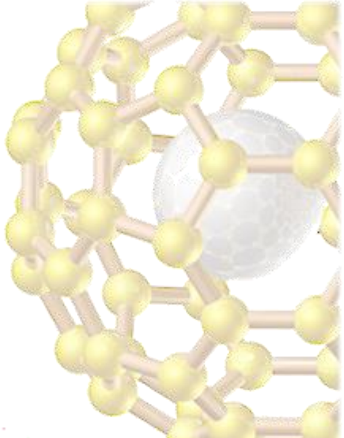
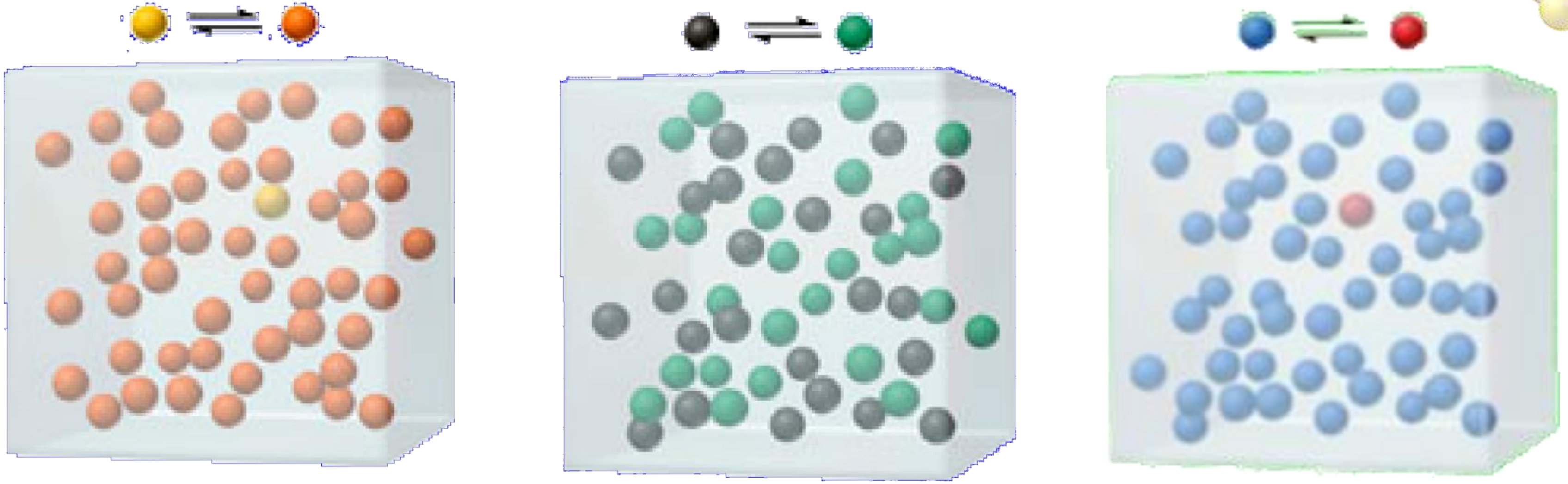
AH Chemistry – Unit 1

Chemical Equilibrium

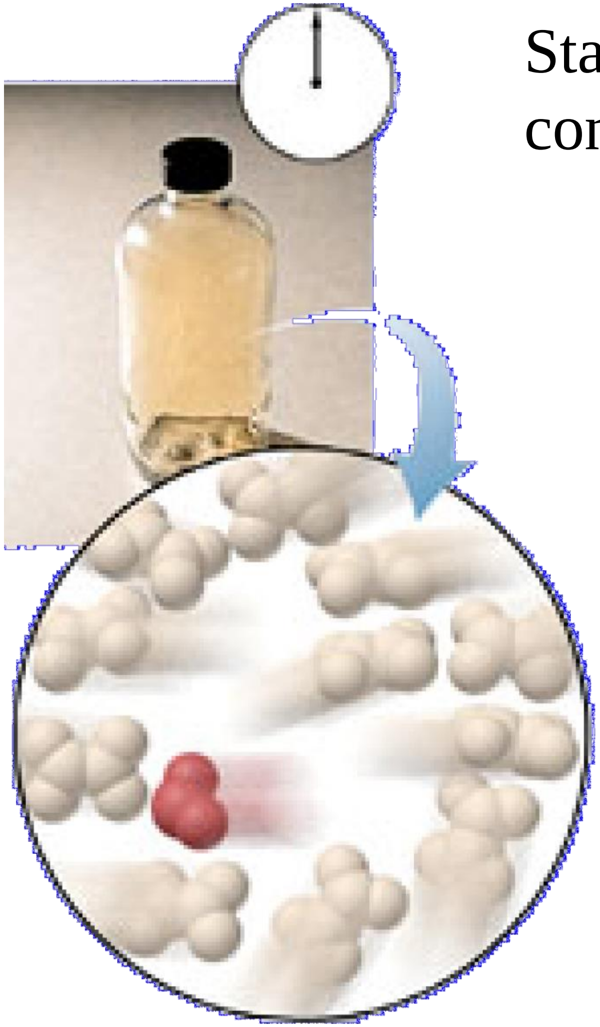
Introduction



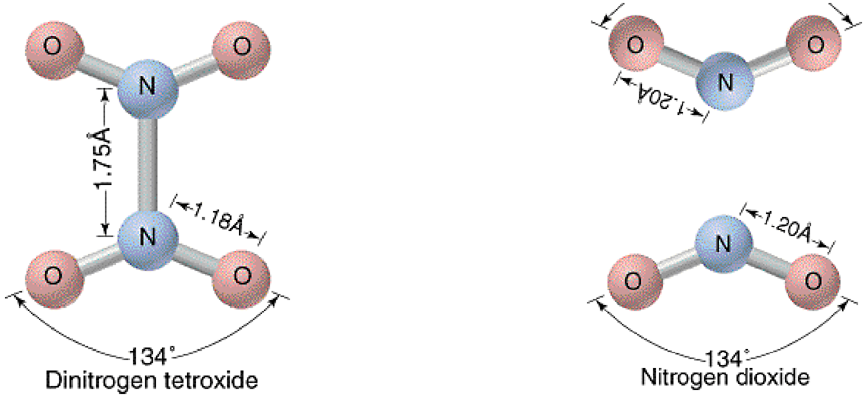


This topic explores various aspects of ***Reversible Reactions***, leading to an appreciation of the importance of ***Equilibria*** in Chemistry.

