

ACIDS, BASES AND SOLUTION EQUILIBRIA

Dr. J. M. Goicoechea

HILARY TERM

Lecture 1

1. Examples of acid-base reactions

2. Introduction to acids and bases

2.1 Definitions and concepts

3. The Brønsted-Lowry Definition

3.1 Protonation equilibria in water

3.2 Polyprotic acids

3.3 The Hammett acidity function

3.4 Factors governing the strengths of acids and bases

a) Gas-phase reactivities

b) Energetics of proton transfer reactions

Solvation effects

Solvent levelling

c) Hydroxyl group acids

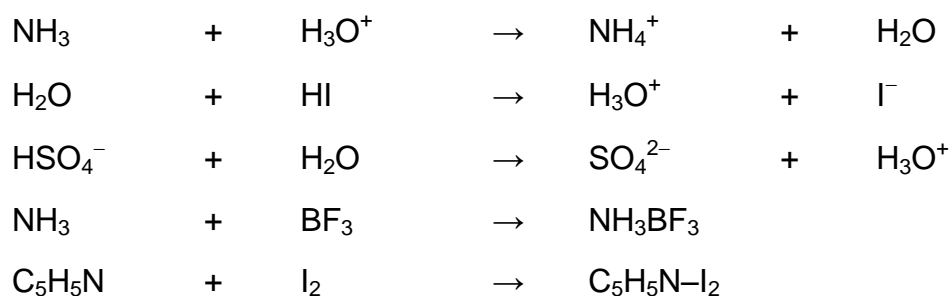
Metal ion acidity

Hydroxo- and oxo-acids: Pauling's rules

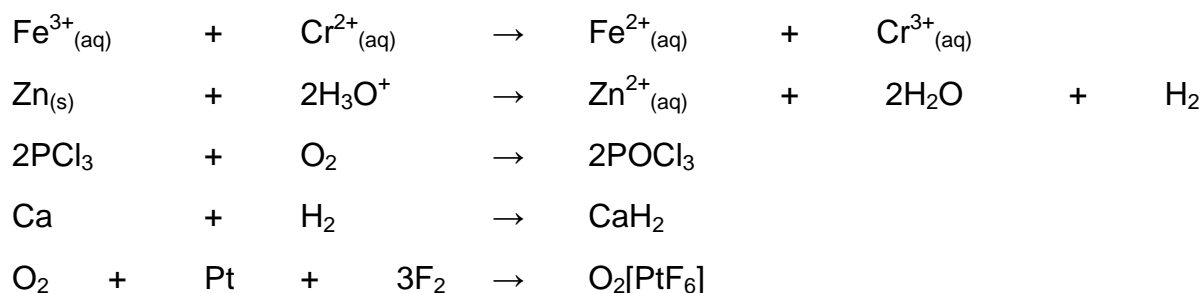
Polymerisation of hydroxyl species

1. Examples of acid-base and redox reactions

Circle the acids:



Circle the oxidants:



By classifying chemicals as Acids/Bases or as Oxidants/Reductants we can predict the affinities and reactivities of a large number of chemical reactions

2. Introduction to acids and bases

2.1 Definitions and concepts

Arrhenius. *A very narrow definition.* Acids and bases dissociate in H_2O , releasing H^+ (H_3O^+) and OH^- respectively. This definition is confined to an aqueous media and requires dissociation of H_2O to H_3O^+ and OH^- .

Brønsted-Lowry. *A narrow definition, but widely used due to the importance of the proton.* An acid is a H^+ donor, and a base a H^+ acceptor. This definition can be applied to a range of solvents.

Lux-Flood. *Narrow.* Used in solid-state chemistry. An acid is an oxide ion acceptor, a base is an oxide ion donor.

Solvent system. For auto-ionising solvents. Acids are agents that increase the concentration of cations; bases increase the concentration of anions.

Lewis. *The most general definition. Extensively used.* An acid is a lone-pair acceptor, a base is an electron pair donor. Coordination chemistry is governed by Lewis acid/base interactions.

