

ACIDS, BASES AND SOLUTION EQUILIBRIA

Dr. J. M. Goicoechea

HILARY TERM

Lecture 2

4. The Lewis definition of acids and bases

4.1 The coordinate bond

- a) Donors and acceptors
- b) Frontier orbitals
- c) Examples of Lewis acids

4.2. Strengths of Lewis acids and bases

- a) How strengths are measured
- b) Acid-base affinities: Observations.
 - 'Hard' and 'Soft' acids and bases
 - The Irving-Williams series
 - Stereochemical factors
 - Solvent effects
 - Hard/soft behaviour in terms of orbital energies

4.3. Other types of Lewis acids and bases

π -acceptor and π -donors

4.4. Quantifying Lewis acid and base strengths

Donor-acceptor numbers

4.5 Extension of acid-base concepts

- a) Superacids and their applications
- b) Generation of reactive carbocations
- c) Coordination chemistry
- d) Multidentate ligands

4. The Lewis definition of acids and bases

4.1 The coordinate bond

a) Donors and acceptors

Lewis acid: **A** Lone pair acceptor

Lewis base: **:B** Lone pair donor

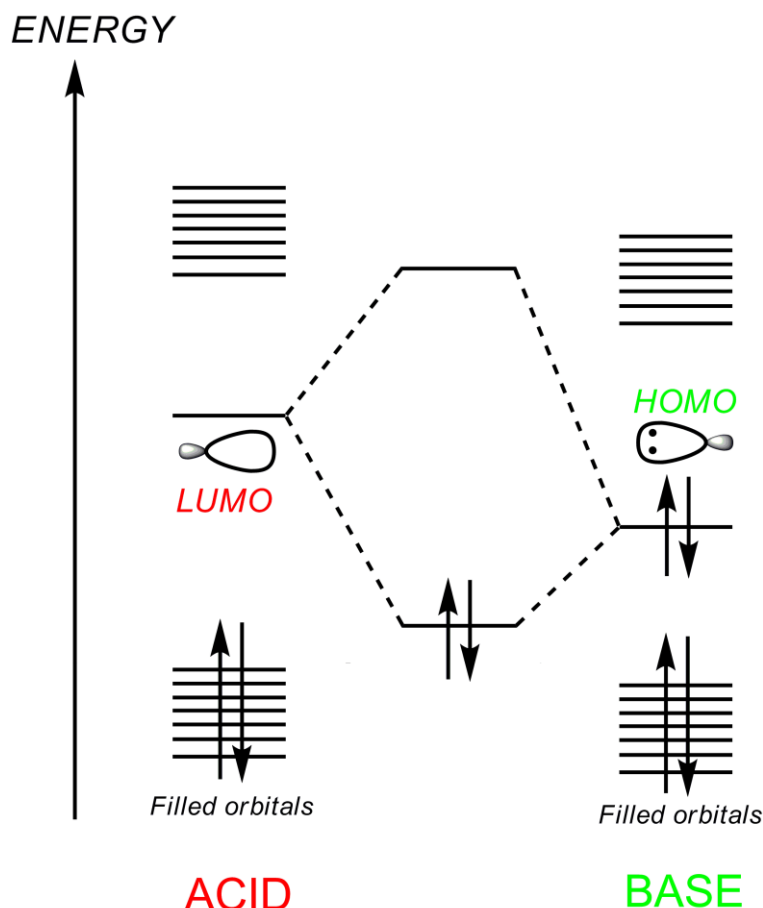
A and **:B** combine to give **A:B**, the bonding orbital generated is occupied by the electrons supplied by **:B**.

A:B is known as an *adduct* or *complex*. The interaction between **A** and **:B** is known as *dative* or *coordinate* bonding.

Breakage of the bond occurs heterolytically to give back the original **A** and **:B**.

b) Frontier orbitals

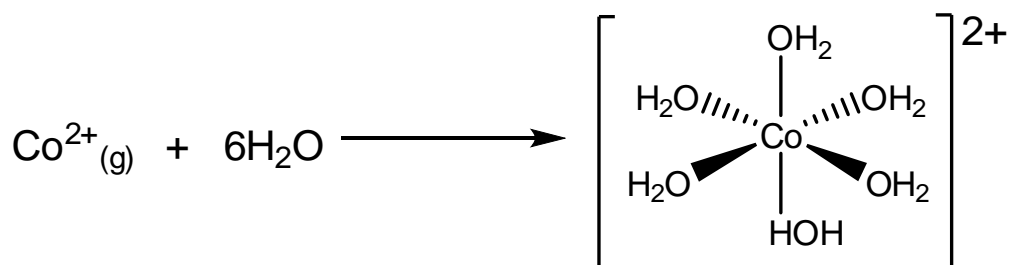
When employing molecular orbital theory, we discuss donors and acceptors in terms of 'frontier orbitals'. We usually think of the base as having a suitable HOMO (highest occupied molecular orbital) whereas the acid possesses a suitable LUMO (lowest unoccupied molecular orbital). The interaction between the full HOMO of the base and the empty LUMO of the acid gives rise to a bonding and an antibonding orbital as pictured below.