Attaining Equilibrium 1

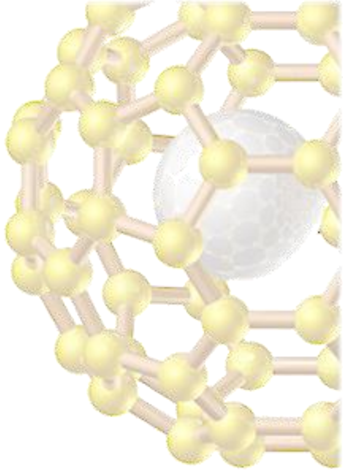


Starting with a frozen sample containing the dimer, $N_2O_{4(g)}$

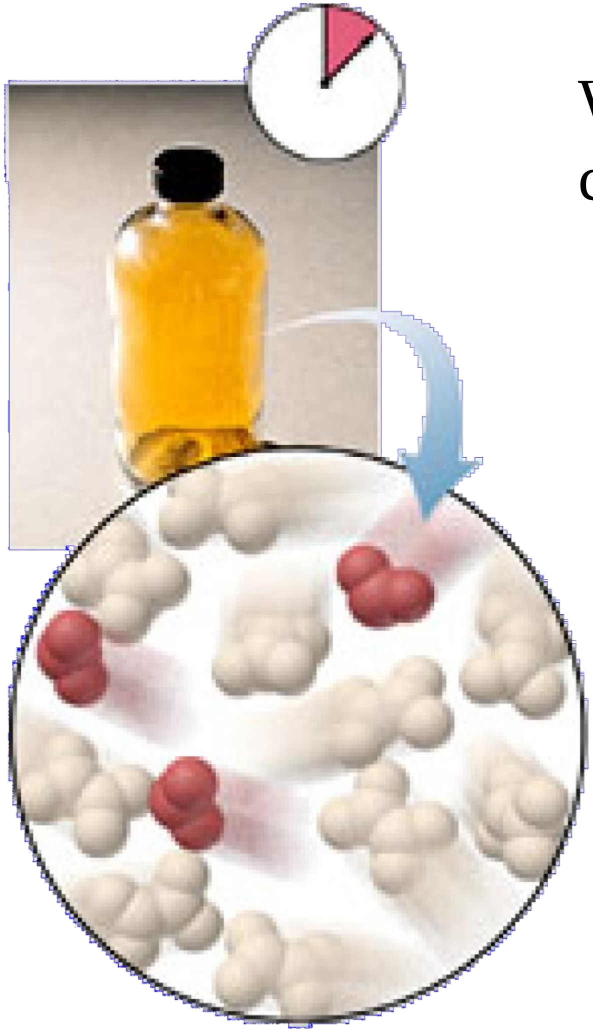


As the sample warms up the only reaction will be:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$



Attaining Equilibrium 2



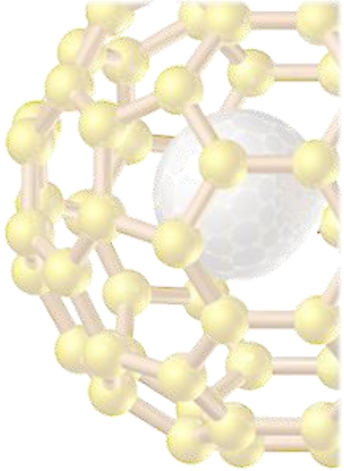
When enough NO_2 has formed, it can react to form N_2O_4.

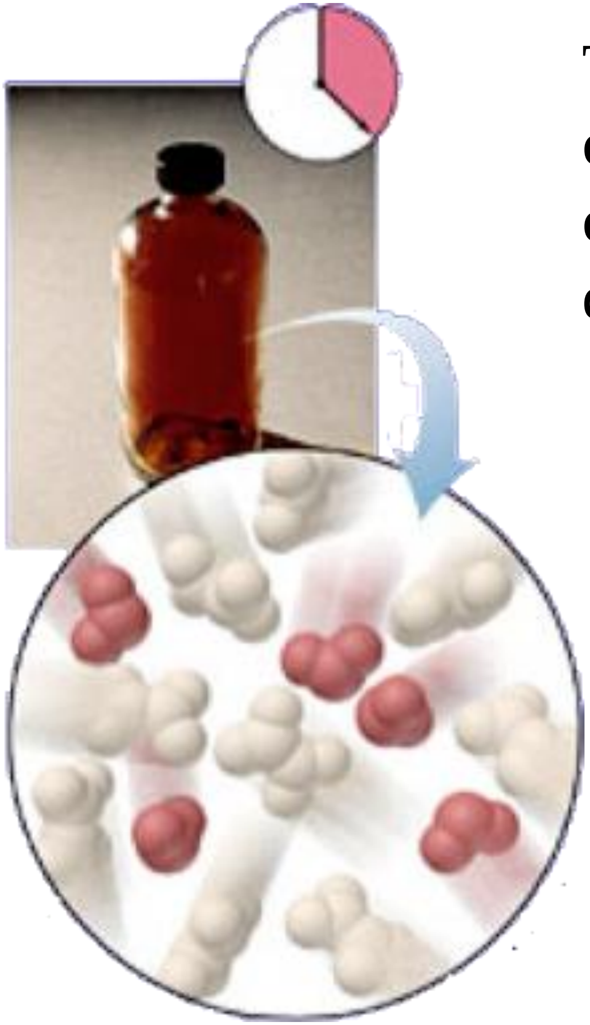
$$2NO_{2(g)} \square N_2O_{4(g)}$$

At this stage the forward reaction will still be faster:

$$N_2O_4 \rightleftharpoons 2NO_2$$

Attaining Equilibrium 3

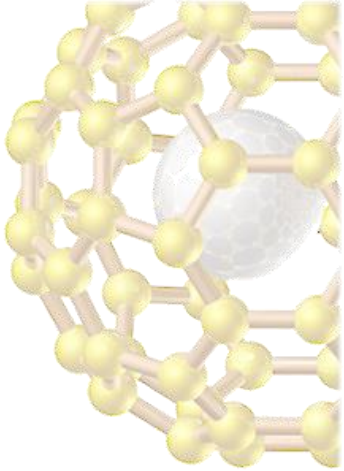




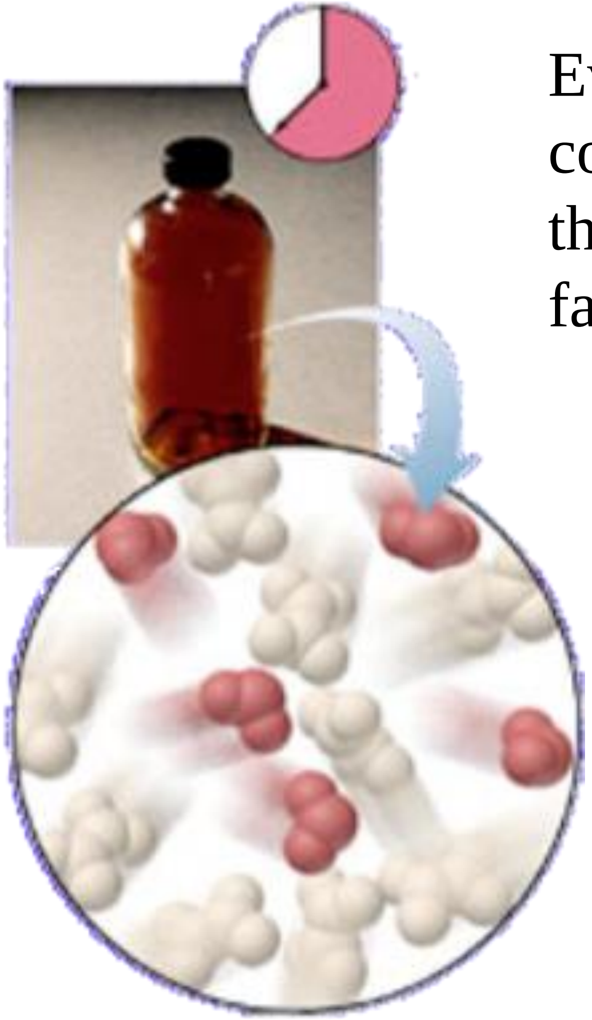
The concentration of NO_2 will continue to increase while the concentration of N_2O_4 will decrease.