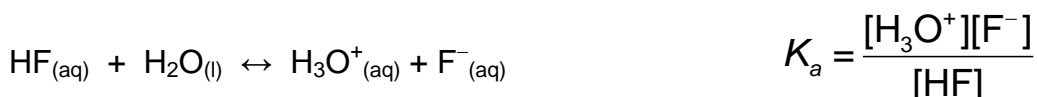
Usanovich. *A very broad definition.* Encompasses all of the previous acid-base concepts. An acid is a substance that forms salts by reacting with bases, it gives up cations or accepts anions or electrons. A base is a species that reacts with acids, it gives up anions, combines with cations or donates electrons.

3. The Brønsted-Lowry definition

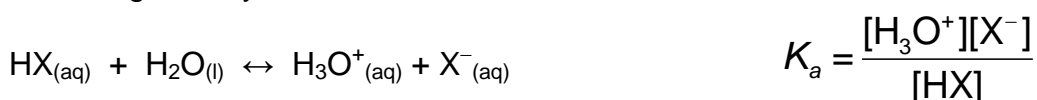
3.1 Protonation equilibria in water

The practical measures of Brønsted acidity and acid-base strength in dilute aqueous solution are pH and p*K*.

The strength of a Brønsted acid, such as HF, in aqueous solution is expressed by its **acidity constant** (or 'acid ionisation constant'), *K_a*:



or more generally:



In this definition, $[\text{X}^-]$ denotes the numerical value of the molar concentration of the species X^- (so, if the molar concentration of HF molecules is 0.001 mol L^{-1} , then $[\text{HF}] = 0.001$).¹ A value of $K_a \ll 1$ implies that $[\text{HX}]$ is large with respect to $[\text{X}^-]$, and so proton retention by the acid is favoured. The experimental value of K_a for hydrogen fluoride in water is 3.5×10^{-4} , indicating that under normal conditions, only a very small fraction of HF molecules are deprotonated in water.

Because water is amphiprotic (it can both donate and accept protons), a proton transfer equilibrium exists even in the absence of added acids or bases. The proton transfer from one water molecule to another is called **autoprotolysis** (or 'autoionisation'). The extent of autoprotolysis and the composition of the solution at equilibrium is described by the autoprotolysis constant of water, *K_w*:



The experimental value of K_w is 1.00×10^{-14} at 25°C. Only a very tiny fraction of water molecules are present as ions in pure water.

Because molar concentrations and acidity constants (*K* values) span many orders of magnitude it is convenient to report them as their common logarithms (logarithms to the base of 10) by using pH and p*K*.

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

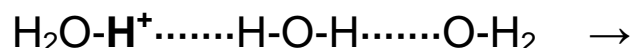
$$\text{pK} = -\log K$$

¹ In precise work, K_a is expressed in terms of the activity of X, $a(\text{X})$, its effective thermodynamic concentration.

At 25° C, for instance, $pK_w = 14.00$. A similar expression applies to any solvent, with pK_w replaced by the appropriate autoprotolysis constant of the solvent, pK_{solv} .

A useful result is that for a simple acid the pK is the pH at which $[HX] = [X^-]$, i.e. the pH at which *half the Brønsted acid molecules HX are deprotonated*.

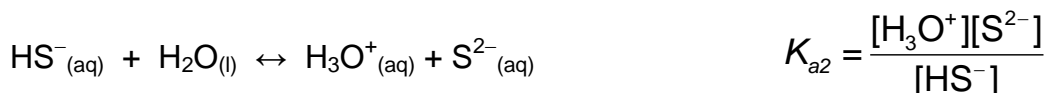
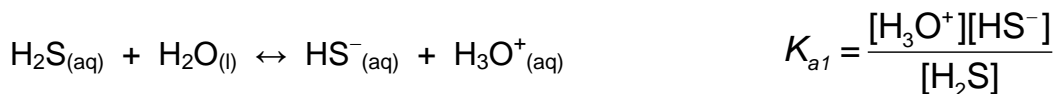
Proton transfer reactions are typically very fast. A particular example is water which ‘conducts’ protons by the **Grotthuss mechanism**. Here, H^+ ‘flips’ through H-bonded networks as water molecules rotate.



