3As + 3NH_4Br \longrightarrow AsH_3 + 3NaBr + 3NH_3 \qquad (9.23)$$

A saturated solution of NH_4NO_3 in liquid NH_3 (which has a vapour pressure of less than 1 bar even at 298 K) dissolves many metal oxides and even some metals. Nitrate to nitrite reduction often accompanies the dissolution of metals. Metals that form insoluble hydroxides under aqueous conditions, form insoluble amides in liquid NH_3, e.g. $Zn(NH_2)_2$. Just as $Zn(OH)_2$ dissolves in the presence of excess hydroxide ion (eq. 9.24), $Zn(NH_2)_2$ reacts with amide ion to form soluble salts containing anion **9.12** (eq. 9.25).

$$Zn^{2+} + 2[OH]^- \longrightarrow Zn(OH)_2 \xrightarrow{\text{excess } [OH]^-} [Zn(OH)_4]^{2-} \qquad (9.24)$$

$$Zn^{2+} + 2[NH_2]^- \longrightarrow Zn(NH_2)_2 \xrightarrow{\text{excess } [NH_2]^-} [Zn(NH_2)_4]^{2-} \qquad (9.25)$$



(9.12)

Parallels can be drawn between the behaviours of metal nitrides in liquid NH_3 and of metal oxides in aqueous media. Many similar analogies can be drawn.

Complex formation between Mg^{2+} and NH_3 leads to $[Mg(NH_3)_6]^{2+}$, isolated as $[Mg(NH_3)_6]Cl_2$. Similarly, in liquid NH_3, $CaCl_2$ forms $[Ca(NH_3)_6]Cl_2$ and this is the reason that anhydrous $CaCl_2$ (which readily absorbs water, see Section 12.5) cannot be used to dry NH_3. Ammine complexes such as $[Ni(NH_3)_6]^{2+}$ can be prepared in aqueous solution by the displacement of aqua ligands by NH_3. Not all hexaammine complexes are, however, directly accessible by this method. Two examples are $[V(NH_3)_6]^{2+}$ and $[Cu(NH_3)_6]^{2+}$. The ion $[V(OH_2)_6]^{2+}$ is readily oxidized in aqueous solution, making the preparation of V(II) complexes in aqueous conditions difficult. In liquid NH_3, dissolution of VI_2 gives $[V(NH_3)_6]I_2$ containing the octahedral $[V(NH_3)_6]^{2+}$ ion. The $[Cu(NH_3)_6]^{2+}$ ion is not accessible in aqueous solution (see Fig. 20.37) but can be formed in liquid NH_3.

Self-study exercises

1. **In eq. 9.10, which reactant acts as a base?**
2. **In eq. 9.22, why does NH_4Br behave as an acid?**

3. Explain why organic amines and amides can function as acids in liquid ammonia.

4. Suggest products for the following reactions:

$$R_2NH + KNH_2 \longrightarrow$$

$$RC(O)NH_2 + KNH_2 \longrightarrow$$

How is KNH_2 functioning in these reactions?

Solutions of s-block metals in liquid NH_3

All of the group 1 metals and the group 2 metals Ca, Sr and Ba dissolve in liquid NH_3 to give metastable solutions from which the group 1 metals can be recovered unchanged. The group 2 metals are recoverable as solids of composition $[M(NH_3)_6]$. Yellow $[Li(NH_3)_4]$ and blue $[Na(NH_3)_4]$ may also be isolated at low temperatures.

Dilute solutions of the metals are bright blue, the colour arising from the short wavelength tail of a broad and intense absorption band in the infrared region of the spectrum. The electronic spectra in the visible region of solutions of all the *s*-block metals are the same, indicating the presence of a species common to all the solutions: this is the solvated electron (eq. 9.26).

$$M \xrightarrow{\text{dissolve in liquid NH}_3} M^+(solv) + e^-(solv) \qquad (9.26)$$

Each dilute solution of metal in liquid NH_3 occupies a volume greater than the sum of the volumes of the metal plus solvent. These data suggest that the electrons occupy cavities of radius 300–400 pm. Very dilute solutions of the metals are paramagnetic, and the magnetic susceptibility corresponds to that calculated for the presence of one free electron per metal atom.

As the concentration of a solution of an *s*-block metal in liquid NH_3 increases, the molar conductivity initially decreases, reaching a minimum at $\approx 0.05\,\text{mol dm}^{-3}$. Thereafter, the molar conductivity increases, and in saturated solution's it is comparable with that of the metal itself. Such saturated solutions are no longer blue and paramagnetic, but are bronze and diamagnetic. They are essentially 'metal-like' and have been described as *expanded metals*. The conductivity data can be described in terms of:

- reaction 9.26 at low concentrations;
- association of $M^+(solv)$ and $e^-(solv)$ at concentrations around $0.05\,\text{mol dm}^{-3}$;
- metal-like behaviour at higher concentrations.

However, in order to explain why the magnetic susceptibilities of solutions *decrease* as the concentration increases, it is necessary to invoke equilibria 9.27 at higher concentrations.

$$\left.\begin{array}{l} 2M^+(solv) + 2e^-(solv) \rightleftharpoons M_2(solv) \\ M(solv) + e^-(solv) \rightleftharpoons M^-(solv) \end{array}\right\} \qquad (9.27)$$

Hydrogen/deuterium isotopic substitution coupled with neutron diffraction studies confirm that the addition of an alkali metal to liquid NH_3 disrupts the hydrogen bonding present in the solvent. In a saturated lithium–ammonia solution (21 mole percent metal), no hydrogen bonding remains between NH_3 molecules. Saturated Li–NH_3 solutions contain tetrahedrally coordinated Li, whereas saturated K–NH_3 solutions contain octahedrally coordinated K.

The blue solutions of alkali metals in liquid NH_3 decompose very slowly, liberating H_2 (eq. 9.28) as the solvent is reduced.

$$2NH_3 + 2e^- \longrightarrow 2[NH_2]^- + H_2 \qquad (9.28)$$

Although reaction 9.28 is thermodynamically favoured, there is a significant kinetic barrier. Decomposition is catalysed by many *d*-block metal ions. Ammonium salts (which are strong acids in liquid NH_3) decompose immediately (eq. 9.29).

$$2[NH_4]^+ + 2e^- \longrightarrow 2NH_3 + H_2 \qquad (9.29)$$

There are numerous applications of sodium in liquid ammonia in organic synthesis,[†] including the well-established Birch reduction. Dilute solutions of alkali metals in liquid NH_3 have many applications as reducing agents in inorganic syntheses. Reactions 9.30 to 9.34 (in which e^- represents the electron generated in reaction 9.26) provide examples and others are mentioned later in the book. In each of reactions 9.30–9.34, the anion shown is isolated as an alkali metal salt, the cation being provided from the alkali metal dissolved in the liquid NH_3.

$$2GeH_4 + 2e^- \longrightarrow 2[GeH_3]^- + H_2 \qquad (9.30)$$

$$O_2 + e^- \longrightarrow \underset{\text{superoxide ion}}{[O_2]^-} \qquad (9.31)$$

$$O_2 + 2e^- \longrightarrow \underset{\text{peroxide ion}}{[O_2]^{2-}} \qquad (9.32)$$

$$[MnO_4]^- + e^- \longrightarrow [MnO_4]^{2-} \qquad (9.33)$$

$$[Fe(CO)_5] + 2e^- \longrightarrow [Fe(CO)_4]^{2-} + CO \qquad (9.34)$$

Early synthetic routes to *Zintl ions* (see Section 14.7) involved reduction of Ge, Sn or Pb in solutions of Na in liquid NH_3. The method has been developed with the addition of the macrocyclic ligand cryptand-222 (crypt-222) (see Section 11.8) which encapsulates the Na^+ ion and allows the isolation of salts of the type $[Na(crypt\text{-}222)]_2[Sn_5]$ (eq. 9.35). Zintl ions produced in this way include $[Sn_5]^{2-}$ (Fig. 9.3), $[Pb_5]^{2-}$, $[Pb_2Sb_2]^{2-}$, $[Bi_2Sn_2]^{2-}$, $[Ge_9]^{2-}$, $[Ge_9]^{4-}$ and $[Sn_9Tl]^{3-}$.

$$Sn \xrightarrow{\text{Na in liquid NH}_3} \underset{\text{Zintl phase}}{NaSn_{1.0-1.7}}$$

$$\xrightarrow[\text{in 1,2-ethanediamine}]{\text{2,2,2-crypt}} [Na(crypt\text{-}222)]_2[Sn_5] \qquad (9.35)$$

[†] For a summary, see: S.B. Raikar (2007) *Synlett*, p. 341.

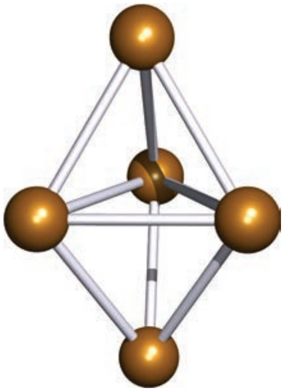


Fig. 9.3 The Zintl ion $[Sn_5]^{2-}$ has a trigonal bipyramidal cluster structure.

A further development in the synthesis of Zintl ions has been to use the reactions of an excess of Sn or Pb in solutions of Li in liquid NH_3. These reactions give $[Li(NH_3)_4]^+$ salts of $[Sn_9]^{4-}$ and $[Pb_9]^{4-}$, and we discuss these Zintl ions further in Section 14.7.

The group 2 metals Ca, Sr and Ba dissolve in liquid NH_3 to give bronze-coloured $[M(NH_3)_x]$ species, and for $M = Ca$, neutron diffraction data confirm the presence of octahedral $[Ca(ND_3)_6]$. Although pale blue solutions are obtained when Mg is added to NH_3, complete dissolution is not observed and no ammine adducts of Mg have been isolated from these solutions. However, combining an Hg/Mg (22 : 1 ratio) alloy with liquid NH_3 produces crystals of $[Mg(NH_3)_6Hg_{22}]$ which contain octahedral $[Mg(NH_3)_6]$ units, hosted within an Hg lattice. This material is superconducting (see Section 28.4) with a critical temperature, T_c, of 3.6 K.

Redox reactions in liquid NH_3

Reduction potentials for the reversible reduction of metal ions to the corresponding metal in aqueous solution and in liquid NH_3 are listed in Table 9.5. The values follow the same general trend, but the oxidizing ability of each metal ion is solvent-dependent. Reduction potentials for oxidizing systems cannot be obtained in liquid NH_3 owing to the ease with which the solvent is oxidized.

Information deduced from reduction potentials, and from lattice energies and solubilities, indicates that H^+ and *d*-block M^{n+} ions have more negative absolute standard Gibbs energies of solvation in NH_3 than in H_2O; for alkali metal ions, values of $\Delta_{solv}G^o$ are about the same in the two solvents. These data are consistent with the observation that the addition of NH_3 to aqueous solutions of *d*-block M^{n+} ions results in the formation of ammine complexes such as $[M(NH_3)_6]^{n+}$ whereas alkali metal ions are not complexed by NH_3 under aqueous conditions.

Table 9.5 Selected standard reduction potentials (298 K) in aqueous and liquid ammonia media; the concentration of each solution is 1 mol dm^{-3}. The value of $E^o = 0.00$ V for the H^+/H_2 couple is defined by convention.

Reduction half-equation	E^o / V in aqueous solution	E^o / V in liquid ammonia
$Li^+ + e^- \rightleftharpoons Li$	−3.04	−2.24
$K^+ + e^- \rightleftharpoons K$	−2.93	−1.98
$Na^+ + e^- \rightleftharpoons Na$	−2.71	−1.85
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76	−0.53
$2H^+ + 2e^- \rightleftharpoons H_2$ (g, 1 bar)	0.00	0.00
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34	+0.43
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80	+0.83

9.7 Liquid hydrogen fluoride

Physical properties

Hydrogen fluoride attacks silica glass (eq. 9.36) thereby corroding glass reaction vessels, and it is only relatively recently that HF has found applications as a non-aqueous solvent. It can be handled in polytetrafluoroethene (PTFE) containers, or, if absolutely free of water, in Cu or Monel metal (a nickel alloy) equipment.

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O \qquad (9.36)$$

Hydrogen fluoride has a liquid range from 190 to 292.5 K (Fig. 9.2). The relative permittivity is 84 at 273 K, rising to 175 at 200 K. Liquid HF undergoes self-ionization (equilibrium 9.37), for which $K_{self} \approx 2 \times 10^{-12}$ at 273 K.

$$3HF \rightleftharpoons \underset{\text{dihydridofluorine(1+) ion}}{[H_2F]^+} + \underset{\text{difluorohydrogenate(1−) ion}}{[HF_2]^-} \qquad (9.37)$$

The difference in electronegativities of H ($\chi^P = 2.2$) and F ($\chi^P = 4.0$) results in the presence of extensive intermolecular hydrogen bonding in the liquid. High-energy X-ray and neutron diffraction studies[†] have been used to show that liquid HF (at 296 K) contains chains of hydrogen-bonded molecules (on average, seven molecules per chain). Interchain hydrogen bonding also exists. In the vapour phase, hydrogen fluoride consists of cyclic $(HF)_x$ species as well as clusters.

Acid–base behaviour in liquid HF

Using the solvent-oriented definition (Section 9.4), a species that produces $[H_2F]^+$ ions in liquid HF is an acid, and one that produces $[HF_2]^-$ is a base.

[†] See: S.E. McLain, C.J. Benmore, J.E. Siewenie, J. Urquidi and J.F.C. Turner (2004) *Angew. Chem. Int. Ed.*, vol. 43, p. 1951 – 'The structure of liquid hydrogen fluoride'.

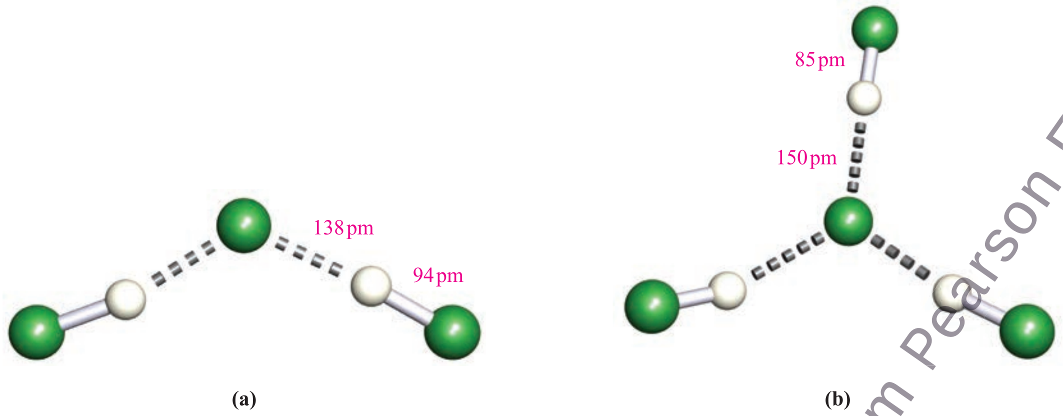


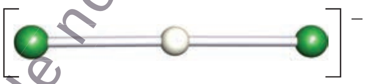
Fig. 9.4 The structures of the anions (a) $[H_2F_3]^-$ and (b) $[H_3F_4]^-$, determined by low-temperature X-ray diffraction for the $[Me_4N]^+$ salts. The distances given are the average values for like internuclear separations; the experimental error on each distance is ±3–6 pm [D. Mootz *et al.* (1987) *Z. Anorg. Allg. Chem.*, vol. 544, p. 159]. Colour code: F, green; H, white.