At normal temperatures, the reverse reaction is more favoured, but the high concentration of N_2O_4 means:

$$\mathbf{N_2O_4 \rightleftharpoons 2NO_2}$$



Attaining Equilibrium 4

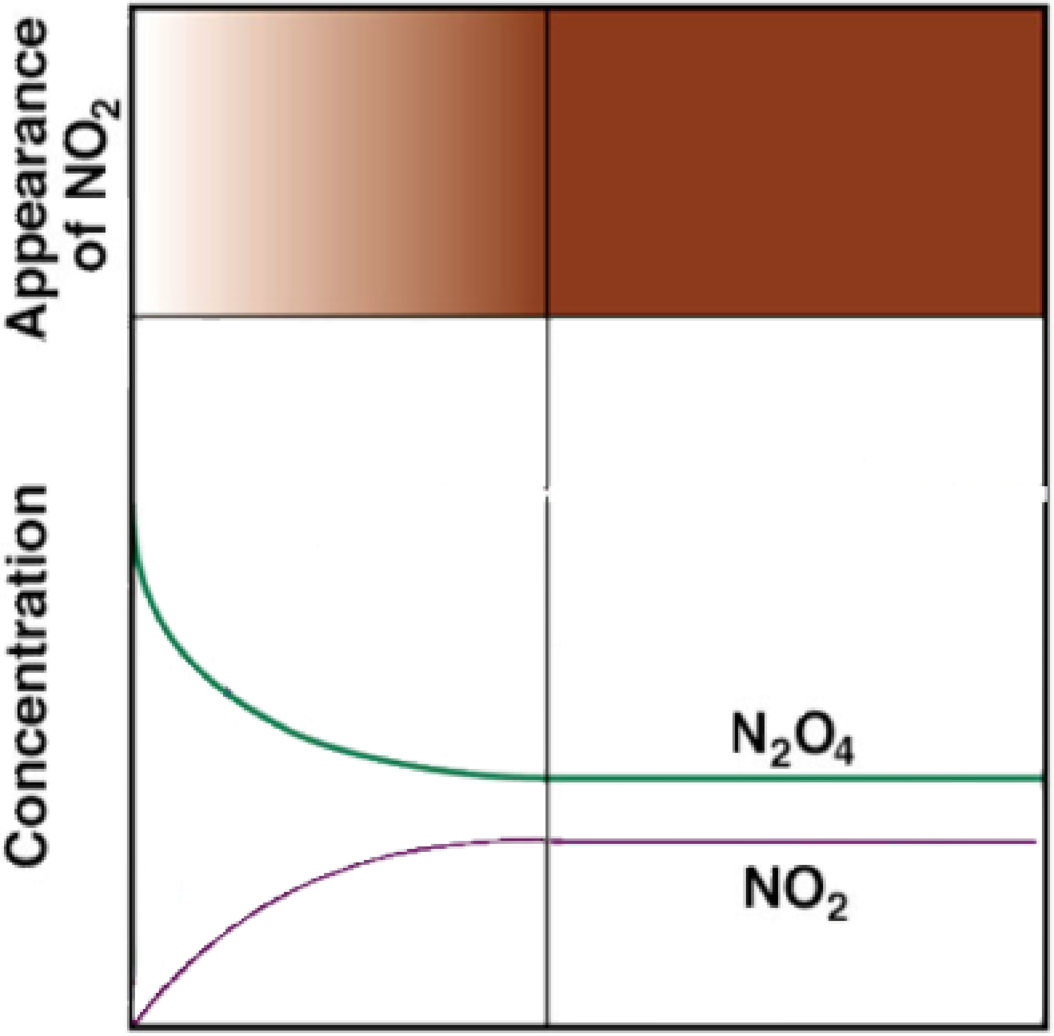


Eventually, however, the rising concentration of NO_2 means that the reverse reaction will become as fast as the forward reaction:

$$\mathbf{N_2O_4 \rightleftharpoons 2NO_2}$$

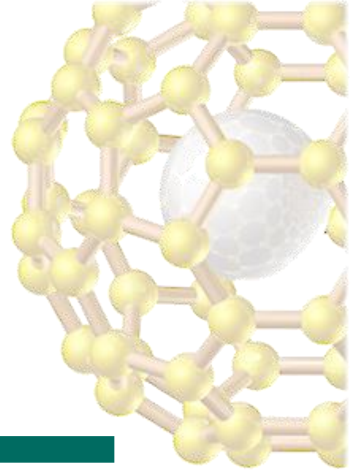
From now on the concentrations of N_2O_4 and NO_2 will not change - the reaction will have reached ***equilibrium***.

Attaining Equilibrium 5



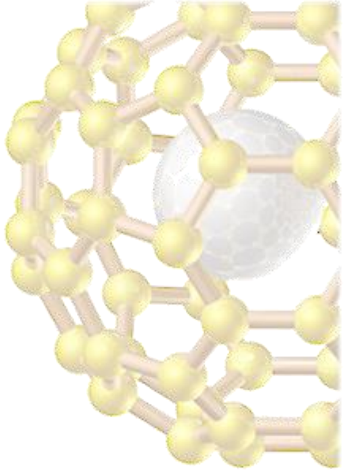
Equilibrium Constant 1

Initial and Equilibrium Concentrations for the N_2O_4 - NO_2 System at 100° C



Initial		Equilibrium		Ratio
$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[NO_2]^2/[N_2O_4]$
0.1000	0.0000	0.0491	0.1018	0.211
0.0000	0.1000	0.0185	0.0627	0.212
0.0500	0.0500	0.0332	0.0837	0.211
0.0750	0.0250	0.0411	0.0930	0.210

Equilibrium Constant 2



No matter the starting composition of reactants and products, the same ratio of concentrations is achieved at equilibrium.

For a general reaction

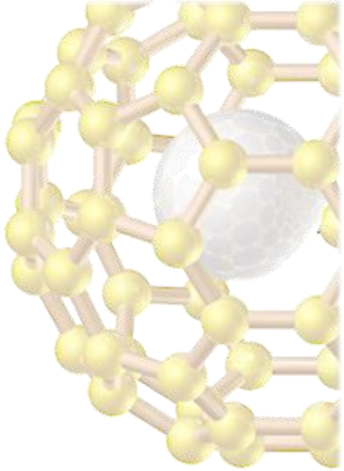
$$aA + bB \rightleftharpoons pP + qQ$$

the equilibrium constant expression is

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[P]^p[Q]^q}{[A]^a[B]^b}$$

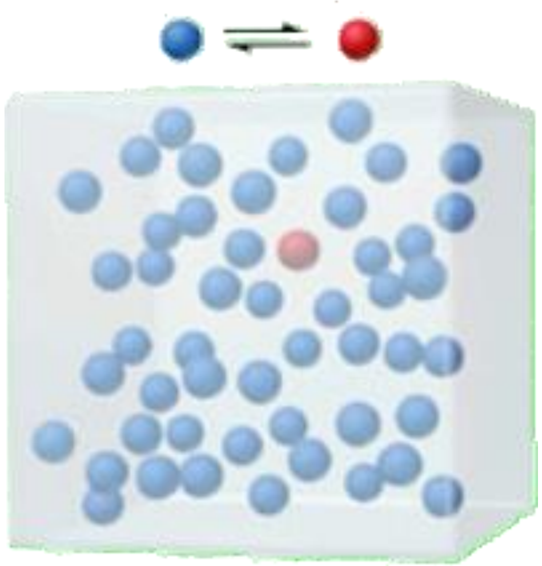
where K_c is the equilibrium constant.