3.2 Polyprotic acids

Acid	HA	A ⁻	K_a	pK_a
Hydriodic	HI	I ⁻	10^{11}	-11
Perchloric	HClO ₄	ClO ₄ ⁻	10^{10}	-10
Hydrobromic	HBr	Br ⁻	10^9	-9
Hydrochloric	HCl	Cl ⁻	10^7	-7
Sulfuric	H ₂ SO ₄	HSO ₄ ⁻	10^2	-2
Nitric	HNO ₃	NO ₃ ⁻	10^2	-2
Hydronium ion	H ₃ O ⁺	H ₂ O	1	0.0
Chloric	HClO ₃	ClO ₃ ⁻	10^{-1}	1
Sulfurous	H ₂ SO ₃	HSO ₃ ⁻	1.5×10^{-2}	1.81
Hydrogensulfate ion	HSO ₄ ⁻	SO ₄ ²⁻	1.2×10^{-2}	1.92
Phosphoric	H ₃ PO ₄	H ₂ PO ₄ ⁻	7.5×10^{-3}	2.12
Hydrofluoric	HF	F ⁻	3.5×10^{-4}	3.45
Formic	HCOOH	HCO ₂ ⁻	1.8×10^{-4}	3.75
Ethanoic	CH ₃ COOH	CH ₃ CO ₂ ⁻	1.74×10^{-5}	4.76
Pyridinium ion	HC ₅ H ₅ N ⁺	C ₅ H ₅ N	5.6×10^{-6}	5.25
Carbonic	H ₂ CO ₃	HCO ₃ ⁻	4.3×10^{-7}	6.37
Hydrogen sulfide	H ₂ S	HS ⁻	9.1×10^{-8}	7.04
Dihydrogenphosphate ion	H ₂ PO ₄ ⁻	HPO ₄ ²⁻	6.2×10^{-8}	7.21
Ammonium ion	NH ₄ ⁺	NH ₃	5.6×10^{-10}	9.25
Hydrocyanic	HCN	CN ⁻	4.9×10^{-10}	9.31
Hydrogencarbonate ion	HCO ₃ ⁻	CO ₃ ²⁻	4.8×10^{-11}	10.32
Hydrogenphosphate ion	HPO ₄ ²⁻	PO ₄ ³⁻	2.2×10^{-13}	12.67
Hydrogensulfide ion	HS ⁻	S ²⁻	1.1×10^{-19}	19

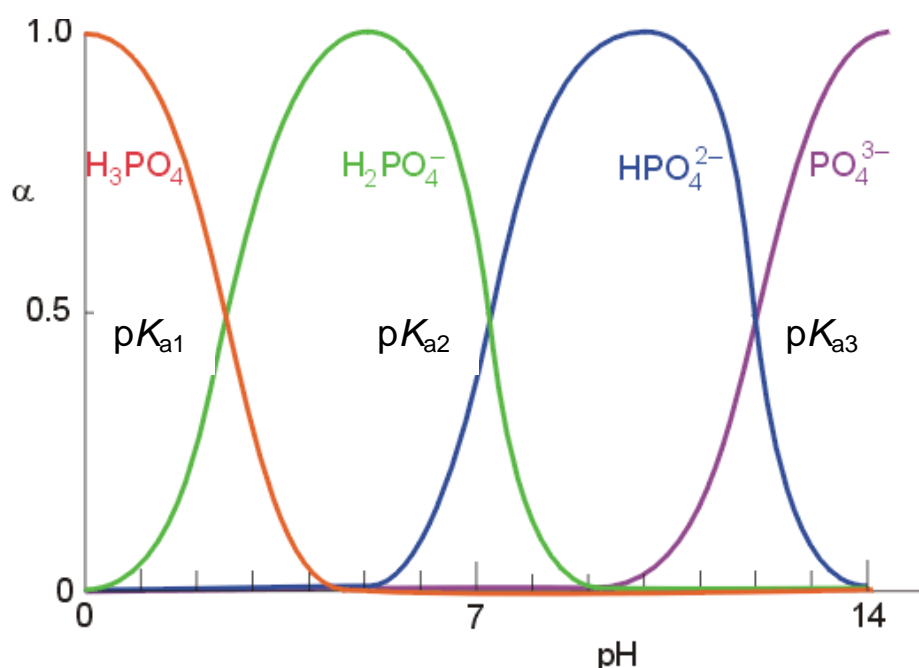
A polyprotic acid is a substance that can donate more than one proton. An example is hydrogen sulphide, H_2S , a diprotic acid. For a diprotic acid, there are two successive proton donations and two acidity constants.