Many organic compounds are soluble in liquid HF, and in the cases of, for example, amines and carboxylic acids, protonation of the organic species accompanies dissolution (eq. 9.38). Proteins react immediately with liquid HF, and it produces very serious skin burns.

$$MeCO_2H + 2HF \longrightarrow [MeC(OH)_2]^+ + [HF_2]^- \qquad (9.38)$$

Most inorganic salts are converted to the corresponding fluorides when dissolved in liquid HF, but only a few of these are soluble. Fluorides of the *s*-block metals, silver and thallium(I) dissolve to give salts such as $K[HF_2]$ and $K[H_2F_3]$, and thus exhibit basic character. The single crystal structures of a number of salts containing $[HF_2]^-$ or $[DF_2]^-$ (i.e. deuterated species) have been determined by X-ray or neutron diffraction techniques; these include $[NH_4][HF_2]$, $Na[HF_2]$, $K[HF_2]$, $Rb[HF_2]$, $Cs[HF_2]$ and $Tl[HF_2]$.

The anion is linear (structure 9.13), and its formation is a consequence of the H and F atoms being involved in strong hydrogen bonding. In the solid state structures reported, the F---F distance is ≈228 pm. This value is greater than twice the H−F bond length in HF (2 × 92 pm), but an H····F hydrogen bond will always be weaker and longer than a 2-centre covalent H−F bond. Comparison of the values gives some indication of the strength of the hydrogen bonding in $[HF_2]^-$. (See also Fig. 5.29 and 9.4.)



(9.13)

Ammonium fluoride is basic in liquid HF. Studies of the Me_4NF–HF system over a range of compositions and temperatures reveal the formation of the compounds of composition $Me_4NF \cdot nHF$ ($n = 2, 3, 5$ or 7). X-ray diffraction studies for compounds with $n = 2$, 3 or 5 have confirmed the structures of $[H_2F_3]^-$ (Fig. 9.4a), $[H_3F_4]^-$ (Fig. 9.4b) and $[H_5F_6]^-$, in which strong hydrogen bonding is an important feature (see Section 10.6).

The molecular fluorides, CF_4 and SiF_4 are insoluble in liquid HF, but F^- acceptors such as AsF_5 and SbF_5 dissolve according to eq. 9.39 to give very strongly acidic solutions. Less potent fluoride acceptors such as BF_3 function as weak acids in liquid HF (eq. 9.40). PF_5 behaves as a *very* weak acid (eq. 9.41). In contrast, ClF_3 and BrF_3 act as F^- donors (eq. 9.42) and behave as bases.

$$EF_5 + 2HF \rightleftharpoons [H_2F]^+ + [EF_6]^- \quad E = \text{As or Sb} \qquad (9.39)$$

$$BF_3 + 2HF \rightleftharpoons [H_2F]^+ + [BF_4]^- \qquad (9.40)$$

$$PF_5 + 2HF \rightleftharpoons [H_2F]^+ + [PF_6]^- \qquad (9.41)$$

$$BrF_3 + HF \rightleftharpoons [BrF_2]^+ + [HF_2]^- \qquad (9.42)$$

Few protic acids are able to exhibit acidic behaviour in liquid HF, on account of the competition between HF and the solute as H^+ donors. Perchloric acid and fluorosulfonic acid (equation 9.43) do act as acids.

$$HOSO_2F + HF \rightleftharpoons [H_2F]^+ + [SO_3F]^- \qquad (9.43)$$

With SbF_5, HF forms a *superacid* (eq. 9.44) which is capable of protonating *very* weak bases including hydrocarbons (see Section 9.9).

$$2HF + SbF_5 \rightleftharpoons [H_2F]^+ + [SbF_6]^- \qquad (9.44)$$

Self-study exercises

1. **Write equations to show how ClF_3 and AsF_5 behave in liquid HF.**
2. **Use the VSEPR model to rationalize why $[H_2F]^+$ and $[BrF_2]^+$ are non-linear.**
3. **Using Fig. 5.29 to help you, give a bonding description for the $[HF_2]^-$ ion.**

Electrolysis in liquid HF

Electrolysis in liquid HF is an important preparative route to both inorganic and organic fluorine-containing compounds, many of which are difficult to access by other routes. Anodic oxidation in liquid HF involves half-reaction 9.45 and with NH_4F as substrate, the products of the subsequent fluorination are NFH_2, NF_2H and NF_3.

$$2F^- \rightleftharpoons F_2 + 2e^- \qquad (9.45)$$

In liquid HF, anodic oxidation of water gives OF_2, of SCl_2 yields SF_6, of acetic acid yields CF_3CO_2H and of Me_3N produces $(CF_3)_3N$.

9.8 Sulfuric acid and fluorosulfonic acid

Physical properties of sulfuric acid

Selected physical properties of H_2SO_4 are given in Table 9.6. It is a liquid at 298 K, and the long liquid range (Fig. 9.2) contributes towards making this a widely used non-aqueous solvent. Disadvantages of liquid H_2SO_4 are its high viscosity (27 times that of water at 298 K) and high value of $\Delta_{vap}H^o$. Both these properties arise from extensive intermolecular hydrogen bonding, and make it difficult to remove the solvent by evaporation from reaction mixtures. Dissolution of a solute in H_2SO_4 is favourable only if new interactions can be established to compensate for the loss of the extensive hydrogen bonding. Generally, this is possible only if the solute is ionic.

Table 9.6 Selected physical properties of sulfuric acid, H_2SO_4.

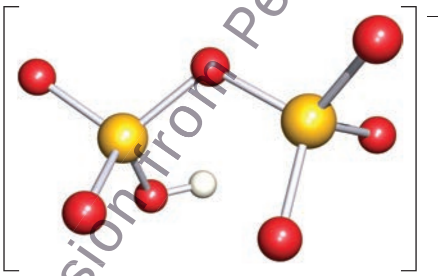
Property / units	Value
Melting point / K	283.4
Boiling point / K	≈603
Density of liquid / $g\,cm^{-3}$	1.84
Relative permittivity	110 (at 292 K)
Self-ionization constant	2.7×10^{-4} (at 298 K)

The value of the equilibrium constant for the self-ionization process 9.46 is relatively large. Other equilibria such as 9.47 are involved to a lesser extent.

$$2H_2SO_4 \rightleftharpoons [H_3SO_4]^+ + \underset{\text{hydrogensulfate ion}}{[HSO_4]^-}$$

$$K_{self} = 2.7 \times 10^{-4} \qquad (9.46)$$

$$2H_2SO_4 \rightleftharpoons [H_3O]^+ + \underset{\mathbf{9.14}}{[HS_2O_7]^-} \quad K_{self} = 5.1 \times 10^{-5} \qquad (9.47)$$



(9.14)

Acid–base behaviour in liquid H_2SO_4

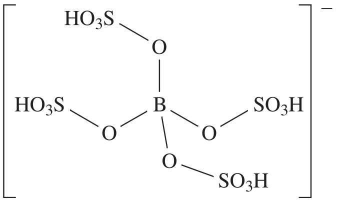
Sulfuric acid is a highly acidic solvent and most other 'acids' are neutral or behave as bases in it. We have already noted the basic behaviour of HNO_3. Initial proton transfer (eq. 9.8) leads to the formation of the 'protonated acid' $[H_2NO_3]^+$ which then eliminates H_2O (eq. 9.9). Overall, reaction 9.48 occurs. Similarly, acetic acid behaves as a base in sulfuric acid (eq. 9.49). A solution of boric acid in H_2SO_4 produces the $[B(HSO_4)_4]^-$ ion (eq. 9.50 and structure **9.15**).

$$HNO_3 + 2H_2SO_4 \longrightarrow [NO_2]^+ + [H_3O]^+ + 2[HSO_4]^- \qquad (9.48)$$

$$MeCO_2H + H_2SO_4 \longrightarrow [MeC(OH)_2]^+ + [HSO_4]^- \qquad (9.49)$$

$$H_3BO_3 + 6H_2SO_4 \longrightarrow [B(HSO_4)_4]^- + 3[H_3O]^+ + 2[HSO_4]^- \qquad (9.50)$$

For the $[B(HSO_4)_4]^-$ ion to be formed, $H[B(HSO_4)_4]$ must act as a strong acid in H_2SO_4 solution. $H[B(HSO_4)_4]$ is a stronger acid even than HSO_3F (see below). The ionization constants (in H_2SO_4) for HSO_3F and $H[B(HSO_4)_4]$ are 3×10^{-3} and 0.4, respectively.



(9.15)

The species '$H[B(HSO_4)_4]$' has not been isolated as a pure compound, but a solution of this acid can be prepared by dissolving boric acid in *oleum* (eq. 9.51) (see Section 16.9) and can be titrated conductometrically against a solution of a strong base such as $KHSO_4$ (eq. 9.52).

$$H_3BO_3 + 2H_2SO_4 + 3SO_3 \longrightarrow [H_3SO_4]^+ + [B(HSO_4)_4]^- \qquad (9.51)$$

$$H[B(HSO_4)_4] + KHSO_4 \longrightarrow K[B(HSO_4)_4] + H_2SO_4 \qquad (9.52)$$

In a *conductometric titration*, the end-point is found by monitoring changes in the electrical conductivity of the solution.[†]

Few species function as strong acids in H_2SO_4 medium. Perchloric acid (a potent acid in aqueous solution) is essentially non-ionized in H_2SO_4 and behaves only as a very weak acid.

In some cases (in contrast to eq. 9.49), the cations formed from carboxylic acids are unstable, e.g. HCO_2H and $H_2C_2O_4$ (eq. 9.53) decompose with loss of CO.

$$\begin{array}{l}CO_2H\\ |\\ CO_2H\end{array} + H_2SO_4 \longrightarrow CO + CO_2 + [H_3O]^+ + [HSO_4]^- \qquad (9.53)$$

The ionic mobilities[‡] of $[H_3SO_4]^+$ and $[HSO_4]^-$ are very high, and the conductivity in H_2SO_4 is almost entirely due to the presence of $[H_3SO_4]^+$ and/or $[HSO_4]^-$. These ions carry the electrical current by proton-switching mechanisms, thus avoiding the need for migration through the viscous solvent.

Self-study exercises

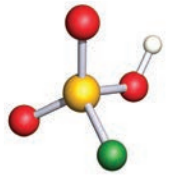
1. **The self-ionization constant for H_2SO_4 is 2.7×10^{-4}. To what equilibrium does this refer?**
2. **When EtOH dissolves in liquid H_2SO_4, $EtOSO_3H$ forms. Write a balanced equation for this reaction, bearing in mind that H_2O acts as a base in H_2SO_4.**
3. **Explain why $[P(OH)_4]^+$ forms when phosphoric acid dissolves in H_2SO_4.**

Table 9.7 Selected physical properties of fluorosulfonic acid, HSO_3F.

Property / units	Value
Melting point / K	185.7
Boiling point / K	438.5
Density of liquid / g cm^{-3}	1.74
Relative permittivity	120 (at 298 K)
Self-ionization constant	4.0×10^{-8} (at 298 K)

Physical properties of fluorosulfonic acid

Table 9.7 lists some of the physical properties of fluorosulfonic acid,[*] HSO_3F, **9.16**. It has a relatively long liquid range (Fig. 9.2) and a high dielectric constant. It is far less viscous than H_2SO_4 (by a factor of ≈16) and, like H_2SO_4 but unlike HF, can be handled in glass apparatus.



(9.16)

Equation 9.54 shows the self-ionization of HSO_3F for which $K_{self} = 4.0 \times 10^{-8}$.

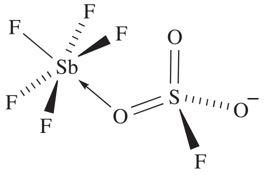
$$2HSO_3F \rightleftharpoons [H_2SO_3F]^+ + [SO_3F]^- \qquad (9.54)$$

9.9 Superacids

A ***superacid*** is a stronger acid than anhydrous H_2SO_4. Superacids are made by dissolving a strong Lewis acid (e.g. SbF_5) in either of the Brønsted acids HF or HSO_3F.

Extremely potent acids, capable of protonating even hydrocarbons, are termed *superacids* and include mixtures of HF and SbF_5 (eq. 9.44) and HSO_3F and SbF_5 (eq. 9.55). The latter mixture is called *magic acid* (one of the strongest acids known) and is available commercially under this name. Antimony(V) fluoride is a strong Lewis acid and forms an adduct with F^- (from HF) or $[SO_3F]^-$ (from HSO_3F). Figure 9.5 shows the crystallographically determined structure of the related adduct $SbF_5OSO(OH)CF_3$.

$$2HSO_3F + SbF_5 \rightleftharpoons [H_2SO_3F]^+ + \underset{\mathbf{9.17}}{[F_5SbOSO_2F]^-} \qquad (9.55)$$



(9.17)

[†] For an introduction to conductometric titrations, see: C.E. Housecroft and E.C. Constable (2010) *Chemistry*, 4th edn, Prentice Hall, Harlow, Chapter 19.

[‡] For discussions of ion transport see: P. Atkins and J. de Paula (2010) *Atkins' Physical Chemistry*, 9th edn, Oxford University Press, Oxford, Chapter 20; J. Burgess (1999) *Ions in Solution: Basic Principles of Chemical Interactions*, 2nd edn, Horwood Publishing, Westergate, Chapter 2.

[*] Fluorosulfonic acid is sometimes called fluorosulfuric acid.

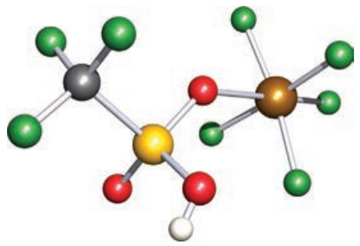


Fig. 9.5 The solid state structure (X-ray diffraction) of SbF$_5$OSO(OH)CF$_3$ [D. Mootz *et al.* (1991) *Z. Naturforsch., Teil B*, vol. 46, p. 1659]. Colour code: Sb, brown; F, green; S, yellow; O, red; C, grey; H, white.

Equilibrium 9.55 is an over-simplification of the SbF$_5$–HSO$_3$F system, but represents it sufficiently for most purposes. The species present depend on the ratio of SbF$_5$: HSO$_3$F, and at higher concentrations of SbF$_5$, species including [SbF$_6$]$^-$, [Sb$_2$F$_{11}$]$^{2-}$, HS$_2$O$_6$F and HS$_3$O$_9$F may exist.