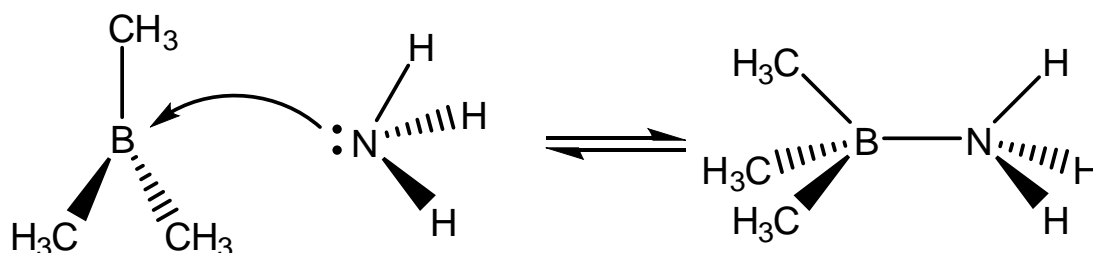
c) Examples of Lewis acids

1) H^+ is a Lewis acid. Any Brønsted acid exhibits Lewis acidity.

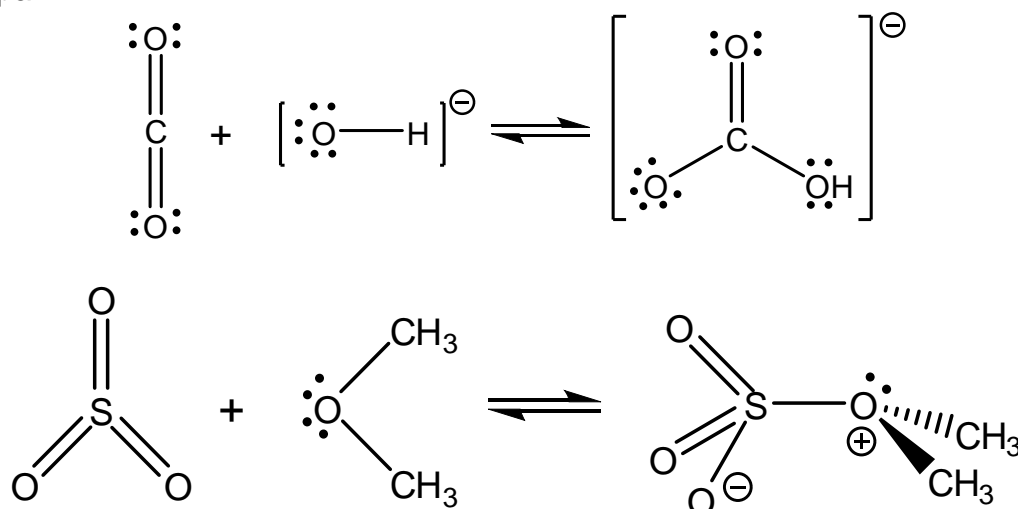
2) Metal cations. In aqueous solution metal cations act as Lewis acids and water molecules (with electron lone-pairs on the oxygen atoms) act as Lewis bases. Note how in aqua ions this is transmitted into Brønsted acidity because coordinated H_2O can release H^+ .



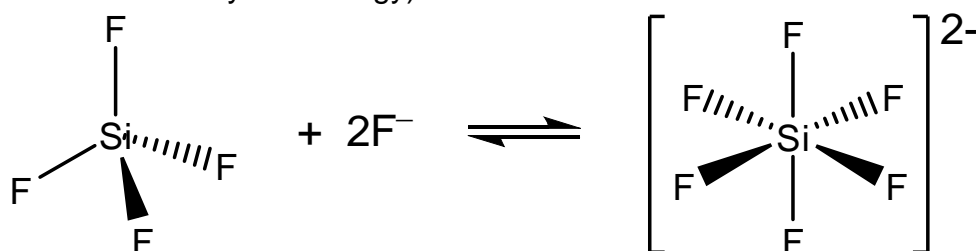
3) Molecules of main-group elements with an incomplete octet.