$K_{\text{a1}} = 9.1 \times 10^{-8}$ ($\text{p}K_{\text{a1}} = 7.04$) and $K_{\text{a2}} \approx 10^{-19}$ ($\text{p}K_{\text{a2}} = 19$). The second acidity constant is almost always smaller than K_{a1} (and hence $\text{p}K_{\text{a2}}$ is generally larger than $\text{p}K_{\text{a1}}$). The decrease in K_{a} is consistent with an electrostatic model of the acid in which, in the second deprotonation, a proton must separate from a centre with one more negative charge than in the first deprotonation. Because additional electrostatic work must be done to remove the positively charged proton, the deprotonation is less favourable.

The clearest representation of the concentrations of the species formed in successive proton transfer equilibria of polyprotic acids is a **distribution diagram**. As an example, the triprotic acid H_3PO_4 releases three protons in succession to give $\text{H}_2\text{PO}_4^{-}$, HPO_4^{2-} and PO_4^{3-} . The fraction of solute present as intact H_3PO_4 molecules is:

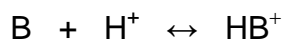
$$\alpha(\text{H}_3\text{PO}_4) = \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^{-}] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]}$$



The distribution diagram shows the fraction of each solute species as a function of pH. Conversely, the diagram indicates the pH of the solution that contains a particular fraction of the species. Thus if $\text{pH} < \text{p}K_{\text{a1}}$ the dominant species is the fully protonated H_3PO_4 molecule. However, if $\text{pH} > \text{p}K_{\text{a3}}$, corresponding to low hydronium ion concentrations, the dominant species is the fully deprotonated PO_4^{3-} ion.

3.3 The Hammett Acidity function

The Brønsted acid concept can be extended to proton donors in non-aqueous solutions, to concentrated solutions and to extremely strong acids whose pK_a values cannot be determined because they are < 0 . For the following reaction:



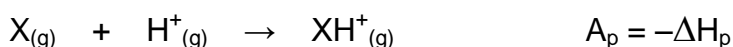
We define the **Hammett acidity function**: $H_0 = pK_{BH^+} - \log\{[BH^+]/[B]\}$

H_0 values are often determined by examining the position of the proton exchange equilibrium with reference dyes (specified H_0) that exhibit a colour change (measured as light absorption) when they change protonation site.

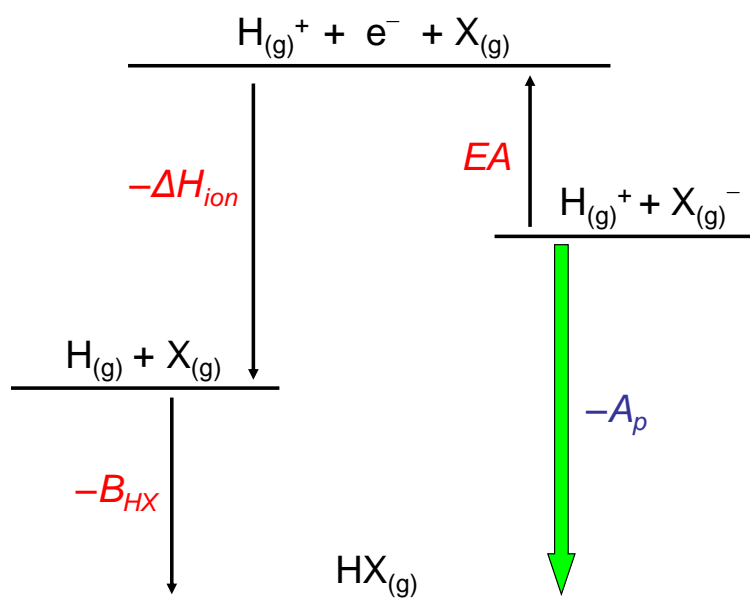
3.4 Factors governing the strengths of acids and bases