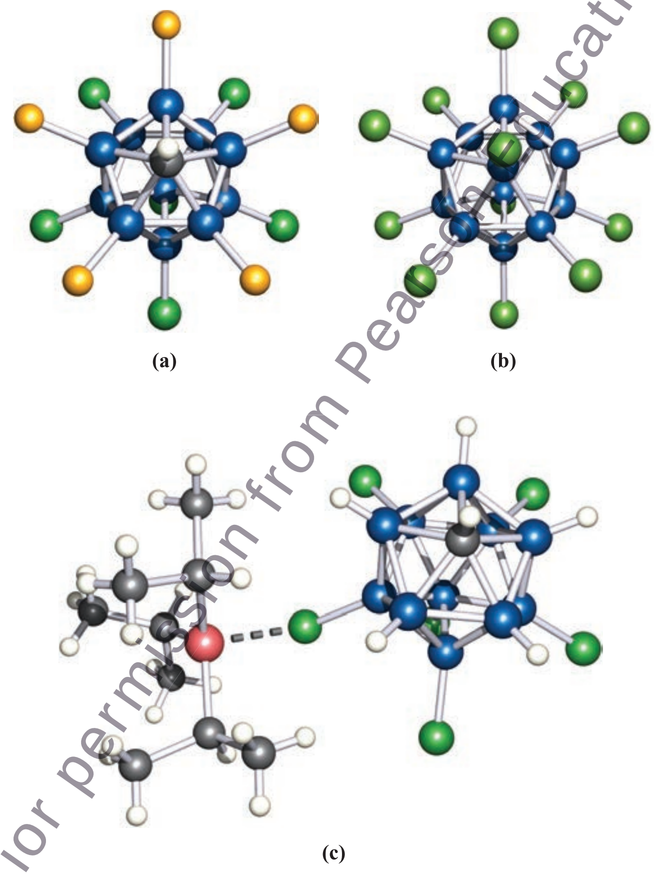
In superacidic media, hydrocarbons act as bases, and this is an important route to the formation of carbenium ions,[†] e.g. eq. 9.56.

$$\mathrm{Me_3CH} + \underset{\substack{\text{generated in}\\ \text{magic acid}}}{[\mathrm{H_2SO_3F}]^+} \longrightarrow [\mathrm{Me_3C}]^+ + \mathrm{H_2} + \mathrm{HSO_3F} \qquad (9.56)$$

Superacids have a wide range of applications and have been used to access species such as [HPX$_3$]$^+$(X=halide), [C(OH)$_3$]$^+$ (by protonation of carbonic acid), [H$_3$S]$^+$ (see Section 16.5), [Xe$_2$]$^+$ (see Section 18.1) and metal carbonyl cations (see Sections 22.9 and 24.4). However, the conjugate bases of traditional superacids are typically strongly oxidizing and strongly nucleophilic, and are not necessarily innocent bystanders in a reaction mixture. A recently developed class of superacids involves icosahedral CB$_{11}$ (*carbaboranes*) or B$_{12}$ cluster cages (see Section 13.11). An advantage of these acids is that they possess chemically inert, extremely weak conjugate bases, and this contrasts with the properties of more traditional superacids. Figures 9.6a and 9.6b show the carbaborane anions [CHB$_{11}$R$_5$X$_6$]$^-$ (R = H, Me, Cl and X = Cl, Br, I) and [B$_{12}$X$_{12}$]$^{2-}$ (X = Cl, Br) which are the conjugate bases of members of this family of superacids. While the anions [CHB$_{11}$R$_5$X$_6$]$^-$ and [B$_{12}$X$_{12}$]$^{2-}$ are chemically unreactive, their conjugate acids are an extremely potent Brønsted acids, stronger than fluorosulfonic acid. The superacids HCHB$_{11}$R$_5$X$_6$ and H$_2$B$_{12}$X$_{12}$ are prepared in two steps (eqs. 9.57 and 9.58, or 9.59 and 9.60).

$$\underset{(\text{e.g. R = Et, }^{i}\text{Pr})}{\mathrm{R_3SiH}} + [\mathrm{Ph_3C}]^+[\mathrm{CHB_{11}R_5X_6}]^- \longrightarrow \mathrm{R_3Si(CHB_{11}R_5X_6)} + \mathrm{Ph_3CH} \qquad (9.57)$$

$$\underset{(\text{e.g. R = Et, }^{i}\text{Pr})}{\mathrm{R_3Si(CHB_{11}R_5X_6)}} \xrightarrow{\text{anhydrous liquid HCl}} \underset{\text{superacid}}{\mathrm{HCHB_{11}R_5X_6}} + \mathrm{R_3SiCl} \qquad (9.58)$$



(a)

(b)

(c)

Fig. 9.6 (a) The [CHB$_{11}$R$_5$X$_6$]$^-$(R = H, Me, Cl and X = Cl, Br, I) anions and (b) the [B$_{12}$X$_{12}$]$^{2-}$ (X = Cl, Br) anions that are the conjugate bases of the family of boron cluster superacids. Colour code: C, grey; B, blue; H, white; R, yellow; X, green. (c) The structure of ^{i}Pr$_3$Si(CHB$_{11}$H$_5$Cl$_6$) (X-ray diffraction) showing the long Si–Cl 'bond' which suggests that the structure approaches an ion-pair [Z. Xie *et al.* (1996) *J. Am. Chem. Soc.*, vol. 118, p. 2922]. Colour code: C, grey; B, blue; Cl, green; Si, pink; H, white.

$$2\mathrm{Et_3SiH} + [\mathrm{Ph_3C}]^+{}_2[\mathrm{B_{12}X_{12}}]^{2-} \longrightarrow (\mathrm{Et_3Si})_2(\mathrm{B_{12}X_{12}}) + 2\mathrm{Ph_3CH} \qquad (9.59)$$

$$(\mathrm{Et_3Si})_2(\mathrm{B_{12}X_{12}}) \xrightarrow{\text{anhydrous liquid HCl}} \underset{\text{superacid}}{\mathrm{H_2B_{12}X_{12}}} + 2\ \mathrm{Et_3SiCl} \qquad (9.60)$$

Reactions 9.58 and 9.60 show the formation of intermediate silylium species which are of interest in their own right (see Section 23.5). Figure 9.6c shows the structure of ^{i}Pr3Si(CHB$_{11}$H$_5$C$_{16}$). The Si–Cl distance is 232 pm, significantly greater than the sum of the covalent radii (217 pm). This indicates that ^{i}Pr$_3$Si(CHB$_{11}$H$_5$C$_{16}$) is tending towards an [^{i}Pr$_3$Si]$^+$[CHB$_{11}$H$_5$C$_{16}$]$^-$ ion-pair, although well-separated ions are clearly not present. Similarly, the solid state structure of (Et$_3$Si)$_2$(B$_{12}$Cl$_{12}$) reveals Et$_3$Si units associated with the B$_2$Cl$_{12}$ cage through long Si–Cl bonds (231 pm). The Et$_3$Si units are flattened and the sum of the C–Si–C bond angles is 348° which approachs the 360° expected for an isolated [Et$_3$Si]$^+$ ion. Treatment of the

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[†] A *carbenium* ion is also called a *carbocation*; the older name of *carbonium* ion is also in use.

intermediates with anhydrous liquid HCl (eqs. 9.58 and 9.60) yields anhydrous $HCHB_{11}R_5X_6$ and $HB_{12}X_{12}$. These superacids protonate most solvents. They can be handled in liquid SO_2, although complete ionization appears to take place, probably with the formation of $[H(SO_2)_2]^+$ (eqs. 9.61 and 9.62).

$$HCHB_{11}R_5X_6 \xrightarrow{\text{liquid } SO_2} [H(SO_2)_2]^+ + [CHB_{11}R_5X_6]^- \qquad (9.61)$$

$$H_2B_{12}X_{12} \xrightarrow{\text{liquid } SO_2} 2[H(SO_2)_2]^+ + [B_{12}X_{12}]^{2-} \qquad (9.62)$$

The exceptional acid strength of these superacids is illustrated by their ability to protonate arenes (e.g. C_6H_6, C_6H_5Me, C_6Me_6). The resultant salts are remarkably thermally stable, e.g. $[C_6H_7]^+[CHB_{11}Me_5Br_6]^-$ is stable to 423 K.

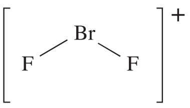
9.10 Bromine trifluoride

Physical properties

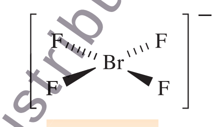
Bromine trifluoride is a pale yellow liquid at 298 K and is an *aprotic* non-aqueous solvent. Selected physical properties are given in Table 9.8 and the compound is discussed further in Section 17.7. Bromine trifluoride is an extremely powerful fluorinating agent and fluorinates essentially every species that dissolves in it. However, massive quartz is kinetically stable towards BrF_3 and the solvent can be handled in quartz vessels. Apparatus made from Cu, Ni or Monel metal (68% Ni and 32% Cu) can also be used; the metal surface becomes protected by a thin layer of metal fluoride.

The self-ionization of BrF_3 (eq. 9.60) has been demonstrated by the isolation and characterization of salt containing the $[BrF_2]^+$ and $[BrF_4]^-$ ions, and by conductometric titrations of them (see below). Using the solvent-based acid–base definitions, an acid in BrF_3 is a species that produces $[BrF_2]^+$ (**9.18**), and a base is one that gives $[BrF_4]^-$ (**9.19**).

$$2BrF_3 \rightleftharpoons [BrF_2]^+ + [BrF_4]^- \qquad (9.63)$$



(9.18)



(9.19)

Table 9.8 Selected physical properties of bromine trifluoride, BrF_3.

Property / units	Value
Melting point / K	281.8
Boiling point / K	408
Density of liquid / g cm^{-3}	2.49
Relative permittivity	107
Self-ionization constant	8.0×10^{-3} (at 281.8 K)

Behaviour of fluoride salts and molecular fluorides in BrF_3

Bromine trifluoride acts as a Lewis acid, readily accepting F^-. When dissolved in BrF_3, alkali metal fluorides, BaF_2 and AgF combine with the solvent to give salts containing the $[BrF_4]^-$ anion, e.g. $K[BrF_4]$ (eq. 9.64), $Ba[BrF_4]_2$ and $Ag[BrF_4]$. On the other hand, if the fluoride solute is a more powerful F^- acceptor than BrF_3, salts containing $[BrF_2]^+$ are formed, e.g. eqs. 9.65–9.67.

$$KF + BrF_3 \longrightarrow K^+ + [BrF_4]^- \qquad (9.64)$$

$$SbF_5 + BrF_3 \longrightarrow [BrF_2]^+ + [SbF_6]^- \qquad (9.65)$$

$$SnF_4 + 2BrF_3 \longrightarrow 2[BrF_2]^+ + [SnF_6]^{2-} \qquad (9.66)$$

$$AuF_3 + BrF_3 \longrightarrow [BrF_2]^+ + [AuF_4]^- \qquad (9.67)$$

A conductometric titration of $[BrF_2][SbF_6]$ against $Ag[BrF_4]$ exhibits a minimum at a 1 : 1 ratio supporting neutralization reaction 9.68.

$$\underset{\text{acid}}{[BrF_2][SbF_6]} + \underset{\text{base}}{Ag[BrF_4]} \longrightarrow Ag[SbF_6] + 2BrF_3 \qquad (9.68)$$

Reactions in BrF_3

Much of the chemistry studied in BrF_3 media involves fluorination reactions, and the preparation of highly fluorinated species. For example, the salt $Ag[SbF_6]$ can be prepared in liquid BrF_3 from elemental Ag and Sb in a 1 : 1 molar ratio (eq. 9.69), and $K_2[SnF_6]$ is produced when KCl and Sn are combined in a 2 : 1 molar ratio in liquid BrF_3 (eq. 9.70). Further examples are given in eqs. 9.71–9.73.

$$Ag + Sb \xrightarrow{\text{in } BrF_3} Ag[SbF_6] \qquad (9.69)$$

$$2KCl + Sn \xrightarrow{\text{in } BrF_3} K_2[SnF_6] \qquad (9.70)$$

$$Ag + Au \xrightarrow{\text{in } BrF_3} Ag[AuF_4] \qquad (9.71)$$

$$KCl + VCl_4 \xrightarrow{\text{in } BrF_3} K[VF_6] \qquad (9.72)$$

$$Ru + KCl \xrightarrow{\text{in } BrF_3} K[RuF_6] \qquad (9.73)$$

In contrast to the situation for H_2SO_4, where we noted that it is difficult to separate reaction products from the solvent by evaporation, BrF_3 can be removed *in vacuo* ($\Delta_{vap}H^o = 47.8\,kJ\,mol^{-1}$). Some of the compounds prepared in liquid BrF_3 can also be made using F_2 as the fluorinating agent, but use of F_2 generally requires higher reaction temperatures and the reactions are not always product-specific.

Non-aqueous solvents that behave similarly to BrF_3 in that they are good oxidizing and fluorinating agents include ClF_3, BrF_5 and IF_5.

Self-study exercises

1. **Suggest how AgF behaves when dissolved in BrF_3.**
[*Ans.* Analogous to reaction 9.64]

2. **When AgF and SbF_5 are dissolved in BrF_3, the product is $Ag[SbF_6]$. Comment on the role of the solvent in this reaction.**

3. **When NaCl and $RhCl_3$ are dissolved in liquid IF_5, a rhodium(V) salt is obtained. Suggest a likely identity for this product.** **[*Ans.* $Na[RhF_6]$]**

4. **When tungsten metal dissolves in BrF_3, a W(VI) compound is formed. (a) What is this product? (b) The oxidation must be accompanied by a reduction process. Suggest the likely reduction product.**
[*Ans.* (a) WF_6; (b) Br_2]

9.11 Dinitrogen tetraoxide

Physical properties

The data in Table 9.9 and Fig. 9.2 emphasize the very short liquid range of N_2O_4. Despite this and the low relative permittivity (which makes it a poor solvent for most inorganic compounds), N_2O_4 has some important preparative uses.

The low electrical conductivity ($1.3 \times 10^{-13}\ \Omega^{-1}\ cm^{-1}$ at 273 K) of liquid N_2O_4 is inconsistent with the presence of ions in the neat liquid. However, when $[Et_4N][NO_3]$ (which has a very low lattice energy) dissolves in liquid N_2O_4, $[NO_3]^-$ ions rapidly exchange between the solute and solvent. This confirms that $[NO_3]^-$ ions can form in liquid N_2O_4. In terms of a solvent-oriented acid-base definition, basic behaviour in N_2O_4 is characterized by the formation of $[NO_3]^-$, and acidic behaviour by the production of $[NO]^+$. Thus, equilibrium 9.74 is useful for understanding reactions in liquid N_2O_4, even though self-ionization does not occur in the pure liquid.

$$N_2O_4 \rightleftharpoons [NO]^+ + [NO_3]^- \qquad (9.74)$$

Table 9.9 Selected physical properties of dinitrogen tetraoxide, N_2O_4.