Equilibrium Constant 3



The equilibrium constant provides information about which of the reactions is ***most favoured*** at that particular temperature

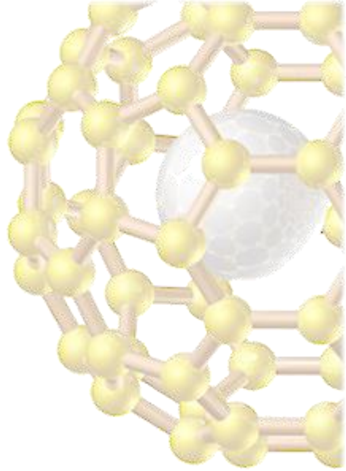
K small $\mathbf{N_{2(g)} + O_{2(g)} \rightleftharpoons 2\,NO_{(g)}}$ $K = 1 \times 10^{-30}$



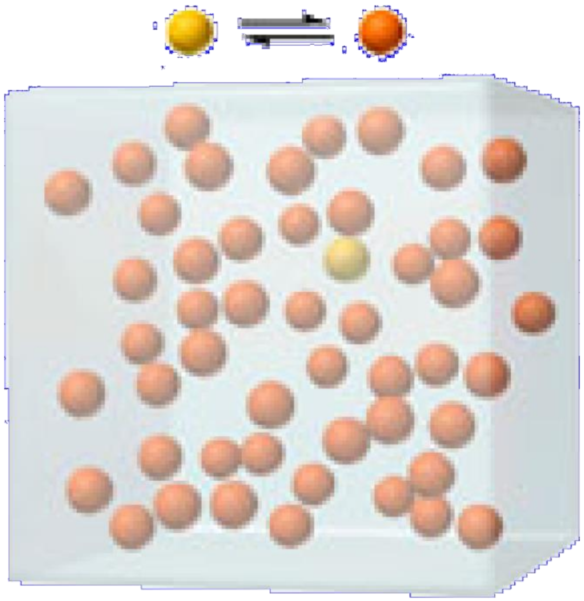
You would predict that under most conditions there would be very little NO produced.

Equilibrium position likely to lie ***well over to left***

Equilibrium Constant 4



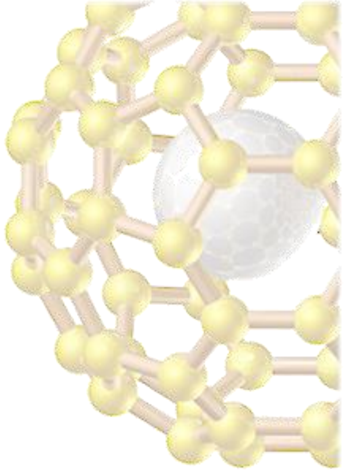
K large $\mathbf{2CO_{(g)} + O_{2(g)} \rightleftharpoons 2\,CO_{2(g)}}$ K = 2 x 10^{22}



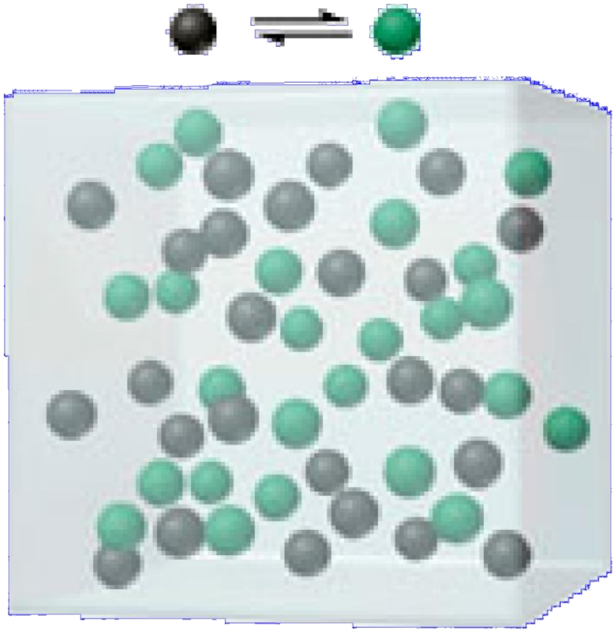
You would predict that under most conditions there would be very little CO left.

Equilibrium position likely to lie ***well over to right***

Equilibrium Constant 5

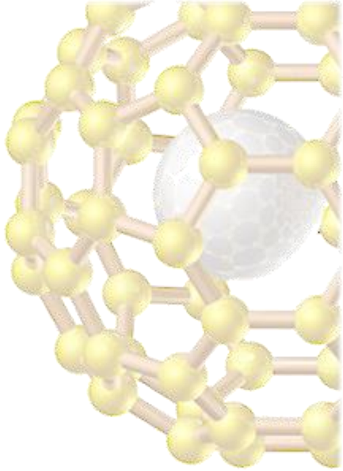


Intermediate K $2BrCl_{(g)} \rightleftharpoons Br_{2(g)} + Cl_{2(g)}$ K = 5



You would predict that under most conditions there would be reasonable amounts of BrCl, Br_2 and Cl_2.

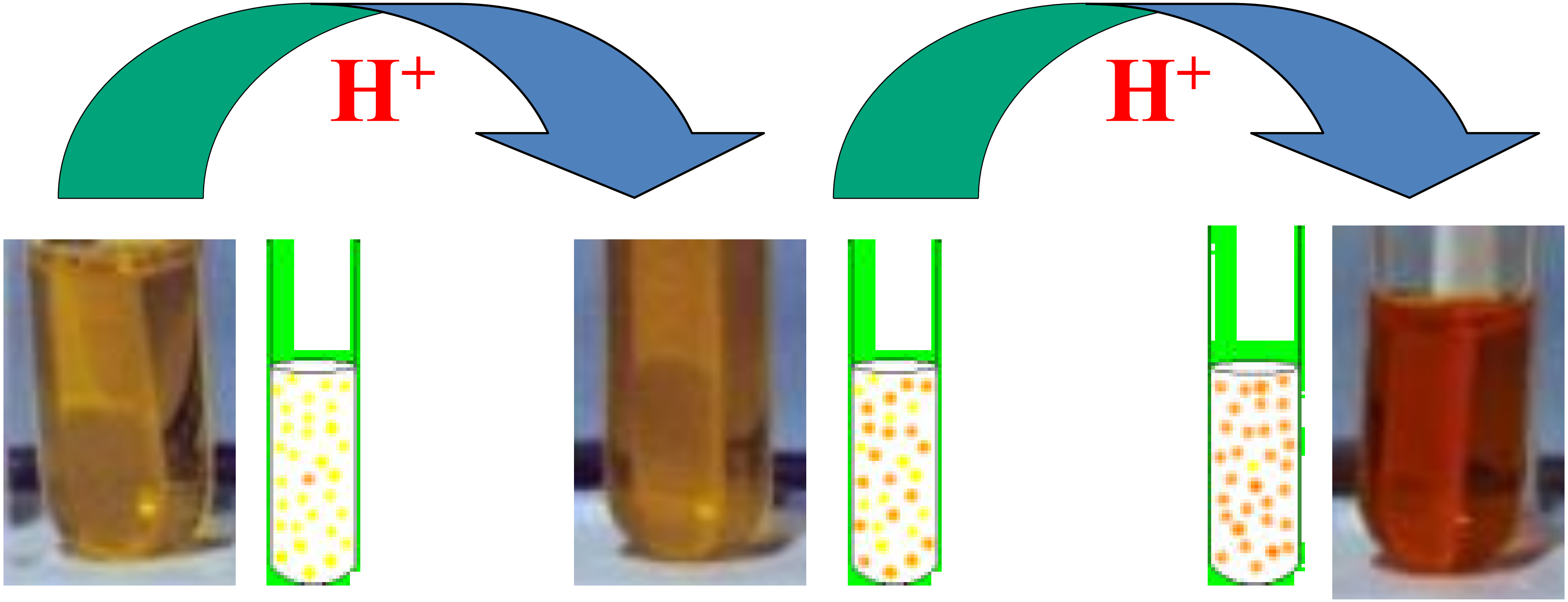
Equilibrium position likely to lie somewhere ***in the middle***