a) Gas-phase reactions

The best way to understand the strength of Brønsted acids is to consider the quantity known as **gas-phase proton affinity (A_p)**. This is defined as the energy released by the process:

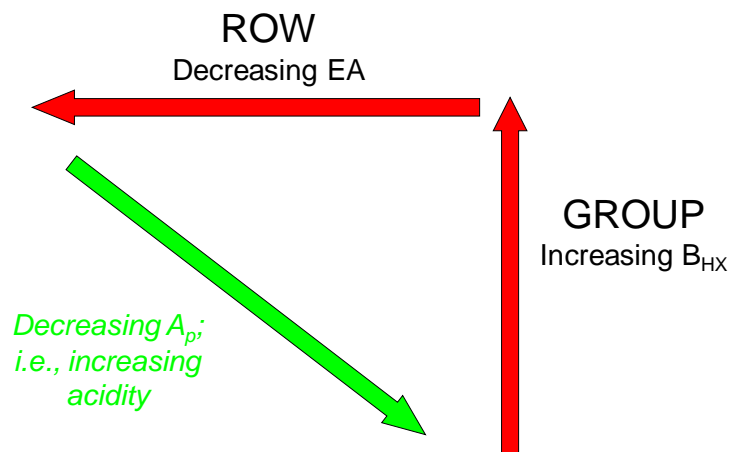


Proton affinities can be measured by ion cyclotron resonance and mass spectrometry. The factors determining A_p are revealed by a thermodynamic cycle, which involves H-X bond dissociation energy, $\Delta H_{ion}(X)$, and the electron affinity of $X_{(g)}$. See below:



$$A_p = B_{HX} + \Delta H_{ion} - EA$$

The variables are BDE(HX) and EA. As a result we expect that the trend across the periodic table will be:



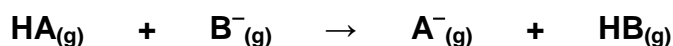
This prediction is borne out by experiment. Data for A_p are given below. However, in solution, the most widely used experimental parameter is the pK ; pK values for aqueous solutions are shown in brackets alongside A_p values.

H^-	CH_3^-	NH_2^-	OH^-	F^-
1675	1745 (49)	1689 (39)	1635 (15.7)	1554 (3.2)
	SiH_3^-	PH_2^-	SH^-	Cl^-
	1554 (35)	1552 (27)	1469 (7.05)	1395 (-6.1)
	GeH_3^-	AsH_2^-	SeH^-	Br^-
	1509 (25)	1515 (23)	1466 (3.8)	1354 (-8)
				I^-
				1315 (-9)

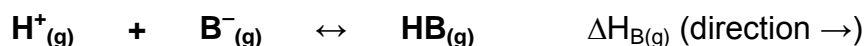
Note the disparities between acid strengths defined by A_p and pK_a . For example, PH_2^- and F^- have almost identical A_p values but F^- has a much lower pK_a . Therefore HF is a much stronger acid in water than PH_2^- . These values are different due to solvent effects which we will discuss in Lecture 2.