Property / units	Value
Melting point / K	261.8
Boiling point / K	294.2
Density of liquid / g cm^{-3}	1.49 (at 273 K)
Relative permittivity	2.42 (at 291 K)

Reactions in N_2O_4

Reactions carried out in liquid N_2O_4 reflect the fact that N_2O_4 is a good oxidizing (see Box 9.1) and nitrating agent. Electropositive metals such as Li and Na react in liquid N_2O_4 liberating NO (eq. 9.75). In this reaction, Li is oxidized to Li^+, and $[NO]^+$ is reduced to NO.

$$Li + N_2O_4 \longrightarrow LiNO_3 + NO \qquad (9.75)$$

Less reactive metals may react rapidly if ClNO, $[Et_4N][NO_3]$ or an organic donor such as MeCN is present. These observations can be explained as follows.

- ClNO behaves as a very weak acid in liquid N_2O_4, ionizing to produce $[NO]^+$. This encourages oxidation of metals as $[NO]^+$ is reduced to NO (eq. 9.76).

$$Sn + 2ClNO \xrightarrow{\text{in liquid } N_2O_4} SnCl_2 + 2NO \qquad (9.76)$$

- $[Et_4N][NO_3]$ acts as a base in liquid N_2O_4 and its action on metals such as Zn and Al produces nitrato complexes (eq. 9.77). This is analogous to the formation of hydroxido complexes in an aqueous system. Figure 9.7 shows the structure of $[Zn(NO_3)_4]^{2-}$. Again, the oxidation of the metal is accompanied by reduction of $[NO]^+$ to NO.

$$\begin{aligned} &Zn + 2[Et_4N][NO_3] + 2N_2O_4 \\ &\qquad \longrightarrow [Et_4N]_2[Zn(NO_3)_4] + 2NO \end{aligned} \qquad (9.77)$$

- Organic donor molecules appear to facilitate reactions with metals by increasing the degree of self-ionization of the solvent as a result of adduct formation with the $[NO]^+$ cation; e.g. Cu dissolves in liquid N_2O_4/MeCN (eq. 9.78), and Fe behaves similarly, dissolving to give $[NO][Fe(NO_3)_4]$.

$$Cu + 3N_2O_4 \xrightarrow{\text{in presence of MeCN}} [NO][Cu(NO_3)_3] + 2NO \qquad (9.78)$$

The presence of $[NO]^+$ cations in compounds such as $[NO][Cu(NO_3)_3]$, $[NO][Fe(NO_3)_4]$, $[NO]_2[Zn(NO_3)_4]$ and $[NO]_2[Mn(NO_3)_4]$ is confirmed by the appearance of a characteristic absorption (ν_{NO}) at $\approx$2300 cm^{-1} in the infrared spectra of the complexes.

Just as hydrolysis of a compound may occur in water (see Section 7.7), solvolysis such as reaction 9.79 can take place in liquid N_2O_4. Such reactions are of synthetic importance as routes to *anhydrous* metal nitrates.

$$ZnCl_2 + 2N_2O_4 \longrightarrow Zn(NO_3)_2 + 2ClNO \qquad (9.79)$$

In many of the reactions carried out in liquid N_2O_4, the products are solvates, for example $[Fe(NO_3)_3]\cdot 1.5N_2O_4$, $[Cu(NO_3)_2]\cdot N_2O_4$, $[Sc(NO_3)_2]\cdot 2N_2O_4$ and $[Y(NO_3)_3]\cdot 2N_2O_4$. Such formulations may, in some cases, be correct, with molecules of N_2O_4 present, analogous to water molecules of crystallization in crystals isolated from an aqueous system. However, the results of X-ray diffraction

APPLICATIONS

Box 9.1 Liquid N_2O_4 as a fuel in the Apollo missions

During the Apollo Moon missions, a propulsion system was required that could be used to alter the velocity of the spacecraft and change its orbit during landing on and take-off from the Moon's surface. The fuel chosen was a mixture of liquid N_2O_4 and derivatives of hydrazine (N_2H_4). Dinitrogen tetraoxide is a powerful oxidizing agent and contact with, for example, $MeNHNH_2$ leads to immediate oxidation of the latter:

$$5N_2O_4 + 4MeNHNH_2 \longrightarrow 9N_2 + 12H_2O + 4CO_2$$

The reaction is highly exothermic, and at the operating temperatures, all products are gases.

Safety is of utmost importance; the fuels clearly must not contact each other before the required moment of landing or lift-off. Further, $MeNHNH_2$ is extremely toxic.

The command module of *Apollo 17* in orbit above the lunar surface.

studies on some solvated compounds illustrate the presence, not of N_2O_4 molecules, but of $[NO]^+$ and $[NO_3]^-$ ions. Two examples are $[Sc(NO_3)_3]\cdot 2N_2O_4$ and $[Y(NO_3)_3]\cdot 2N_2O_4$, for which the formulations $[NO]_2[Sc(NO_3)_5]$ and $[NO]_2[Y(NO_3)_5]$ have been crystallographically confirmed. In the $[Y(NO_3)_5]^{2-}$ anion, the Y(III) centre is 10-coordinate with bidentate nitrato ligands, while in $[Sc(NO_3)_5]^{2-}$, the Sc(III) centre is 9-coordinate with one $[NO_3]^-$ ligand being monodentate.

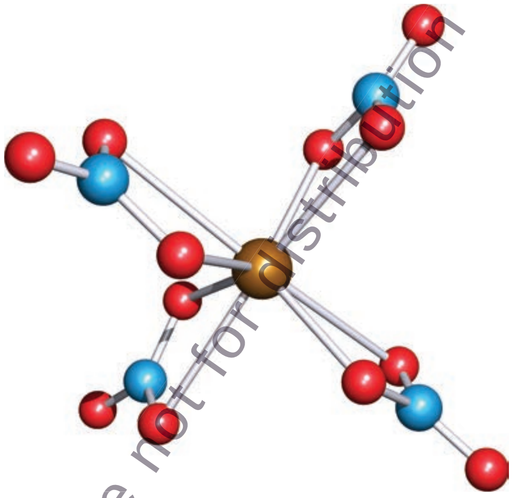


Fig. 9.7 The solid state structure (X-ray diffraction) of the $[Zn(NO_3)_4]^{2-}$ anion in the salt $[Ph_4As]_2[Zn(NO_3)_4]$. Each $[NO_3]^-$ ligand is coordinated to the Zn(II) centre through two O atoms, with one short (average 206 pm) and one long (average 258 pm) Zn–O interaction [C. Bellitto *et al.* (1976) *J. Chem. Soc., Dalton Trans.*, p. 989]. Colour code: Zn, brown; N, blue; O, red.

Self-study exercises

1. **In reaction 9.76, why is ClNO considered to act as a weak acid?**
2. **Reaction of uranium metal with N_2O_4 in $N_2O_4/MeNO_2$ solvent yields $[UO_2(NO_3)_3]^-$ in which the U centre is 8-coordinate. Suggest (a) a structure for $[UO_2(NO_3)_3]^-$, and (b) the identity of the counterion.**
   [*Ans.* See M.-J. Crawford *et al.* (2005) *Inorg. Chem.*, vol. 44, p. 8481]
3. **Write an equation for the reaction of Na metal in liquid N_2O_4. [*Ans.* Analogous to reaction 9.75]**
4. **Why is the following reaction classified as a neutralization process?**

$$AgNO_3 + NOCl \xrightarrow{\text{in liquid } N_2O_4} AgCl + N_2O_4$$

9.12 Ionic liquids

The use of *ionic liquids* (also called *molten salts*) as reaction media is a relatively new area, although molten conditions have been well established in industrial processes (e.g. the Downs process, Fig. 11.2) for many years. While some 'molten salts' are hot as the term suggests, others operate at ambient temperatures and the term 'ionic liquids' is more appropriate. Although the terms 'ionic liquids' and 'molten salts' are sometimes used interchangeably, we make a clear distinction between them, using 'ionic liquid' only for a salt with a melting point $\leq$373 K.

Molten salt solvent systems

When an ionic salt such as NaCl melts, the ionic lattice (see Fig. 6.16) collapses, but some order is still retained. Evidence for this comes from X-ray diffraction patterns, from which *radial distribution functions* reveal that the average coordination number (with respect to cation–anion interactions) of each ion in liquid NaCl is $\approx$4, compared with 6 in the crystalline lattice. For cation–cation or anion–anion interactions, the coordination number is higher, although, as in the solid state, the internuclear distances are larger than for cation–anion separations. The solid-to-liquid transition is accompanied by an increase in volume of $\approx$10–15%.

The term *eutectic* is commonly encountered in this field. The reason for forming a eutectic mixture is to provide a molten system at a convenient working temperature. For example, the melting point of NaCl is 1073 K, but is lowered if $CaCl_2$ is added as in the Downs process.

> A *eutectic* is a mixture of two substances and is characterized by a sharp melting point lower than that of either of the components; a eutectic behaves as though it were a single substance.

Other alkali metal halides behave in a similar manner to NaCl, but metal halides in which the bonding has a significant covalent contribution (e.g. Hg(II) halides) form melts in which equilibria such as 9.80 are established. In the solid state, $HgCl_2$ forms a molecular lattice, and layer structures are adopted by $HgBr_2$ (distorted CdI_2 lattice) and HgI_2.

$$2HgBr_2 \rightleftharpoons [HgBr]^+ + [HgBr_3]^- \qquad (9.80)$$

In terms of the solvent-oriented description of acid–base chemistry in a non-aqueous solvent, eq. 9.80 illustrates that, in molten $HgBr_2$, species producing $[HgBr]^+$ ions may be considered to act as acids, and those providing $[HgBr_3]^-$ ions function as bases. In most molten salts, however, the application of this type of acid–base definition is not appropriate.

An important group of molten salts with more convenient operating temperatures contain the $[AlCl_4]^-$ ion. An example is an NaCl–Al_2Cl_6 mixture. The melting point of Al_2Cl_6 is 463 K (at 2.5 bar), and its addition to NaCl (melting point, 1073 K) results in a 1:1 medium with a melting point of 446 K. In this and other Al_2Cl_6–alkali metal chloride melts, equilibria 9.81 and 9.82 are established, with the additional formation of $[Al_3Cl_{10}]^-$ (see Section 13.6).

$$Al_2Cl_6 + 2Cl^- \rightleftharpoons 2[AlCl_4]^- \qquad (9.81)$$

$$2[AlCl_4]^- \rightleftharpoons [Al_2Cl_7]^- + Cl^- \qquad (9.82)$$

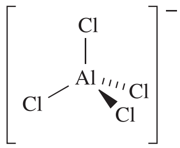
Manufacturing processes in which metals are extracted from molten metal salts are important examples of the uses of molten salts and include the Downs process, and the production of Li by electrolysis of molten LiCl, and of Be and Ca from $BeCl_2$ and $CaCl_2$, respectively.

Some unusual cations have been isolated as products from reactions in molten salt media. For example, the reaction of Bi and $BiCl_3$ in KCl–$BiCl_3$ solvent at $\approx$570 K yields $[Bi_9]_2[BiCl_5]_4[Bi_2Cl_8]$ which contains $[Bi_9]^{5+}$, $[BiCl_5]^{2-}$ and $[Bi_2Cl_8]^{2-}$. In a melt containing $AlCl_3$ and MCl (M = Na or K) at $\approx$530 K, Bi and $BiCl_3$ react to form $[Bi_5]^{3+}$ (a trigonal bipyramidal species like $[Sn_5]^{2-}$, Fig. 9.3) and $[Bi_8]^{2+}$, which are isolated as the $[AlCl_4]^-$ salts.

Ionic liquids at ambient temperatures

> An *ionic liquid* is an ionic salt that is a liquid below 373 K.

Interest in the development and applications of ionic liquids continues to grow rapidly, one of the main reasons being that these solvents have implications for green chemistry (see Box 9.2). The first generation of ionic liquids were salts containing alkylpyridinium or dialkylimidazolium cations (Fig. 9.8) with $[AlCl_4]^-$ (**9.20**) or $[Al_2Cl_7]^-$ (**9.21**) anions.



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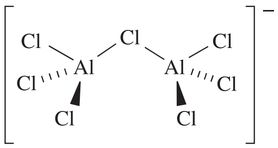


(9.21)

For example, reaction between Al_2Cl_6 and *n*-butylpyridinium chloride, [pyBu]Cl, produces $[pyBu][AlCl_4]$ (eq. 9.83). This family of ionic liquids suffers from the fact that the $[AlCl_4]^-$ ion readily hydrolyses. Replacement of $[AlCl_4]^-$ by $[BF_4]^-$ or $[PF_6]^-$ increases the stability of the ionic liquids to air and water.

$$Al_2Cl_6 + 2[pyBu]Cl \longrightarrow 2[pyBu][AlCl_4] \qquad (9.83)$$

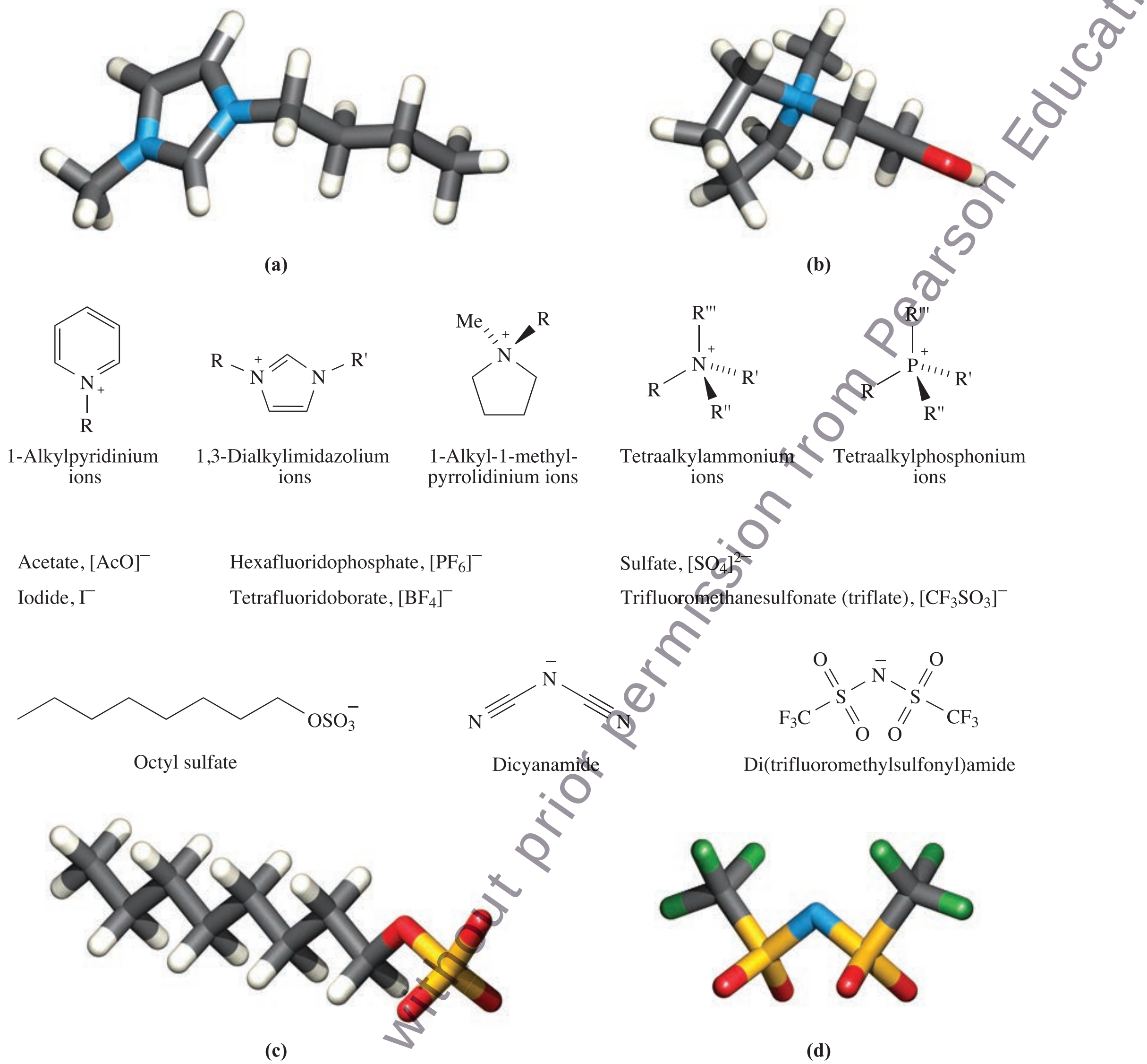
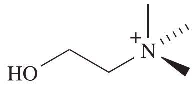


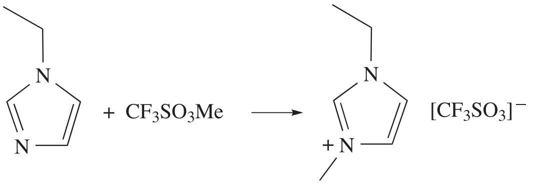
Fig. 9.8 Some of the most commonly used cations and anions in ionic liquids. In the cations, the organic groups, R, R′ etc., may be unsubstituted alkyl groups or may be functionalized, e.g. (a) 1-butyl-3-methylimidazolium cation and (b) 1-(2-aminoethyl)-1-methylpyrrolidinium cation. Structures (c) and (d) show the octyl sulfide and di(trifluoromethylsulfonyl)amide anions. Colour code: C, grey; H, white; N, blue; O, red; S, yellow; F, green.

