Chapter 9

Non-aqueous media

Relative permittivity

Acid-base behavior in non-aqueous solvents

Liquid NH_3, HF, H_2SO_4, BrF_3, N_2O_4

Ionic liquids

Supercritical fluids

Categories of non-aqueous solvents

Protic Solvents

(HF, H_2SO_4, $MeOH$)

Aprotic Solvents

(N_2O_4, BrF_3)

Coordinating Solvents

($MeCN$, Et_2O, Me_2CO)

In Vacuum $\text{Coulombic potential energy} = \dfrac{e^2}{4\pi\varepsilon_0 r}$ (9.1)

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

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.

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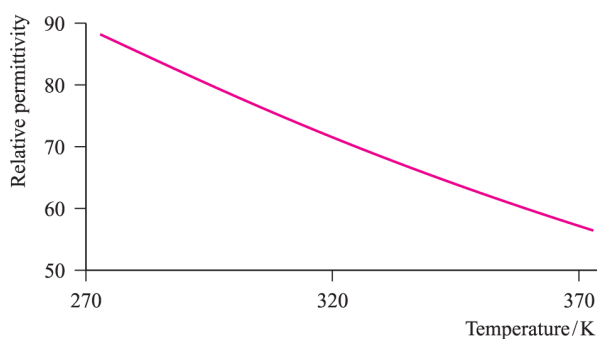

Variation in the relative permittivity (dielectric constant) of water as a function of temperature.

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

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.

Strengths of acids and bases

$$HX\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (l) + X^-\ (aq)$$
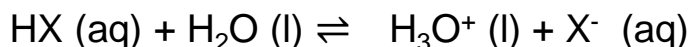
Strength of acid HX depends on relative proton donor abilities of HX and H_3O^+

Tabulated values of K_a (or K_b) generally refer to the ionizations of acids in aqueous solution, thus when we consider HCl a strong acid in aqueous medium.

•Note, because of the **common ion effect**, if HCl is dissolved in acetic acid, the extent of ionization is less than in water and HCl acts as a weak acid.
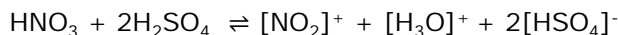
•Non-aqueous solvents that are good proton acceptors (e.g. NH_3) enable acids to ionize.

•In a basic solvent, all acids are strong. The solvent is noted to exhibit a **levelling effect** on the acid, since the strength of the dissolved acid cannot exceed that of the protonated solvent.
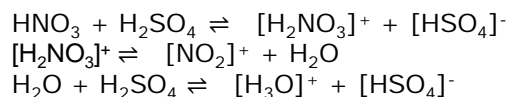
•In aqueous solution, no acidic species can exist that is a stronger acid than H_3O^+.

'Acids' in acidic solvents

Effect of dissolving an 'acid' in acidic non-aqueous solvents enables us to realize that just because a compound is named an 'acid', it may not behave as one in non-aqueous media.

$$HNO_3 + 2H_2SO_4 \rightleftharpoons [NO_2]^+ + [H_3O]^+ + 2[HSO_4]^-$$

The above reaction may be described as the sum of:

$$HNO_3 + H_2SO_4 \rightleftharpoons [H_2NO_3]^+ + [HSO_4]^-$$
$$[H_2NO_3]^+ \rightleftharpoons [NO_2]^+ + H_2O$$
$$H_2O + H_2SO_4 \rightleftharpoons [H_3O]^+ + [HSO_4]^-$$

Formation of $[NO_2]^+$ is important in the nitration of aromatic compounds
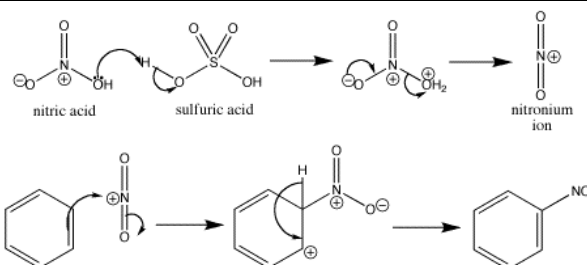
Acids and bases: a solvent oriented definition