b) Energetics of proton transfer reactions

Consider the exchange of a proton between species A^- and species B^- :



now treat this as two half-reactions involving competition for a free H^+ :



$$\begin{aligned}\text{Subsequently, } \Delta H_{\text{rxn}} &= \Delta H_{\text{B(g)}} - \Delta H_{\text{A(g)}} \\ &= A_{\text{p(A)}} - A_{\text{p(B)}}\end{aligned}$$

The reaction is favourable if $A_{\text{p(B)}} > A_{\text{p(A)}}$

Solvation effects

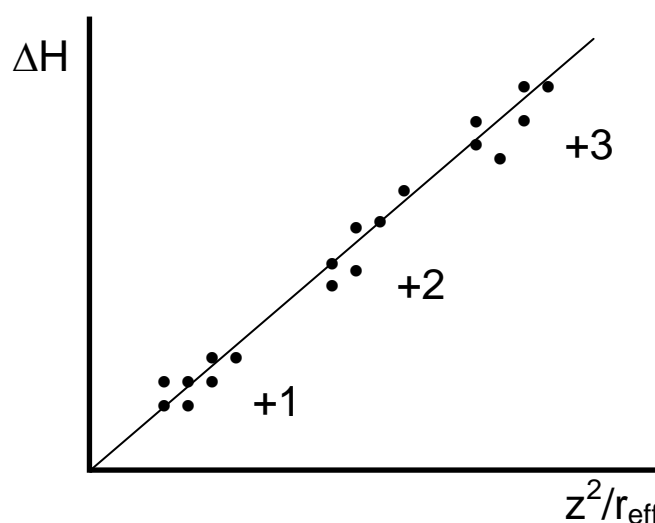
First consider the solvation energies of gaseous ions. Derived from simple electrostatics.

Energy changes when gaseous ion transferred to a dielectric medium

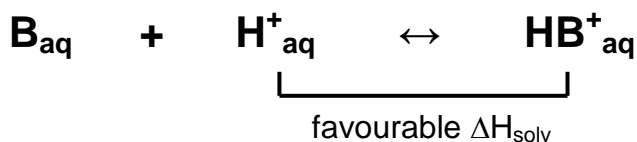
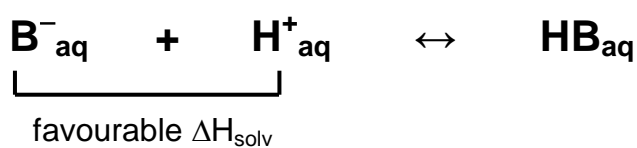
Born equations:

$$\Delta G = \frac{-N_A e^2 z^2}{8\pi\epsilon_0 r} \left(1 - \frac{1}{\epsilon}\right)$$

$$\Delta H = \Delta G + T\Delta S$$



Now consider acid-base reactions in a solvent:



Inclusion of solvation effects leads to some alterations of the proton affinity values (A_{p}'). These values are shown in *italics*. The most widely used experimental parameter is the pK , and data for aqueous solution are also shown. Strong acids have low values of A_{p}' .

A_p and A_p' (*italics*); kJ mol^{-1} . $\text{p}K_a$ values in brackets.

H^-	CH_3^-	NH_2^-	OH^-	F^-
1674	1743 1380 (49)	1689 1351 (39)	1632 1188 (15.7)	1554 1150 (3.2)
	SiH_3^-	PH_2^-	SH^-	Cl^-
	1554 (35)	1548 (27)	1474 1283 (7.05)	1395 1090 (-6.1)
	GeH_3^-	AsH_2^-	SeH^-	Br^-
	1509 (25)	1500 (23)	1420 (3.8)	1315 1079 (-8)
				I^-
				1314 1068 (-9)

Although A_p' values relate to enthalpy (ΔH), solvation also contributes another factor, entropy (ΔS).