Currently favoured ionic liquids comprise combinations of cations and anions such as those in Fig. 9.8. By varying (i) the substituents in the cations and (ii) the combinations of anions and cations, a huge number of ionic liquids with differing physical properties (e.g. melting point, viscosity, mobility of ions in solution) can be prepared. A third group of ionic liquids has been designed for use in biocatalysis. These comprise biodegradable, low-toxicity cations and/or anions, for example the choline cation (**9.22**) with alkyl sulfates, alkyl phosphates or anions derived from sugars or amino acids.[†]



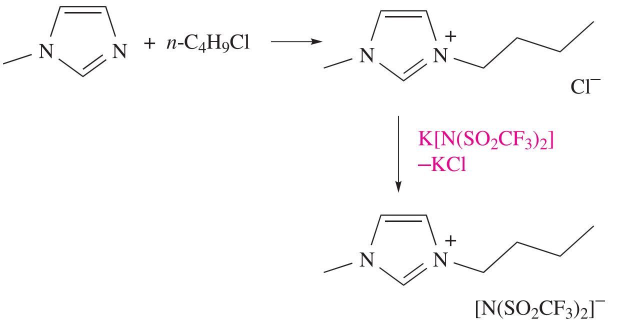
(9.22)

Some ionic liquids can be formed by the direct reaction of the N- or P-containing base with an alkylating agent. The latter may provide the desired counter-ion directly (e.g. eq. 9.84), or alkylation may be followed by anion exchange (scheme 9.85).



(9.84)

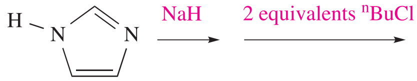
[†] See: J. Gorke, F. Srienc and R. Kazlauskas (2010) *Biotechnol. Bioprocess Eng.*, vol. 15, p. 40—'Toward advanced ionic liquids. Polar, enzyme-friendly solvents for biocatalysis'.

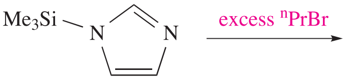


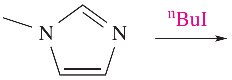
(9.85)

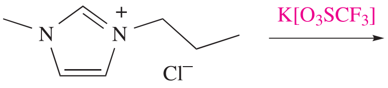
Self-study exercises

1. **The following are routes to 1,3-dialkylimidazolium-based ionic liquids. What is the product is each case? Comment on the roles of the reagents.**

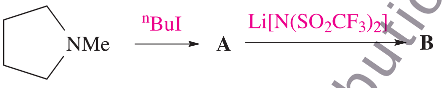








2. **Ionic liquid B can be made in two steps:**



Identify A and B. Which step is a metathesis reaction?

The reason that ionic liquids possess such low melting points is that they contain large, unsymmetrical cations usually combined with polyatomic anions (Fig. 9.8). Such ions pack less efficiently in the solid state than symmetrical ions (e.g. $[NH_4]^+$ with Br^-). The relatively poor packing results in low lattice energies (Table 9.10) which, in turn, lead to low melting compounds. The melting point can be tuned by altering the substituents in a given cation. For example, in a series of salts containing different 1-alkyl-3-methylimidazolium cations and a common anion, the melting point decreases as the n-alkyl chain lengthens. However, once the n-alkyl substituent contains more than eight C atoms, the melting point starts to increase because it is energetically favourable for the longer alkyl chains to be aligned parallel to one another with van der Waals forces operating between them. Melting points are also affected by hydrogen bonding. If the ionic liquid is a hexafluoridophosphate salt, the organic cation and $[PF_6]^-$ ion can engage in weak C–H$\cdots$F non-classical hydrogen bonds (see Section 10.6) in the solid state. This increases the melting point (although not as significantly as would be the case for O–H$\cdots$O or N–H$\cdots$O hydrogen bonds). In contrast, the melting points and viscosities of ionic liquids containing $[N(SO_2CF_3)_2]^-$ are low because the negative charge is delocalized over the two SO_2 units, thereby preventing directionalized cation$\cdots$anion interactions.

Ionic liquids are sometimes termed 'task specific', meaning that the large pool of cations and anions available permits the design of a solvent with quite specific properties. The low volatility of ionic liquids gives them a 'green' advantage over volatile organic solvents. Ionic liquids have long liquid ranges, and many are non-flammable and thermally stable. However, it is important to assess both the synthetic route to the ionic liquid as well as the properties of the material itself before labelling the compound environmentally friendly.[†]

Some of the first applications of room temperature ionic liquids (mp < 298 K) were in solution electrochemistry, for electrodeposition (electroplating) of metals and as electrolytes in batteries. What advantages do ionic liquids have over conventional solvents (e.g. MeCN) for cyclic voltammetry? In Box 8.2, we pointed out that a supporting electrolyte is added to the solvent in a cyclic voltammetry experiment to ensure a high enough electrical conductivity. Since an ionic liquid is composed of ions, no supporting electrolyte is needed. However, the mobility (not just the number) of ions affects conductivity. The large ions typically present in an ionic liquid exhibit low mobilities and this offsets the advantage of having a solvent composed entirely of ions. Many ionic liquids are too viscous to be used for solution electrochemical studies. Compared with traditional solvents, ionic liquids composed of imidazolium cations with $[AlCl_4]^-$, $[BF_4]^-$, $[CF_3CO_2]^-$, $[CF_3SO_3]^-$ or $[N(SO_2CF_3)_2]^-$ and which exhibit wide potential windows (see Box 8.2) of ≤ 6 V, represent possible alternative media for cyclic voltammetry and similar electrochemical measurements.

Commerical electroplating of metals (e.g. Ni, Cu, Zn, Ag, Au) involves the deposition of the metal at the cathode from an aqueous electrolyte in a Galvanic cell. Electrodeposition of Al is an exception; during electrolysis, H_2O is reduced at

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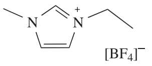
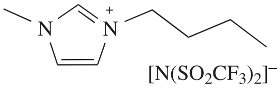
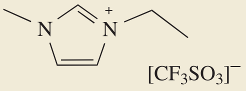
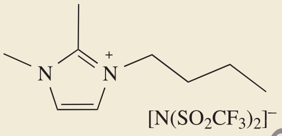
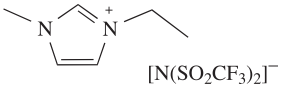
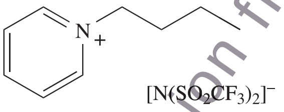
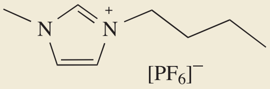
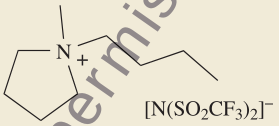
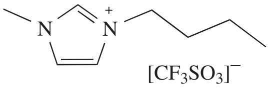
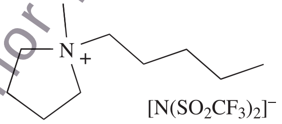
[†] See: M. Deetlefs and K.R. Seddon (2010) *Green Chem.*, vol. 12, p. 17 – 'Assessing the greenness of some typical laboratory ionic liquid preparations'; M. Smiglak *et al.* (2006) *Chem. Commun.*, p. 2554 – 'Combustible ionic liquids by design: is laboratory safety another ionic liquid myth?'.

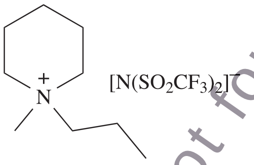
Table 9.10 Calculated values of lattice enthalpies ($\Delta_{\text{lattice}}H^\circ$) for selected ionic liquids. Values refer to the process: gaseous ions → ionic solid. (See Chapter 6 for definitions of lattice energy and lattice enthalpy.)

Ionic liquid	$\Delta_{\text{lattice}}H^\circ$/kJmol^{-1}	Ionic liquid	$\Delta_{\text{lattice}}H^\circ$/kJmol^{-1}
 $[BF_4]^-$	−492	 $[N(SO_2CF_3)_2]^-$	−420
 $[CF_3SO_3]^-$	−464	 $[N(SO_2CF_3)_2]^-$	−412
 $[N(SO_2CF_3)_2]^-$	−425	 $[N(SO_2CF_3)_2]^-$	−420
 $[PF_6]^-$	−457	 $[N(SO_2CF_3)_2]^-$	−414
 $[CF_3SO_3]^-$	−449	 $[N(SO_2CF_3)_2]^-$	−411

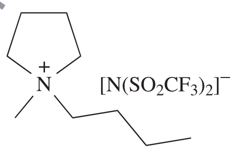
Data: I. Krossing *et al.* (2006) *J. Am. Chem. Soc.*, vol. 128, p. 13427; I. Krossing *et al.* (2007) *J. Am. Chem. Soc.*, vol. 129, p. 11296.

the cathode before Al^{3+} is reduced. Thus, commercial electrodeposition of Al is carried out using Et_3Al (which is pyrophoric) in toluene. A safer alternative is electrodeposition of Al from $AlCl_3$ or related precursor in an ionic liquid. Possible solvents are **9.23** and **9.24**,[†] and further research development should lead to commercial application in the near future. Other metals that could be electroplated using ionic liquids include Mg, Ti, Mo and W.

A ***pyrophoric*** material is one that spontaneously ignites in air.

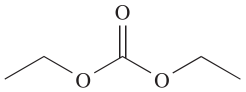


(9.23)



(9.24)

Rechargeable lithium-ion batteries have widespread commercial applications in portable electronic devices (see Box 11.3). However, safety issues associated with the use of flammable organic electrolytes have been a barrier to the development of large lithium-ion batteries of the current composition for use in electric or hybrid electric vehicles (see Box 11.3). The electrolyte in commercial batteries is typically $LiPF_6$ in an alkyl carbonate. The physical properties of ionic liquids suggest that they could be applied in lithium-ion batteries, and among those tested, compound **9.23** functions well. Cell performance is enhanced by adding $Li[N(SO_2CF_3)_2]$ (0.3 mole per kg of **9.23**), and further improved if diethyl carbonate (**9.25**) is added as a co-solvent. The amount of diethyl carbonate must be limited to maintain an electrolyte of low flammability. Although promising,[†] the application of ionic liquids in lithium-ion batteries has not yet (as of 2010) been commercialized.

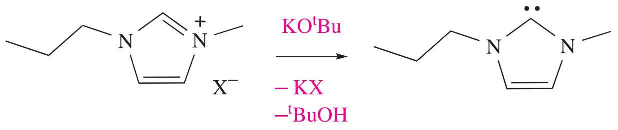


(9.25)

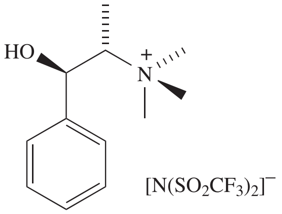
[†] See: T. Rodopoulos, L. Smith, M. D. Horne and T. Rüther (2010) *Chem. Eur. J.*, vol. 16, p. 3815.

[†] See: A. Lewandowski and A. Świderska-Mocek (2009) *J. Power Sources*, vol. 194, p. 601; H.F. Xiang, B. Yin, H. Wang, H.W. Lin, X.W. Ge, S. Xie and C.H. Chen (2010) *Electrochim. Acta*, vol. 55, p. 5204.

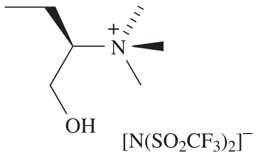
Ionic liquids are now used in place of organic solvents in a wide range of organic transformations including Diels-Alder reactions, Friedel-Crafts alkylations and acylations, C–C bond-forming Heck reactions, and syntheses of heterocyclic systems. However, imidazolium-based ionic liquids tend to react with strong bases (e.g. Grignard reagents or KO^{t}Bu), being deprotonated at the C2 position to give a carbene:



They should therefore not be used under such conditions. Nonetheless, many ionic liquids are good solvents for a wide range of organometallic compounds, thus enabling them to be used in homogeneous catalysis. Asymmetric syntheses may be carried out using chiral catalysts in achiral ionic liquids. Enantiomerically pure ionic liquids containing chiral cations such as **9.26** (mp 327 K) and **9.27** (mp < 255 K) are also available.



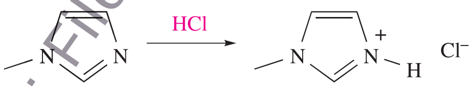
(9.26)



(9.27)

The first industrial process to involve ionic liquids was introduced by BASF in 2002. Called BASIL™, this technology addresses the problem of HCl formed as a byproduct in the synthesis of alkoxyphenylphosphines (eq. 9.86). Before the advent of ionic liquids, HCl was scavenged by a tertiary amine, forming a solid [R$_3$NH]Cl salt which was separated by filtration. On a commercial scale, this operation is expensive. BASF now uses 1-methylimidazole to scavenge HCl (eq. 9.87). 1-Methylimidazolium chloride is an ionic liquid (mp 348 K) which is immiscible with the reaction solvent. Separation of the two liquid phases is achieved at a lower cost than the filtration previously needed. Deprotonation of the 1-methylimidazolium cation regenerates imidazole which is recycled.