4) Molecules such as CO₂ and SO₃ which can rearrange valence electrons and accept an electron pair.



5) Molecules of heavier elements large enough to accept more electron pairs (or having empty orbitals of sufficiently low energy).



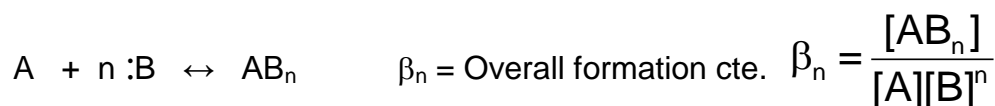
4.2 Strengths of Lewis acids and bases

a) How strengths are measured

There are far more variables than for Brønsted acidity since Lewis acids differ widely in their structures.

Most simply: $A + :B \leftrightarrow AB$ $K_f = \text{formation constant.}$ $K_f = \frac{[AB]}{[A][B]}$

This can be extended to consider multiple equilibria:



Techniques for measuring formation constants:

Spectral changes: e.g. UV-visible spectrophotometry

Electrochemistry: e.g. for ions (conductivity) or for redox active species (voltammetry)

Calorimetry: measure ΔH

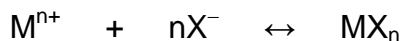
b) Acid-base affinities: Observations

‘Hard’ and ‘Soft’ acids and bases

Aside from obvious steric effects, the strengths of Lewis acids depend upon factors such as bond strengths and solvation effects.

We will focus on observations, treating these empirically.

Consider the reaction between an acid (= metal ion) and a base X^- (= halide), to give an adduct (complex):



For Mg^{2+} in water the order of stability of MX_n is: $F^- > Cl^- > Br^- > I^-$. This behaviour is referred to as 'Class A'.

However, for Hg^{2+} in water the order of stability of MX_n is: $I^- > Br^- > Cl^- > F^-$. This behaviour is referred to as 'Class B'.

More generally, we use the terms ‘*Hard*’ and ‘*Soft*’ acids and bases (HSAB).

Mg^{2+} is a ‘Hard’ acid. F^- is a ‘Hard’ base.

Hg^{2+} is a ‘Soft’ acid. I^- is a ‘Soft’ base.

The HSAB classification is extensively used in coordination chemistry. As an empirical guide it is very useful in helping predict reaction outcomes. *Hard goes with Hard, Soft goes with Soft.*

Examples:

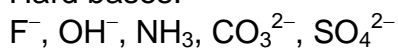
Hard acids:

H^+ , Group I and II metal ions, Al^{3+} , Lanthanides (M^{3+}).

Early d-block metals in high oxidation states, e.g. Ti^{4+} .

A tendency to be non-polarisable. Small/highly charged ions are good examples.

Hard bases:



A tendency to be non-polarisable. Ions based on the 2p elements are good examples.

Soft acids:

Late and heavier d-block elements and heavy p-block metal ions, particularly in low oxidation states e.g. Cu^+ , Ag^+ , Hg^{2+} , Hg_2^{2+} , Tl^+ .

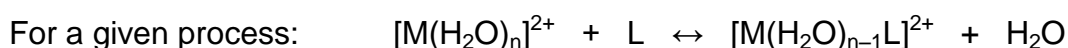
Soft acids tend to be larger and more polarisable.

Soft bases:

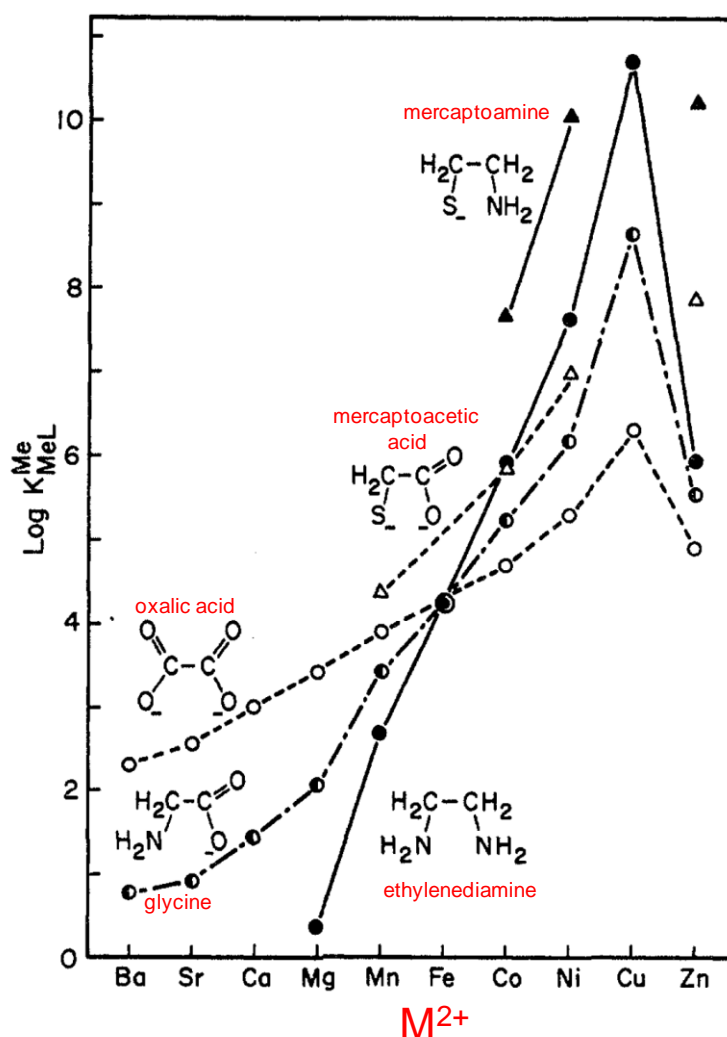


A tendency to involve elements from the 3p and lower rows.

The Irving-Williams series



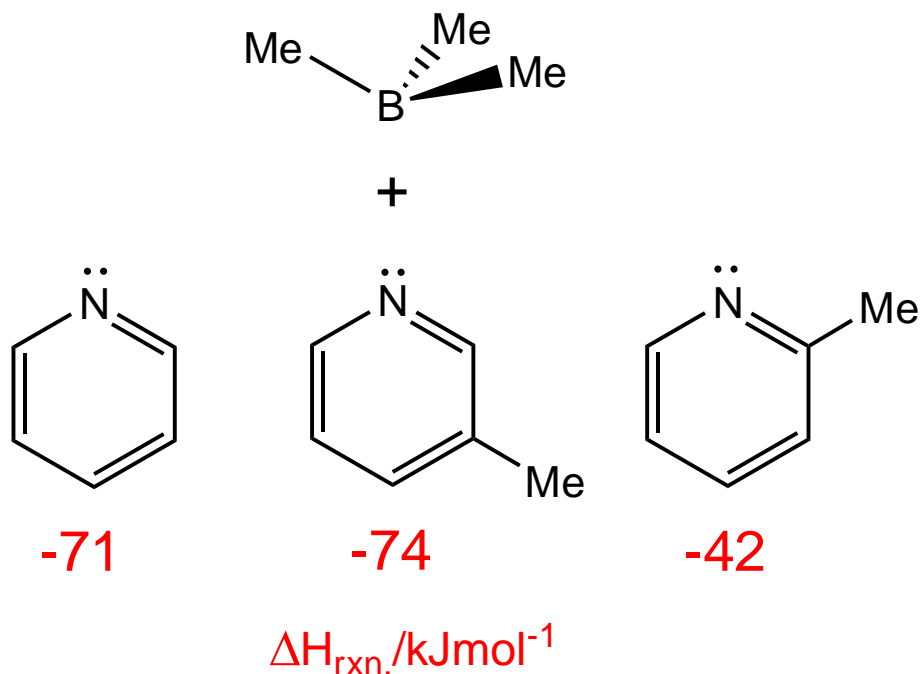
The formation constant reflects a general increase in bond strength as size of metal decreases. Note here also the switch in preference to favour *Soft* donors as the d-block is crossed left to right. K_f : $\text{Ba}^{2+} < \text{Ca}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$.



Stereochemical factors

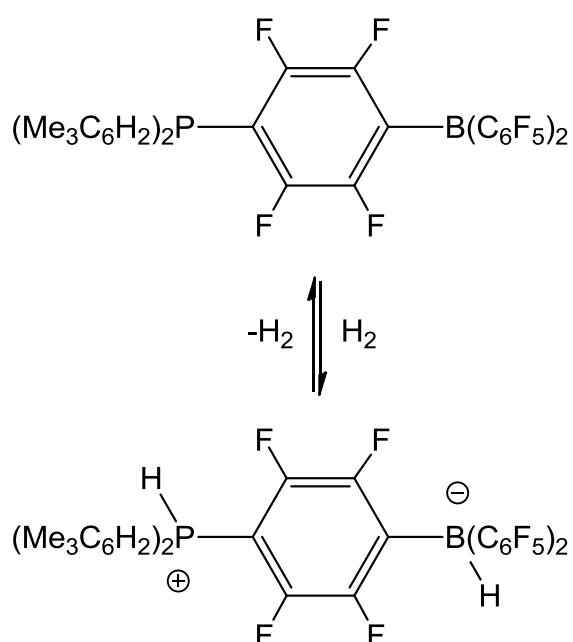
Stereochemical effects represent an immediate contrast with proton-base interactions.