[*] note that $\text{p}K$ refers to a dissociation constant

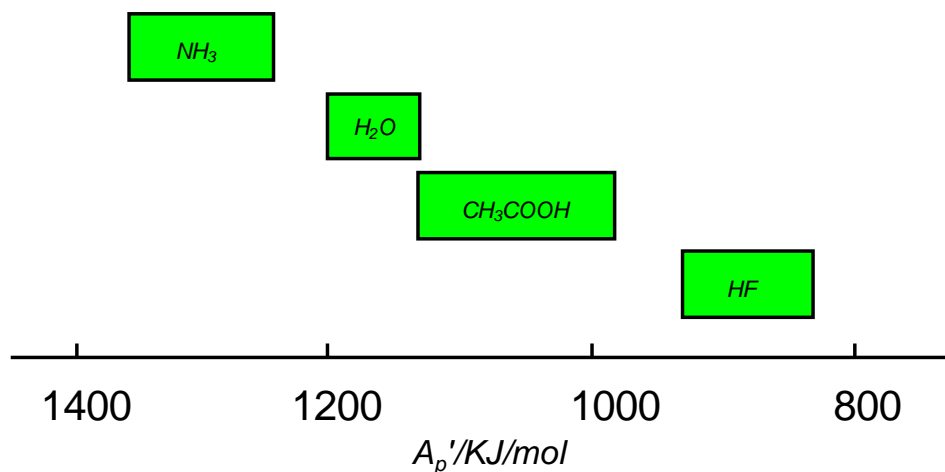
For each species, generally: increased solvation $\Delta S < 0$; decreased solvation $\Delta S > 0$.

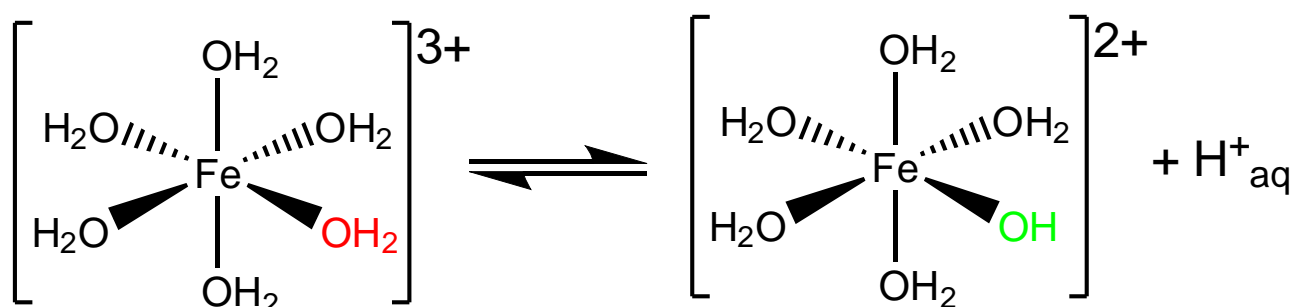
Solvent levelling



the autoprotolysis constant K_{auto} is $[\text{H}_2\text{Y}^+][\text{Y}^-]$, and $\text{p}K_{\text{auto}} = -\log K_{\text{auto}}$

- 1) Strongest acid is H_2Y^+ , and strongest base is Y^-
- 2) Range of solute acid-base discrimination is proportional to $\text{p}K_{\text{aut}}$.



c) Hydroxyl group acids**Metal aqua ion acidity**

$\text{Fe}^{3+}_{\text{aq}}$ ($\text{pK} = 2$) is as acidic as carboxylic acids.

Hydroxo- and Oxo- acids

Of wide importance: predictions about their strengths can be made using empirical rules devised by Pauling.

1) $\text{O}_p\text{E}(\text{OH})_q$ $\text{pK} = 8 - 5p$

2) pK increases by 5 units for each successive deprotonation

Compare acidities of:

H_3PO_4 [= $\text{OP}(\text{OH})_3$]

H_2SO_4 [= $\text{O}_2\text{S}(\text{OH})_2$]

HClO_4 [= $\text{O}_3\text{Cl}(\text{OH})$]

What about H_3BO_3 ?

