The equilibrium constant K_c

If you have an equilibrium reaction you can describe it with K_c.

It describes how much of a reaction is on the left or right side.

High K_c: $\longrightarrow$

Low K_c: $\longleftarrow$

The only thing that changes the value of Kc for a reaction is the temperature.

$$aA + bB \rightleftharpoons cC + dD$$

$$\boxed{K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}}$$

[ ] means concentration in moles/dm^3

The ionisation of water

Water will fall apart into ions a little bit by itself.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$\boxed{K_c = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]}}$$

$$[H_2O] = \frac{n}{V} = \frac{m/M}{V} = \frac{1000/18}{1} = 55.6 \text{ mol/dm}^3$$

A constant that is always the same.

Since $[H_2O]$ is always the same one can introduce a new constant K_w that is called the ionic product constant of water:

$$\boxed{K_w = [H_3O^+][OH^-] = 10^{-14} \quad \text{at } 25\ ^\circ C}$$

The definitions of Acids and Bases

The Arrhenius definition

Acids: A substance that forms H^+ ions when mixed with water.
Bases: A substance that forms OH^- ions when mixed with water.

The Brönsted-Lowry definition

Acids: A substance that is a proton (H^+) donator.

Bases: A substance that is a proton (H^+) acceptor.

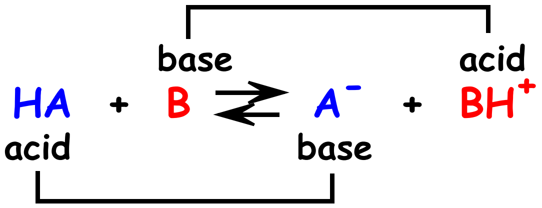
The Lewis definition

Acids: A substance that is an electron pair acceptor.

Bases: A substance that is an electron pair donator.

Conjugate acid-base pairs

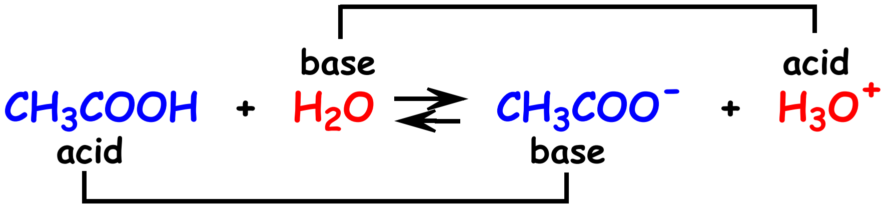
If there is a donator (acid) there has to be an acceptor (base) in a reaction.
The acid and base in a conjugate acid-base pair differs with just one H^+



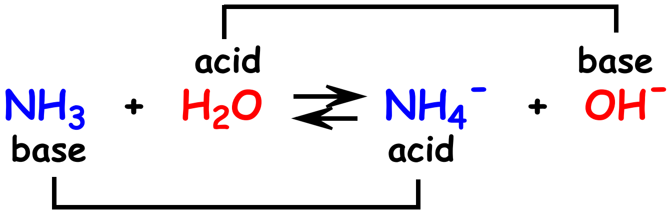
$$\underset{\text{acid}}{HA} + \overset{\text{base}}{B} \rightleftharpoons \underset{\text{base}}{A^-} + \overset{\text{acid}}{BH^+}$$

Amphoteric substances

A substance that sometimes acts as an acid and sometimes as a base is called an amphoteric substance. Water is such a substance.



$$\underset{\text{acid}}{CH_3COOH} + \overset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{base}}{CH_3COO^-} + \overset{\text{acid}}{H_3O^+}$$



$$\underset{\text{base}}{NH_3} + \overset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{acid}}{NH_4^-} + \overset{\text{base}}{OH^-}$$

The pH and pOH scales

The pH and pOH values give the concentration of H^+ and OH^- ions in a liquid.

Large pH and pOH values means small concentration because

$pH = -\log[H^+]$ $[H^+] = 10^{-pH}$

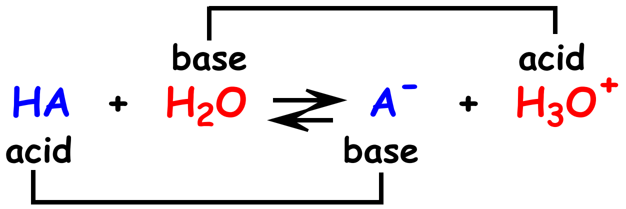
$pOH = -\log[OH^-]$ $[OH^-] = 10^{-pOH}$