Ground state steric interactions:

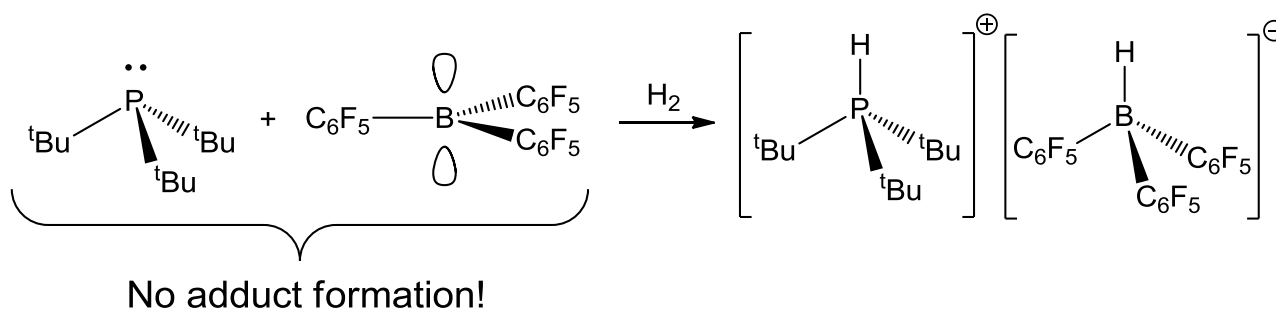


Frustrated Lewis pairs:

Steric clash so great that the Lewis acid and base do not form an adduct. This results in unquenched reactivity which allows such species to activate small molecules such as dihydrogen.



In this example the phosphine (Lewis base) and borane (Lewis acid) activate dihydrogen to give a Zwitterion. This is a reversible process.



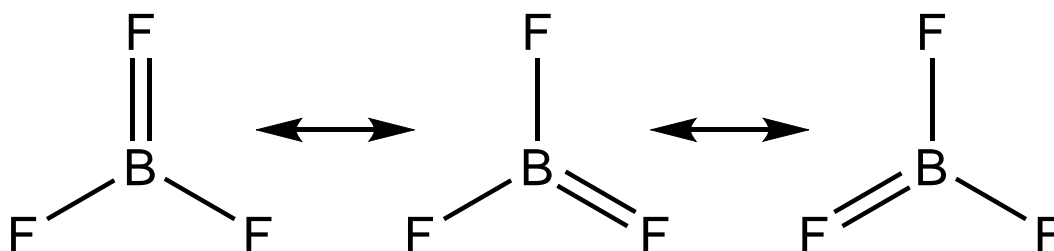
A sterically bulky phosphine (tris(*tert*-butyl)phosphine) and Lewis acidic borane activate dihydrogen to give a 1:1 electrolyte. In this instance the process is irreversible (i.e. the phosphine and borane cannot be regenerated by heating or under vacuum).

Changes in shape and internal bonding:

Consider the reaction: $X_3B + :NR_3 \leftrightarrow X_3B:NR_3$

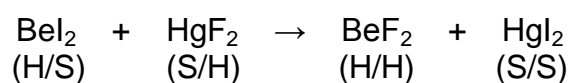
This is a reaction between a 'Hard' acid and a 'Hard' base to give a complex. On the basis of the inductive effect we expect an order of K_f : $F^- > Cl^- > Br^- > I^-$, due to the greater electronegativity of the fluoride anion.

However, BF_3 is the weakest acid. This is because p-p π -bonding is strongest for the 2p elements and more energy is required to distort the planar BF_3 molecule to the pyramidal geometry required for adduct formation.



Solvent effects

The metathesis reaction shown below is exothermic, as predicted by the HSAB rule. It can be studied in the *gas phase*.



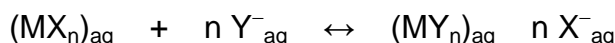
Heats of atomisation (KJ mol^{-1} ; $\text{MX}_2 \rightarrow \text{M} + 2\text{X}$):



So contrary to 'Soft likes Soft', Hg-I bonds are actually the weakest. The reaction is driven by the very strong (ionic) bonding between Be and F.