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.

$$2H_2O \rightleftharpoons [H_3O]^+ + [OH]^-$$
    hydronium hydroxide
    ion   **ion**
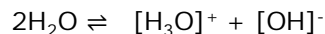
$$2NH_3 \rightleftharpoons [NH_4]^+ + [NH_2]^-$$
    ammonium amide
    ion   **ion**

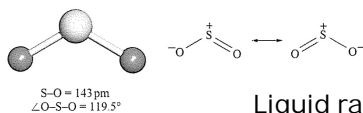Non-aqueous solvents that are self-ionizing may be classified as:
1) proton containing (NH_3, HF, H_2SO_4, $HOSO_2F$)
2) aprotic (BrF_3, N_2O_4)

Dinitrogen tetroxide, N_2O_4, undergoes self-ionization.

$$N_2O_4 \rightleftharpoons [NO]^+ + [NO_3]^-$$

In this solvent medium, nitrosyl salts behave as acids and metal nitrates (MNO_3) act as bases.

Non-ionizing non-aqueous solvents

S–O = 143 pm
∠O–S–O = 119.5°

Physical properties of 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)

Liquid ranges for water and selected non-aqueous solvents.

Bromide trifluoride
Dinitrogen tetraoxide
Fluorosulfonic acid
Hydrogen fluoride
Sulfuric acid
Sulfur dioxide
Ammonia
Water

200   300   400   500   600
Liquid range/K
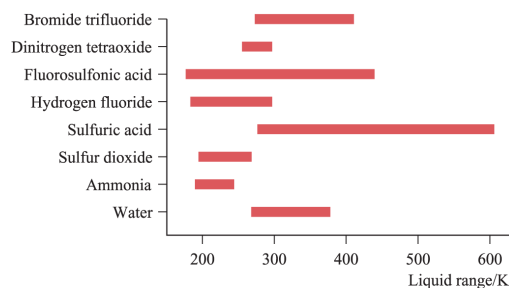
Liquid SO$_2$ is an inert solvent for both organic and inorganic compounds
•Good ionizing medium for compounds related to Ph$_3$CCl (giving [Ph$_3$C]$^+$)
•Useful in synthesis of group 16 and 17 cations species (e.g. I$_3^+$ and I$_5^+$)

$$3 \text{ AsF}_5 + 5\text{I}_2 \xrightarrow{\text{liquid SO}_2} 2[\text{I}_5][\text{AsF}_6] + \text{AsF}_3$$
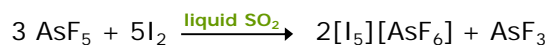
Liquid ammonia

Property / units	NH$_3$	H$_2$O
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}

•Relative permittivity of NH$_3$ (25) is lower than that of water (79), thus the ability of liquid ammonia to dissolve ionic compounds is less than that of H$_2$O.
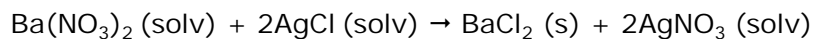
•   Exceptions include [NH$_4$]$^+$ salts, iodides, and nitrates which are readily soluble

AgI, K$_{sp}$ = 8.3 × 10^{-17}, is sparingly soluble in water, but dissolves easily in liquid NH$_3$ (solubility = 206.8 g per 100 g of NH$_3$)

•   The Ag$^+$ and I$^-$ interact strongly with the solvent, and Ag$^+$ forms an ammine complex.

In aqueous solution:

$BaCl_2$ (aq) + $2AgNO_3$ (aq) → $2AgCl$ (s) + $Ba(NO_3)_2$ (aq)

In NH_3:

$Ba(NO_3)_2$ (solv) + $2AgCl$ (solv) → $BaCl_2$ (s) + $2AgNO_3$ (solv)

Solubility of AgCl is 0.29 g/100 g liquid NH_3 compared with 1.91×10^{-4} g per 100 g H_2O

In NH_3:

KNO_3 (solv) + $AgCl$ (solv) → KCl (s) + $AgNO_3$ (solv)
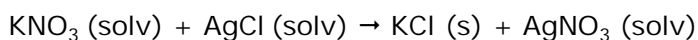
Neutralization reactions in liquid ammonia