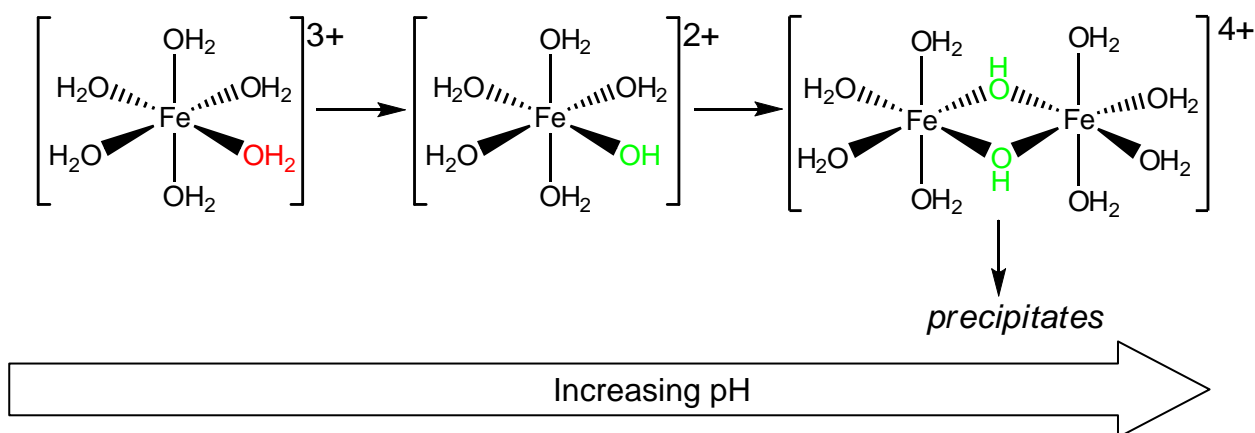
This is correctly formulated as $\text{B}(\text{OH})_3$, however $\text{B}(\text{OH})_3$ is not deprotonated at a hydroxide site. Instead, $\text{B}(\text{OH})_3$ acts as a Lewis acid and the acid base equilibrium is:



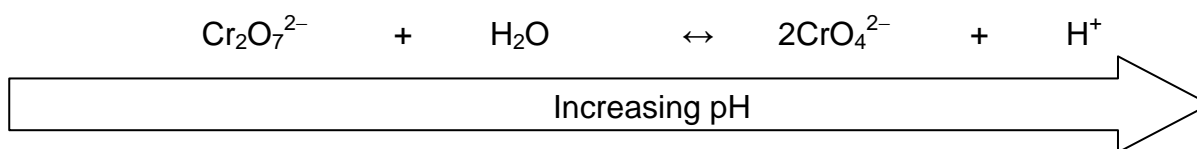
Thus a Lewis acid that accepts a hydroxide ion in water produces the same effect as a Brønsted acid.

Polymerisation reactions and polyoxo species

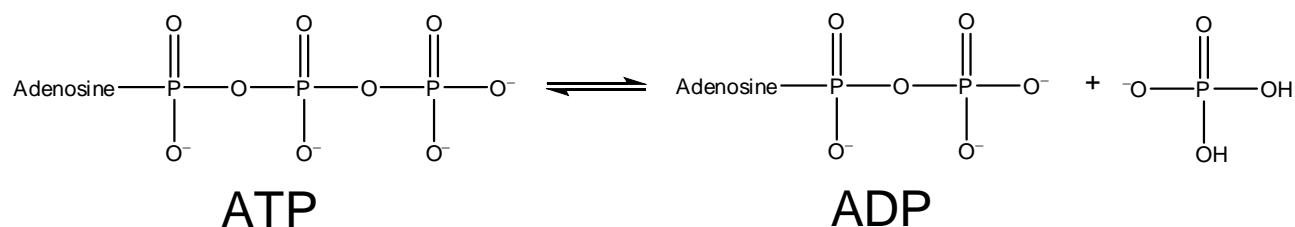
Polmerisation of aqua-cations at high pH



Condensation of oxo-anions at low pH



An important example of this is ATP (adenosine triphosphate):



Further reading:

Shriver and Atkins, 5th edition (2009).Housecroft and Sharpe, 2nd editions (2005).