The following rule is true when the temperature is 25 °C

$$\boxed{pH + pOH = 14}$$

Dissociation constants

An acid will in water dissociate with the following reaction



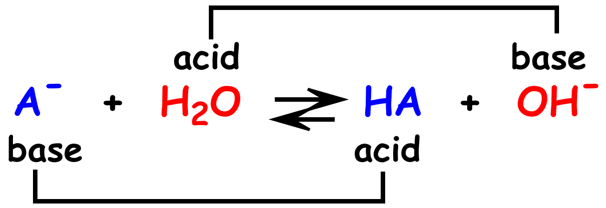
$$\underset{acid}{HA} + \overset{base}{H_2O} \rightleftharpoons \underset{base}{A^-} + \overset{acid}{H_3O^+}$$

Example: $HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$

This reaction has an acid dissociation constant:

$$\boxed{K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}}$$

The A^- ions will also react with water and so there is a second reaction that creates OH^- ions:



$$\underset{base}{A^-} + \overset{acid}{H_2O} \rightleftharpoons \underset{acid}{HA} + \overset{base}{OH^-}$$

Example: $Cl^- + H_2O \rightleftharpoons HCl + OH^-$

This reaction has an acid dissociation constant:

$$\boxed{K_b = \frac{[OH^-]\,[HA]}{[A-]}}$$

In the end there will be a mixture of HA, A^-, H_3O^+ and OH^- in the water.

K_a and K_b are constants but depends on temperature.
They give the strength of the acid or base.

$$pK_a = -\log[K_a] \qquad K_a = 10^{-pKa}$$

$$pK_b = -\log[K_b] \qquad K_b = 10^{-pKb}$$

The following rule is true when the temperature is 25 °C

$$\boxed{pK_a + pK_b = 14}$$

The larger the pK_a the weaker the acid.
The larger the pK_b the weaker the base.

Strong acids

Strong acids (pK_a is negative) dissolve almost totally in water:

	HA	+	H_2O	$\rightarrow$	A^-	+	H_3O^+
initially:	$[HA]_{initially}$				0		0
finally:	$[HA]_{finally} \approx 0$				$[A^-]$		$[H_3O^+]$

Very small number

$$\boxed{[A^-] = [H_3O^+] = [HA]_{initially}}$$

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]_{finally}} = \frac{[HA]^2_{initially}}{[HA]_{finally}} = \text{Very large number}$$

Very small number

$$pH = -\log[H_3O^+] = -\log[HA]_{initially}$$

Strong bases

Strong bases dissolve almost totally in water:

	B	+	H_2O	$\rightarrow$	BH^+	+	OH^-
initially:	$[B]_{initially}$				0		0
finally:	$[B]_{finally} \approx 0$				$[BH^+]$		$[OH^-]$

Very small number

$$\boxed{[BH^+] = [OH^-] = [B]_{initially}}$$

$$K_b = \frac{[OH^-]\,[BH^+]}{[B]_{finally}} = \frac{[B]^2_{initially}}{[B]_{finally}} = \text{Large number}$$

Very small number

$$pOH = -\log[OH^-] = -\log[B]_{initially}$$

Examples of strong acids and bases

Strong acids:

	K_a	pK_a
H_2SO_4	10^3	-3
HNO_3	10^1	-1
HCl	10^8	-8
HBr	10^9	-9
$HClO_4$	10^{10}	-10

Strong bases:

	K_b	pK_b
LiOH	2.5	-0.4
NaOH	0.6	+0.2
KOH	0.3	+0.5

Weak acids

Weak acids (pK_a is positive) dissolve hardly at all in water:

	HA	+	$H_2O \rightleftharpoons$	A^-	+	H_3O^+
initially:	$[HA]$			0		0
finally:	$[HA]$			$[A^-]$		$[H_3O^+]$

$$\boxed{[HA]_{final} = [HA]_{initial} \text{ and } [A^-] = [H_3O^+]}$$

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]} = \frac{[H_3O^+]^2}{[HA]}$$

$$pH = -\log[H_3O^+] = -\log\sqrt{K_a[HA]}$$

Weak bases

Weak bases dissolve hardly at all in water:

	B	+	$H_2O \rightarrow$	BH^+	+	OH^-
initially:	$[B]$			0		0
finally:	$[B]$			$[BH^+]$		$[OH^-]$

$$\boxed{[B]_{final} = [B]_{initial} \text{ and } [BH^+] = [OH^-]}$$

$$K_b = \frac{[OH^-]\,[BH^+]}{[B]} = \frac{[OH^-]^2}{[B]}$$

$$pOH = -\log[OH^-] = -\log\sqrt{K_b[B]}$$

Examples of weak acids and bases

Weak acids:

	K_a	pK_a
CH_3COOH	$2x10^{-5}$	4.8
$C_6H_8O_7$	$8x10^{-4}$	3.1
H_2CO_3	$4x10^{-7}$	6.4

Weak bases:

	K_b	pK_b
NH_3	$2x10^{-5}$	4.8
CH_3NH_2	$4x10^{-4}$	3.4
$C_2H_5NH_2$	$4x10^{-4}$	3.3