Phenolphthalein

Acid + Base → Salt + Ammonia

NH_4Br + KNH_2 → KBr + $2NH_3$
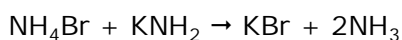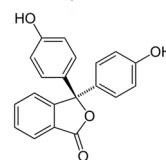
Influence of solvent on acids

H_2NSO_2OH (aq) + H_2O(l) ⇌ H_3O^+ (aq) + $[H_2NSO_2O]^-$ (aq)
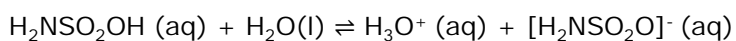
K_a = 1.01 x 10^{-1}; a monoprotic acid in aqueous solution

sulfamic acid

H_2NSO_2OH(aq) + $2KNH_2$(l) ⇌ $K_2[HNSO_2O]$ + $2NH_3$ (aq)
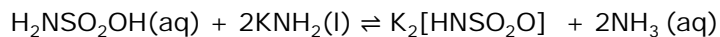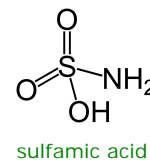
a diprotic acid in liquid NH_3

The levelling effect of NH_3 means the strongest acid possible in this medium is NH_4^+, thus solutions of ammonium halides may be used as acids:

Mg_2Si + $4NH_4Br$ → SiH_4 + $2MgBr_2$ + $4NH_3$

Na_3As + $3NH_4Br$ → AsH_3 + $3NaBr$ + $3NH_3$
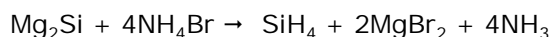
Solutions of s-block metals in liquid NH₃

All Group 1 metals and group 2 metals Ca, Sr, and Ba dissolve in liquid NH_3.

Dilute solutions of the metals are bright blue, color arising from a broad and intense absorption in the IR region.

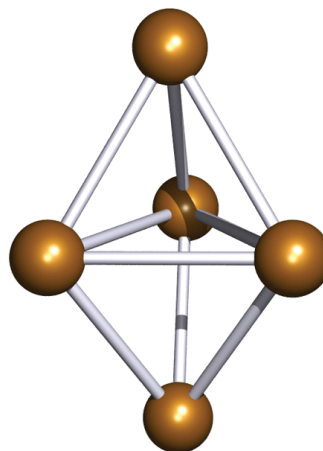$$M \xrightarrow{\text{dissolve in liquid } NH_3} M^+(solv) + e^-(solv)$$

Dilute solutions occupy a volume greater than the sum of the metal plus solvent, with electrons occupying cavities of radius 300-400 pm.
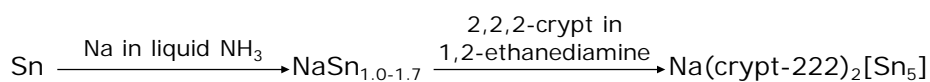
• Dilute solutions are paramagnetic and the magnetic response corresponds to that of one free electron per metal atom.

• Molar conductivity initially decreases with increasing concentration, reaching a minimum near 0.05 M. Conductivity increases at higher concentrations and in saturated solutions the concentration is comparable with the solid metal.

• Saturated solutions are not blue and paramagnetic, but instead are bronze and diamagnetic.

    • Termed expanded metals and sometimes called an electride

• Decompose slowly $2NH_3 + 2e^- \rightarrow 2[NH_2]^- + H_2$

• Used as a *reducing agent* in a variety of reactions

Zintl ions

Early synthetic routes for Zintl ions involved reductions of Ge, Sn, or Pb in solutions of Na in liquid NH_3.

Zintl ion $[Sn_5]^{2-}$

$$Sn \xrightarrow{\text{Na in liquid } NH_3} NaSn_{1.0-1.7} \xrightarrow[\text{1,2-ethanediamine}]{\text{2,2,2-crypt in}} Na(crypt\text{-}222)_2[Sn_5]$$

Redox Reactions in liquid NH_3

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

Selected standard reduction potentials (298 K) in aqueous and liquid ammonia media
- The oxidizing ability of each metal ion is solvent dependent.