(9.86)



(9.87)

Applications of ionic liquids in inorganic chemistry range from the isolation of molecular species to uses in material chemistry. The choice of an ionic liquid allows access to species that are insoluble in common organic solvents or are unstable in aqueous media. The organic cations in the solvent are often incorporated into the products and can act as templates to facilitate the assembly of 3-dimensional frameworks.

Ionic liquids containing inorganic halide anions may act as a source of halide, thereby functioning as a reagent as well as a solvent. For example, reactions of Bi_2O_3 or V_2O_5 in [Bupy][AlCl$_4$] ([Bupy]$^+$ = *N*-butylpyridinium ion) at 373 K with Bi or In metal as reducing agent produces [Bupy]$_4$[Bi$_4$Cl$_{16}$] or [Bupy]$_4$[V$_4$O$_4$Cl$_{12}$] (Figs. 9.9a and 9.9b). The cluster ion [Zr$_6$MnCl$_{18}$]$^{5-}$ (Fig. 9.9c) and related anions may be 'cut out' from solid state precursors that possess extended structures. Solid $Li_2Zr_6MnCl_{15}$ comprises octahedral Zr$_6$Mn-units connected by bridging Cl atoms. Heating $Li_2Zr_6MnCl_{15}$ in [EMim][AlCl$_4$] ([EMim]$^+$ = 1-ethyl-3-methylimidazolium ion) yields the [EMim]$_5$[Zr$_6$MnCl$_{18}$].

Anions used in ionic liquids include some which may coordinate to metal ions, e.g. [AcO]$^-$, [CF$_3$SO$_3$]$^-$ and [N(SO$_2$CF$_3$)$_2$]$^-$. Since the charge in [N(SO$_2$CF$_3$)$_2$]$^-$ is delocalized over the ion, it is typically considered to be only weakly coordinating. However, in an appropriate ionic liquid (i.e. in the absence of competing ligands such as H_2O or solvent), [N(SO$_2$CF$_3$)$_2$]$^-$ binds to a range of metal ions and its coordination chemistry is now well developed for *s*- and *f*-block metal ions (see also Chapter 27). Reactions 9.88-9.91 give examples ([MPpyr]$^+$ = *N*-methyl-*N*-propylpyrrolidinium ion, [BMpyr]$^+$ = *N*-butyl-*N*-methylpyrrolidinium ion). The [N(SO$_2$CF$_3$)$_2$]$^-$ ion coordinates through one or two of its oxygen atoms. In [Ca{N(SO$_2$CF$_3$)$_2$}$_4$]$^{2-}$ (Fig. 9.10a) and [Yb{N(SO$_2$CF$_3$)$_2$}$_4$]$^{2-}$, the metal ion is in a square antiprismatic environment (8-coordinate) with four bidentate ligands. In [Pr{N(SO$_2$CF$_3$)$_2$}$_5$]$^{2-}$ and [Nd{N(SO$_2$CF$_3$)$_2$}$_5$]$^{2-}$ (Fig. 9.10b), the metal ion is 9-coordinate with one monodentate and four bidentate ligands.

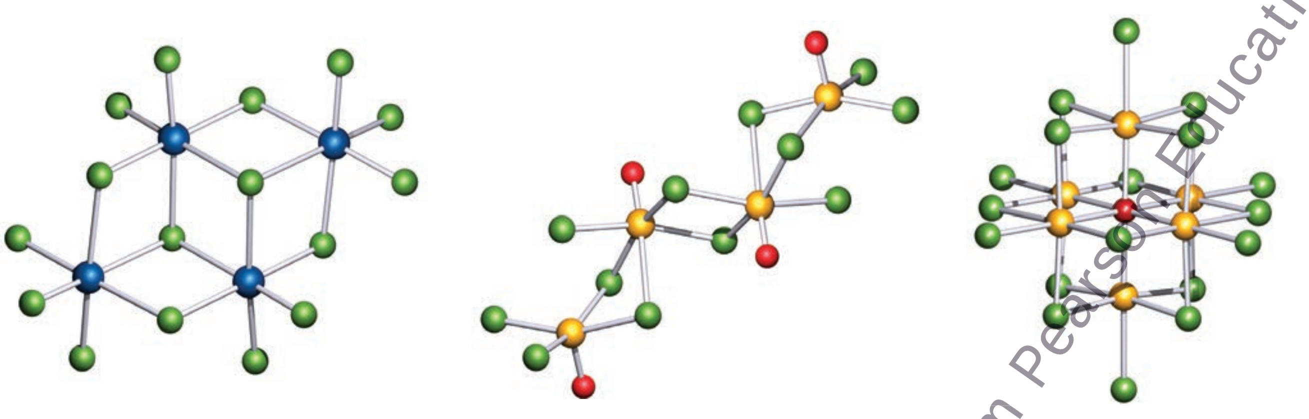
$$\mathrm{CaI_2} + \text{excess } [\mathrm{MPpyr}][\mathrm{N(SO_2CF_3)_2}] \xrightarrow{\text{390 K, under vacuum}} [\mathrm{MPpyr}]_2[\mathrm{Ca\{N(SO_2CF_3)_2\}_4}] \qquad (9.88)$$

$$\mathrm{YbI_2} + \text{excess } [\mathrm{MPpyr}][\mathrm{N(SO_2CF_3)_2}] \quad r \xrightarrow{\text{390 K, under vacuum}} [\mathrm{MPpyr}]_2[\mathrm{Yb\{N(SO_2CF_3)_2\}_4}] \qquad (9.89)$$

$$\mathrm{Pr\{N(SO_2CF_3)_2\}_3} + \text{excess } [\mathrm{BMpyr}][\mathrm{N(SO_2CF_3)_2}] \xrightarrow{\text{390 K, under vacuum}} [\mathrm{BMpyr}]_2[\mathrm{Pr\{N(SO_2CF_3)_2\}_5}] \qquad (9.90)$$

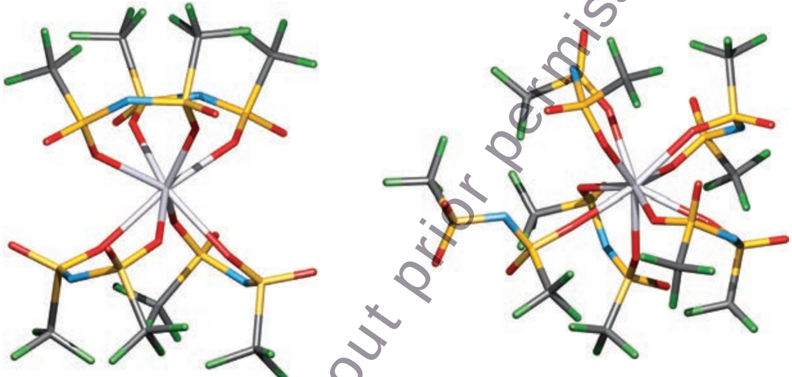
$$\mathrm{Nd\{N(SO_2CF_3)_2\}_3} + \text{excess } [\mathrm{BMpyr}][\mathrm{N(SO_2CF_3)_2}] \xrightarrow{\text{390 K, under vacuum}} [\mathrm{BMpyr}]_2[\mathrm{Pr\{N(SO_2CF_3)_2\}_5}] \qquad (9.91)$$

In reactions 9.90 and 9.91, the precursor is the di(trifluoromethylsulfonyl)amido salt of the metal rather than a



(a) (b) (c)

Fig. 9.9 The structures (X-ray diffraction) of (a) the $[Bi_4Cl_{16}]^{4-}$ ion in $[Bupy]_4[Bi_4Cl_{16}]$ (colour code: Bi, blue; Cl, green), (b) the $[V_4O_4Cl_{12}]^{4-}$ ion in $[Bupy]_4[V_4O_4Cl_{12}]$ (colour code: V, yellow; O, red; Cl, green) [P. Mahjoor *et al.* (2009) *Cryst. Growth Des.*, vol. 9, p. 1385], and (c) the $[Zr_6MnCl_{18}]^{5-}$ anion from the 1-ethyl-3-methylimidazolium salt [D. Sun *et al.* (2000) *Inorg. Chem.*, vol. 39, p. 1964]. Colour code: Zr, yellow; Mn, red; Cl, green.



(a) (b)

Fig. 9.10 Stick-representations of the structures (X-ray diffraction) of (a) the $[Ca\{N(SO_2CF_3)_2\}_4]^{2-}$ anion in $[MPpyr]_2[Ca\{N(SO_2CF_3)_2\}_4]$ [A. Babai *et al.* (2006) *Inorg. Chem.*, vol. 45, p. 1828], and (b) the $[Nd\{N(SO_2CF_3)_2\}_5]^{2-}$ ion in $[BMpyr]_2[Nd\{N(SO_2CF_3)_2\}_5]$ [A. Babai *et al.* (2006) *Dalton Trans.*, p. 1828.]. Colour code: Ca or Nd, silver; O, red; N, blue; S, yellow; C, grey; F, green.

halide as in eqs. 9.88 and 9.89. If PrI_3 is reacted with $[BMpyr][N(SO_2CF_3)_2]$, the product is $[BMpyr]_4[PrI_6][N(SO_2CF_3)_2]$ containing the octahedral $[PrI_6]^{3-}$ ion and a non-coordinated $[N(SO_2CF_3)_2]^-$ ion. Separation of products from ionic liquid solvents is facile if the product is insoluble (separation is by filtration or removal of the solvent by cannula). However, if the product is soluble, separation may be difficult since the low volatility of ionic liquids prevents their ready evaporation. If the product is volatile, it can be separated by distillation because the ionic liquid has such a low vapour pressure.

In materials chemistry, ionic liquids are used in a variety of ways, e.g. routes to nanoparticles (some of which have catalytic applications) and to metal-organic frameworks (MOFs). Zeolites represent an important class of crystalline materials (see Section 14.9) with many applications in catalysis and gas/liquid absorption. Their synthesis under hydrothermal conditions (i.e. high temperatures and pressure in aqueous media) from Al_2O_3, SiO_2 and Na_2O or similar precursors requires an organic template to direct the assembly of the 3-dimensional array with template ions (e.g. alkyl ammonium cations) occupying the pores in the open network structure. Using ionic liquids in place of hydrothermal conditions has several advantages: (i) the low vapour pressure of an ionic liquid means that the synthesis takes place at ambient pressures, (ii) the organic template is provided by the ionic liquid, resulting in there being no competition between solvent and template during crystallization, and (iii) new structure types may be assembled. This is an area that is actively being developed, although industrial manufacture of synthetic zeolites remains (as of 2010) reliant on hydrothermal methods.†

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† See: R.E. Morris (2009) Chem. *Commun.*, p. 2990; Z. Ma, J. Yu and S. Dai (2010) Adv. Mater., vol. 22, p. 261.

9.13 Supercritical fluids

Properties of supercritical fluids and their uses as solvents

> Above its critical temperature and critical pressure, an element or compound is in its ***supercritical fluid*** state.

Since the 1990s, the chemical literature has seen a huge increase in the publication of papers describing the properties and applications of *supercritical fluids*, in particular, supercritical carbon dioxide and water. One of the driving forces for this interest is the search for green solvents to replace volatile organics (see Box 9.2). The meaning of the term *supercritical* is explained in Fig. 9.11 which shows a pressure–temperature phase diagram for a one-component system. The solid blue lines represent the boundaries between the phases. The hashed line illustrates the distinction between a vapour and a gas:

> A ***vapour*** can be liquefied by increasing the pressure, but a ***gas*** cannot.

Above the critical temperature, T_{critical}, the gas can no longer be liquefied, no matter how high the pressure is increased. If a sample is observed as the critical point is reached, the meniscus at the liquid–gas interface disappears, signifying that there is no longer a distinction between the two phases. At temperatures and pressures above the critical temperature and pressure (i.e. above the critical point), a substance becomes a supercritical fluid.

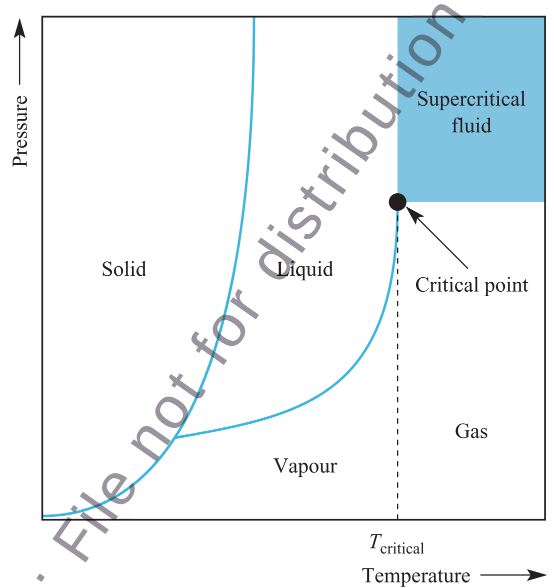


Fig. 9.11 A simple pressure–temperature phase diagram for a one-component system.

A supercritical fluid possesses solvent properties that resemble those of a liquid, but also exhibits gas-like transport properties. Thus, not only can a supercritical fluid dissolve solutes, but it is also miscible with ordinary gases and can penetrate pores in solids. Supercritical fluids exhibit lower viscosities and higher diffusion coefficients than liquids. The density of a supercritical fluid increases as the pressure increases, and as the density increases, the solubility of a solute in the supercritical fluid increases dramatically. The fact that the properties can be tuned by varying the pressure and temperature is advantageous in terms of the applications of these fluids as extraction agents. Using a supercritical fluid for the extraction of a given material from a feedstock involves the partitioning of the material into the supercritical liquid, followed by a change in temperature and pressure that results in isolation of the pure solute by vaporization of the solvent, e.g. CO_2. Finally, the supercritical fluid can be recycled by reversing the change in temperature and pressure conditions (see the figure in Box 9.3).

Table 9.11 lists the critical temperatures and pressures of selected elements compounds that are used as supercritical fluids. Combined with its easy accessibility, low cost, non-toxicity, chemical inertness and non-inflammability, the critical temperature and pressure of CO_2 are convenient enough to make supercritical CO_2 ($scCO_2$) of great value as a solvent, and Box 9.3 gives examples of its commercial applications.

Although $scCO_2$ is a 'clean' alternative to organic solvents for a range of extraction processes, it is non-polar.

Table 9.11 Critical temperatures and pressures of selected elements and compounds with applications as supercritical fluids.

Compound or element	Critical temperature / K	Critical pressure / MPa[†]
Xenon	289.8	5.12
Carbon dioxide	304.2	7.38
Ethane	305.4	4.88
Propane	369.8	4.25
Ammonia	405.6	11.28
Pentane	469.7	3.37
Ethanol	516.2	6.38
Toluene	591.8	4.11
1,2-Ethanediamine	593.0	6.27
Water	647.3	22.05

[†] To convert to bar, multiply by 10.