Competitive effects like this are important for 'simple' reactions in solution. The 'free' (unbound) species is not 'free' at all but bound instead in a *solvato* complex. Small ions are more strongly solvated and this contributes to the HSAB observations.

Subsequently, a ligand exchange reaction such as:

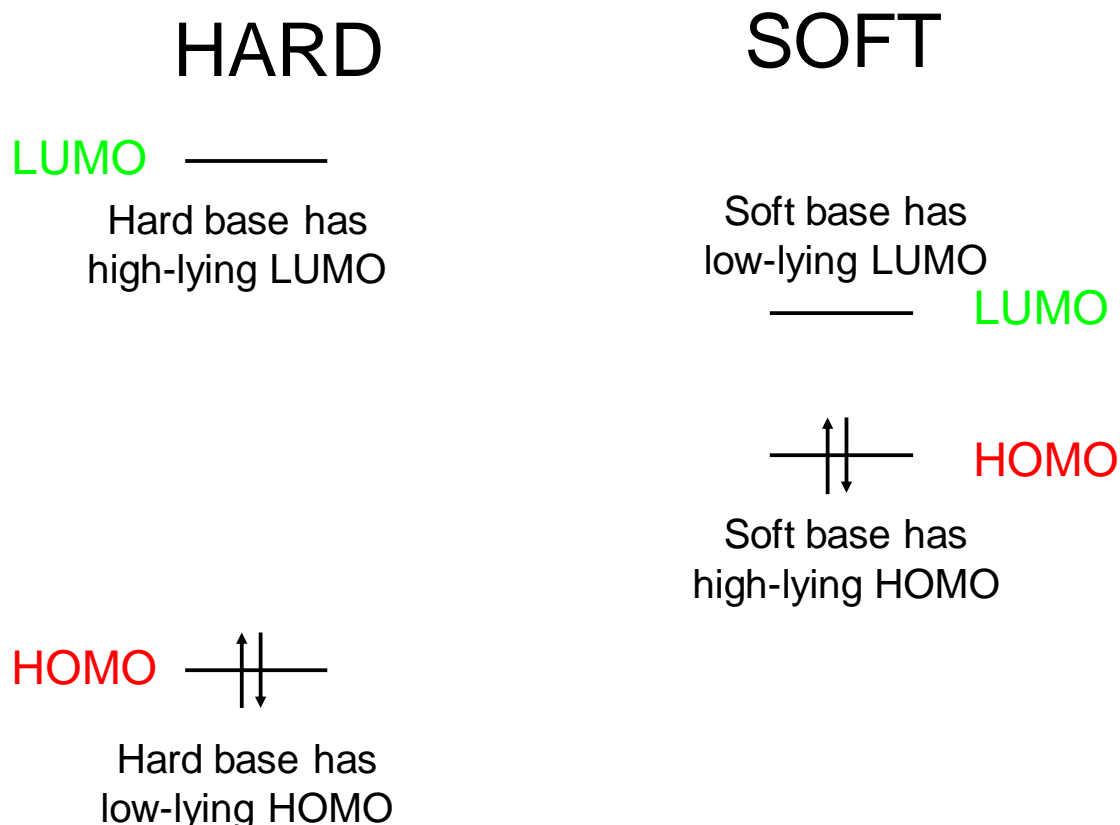


may be favoured because X^- is more strongly solvated than Y^- .

Hard-soft behaviour rationalised in terms of orbital energies

Hard species are non-polarisable, soft species are polarisable.

Polarisability can be expressed in terms of the separation between HOMO and LUMO.



Non-polarisable acids or bases have a large HOMO/LUMO gap – a tendency to form ionic bonds.

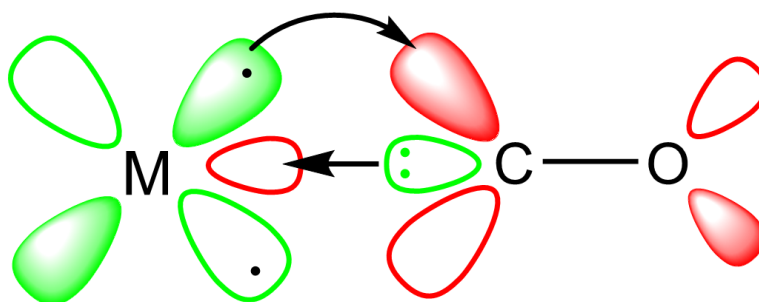
Polarisable acids or bases have a small HOMO/LUMO gap – a tendency to form covalent bonds.