Liquid HF

Corrodes glass containers, must be used in PTFE or dry Cu or Monel metal

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$

Liquid range: 190 to 292.5 K
Relative permittivity 84 at 273 K; 175 at 200 K

Liquid HF undergoes self-ionization: K_{self} =2 x10^{-12} at 273 K

$$3HF \rightleftharpoons [H_2F]^+ + [HF_2]^-$$

dihydridofluorine(1+) ion   difluorohydrogenate(1-) ion

Large electronegativity difference between H (x^P = 2.2) and F (x^P = 4.0) results in the presence of extensive intermolecular hydrogen bonding in the liquid.
- Hydrogen bonded molecules (~7 molecules on average) in liquid phase
- Cyclic $(HF)_x$ species are present in the gas phase

Acid – Base behavior liquid HF
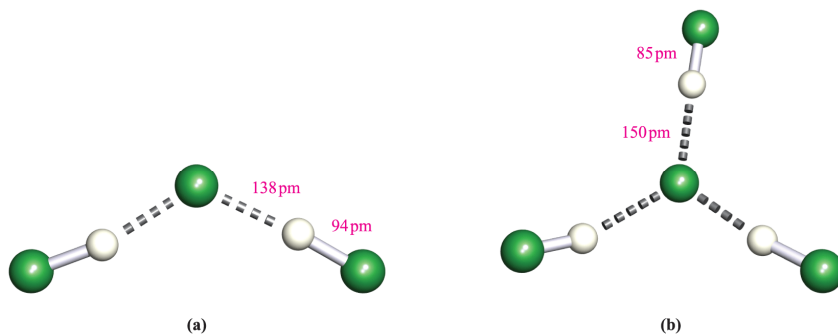
The structures of the anions (a) $[H_2F_3]^-$ and (b) $[H_3F_4]^-$, determined by low-temperature X-ray diffraction for the $[Me_4N]^+$ salts.

Sulfuric acid

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)

$2H_2SO_4 \rightleftharpoons [H_3SO_4]^+ + [HSO_4]^-$ $K_{self} = 2.7 \times 10^{-4}$

$2H_2SO_4 \rightleftharpoons [H_3O]^+ + [HS_2O_7]^-$ $K_{self} = 5.1 \times 10^{-5}$
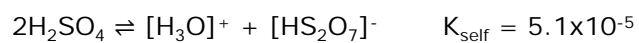
Fluorosulfonic acid, HSO_3F

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)

$$2HSO_3F \rightleftharpoons [H_2SO_3F]^+ + [SO_3F]^-$$
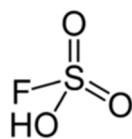
Superacids

Superacids, stronger acid than anhydrous H_2SO_4. Made by dissolving a strong Lewis acid (e.g. SbF_5) in either of the bronsted acids HF or HSO_3F capable of protonating even hydrocarbons, include mixtures of:
•HF and SbF_5
•HSO_3F and SbF_5 (called magic acid)

$$2HSO_3F + SbF_5 \rightleftharpoons [H_2SO_3F]^+ + [F_5SbOSO_2F]^-$$

$SbF_5OSO(OH)CF_3$

10

Carborane Superacids

(a)

[CHB$_{11}$R$_5$X$_6$]$^-$(R = H, Me, Cl and X = Cl, Br, I)

(b)

[B$_{12}$X$_{12}$]$^{2-}$(X = Cl, Br)

(c)