Acid + Metal

Acid + Metal → Salt + Hydrogen

$$2HCl + Zn \rightarrow ZnCl_2 + H_2$$

$$2H^+ + 2Cl^- + Zn \rightarrow Zn^{2+} + 2Cl^- + H_2$$

spectator ions

effervescence
gas bubbles

Acid + Base

Acid + Base → Salt + Water

$$HCl + NaOH \rightarrow NaCl + H_2O$$

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$$

neutralisation reaction

Acid + Carbonate

Acid + Carbonate → Salt + Water + Carbon dioxide

$$2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2$$

$$2H^+ + 2Cl^- + Ca^{2+} + CO_3^{2-} \rightarrow Ca^{2+} + 2Cl^- + H_2O + CO_2$$

effervescence

Buffers

Start with a weak acids that dissolve hardly at all in water:

$HA + H_2O \rightleftarrows A^- + H_3O^+$ with $[HA]_{final} = [HA]_{initial}$

Add the salt of that acid to the water and it will dissolve completly:

$MA \rightarrow M^+ + A^-$ with $[A^-] = [MA]$

In this way one has a solution with a high concentration of both HA and A^-

If one add a little bit of acid (i.e. H_3O^+) it will react with A^-

$A^- + H_3O^+ \rightarrow HA + H_2O$

but there is a lot of A^- so the pH will not change much.

If one add a little bit of base (i.e. OH^-) it will react with HA

$HA + OH^- \rightarrow A^- + H_2O$

but there is a lot of HA so the pH will not change much.

Buffer equations

Weak acid + salt: $[H_3O^+] = K_a \frac{[Acid]}{[Salt]}$

$$pH = pK_a + \log \frac{[Salt]}{[Acid]} = pKa$$

If [Acid] = [Salt]

Weak base + salt: $[OH^-] = K_b \frac{[Base]}{[Salt]}$

$$pOH = pK_b + \log \frac{[Salt]}{[Base]} = pKb$$

If [Base] = [Salt]

Salt Hydrolysis

Salt hydrolysis is the reverse of neutralization

Salt + Water → Acid + Base

$MA + H_2O \rightarrow M^+ + A^-$

$+ H_2O \rightleftharpoons HA + OH^-$ K_b

$+ H_2O \rightleftharpoons MOH + H^+$ K_a

Ka = Kb the solution is neutral

Ka > Kb the solution is acidic

Ka < Kb the solution is basic

Spectator ions comes from the neutralization of very strong acids and bases and they hardly react with water at all.

Group 1: Li^+ Na^+ K^+ Rb^+ Cs^+ Fr^+

Group 2: Be^+ Mg^{2+} Ca^{2+} Ba^{2+} Sr^{2+} Ra^{2+}

$MA + H_2O \rightarrow M^+ + A^-$

I^- Br^- Cl^- NO_3^- ClO_4^-

Does a salt give an acid or a base ?

There are 4 possibilites depending on how the salt is made.

$\times$ = spectator

How the salt is made: Strong base + Strong acid

1) $MA + H_2O \rightarrow \cancel{M^+} + \cancel{A^-}$ Neutral

acid + base

How the salt is made: Weak base + Strong acid

2) $MA + H_2O \rightarrow M^+ + \cancel{A^-}$ Weak acid

acid + base

$+ H_2O \rightleftharpoons MOH + H^+$

How the salt is made: Strong base + Weak acid

3) $MA + H_2O \rightarrow \cancel{M^+} + A^-$ Weak base

acid + base

$+ H_2O \rightleftharpoons HA + OH^-$

How the salt is made: Weak base + Weak acid

4) $MA + H_2O \rightarrow M^+ + A^-$ Depends (on Ka and Kb)

acid + base

$+ H_2O \rightleftharpoons HA + OH^-$

$+ H_2O \rightleftharpoons MOH + H^+$

Rules regarding salt hydrolysis

Spectators

Group 1: Li^+ Na^+ K^+ Rb^+ Cs^+ Fr^+

Group 2: Be^+ Mg^{2+} Ca^{2+} Ba^{2+} Sr^{2+} Ra^{2+}

$$MA + H_2O \rightarrow M^+ + A^-$$

I^- Br^- Cl^- NO_3^- ClO_4^-

$$MA + H_2O \rightarrow \cancel{M^+} + \cancel{A^-}$$

Neutral

Comes from Strong Base + Strong Acid

$$MA + H_2O \rightarrow M^+ + \cancel{A^-}$$

Weak acid

$$+ H_2O \rightleftharpoons MOH + H^+$$

Comes from Weak Base + Strong Acid

$$MA + H_2O \rightarrow \cancel{M^+} + A^-$$

Weak base

$$+ H_2O \rightleftharpoons HA + OH^-$$

Comes from Strong Base + Weak Acid