4.3. Other types of Lewis acids and bases

A more complete understanding of how species act as acids or bases requires greater knowledge of molecular orbital theory, but we will touch upon some examples here.

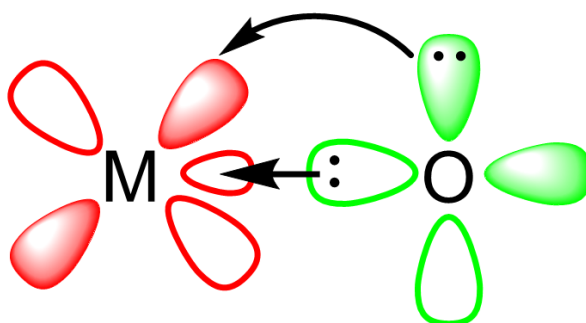
π -acceptor ligands (π -acids)

CO, CN^- , O_2 . Ligands such as these use their anti-bonding π -orbitals as acceptor orbitals.



π -donor ligands (π -bases)

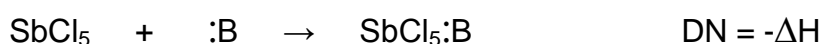
O^{2-} , F^- . Stabilise strong Lewis acids (typically elements in high oxidation states) by using full $2p_{x(y)}$ orbitals as electron-pair donors in addition to the $2p_z$ used in σ -bonding. This is equivalent to the idea that highest oxidation states of an element are manifested in compounds with oxygen.



4.4. Quantifying Lewis acid and base strengths

Donor-acceptor numbers

The *donor number* (DN) of a base is obtained by measuring the enthalpy of reaction with $SbCl_5$ in 1,2-dichloroethane.



Acceptor numbers (AN) for acids have been obtained using nuclear magnetic resonance spectroscopy (NMR), with triethylphosphine oxide as the reference base and measuring the ^{31}P chemical shifts upon adduct formation.

The properties of commonly used solvents are readily gauged from their donor/acceptor numbers.

SOLVENT	DN	AN	ϵ
Pyridine	33.1	14.2	12.3
DMSO	29.8	19.3	45
Diethylether	19.2	3.9	4.3
H ₂ O	18	54.8	81.7
Ethanoic acid	-	52.9	6.2
Acetone	17	12.5	20.7
Acetonitrile	14.1	19.3	36
Benzene	0.1	8.2	2.3
CCl ₄	-	8.6	2.2
SbCl ₅	-	100	-
CF ₃ COOH	-	105.3	-

The Drago-Wayland Equation

Consider the gas phase reaction: $A_{(g)} + :B_{(g)} \rightarrow A-B_{(g)}$

Drago and Wayland proposed the equation:

$$-\Delta H = E_A E_B + C_A C_B$$

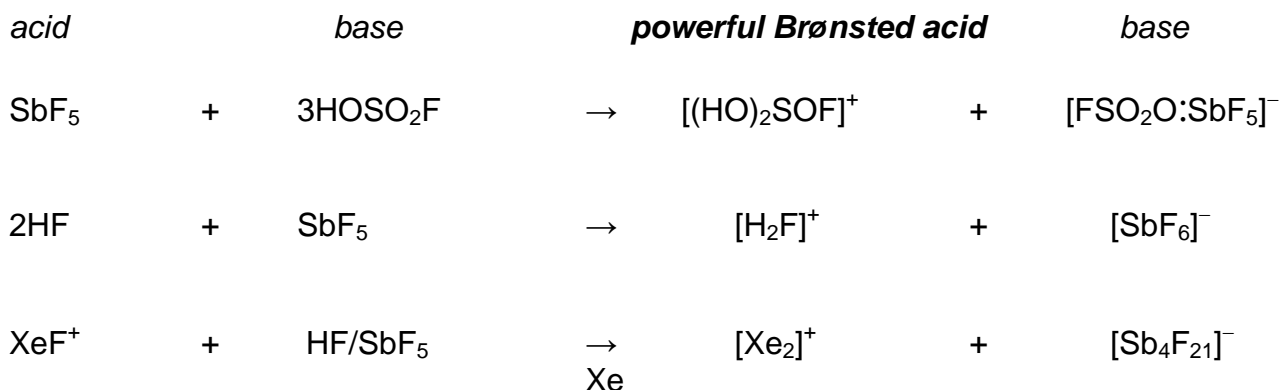
where ΔH is the standard enthalpy of the reaction, and E_A , E_B and C_A , C_B values represent the abilities of the acid and base to participate respectively in ionic and covalent interactions. Large enthalpies result from combinations of acids and bases with either large E or large C values.