ENVIRONMENT

Box 9.2 Green chemistry

With the constant drive to protect our environment, 'green chemistry' is now at the forefront of research and is starting to be applied in industry. In its *Green Chemistry Program*, the US Environmental Protection Agency (EPA) defines green chemistry as 'chemistry for pollution prevention, and the design of chemical products and chemical processes that reduce or eliminate the use of hazardous substances.' The European Chemical Industry Council (CEFIC) works through its programme *Sustech* to develop sustainable technologies. Some of the goals of green chemistry are the use of renewable feedstocks, the use of less hazardous chemicals in industry, the use of new solvents to replace, for example, chlorinated and volatile organic solvents, the reduction in the energy consumption of commercial processes, and the minimizing of waste chemicals in industrial processes.

Anastas and Warner (see Further reading) have developed 12 principles of green chemistry. These clearly illustrate the challenges ahead for research and industrial chemists:

- It is better to prevent waste than to treat or clean up waste after it is formed.
- Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- Chemical products should be designed to preserve efficacy of function while reducing toxicity.
- The use of auxiliary substances (e.g. solvents, separation agents) should be made unnecessary whenever possible and innocuous when used.
- Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
- A raw material feedstock should be renewable rather than depleting whenever technically and economically practical.
- Unnecessary derivatization (e.g. protection/deprotection steps) should be avoided whenever possible.
- Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- Chemical products should be designed so that at the end of their function they do not persist in the environment, but break down into innocuous degradation products.
- Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.
- Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions and fires.

At the beginning of the 21st century, green chemistry represents a move towards a sustainable future. The journal *Green Chemistry* (published by the Royal Society of Chemistry since 1999) is a forum for key developments in the area. The American Chemical Society Green Chemistry Institute (ACS Green Chemistry Institute®) has been established with its goal being 'to enable and catalyse the implementation of green chemistry and green engineering into all aspects of the global chemical enterprise'. In the US, the Presidential Green Chemistry Challenge Awards were initiated in 1995 to encourage the development of green technologies, at both academic and commercial levels (see Box 15.1).

A bee-eater in the Camargue, France: our wildlife depends on a clean environment.

Further reading

P.T. Anastas and J.C. Warner (1998) *Green Chemistry Theory and Practice*, Oxford University Press, Oxford.

J.H. Clark and S.J. Tavener (2007) *Org. Process Res. Develop.*, vol. 11, p. 149 - 'Alternative solvents: shades of green'.

I. T. Horváth and P. T. Anastas (eds.) (2007) *Chem. Rev.*, vol. 107, issue 6 presents a series of articles on the theme of green chemistry.

R.A. Sheldon (2005) *Green Chem.*, vol. 7, p. 267 – A review: 'Green solvents for sustainable organic synthesis: state of the art'.

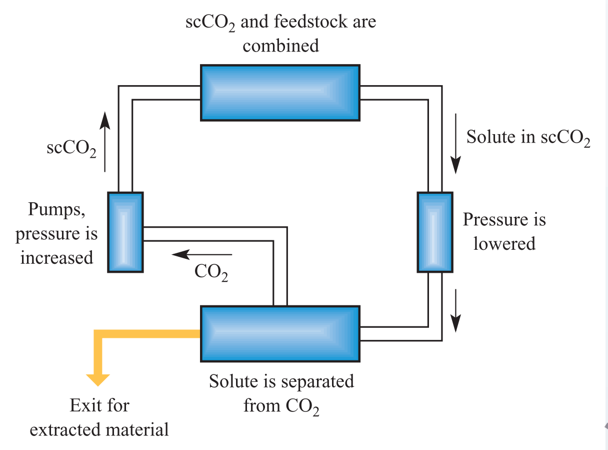
http://www.epa.gov/gcc

http://www.greenchemistrynetwork.org/

APPLICATIONS

Box 9.3 Clean technology with supercritical CO_2

Some of the areas in which supercritical CO_2 ($scCO_2$) is commercially important are summarized in Fig. 9.12. Extraction processes in the food, tobacco (nicotine extraction) and pharmaceutical industries dominate. Supercritical CO_2 is a selective extracting agent for caffeine, and its use in the decaffeination of coffee and tea was the first commercial application of a supercritical fluid, followed by the extraction of hops in the brewing industry. Solvent extractions can be carried out by batch processes, or by a continuous process in which the CO_2 is recycled as shown schematically below:



Examples of industrial autoclaves containing $scCO_2$ are illustrated in the photograph opposite. Such autoclaves are used to decafeinate tea and coffee and to manufacture spice extracts.

Cholesterol (high levels of which in the blood are associated with heart complaints) is soluble in $scCO_2$, and this medium has been used to extract cholesterol from egg yolk, meat and milk. There is potential for wider application of $scCO_2$ in the production of foodstuffs with reduced cholesterol levels.

The extraction of pesticides from rice is carried out commercially using $scCO_2$. Many studies have been carried out to investigate the ability of $scCO_2$ to extract flavours and fragrances from plants, e.g. from ginger root, camomile leaf, vanilla pod, mint leaf, lavender flower and lemon peel. Commercial applications within the food industry include cleaning of rice grains, the extraction of flavours and spices, and the extraction of colouring agents, e.g. from red peppers. Supercritical CO_2 can be used to extract compounds from natural products. One example is the anti-cancer drug taxol which may be extracted from the bark of the Pacific yew tree (although the drug can also be synthesized in a multi-step process).

The technique of supercritical fluid chromatography (SFC) is similar to HPLC (see Section 4.2) but has major advantages over the latter: separation is more rapid and the use of organic solvents is minimized. The pharmaceutical industry applies SFC to the separation of chiral and natural products.

The development of new technologies for the manufacture of high-purity polymers using $scCO_2$ in place of organic solvents is an active area of research, and the reduction of large amounts of toxic waste during polymer production is a prime target for the polymer industry. In 2002, DuPont introduced the first commercial Teflon resins manufactured using $scCO_2$ technology.

Commercial applications of $scCO_2$ in dry cleaning clothes, cleaning of optical and electronics components and of heavy-duty valves, tanks and pipes are growing steadily. Tetrachloroethene is still used as the solvent in textile dry cleaning, but alternative methodologies based on $scCO_2$ overcome the negative impact that volatile and chlorinated organics have on the environment. In 2006, the Fred Butler® cleaning company was launched in Europe and has won awards for its innovative $scCO_2$-based textile cleaning process. Hangers® cleaners are responsible for the growing use of $scCO_2$ in dry cleaning facilities in the US.

Supercritical CO_2 has found applications within materials processing. The *rapid expansion of supercritical solutions* (RESS) involves saturating the supercritical fluid with a given solute followed by rapid expansion (by reduction in pressure) through a nozzle. The result is the nucleation of the solute (e.g. a polymer such as PVC) and the production of a powder, thin film or fibre as required. Union Carbide has developed a process (UNICARB®) in which $scCO_2$ is used in place of organic solvents for spraying paint onto a range of substrates including vehicles.

The textile industry uses huge amounts of water (>100 dm^3 per kg of fibre), and dyeing of fibres is one of the processes during fabric production that depends on water. Under 25 MPa pressure and at 390 K, $scCO_2$ penetrates textile fibres and can be used as a medium for dyeing. This technology entered the textile industry in 2010: DyeCoo™ Textile Systems (Netherlands) manufacture $scCO_2$-based industrial dyeing equipment and the Yeh Group (Thailand) has began production of DryDye™ fabrics using the $scCO_2$ technology. Recycling of $scCO_2$ replaces the output of waste water from traditional dyeing processes.

In the examples given above, supercritical CO_2 is used in what is termed 'clean technology' with drastic reductions in the use of organic solvents, and the 21st century should see an increase in the use of supercritical fluids in commercial processes.

Industrial autoclaves using $scCO_2$ in a food processing plant.

While the behaviour of $scCO_2$ does not parallel a typical non-polar organic solvent, its ability to extract polar compounds is still relatively poor. The dissolution of polar compounds can be aided by introducing a subcritical co-solvent (a modifier) to $scCO_2$, and two common choices are H_2O and MeOH. The use of surfactants that possess a water-soluble head and CO_2-compatible tail permits water 'pockets' to be dispersed within $scCO_2$. As a result, aqueous chemistry can be carried out in what is essentially a non-aqueous environment. An advantage of this system is that reagents not normally soluble in water, but soluble in $scCO_2$, can be brought into intimate contact with water-soluble reagents.

Two other well-studied solvents are supercritical NH_3 and H_2O. The critical temperature and pressure of supercritical NH_3 are accessible (Table 9.11), but the solvent is chemically very reactive and is relatively hazardous for large-scale applications. Supercritical H_2O has a relatively high critical temperature and pressure (Table 9.11) which limit its uses. Even so, it has important applications as a solvent. At its critical point, the density of water is $0.32\,\mathrm{g\,cm^{-3}}$. The density of the supercritical phase can be controlled by varying the temperature and pressure. Unlike subcritical H_2O, supercritical H_2O behaves like a *non-polar* solvent. Thus, it is a poor solvent for inorganic salts, but dissolves non-polar organic compounds. This is the basis for its use in *supercritical water oxidation* (or *hydrothermal oxidation*) of toxic and hazardous organic wastes. In the presence of a suitable oxidizing agent, liquid organic waste in scH_2O is converted to CO_2, H_2O, N_2 and other gaseous products with efficiencies approaching 100%. The operating temperatures are low enough to prevent the formation of environmentally undesirable products such as oxides of nitrogen and sulfur. In the waste-water industry, sludge disposal can be effected using supercritical water oxidation, and, in 2001, the first commercial plant designed for this purpose commenced operation in Texas, USA.

Initial commercial applications of supercritical fluids were coffee decaffeination (in 1978) and hops extraction (in 1982). Together, these uses accounted for over half of the world's supercritical fluid production processes in 2001 (Fig. 9.12).

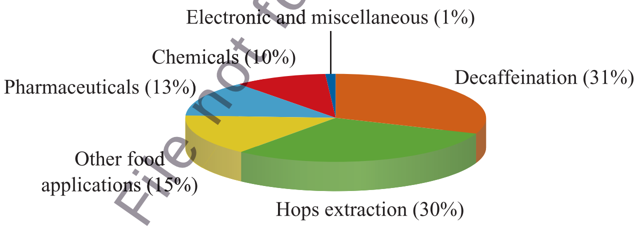


Fig. 9.12 Percentage contributions to the 2001 global US\$960 million value of commercial production using supercritical fluid processing [data: Kline & Company, Inc., www.klinegroup.com].

Supercritical fluids as media for inorganic chemistry

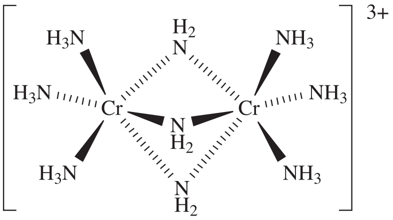
In this section, we describe selected examples of inorganic reactions that are carried out in $scCO_2$ supercritical water (scH_2O) and ammonia ($scNH_3$), critical temperatures and pressures of which are listed in Table 9.11. An important application of scH_2O is in the hydrothermal generation of metal oxides from metal salts (or supercritical hydrothermal crystallization). Equations 9.92 and 9.93 summarize the proposed steps for conversion of metal nitrates to oxides where, for example, M = Fe(III), Co(II) or Ni(II).

$$M(NO_3)_{2x} + 2xH_2O \xrightarrow{scH_2O} M(OH)_{2x}(s) + 2xHNO_3 \qquad \textit{Hydrolysis} \quad (9.92)$$

$$M(OH)_{2x}(s) \xrightarrow{scH_2O} MO_x(s) + xH_2O \qquad \textit{Dehydration} \quad (9.93)$$

By altering the precursor, different oxides of a given metal can be obtained. By adjusting the temperature and pressure of the scH_2O medium, it is possible to control particle size. Such control is important for the production of optical TiO_2 coatings (see Box 21.3).

In Section 9.6, we described metal ammine and amido complex formation in liquid NH_3. In $scNH_3$, $FeCl_2$ and $FeBr_2$ form the complexes $[Fe(NH_3)_6]X_2$ (X=Cl, Br) at 670 K, while reactions of Fe or Mn and I_2 in $scNH_3$ yield $[M(NH_3)_6]I_2$ (M=Fe or Mn). At 600 MPa and 670–870 K, the reaction of Mn with $scNH_3$ gives the manganese nitride, Mn_3N_2. Single crystals of this compound can be grown by adding I_2, K or Rb to the reaction mixture, resulting in the formation of $[Mn(NH_3)_6]I_2$, $K_2[Mn(NH_2)_4]$ or $Rb_2[Mn(NH_2)_4]$ prior to Mn_3N_2. Similarly, γ-Fe_4N is obtained from $[Fe(NH_3)_6]I_2$ in $scNH_3$ at 600–800 MPa and 730–850 K. The reaction of CrI_2 in $scNH_3$ at 773 K and 600 MPa yields $[Cr_2(NH_3)_6(\mu\text{-}NH_2)_3]I_3$ which contains cation **9.28**.



(9.28)

Supercritical amines have been found to be useful solvents for the assembly of complex metal sulfides, including $K_2Ag_6S_4$ (reaction 9.94), $KAgSbS_4$, Rb_2AgSbS_4, KAg_2SbS_4, KAg_2AsS_4 and $RbAg_2SbS_4$. Use of $scNH_3$ allows these solid state compounds to be prepared at lower temperatures than more traditional routes used to synthesize related compounds such as $SrCu_2SnS_4$.

$$K_2S_4 + 6Ag \xrightarrow{scNH_3} K_2Ag_6S_4 \qquad (9.94)$$

If the K^+ or Rb^+ ions in this type of compound are replaced by Fe^{2+} (eq. 9.90), Mn^{2+}, Ni^{2+}, La^{3+} (eq. 9.91) or Yb^{3+} (reaction 9.92), the products contain $[M(NH_3)_n]^{2+}$ or $[M(NH_3)_n]^{3+}$ ions. For La^{3+} and Yb^{3+}, these represent the first examples of homoleptic lanthanoid ammine complexes.

A *homoleptic complex* is of the type $[ML_x]^{n+}$ where all the ligands are identical. In a *heteroleptic complex*, the ligands attached to the metal ion are not all identical.

$$16Fe + 128Cu + 24Sb_2S_3 + 17S_8 \xrightarrow{scNH_3} 16[Fe(NH_3)_6][Cu_8Sb_3S_{13}] \qquad (9.95)$$

$$La + Cu + S_8 \xrightarrow{scNH_3} [La(NH_3)_8][Cu(S_4)_2] \qquad (9.96)$$

$$Yb + Ag + S_8 \xrightarrow{scNH_3} [Yb(NH_3)_9][Ag(S_4)_2] \qquad (9.97)$$

Extractions of organic compounds dominate the applications of $scCO_2$ (see Box 9.3). The extraction of metal ions (especially toxic heavy metal ions) from contaminated sources currently uses chelating ligands and conventional solvents. In order that $scCO_2$ may be used as the extracting medium, ligands must be designed that are both efficient at binding metal ions and are highly soluble in $scCO_2$. For example, 2,2'-bipyridine (bpy, see Table 7.7) forms many metal complexes with high stability constants, but is not readily soluble in $scCO_2$. Extraction of metal ions using bpy is achieved if the ligand is functionalized with long, fluoroalkyl chains. In general, the presence of perfluorinated alkyl 'tails' on the periphery of a ligand significantly increases the solubility of the ligand and its metal complexes in $scCO_2$.