^{i}Pr$_3$Si(CHB$_{11}$H$_5$Cl$_6$)
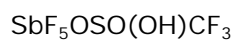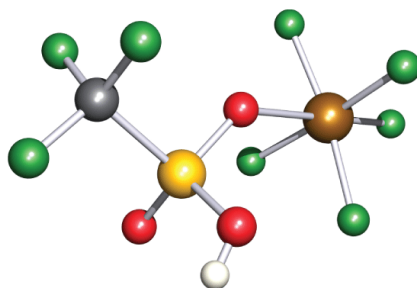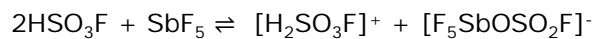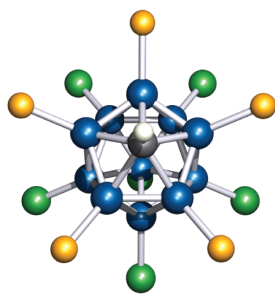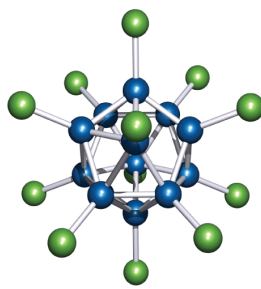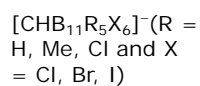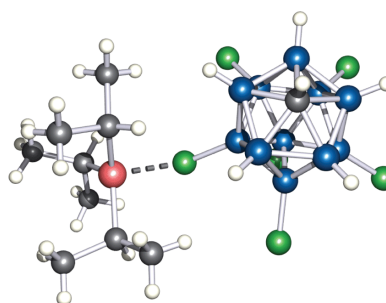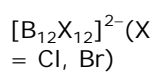
The long Si–Cl 'bond' which suggests that the structure approaches an ion-pair.

BrF$_3$

Good oxidizing and fluorinating agent

| 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)

Ag + Sb –liquid BrF$_3$ → Ag[SbF$_6$]

Ag + Au –liquid BrF$_3$ → Ag[AuF$_4$]

Dinitrogen tetroxide

Good oxidizing and nitrating agent

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)

$$Li + N_2O_4 \rightarrow LiNO_3 + NO$$

$[Zn(NO_3)_4]^{2-}$
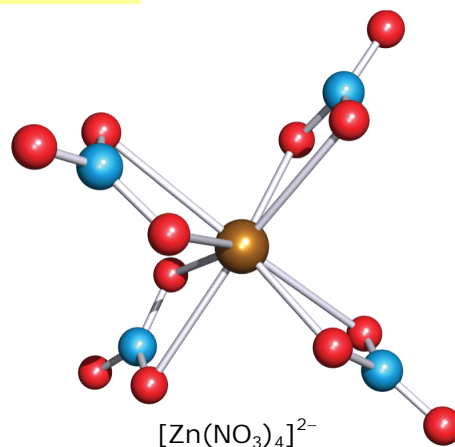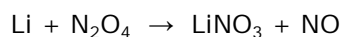
Molten salt solvent systems

Molten salts: NaCl(s) –heat, T = 1073 K→ NaCl(l)

$2HgBr_2 \rightleftharpoons [HgBr]^+ + [HgBr_3]^-$

Consider the **eutectic**, a mixture of two substances that is characterized by a sharp melting point lower than that of either of the components. A eutectic acts as a single substance.
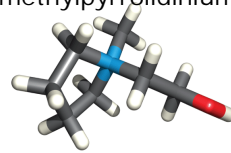

CaCl$_2$ - NaCl
Data from FTsalt - FACT salt databases
FactSage

NaCl-Al$_2$Cl$_6$ mixture

(a)   (b)