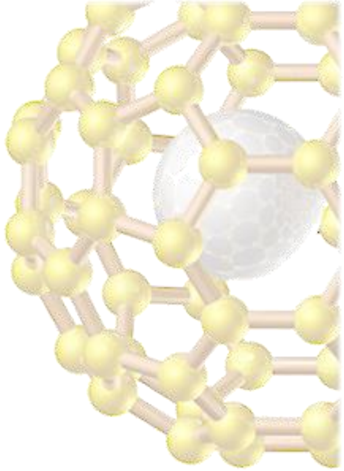


Equilibrium Position and K

Consider the chromate/dichromate equilibrium

$$2CrO_4^{2-}{}_{(aq)} + 2H^+ \rightleftharpoons Cr_2O_7^{2-}{}_{(aq)} + H_2O_{(l)}$$





Equilibrium Position and K

$$2CrO_4^{2-}{}_{(aq)} + 2H^+ \rightleftharpoons Cr_2O_7^{2-}{}_{(aq)} + H_2O_{(l)}$$

Visually, we would see the mixture change from yellow to orange.

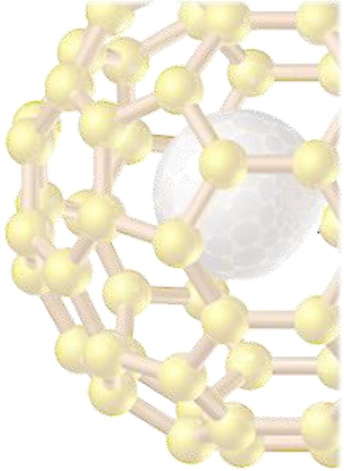
We would say that the equilibrium has shifted to the right.

We might talk in terms of [Products] increasing
[Reactants] decreasing

Does this mean that K has increased, since

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

Equilibrium Position and K



$$2CrO_4^{2-}{}_{(aq)} + 2H^+ \rightleftharpoons Cr_2O_7^{2-}{}_{(aq)} + H_2O_{(l)}$$

In fact, K is not just about CrO_4^{2-} and $Cr_2O_7^{2-}$:

$$K_c = \frac{[Cr_2O_7^{2-}]\,[H_2O]}{[CrO_4^{2-}]^2\,[H^+]^2}$$

$[H_2O]$ will be so large that any change will be negligible

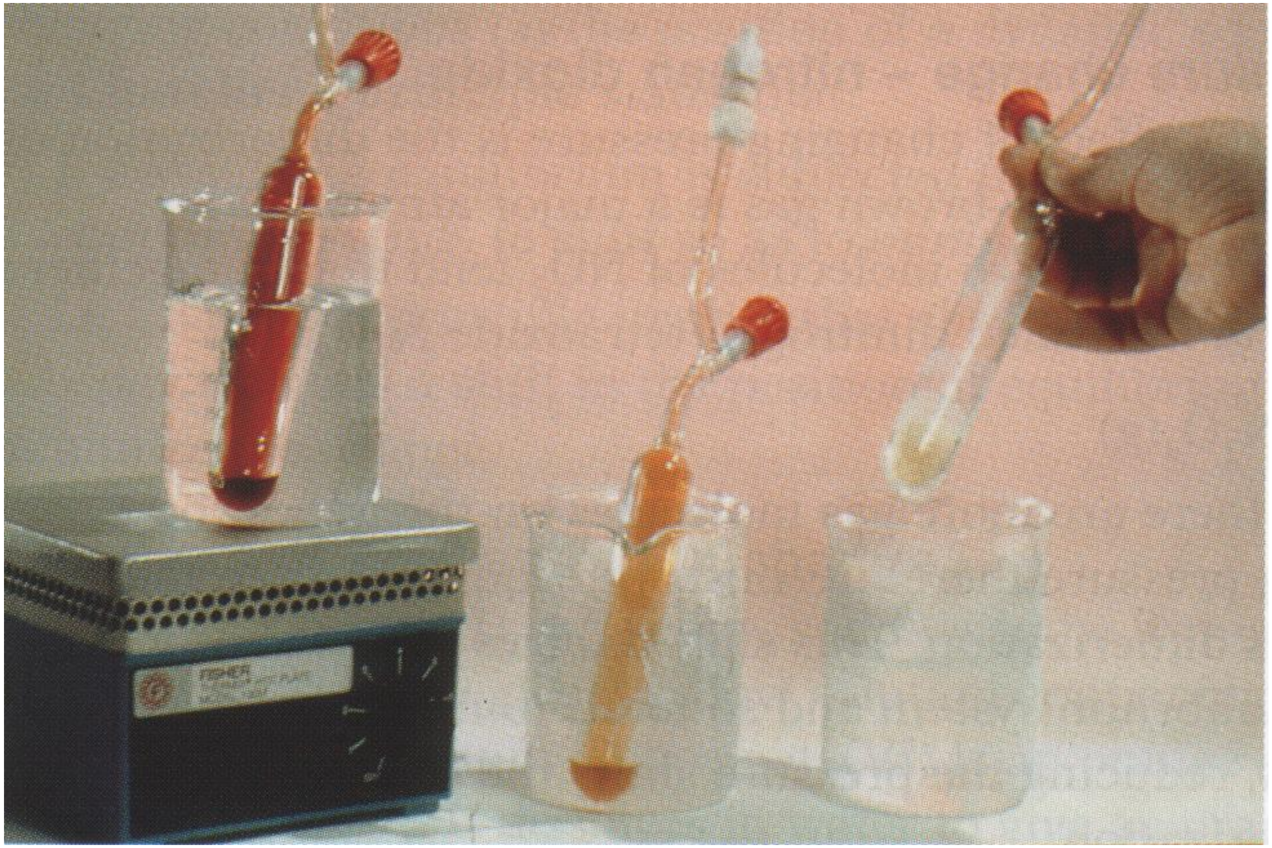
$[H^+]$ will have increased

Overall the ratio of products to reactants will ***remain the same***.

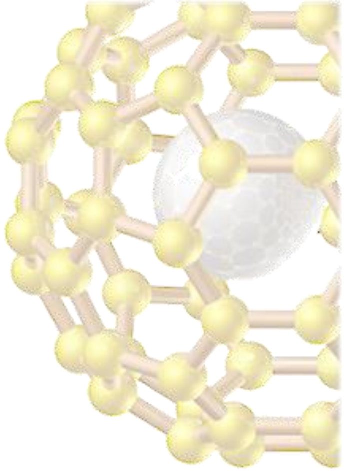
K_c is ***a constant*** that is unaffected by changes in concentration.