	E	C
acids		
SbCl ₅	15.1	10.5
BMe ₃	12.6	3.48
SO ₂	1.88	1.65
Iodine	2.05	2.05
bases		
NH ₃	2.78	7.08
Benzene	0.23	2.9
Pyridine	1.17	6.40
Methylamine	1.30	5.88

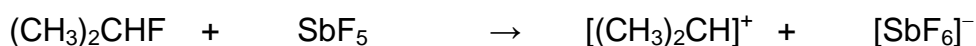
4.5 Extension of acid-base concepts

a) Superacids and their applications

Strong Lewis acids create strong Brønsted acids



b) Generation of reaction carbocations



c) Coordination chemistry

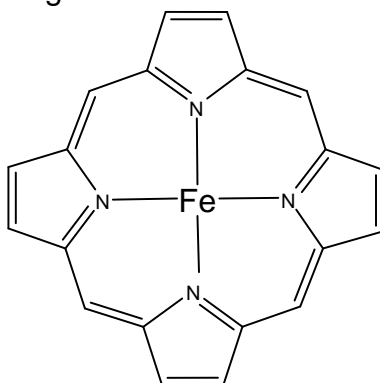
Metal ions (acids) form stable complexes with ligands (bases): $[\text{ML}_x]^{n+}$.

Some are very stable, e.g. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. Here, the complex is also termed '*inert*' (kinetically stable) since exchange with solvent water molecules is very slow. However, if we consider $[\text{Ni}(\text{CN})_4]^{2-}$, the complex is also stable but exchange of CN^- ligands with others in solution is very fast.

d) Multidentate ligands

Familiar ones may be EDTA (used in volumetric determination of Cu in 1st year practical labs).

Protoporphyrin XI is the organic ring coordinated to Fe in haemoglobin.

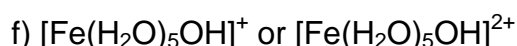
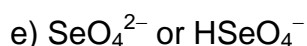
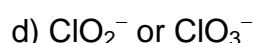
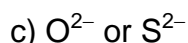
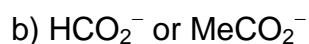
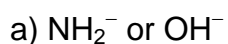


5. Questions

- 1) List the following acids in order of their strength in aqueous solution



- 2) For each of the given pairs, identify the stronger Brønsted base



- 3) List the following acids in order of their strength when reacting with NH_3 .

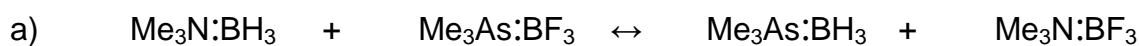


- 4) AlF_3 is insoluble in liquid HF , but dissolves if NaF is present. When BF_3 is added to the solution AlF_3 precipitates. Comment

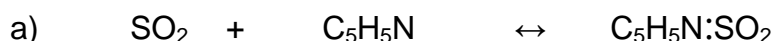
- 5) The conductivity of BrF_3 is enhanced by adding either AgF or SnF_4 . Explain this enhancement, using the appropriate equations.

- 6) Describe how PF_3 can act as a Lewis acid towards F^- and as a Lewis base toward BH_3 .

- 7) Predict the directions of the following reactions in the gas phase.



- 8) Use the Wayland-Drago parameters tabulated in textbooks to calculate the approximate energy changes for the following reactions.



(THF = tetrahydrofuran)

- 9) $\text{Zn}(\text{NO}_3)_2$ is dissolved in H_2O . Slow addition of 2M NH_3 leads first to the formation of a grey precipitate then to a clear colourless solution. Explain the reactions occurring.
- 10) H_3BO_3 and CO_2 are often regarded as acids. Explain the true basis of this activity and propose other examples in which a species appears to behave as a Brønsted acid.
- 11) Identify the principal factors, intrinsic and extrinsic, that underlie the distinctions between 'hard' and 'soft' species in chemical reactions.
- 12) Explain why glass cannot be used in apparatus for handling HF.
- 13) Explain why ammonia is usually considered a better donor than water but is a poorer solvent for most polar molecules.
- 14) Explain the principles by which the unusual cations Se_4^{2+} , Se_8^{2+} can be prepared by exploiting super-acid chemistry (for example $\text{SbF}_5/\text{HSO}_3\text{F}$).