Al$_2$Cl$_6$ + 2Cl$^-$ ⇌ 2[AlCl$_4$]$^-$
2[AlCl$_4$]$^-$ ⇌ [Al$_2$Cl$_7$]$^-$ + Cl$^-$
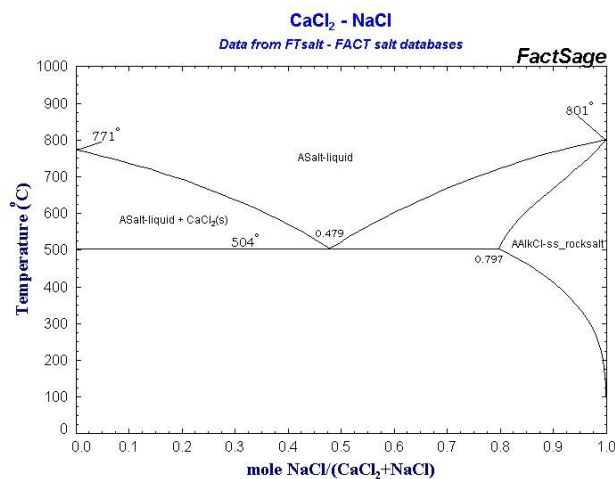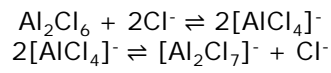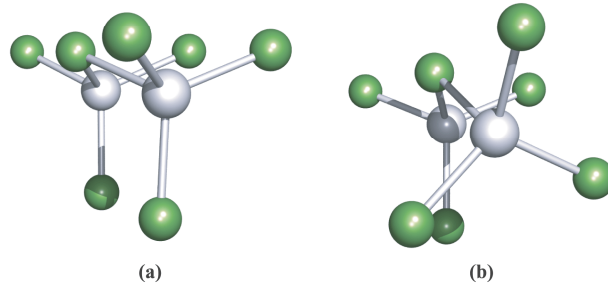
From NaCl-Al$_2$Cl$_6$
mixture (T$_{melt}$ = 446 K)
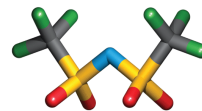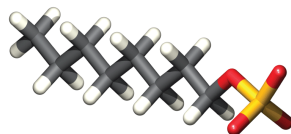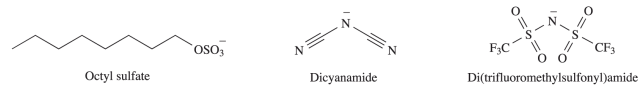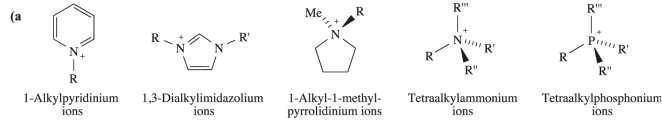
1-butyl-3-
methylimidazolium
cation
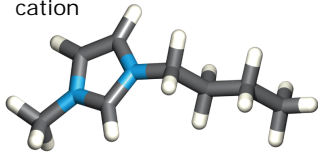
Commonly used ions in ionic liquids

1-(2-hydroxyethyl)-1-
methylpyrrolidinium cation

Ionic Liquids

an ionic salt
that is a liquid
below 373 K


(a

1-Alkylpyridinium
ions

1,3-Dialkylimidazolium
ions

1-Alkyl-1-methyl-
pyrrolidinium ions

Tetraalkylammonium
ions

Tetraalkylphosphonium
ions

Acetate, [AcO]$^-$ Hexafluoridophosphate, [PF$_6$]$^-$ Sulfate, [SO$_4$]$^{2-}$

Iodide, I$^-$ Tetrafluoridoborate, [BF$_4$]$^-$ Trifluoromethanesulfonate (triflate), [CF$_3$SO$_3$]$^-$

Octyl sulfate

Dicyanamide

Di(trifluoromethylsulfonyl)amide

(c)   (d)

13

Ionic liquid	$\Delta_{lattice}H^\circ$/kJmol^{-1}	Ionic liquid	$\Delta_{lattice}H^\circ$/kJmol^{-1}
[structure] [BF$_4$]$^-$	−492	[structure] [N(SO$_2$CF$_3$)$_2$]$^-$	−420
[structure] [CF$_3$SO$_3$]$^-$	−464	[structure] [N(SO$_2$CF$_3$)$_2$]$^-$	−412
[structure] [N(SO$_2$CF$_3$)$_2$]$^-$	−425	[structure] [N(SO$_2$CF$_3$)$_2$]$^-$	−420
[structure] [PF$_6$]$^-$	−457	[structure] [N(SO$_2$CF$_3$)$_2$]$^-$	−414
[structure] [CF$_3$SO$_3$]$^-$	−449	[structure] [N(SO$_2$CF$_3$)$_2$]$^-$	−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.