Effect of Temperature 1

$$N_2O_4 \rightleftharpoons 2NO_2$$



Effect of Temperature 2



$$N_2O_4 \rightleftharpoons 2NO_2$$

Low temperature favours the ***exothermic*** reaction:

$$N_2O_4 \leftharpoondown 2NO_2$$

The ***equilibrium position*** will shift to the left.

$$N_2O_4 \leftharpoondown 2NO_2$$

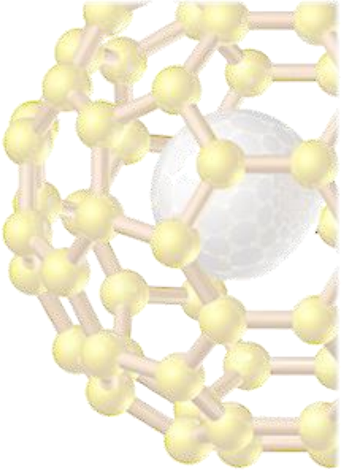
[Reactants] increases

[Products] decreases

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

As temperature drops the value of K will decrease. K is ***temperature dependent***.

Effect of Temperature 3



$$N_2O_4 \rightleftharpoons 2NO_2$$

High temperature favours the ***endothermic*** reaction:

$$N_2O_4 \longrightarrow 2NO_2$$

The ***equilibrium position*** will shift to the right.

$$N_2O_4 \longrightarrow 2NO_2$$

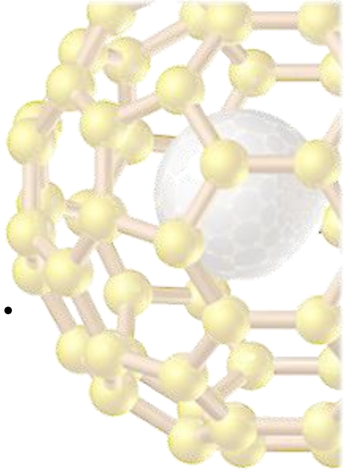
[Reactants]
decreases

[Products]
increases

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

As temperature drops the value of K will increase. K is ***temperature dependent***.

Effect Of a Catalyst



A catalyst lowers the activation energy barrier for a reaction.

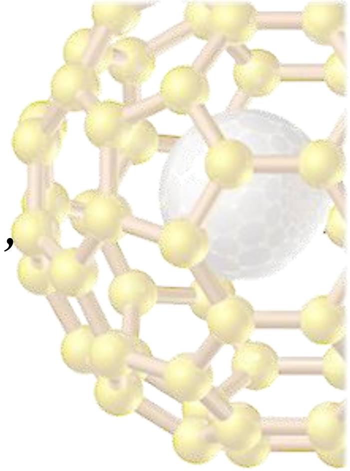
A catalyst speeds up a reaction.

A catalyst lowers the activation energy for the forward and the backward reaction equally.

Therefore, a catalyst will decrease the time taken to reach equilibrium.

A catalyst does not effect the composition of the equilibrium mixture.

Effective Concentrations



In some circumstances chemicals don’t ‘*punch their weight’*

e.g. 0.1 M Na Cl has a conductivity of 80.

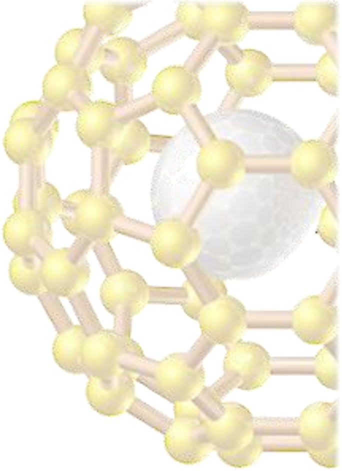
0.2 M NaCl has twice as many ions but its conductivity is 120 not 160

At the higher concentration, there are more and stronger interactions between ions and their conductivity is reduced as a result.

The 0.2 M Na Cl is behaving as if it has an ***effective concentration*** of 0.15 M.

Though beyond the scope of the Advanced Higher Course, we need The concept of effective concentration to explain units of K.

Units for Equilibrium Constants

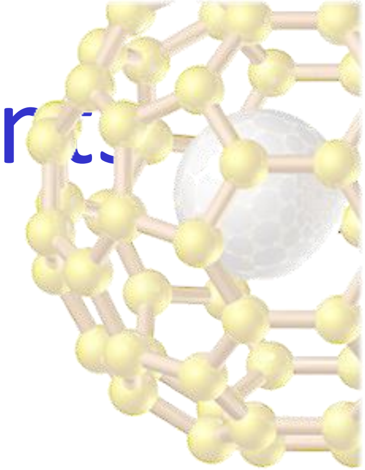


Strictly speaking K is based on ***effective concentrations*** present in the equilibrium mixture rather than ***actual concentrations***.

A value known as the ***activity***, a, is used, which is a measure of the effective concentration relative to a standard concentration.

$$a(P) = \frac{\text{effective [P]}}{\text{standard [P]}} \qquad K_c = \frac{a(P)^q}{a(R)^s}$$

Units for Equilibrium Constants



$$a(P) = \frac{\text{effective [P]}}{\text{standard [P]}} \qquad K_c = \frac{a(P)^q}{a(R)^s}$$

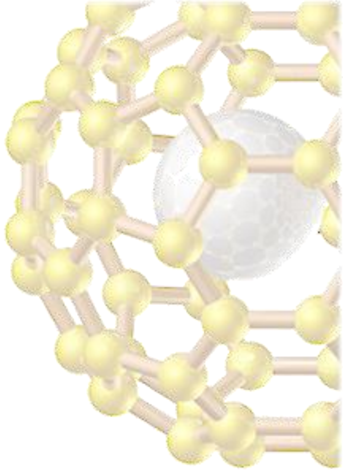
The significant point is that activities involve dividing a concentration in mol l^{-1} by another concentration in mol l^{-1}.

Activities, *a*, are ***without units*** and so, therefore, is K.

Standard concentration is 1 mol l^{-1} and at low concentrations, effective concentration is very close to actual concentration.

This allows us to use actual concentrations to calculate K - but assigning units to K is pointless (and wrong!).

Gas Equilibria



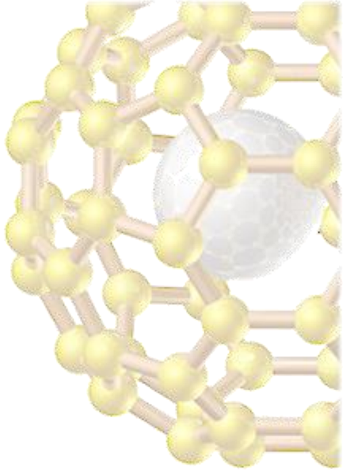
Though we could use moles l^{-1} to describe the ‘concentration’ of a gas, it’s not really satisfactory.