KEY TERMS

The following terms were introduced in this chapter. Do you know what they mean?

- ☐ non-aqueous solvent
- ☐ relative permittivity
- ☐ coordinating solvent
- ☐ protic solvent
- ☐ aprotic solvent
- ☐ solvent-oriented acid and base
- ☐ levelling effect
- ☐ differentiating effect
- ☐ conductiometric titration
- ☐ superacid
- ☐ molten salt
- ☐ ionic liquid
- ☐ eutectic
- ☐ pyrophoric
- ☐ supercritical fluid

FURTHER READING

General: non-aqueous solvents

J.R. Chipperfield (1999) *Non-aqueous Solvents*, Oxford University Press, Oxford – A book in the OUP 'Primer' series which gives a good introduction to the topic.

R.J. Gillespie and J. Passmore (1971) *Accounts of Chemical Research*, vol. 4, p. 413 – An article that highlights the uses of non-aqueous solvents (HF, SO_2 and HSO_3F) in the preparation of polycations.

K.M. Mackay, R.A. Mackay and W. Henderson (2002) *Modern Inorganic Chemistry*, 6th edn, Blackie, London – Chapter 6 includes a general introduction to non-aqueous solvents.

G. Mamantov and A.I. Popov, eds (1994) *Chemistry of Nonaqueous Solutions: Recent Advances*, VCH, New York – A collection of reviews covering up-to-date topics in the field of non-aqueous solvents.

T.A. O'Donnell (2001) *Eur. J. Inorg. Chem*, p. 21 – A review illustrating the generality of inorganic solute speciation in different ionizing solvents.

Superacids

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G.A. Olah, G.K.S. Prakash, J. Sommer and A. Molnar (2009) *Superacid Chemistry*, 2nd edn, Wiley-VCH, Weinheim.

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E.W. Castner, Jr. and J.F. Wishart (2010) *J. Chem. Phys.*, vol. 132, p. 120901.

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P. Wasserscheid and T. Welton (eds) (2008) *Ionic Liquids in Synthesis*, 2nd edn, Wiley-VCH, Weinheim (2 volumes).

Supercritical fluids

J.A. Darr and M. Poliakoff (1999) *Chem. Rev.*, vol. 99, p. 495; other articles in this same issue of *Chem. Rev.* deal with various aspects of supercritical fluids.

P. Licence and M. Poliakoff (2008) *NATO Science Series II*, Springer, Düsseldorf, vol. 246, p. 171.

P. Raveendran, Y. Ikushima and S.L. Wallen (2005) *Acc. Chem. Res.*, vol. 38, p. 478.

H. Weingärtner and E.U. Franck (2005) *Angew. Chem. Int. ed.*, vol. 44, p. 2672.

PROBLEMS

9.1 (a) Give four examples of non-aqueous solvents commonly used in *organic* chemistry, and give one example of a reaction that is carried out in each solvent. (b) Assess the relative importance of the use of aqueous and non-aqueous media in organic and inorganic *general* synthesis.

9.2 Explain what is meant by the relative permittivity of a solvent. What information does this property provide in terms of assisting you to choose a solvent for a given reaction?

9.3 Which of the following solvents are polar: (a) acetonitrile; (b) water; (c) acetic acid; (d) fluorosulfonic acid; (e) dichloromethane; (f) bromine trifluoride; (g) hexane; (h) THF; (i) DMF; (j) liquid sulfur dioxide; (k) benzene?

9.4 Suggest likely products for the following reactions (which are balanced on the left-hand sides) in liquid NH_3.

(a) $ZnI_2 + 2KNH_2 \longrightarrow$

(b) Zinc-containing product of (a) with an excess of KNH_2

(c) $Mg_2Ge + 4NH_4Br \longrightarrow$

(d) $MeCO_2H + NH_3 \longrightarrow$

(e) $O_2 \xrightarrow{\text{Na in liquid NH}_3}$

(f) $HC{\equiv}CH + KNH_2 \longrightarrow$

How does reaction (d) differ from the behaviour of $MeCO_2H$ in aqueous solution?

9.5 Discuss the following observations:

(a) Zinc dissolves in a solution of sodium amide in liquid NH_3 with liberation of H_2; careful addition of ammonium iodide to the resulting solution produces a white precipitate which dissolves if an excess of ammonium iodide is added.

(b) Addition of K to H_2O results in a vigorous reaction; addition of K to liquid NH_3 gives a bright blue solution, which over a period of time liberates H_2.

9.6 Early in the study of chemical reactions in liquid NH_3, it was noted that nitrogen compounds behave in liquid NH_3 in a manner similar to analogous oxygen-containing species in water. For example, $K[NH_2]$ has an analogue in $K[OH]$, and $[NH_4]Cl$ is analogous to $[H_3O]Cl$. What would be the corresponding compounds in the nitrogen system to the following from the oxygen system: (a) H_2O_2; (b) HgO; (c) HNO_3; (d) MeOH; (e) H_2CO_3; (f) $[Cr(OH_2)_6]Cl_3$?

9.7 Give an explanation for the following observations: AlF_3 has only a low solubility in liquid HF, but a combination of NaF and AlF_3 leads to dissolution of the reagents; when BF_3 is added to the solution, a precipitate forms.

9.8 Write equations to show what happens when each of the following dissolves in liquid HF: (a) ClF_3; (b) MeOH; (c) Et_2O; (d) CsF; (e) SrF_2; (f) $HClO_4$.

9.9 $H_2S_2O_7$ functions as a monobasic acid in H_2SO_4. (a) Write an equation to show what happens when $H_2S_2O_7$ dissolves in H_2SO_4. (b) Assess the strength of $H_2S_2O_7$ as an acid given that the ionization constant is 1.4×10^{-2}.

9.10 Give equations to show how the following compounds behave in H_2SO_4: (a) H_2O; (b) NH_3; (c) HCO_2H given that it decomposes; (d) H_3PO_4 given that only one H^+ is transferred between one molecule of H_3PO_4 and one molecule of H_2SO_4; (e) HCl given that HCl acts as an acid and one molecule of HCl reacts with two molecules of H_2SO_4.

9.11 Compare the behaviour of nitric acid in aqueous and sulfuric acid solutions, giving examples from both inorganic and organic chemistries of the uses of HNO_3 in these two media.

9.12 Discuss the following observations:

(a) The alkene $Ph_2C{=}CH_2$ forms a conducting solution in liquid HCl; when such a solution is titrated conductometrically with a solution of BCl_3

in liquid HCl, a sharp end-point is reached when the molar ratio of $Ph_2C{=}CH_2{:}BCl_3$ is 1 : 1.

(b) The following reaction can be described as a neutralization. Explain why this is, identify compound **A**, and determine *x*.

$$[BrF_2]_2[SnF_6] + 2K[BrF_4] \longrightarrow \mathbf{A} + x BrF_3$$

9.13 Confirm that the structures of $[BrF_2]^+$ and $[BrF_4]^-$ (**9.18** and **9.19**) are consistent with the VSEPR model.

9.14 How would you attempt to demonstrate that $AsCl_3$ ionizes slightly according to the equation:

$$2AsCl_3 \rightleftharpoons [AsCl_2]^+ + [AsCl_4]^-$$

and that there exist acids and bases in the $AsCl_3$ system?

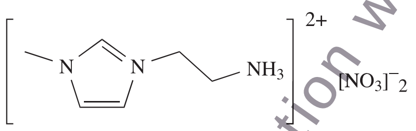
9.15 (a) Describe the bonding in the $[Al_2Cl_7]^-$ anion (**9.21**).

(b) Equilibria 9.81 and 9.82 describe part of the NaCl–Al_2Cl_6 system; additionally $[Al_3Cl_{10}]^-$ is present. Write an equation to show how $[Al_3Cl_{10}]^-$ may be formed, and suggest a structure for this anion.

9.16 Suggest structures for the $[BiCl_5]^{2-}$ and $[Bi_2Cl_8]^{2-}$ anions, the formation of which was described in Section 9.12.

9.17 (a) Give three examples of commonly used ionic liquids. What general properties make ionic liquids attractive in 'green chemistry'? Are the properties of the liquid itself all that determines whether the ionic liquid is environmentally friendly?

(b) The compound shown below was treated with one equivalent of NaOH in methanol to give the ionic liquid **X**:



The positive mode electrospray mass spectrum of **X** exhibits a peak at *m*/*z* 126. Compound **X** reacts with chloroauric acid, $HAuCl_4$, to give a salt, **Y**, which contains two square planar Au(III) environments. The anion in **Y** has D_{4h} symmetry. The ^{1}H NMR spectrum of a DMSO-d_6 solution of **Y** exhibits the following signals: δ/ppm 9.07 (s, 1H), 7.92 (br, 2H), 7.74 (overlapping signals, 2H), 4.38 (t, 2H), 3.86 (s, 3H), 3.34 (m, 2H). The electrospray mass spectrum of **Y** shows peak envelopes at *m*/*z* 428 and 126 (positive mode), and 339 (negative mode). The peak envelope at *m*/*z* 339 consists of four peaks, and that at *m*/*z* 428 exhibits three dominant peaks at *m*/*z* 428, 429 and 432. Identify **X** and **Y**, and interpret the data. Rationalize the appearance of the mass spectra.

[Data: B. Ballarin *et al.* (2010) *Inorg. Chim. Acta*, vol. 363, p. 2055]

9.18 (a) An ionic liquid can be formed by adding $ZnCl_2$ to (2-chloroethyl)trimethylammonium chloride, XCl. When the ratio of $ZnCl_2$: XCl = 2 : 1, fast atom bombardment mass spectrometry shows the presence of $[Zn_xCl_y]^{z-}$ ions with *m*/*z* = 171, 307 and 443. Suggest identities for these ions and write a series of equilibria to account for their formation.

[Data: A. P. Abbott *et al.* (2004) *Inorg. Chem.*, vol. 43, p. 3447]

9.19 (a) With the aid of a phase diagram, explain what is meant by a supercritical fluid. Give examples of commercial processes that involve the use of supercritical fluids.

(b) Even though CO_2 is classified as a 'greenhouse gas' (see Box 14.7), why is the use of supercritical CO_2 regarded as being environmentally friendly?

OVERVIEW PROBLEMS

9.20 (a) Which of the following compounds behave as acids in liquid HF: ClF_3, BF_3, SbF_5, SiF_4? Write equations to explain this behaviour.

(b) The salt $[S_8][AsF_6]_2$ can be isolated from the following reaction:

$$S_8 + 3AsF_5 \xrightarrow{\text{liquid HF}} [S_8][AsF_6]_2 + AsF_3$$

What roles does AsF_5 play in this reaction?

(c) By first considering its reaction in H_2O, suggest how Na might react in liquid N_2O_4.

9.21 When gallium is dissolved in a solution of KOH in liquid NH_3, a salt K[**I**] is formed which is an amido complex of Ga(III). Heating one equivalent of K[**I**] at 570 K under vacuum liberates two equivalents of NH_3, and produces a Ga(III) imido complex K[**II**]. Partial neutralization of K[**I**] with NH_4Cl yields $Ga(NH_2)_3$. Suggest identities for the salts K[**I**] and K[**II**], and write equations for the thermal decomposition and partial neutralization reactions of K[**I**]. ***Hint:*** an *imido* complex formally contains NH^{2-}.

9.22 (a) $SbCl_3$ may be used as a non-aqueous solvent above its melting point. Suggest a possible self-ionization process for this solvent.

(b) Explain why the reaction of NOCl with $AgNO_3$ in liquid N_2O_4 can be classed as a neutralization process. Write an equation for the reaction and compare it with that of HCl with $Ca(OH)_2$ in aqueous solution.

(c) In water, Cr^{3+} precipitates as $Cr(OH)_3$ at pH 7, forms $[Cr(OH_2)_6]^{3+}$ in strongly acidic solution (e.g. $HClO_4$), and $[Cr(OH)_4]^-$ in basic solution. Suggest what Cr(III) species are present in liquid NH_3 as the pH is varied.

9.23 Suggest explanations for the following observations.

(a) In aqueous solution, $AgNO_3$ and KCl react to give a precipitate of AgCl, whereas in liquid NH_3, KNO_3 and AgCl react to produce a precipitate of KCl.

(b) Mg dissolves in a concentrated solution of NH_4I in liquid NH_3.

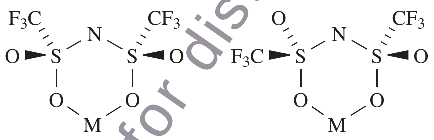
(c) Most common 'acids' behave as bases in liquid H_2SO_4.

(d) $HClO_4$ is fully ionized in water and is strongly dissociated in pure (glacial) acetic acid; in liquid HSO_3F, the following reaction occurs:

$$KClO_4 + HSO_3F \longrightarrow KSO_3F + HClO_4$$

INORGANIC CHEMISTRY MATTERS

9.24 Ionic liquids may have future applications in lithium-ion batteries. A combination of $Li[N(SO_2CF_3)_2]$ and $[EMIm][N(SO_2CF_3)_2]$ (EMim = 1-ethyl-3-methylimidazolium ion) has been used as a model for a room temperature ionic liquid electrolyte. From this mixture, crystals of $Li_2[EMIm][N(SO_2CF_3)_2]_3$ have been isolated. The structure (X-ray diffraction) shows each Li^+ ion to be in a 5-coordinate environment, bound by $[N(SO_2CF_3)_2]^-$ ions. The latter adopt either bi- or monodentate modes and coordinate through *O*-donors. (a) When adopting a bidentate mode, why is it more favourable for a $[N(SO_2CF_3)_2]^-$ ligand (Fig. 9.8d) to coordinate through two O atoms attached to different S atoms rather than through the two O atoms of one CF_3SO_2 group? (b) What coordination geometries are usually associated with a coordination number of five? Comment on the energy difference(s) between them. (c) The diagrams below show the two possible arrangements of CF_3 groups when $[N(SO_2CF_3)_2]^-$ acts as an *O*,*O*′-donor to metal ion M^{n+}. Explain how these arise.



[Data: K. Matsumoto *et al.* (2006) *Solid State Sci.*, vol. 8, p. 1103]

9.25 In the pharmaceutical industry, the active ingredients in drugs are usually manufactured as crystalline solids, and a recurring problem is that of polymorphism. It has been suggested that producing the active pharma ingredients as room temperature ionic liquids could be advantageous. (a) What is polymorphism? (b) Why is polymorphism problematical to the pharmaceutical industry? (c) Distinguish between an 'ionic liquid' and a 'room temperature ionic liquid'. Discuss some of the advantages that room temperature ionic liquids might have over crystalline solids in active pharma ingredients. (d) Hydrochloride salts, RNH_3Cl, or quaternary ammonium salts, R_4NCl, are common among active pharma ingredients. How would these be converted into ionic liquids? Comment on whether inorganic anions such as $[AlCl_4]^-$ or $[BF_4]^-$ would be suitable in these ionic liquids.