Calculated values of lattice enthalpies ($\Delta_{lattice}H^\circ$) for selected ionic liquids. Values refer to the process: gaseous ions → ionic solid

(a)
$[Bi_4Cl_{16}]^{4-}$

(b)
$[V_4O_4Cl_{12}]^{4-}$

(c)
$[Zr_6MnCl_{18}]^{5-}$

(a)
$[Ca\{N(SO_2CF_3)_2\}_4]^{2-}$

(b)
$[Nd\{N(SO_2CF_3)_2\}_5]^{2-}$
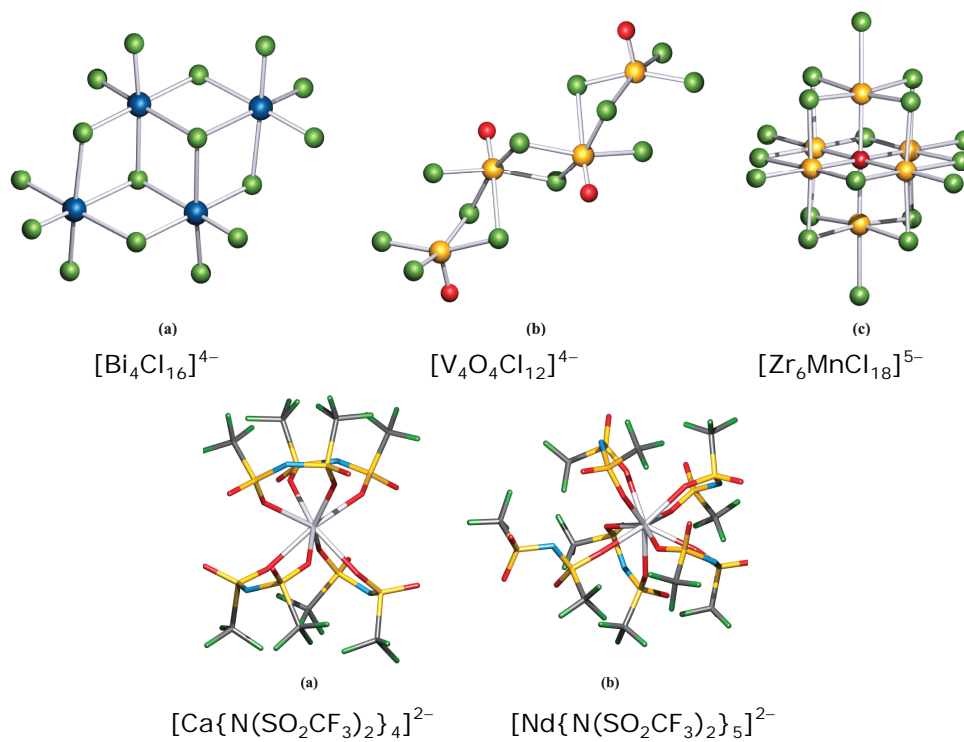
Supercritical fluids

Pressure–temperature phase diagram for a one-component system.
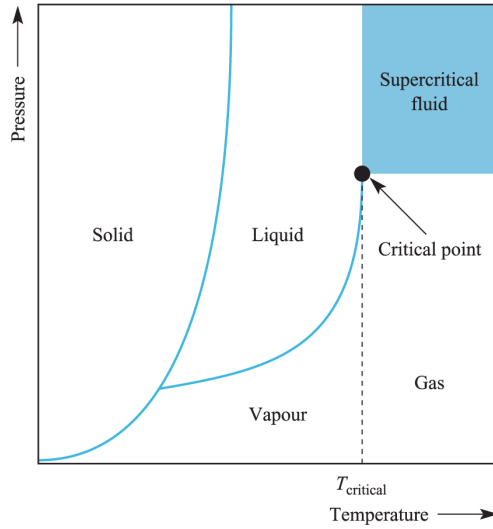
Critical temperatures and pressures

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.

Primary commercial applications of supercritical fluids:
coffee decaffeination, hops extraction

Electronic and miscellaneous (1%)
Chemicals (10%)
Pharmaceuticals (13%)
Other food applications (15%)
Decaffeination (31%)
Hops extraction (30%)