Physicists will know that (for an ideal gas):

$$PV = n\,R\,T$$

where,

P = pressure
V = volume
n = moles of gas
R = a constant
T = temperature



Gas Equilibria

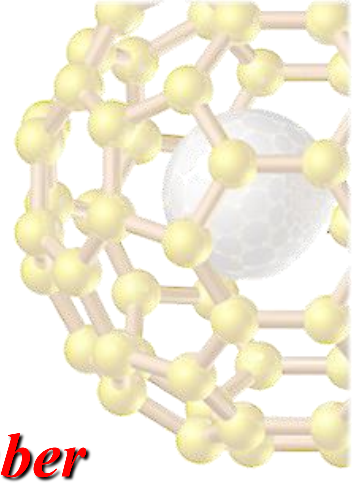
$$PV = n R T$$

From this equation we can see that:

P is proportional to n / V

Therefore, we can use pressures instead of concentrations in our equilibrium expression.

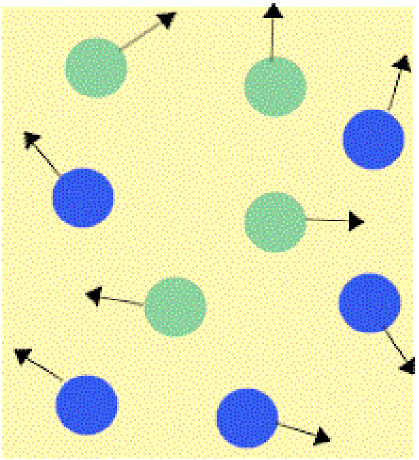
But there is only one value for pressure, even if there is a mixture of gases.



Partial Pressures

However, pressure depends on a ***number*** of gas particles pushing against a surface.

The pressure of a mixture of gases is due to the ***total number*** of particles present.

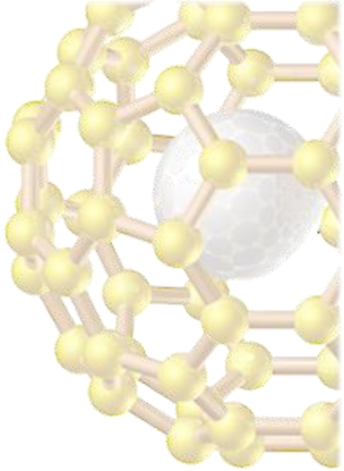


The pressure exerted by a particular group of particles is called their ***partial pressure*** and is:

Partial pressure = (particles in group/ particles in total) x P

Partial pressures, or even moles, of gases can be used in to derive equilibrium constants.

Special K - Solubility Products



The dissolving of a substance can be considered a reversible reaction:

$$\mathbf{Ba^{2+}SO_4{}^{2-}{}_{(s)} + aq \rightleftharpoons Ba^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}}$$

$$\mathbf{K = \frac{[\,Ba^{2+}\,][\,SO_4{}^{2-}\,]}{[\,Ba^{2+}SO_4{}^{2-}\,][\,aq\,]}}$$

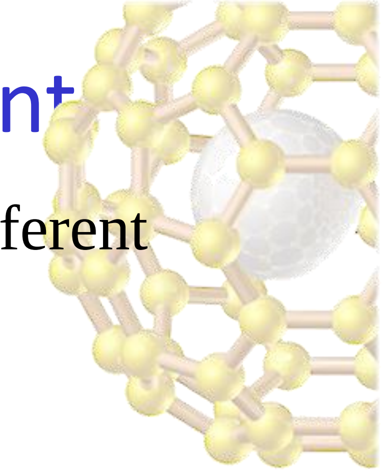
$[Ba^{2+}SO_4{}^{2-}]$ has activity of 0

[aq] remains constant

$$\mathbf{K_{sp} = [\,Ba^{2+}\,][\,SO_4{}^{2-}\,]}$$

This gives a much better measure of solubility.

Special K - Partition Coefficient



When a solute is soluble in two different immiscible solvents, the following equilibrium is set up:

$$\mathbf{K} = \frac{\textbf{[solute] in solvent A}}{\textbf{[solute] in solvent B}}$$

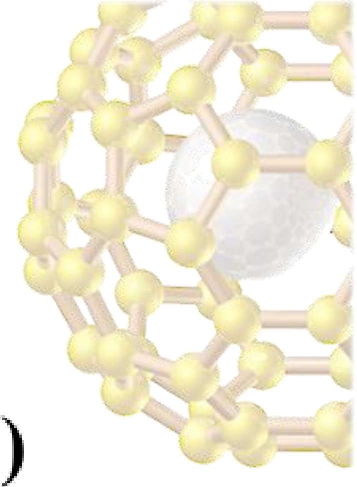
Applications of partition coefficients include:

solvent extraction

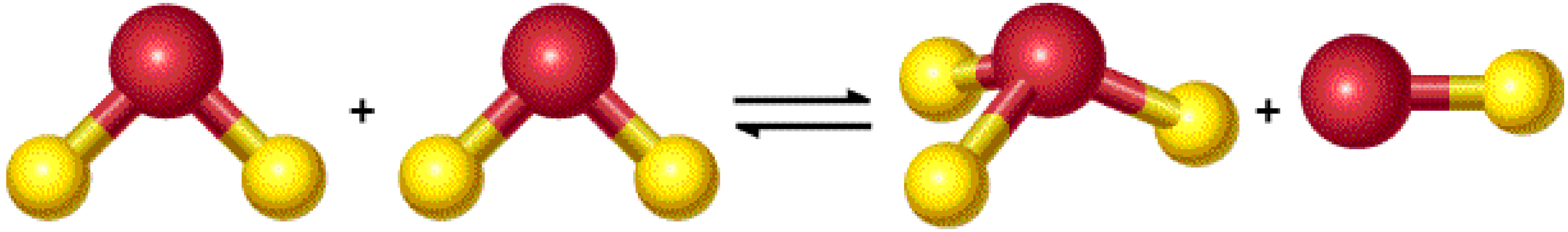
paper chromatography

gas chromatography

Acid Base Equilibria

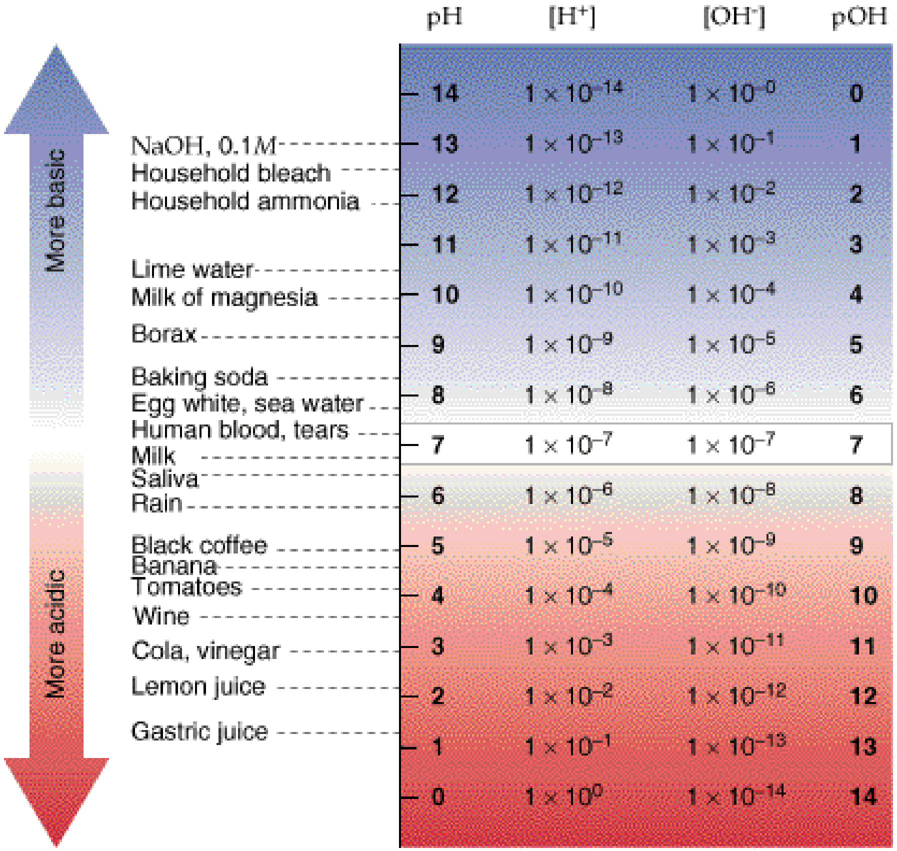


$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

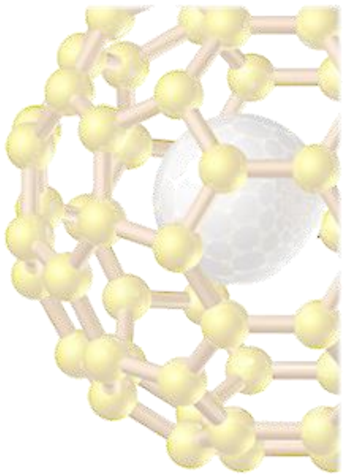


This topic explores various aspects of ***Equilibria involving ions***, leading to a greater understanding of ***Weak Acids*** and ***Weak Bases***.

pH & pH Scale



pH	$[H^+]$	$[OH^-]$	pOH
14	1×10^{-14}	1×10^{-0}	0
13	1×10^{-13}	1×10^{-1}	1
12	1×10^{-12}	1×10^{-2}	2
11	1×10^{-11}	1×10^{-3}	3
10	1×10^{-10}	1×10^{-4}	4
9	1×10^{-9}	1×10^{-5}	5
8	1×10^{-8}	1×10^{-6}	6
7	1×10^{-7}	1×10^{-7}	7
6	1×10^{-6}	1×10^{-8}	8
5	1×10^{-5}	1×10^{-9}	9
4	1×10^{-4}	1×10^{-10}	10
3	1×10^{-3}	1×10^{-11}	11
2	1×10^{-2}	1×10^{-12}	12
1	1×10^{-1}	1×10^{-13}	13
0	1×10^{0}	1×10^{-14}	14



In most solutions $[H^+]$ is quite small.

For strong acids it is usually easy to convert [acid] □ $[H^+]$

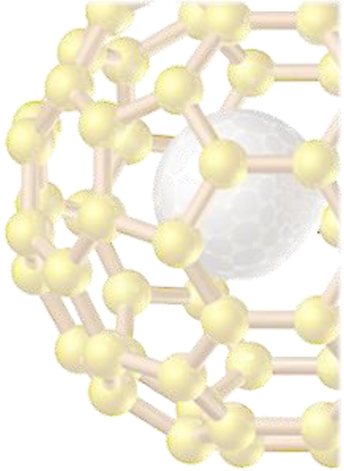
Then:

$$pH = -\log[H^+]$$

and:

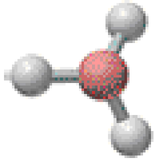
$$pOH = -\log[OH^-]$$

The H^+ Ion in Water



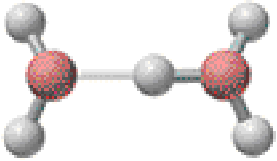
The $H^+_{(aq)}$ ion is simply a ***proton*** with no electrons.

In water, the $H^+_{(aq)}$ form clusters.

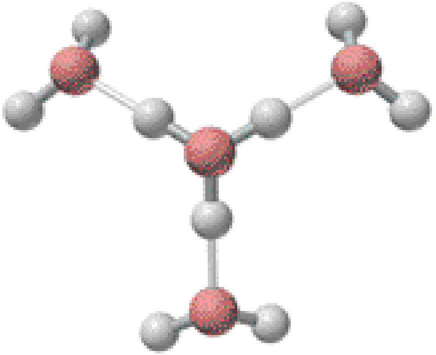


The simplest cluster is $H_3O^+_{(aq)}$.

(Called the ***hydronium ion***)

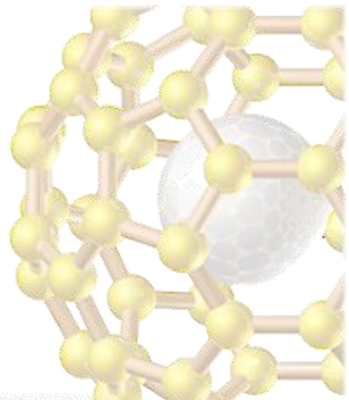


Larger clusters are $H_5O_2^+$ and $H_9O_4^+$.

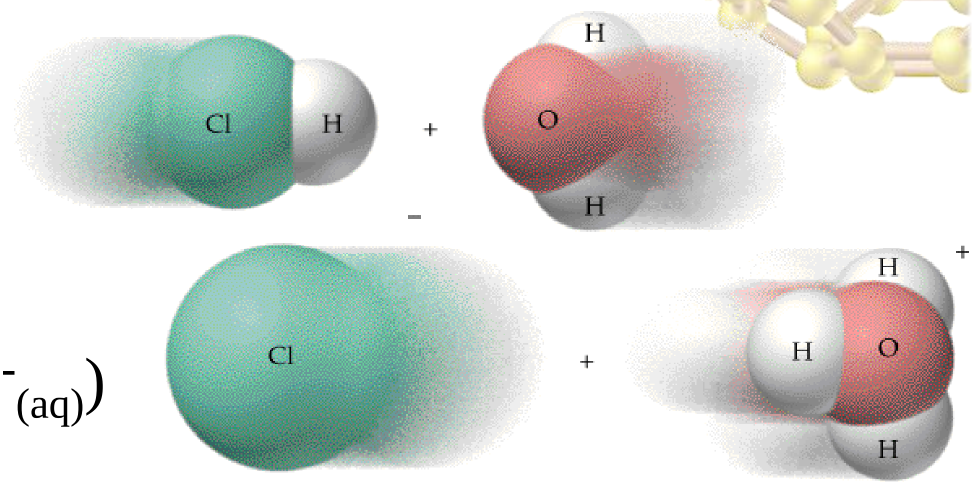


Generally we use $H^+_{(aq)}$ and $H_3O^+_{(aq)}$ interchangeably.

Brønsted-Lowry Acids and Bases



All about the $H^+_{(aq)}$ ion.



Brønsted-Lowry ***acid donates H^+***

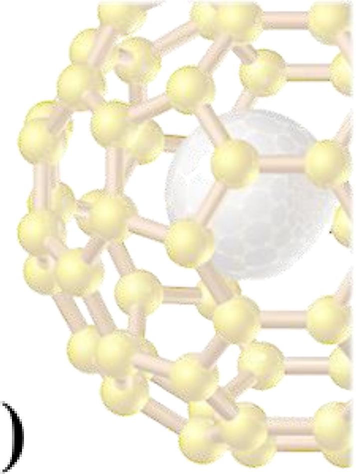
Brønsted-Lowry ***base accepts H^+***

(Base does not need to contain $OH^-_{(aq)}$)

Consider $HCl_{(aq)} + H_2O_{(l)}$ □ $H_3O^+_{(aq)} + Cl^-_{(aq)}$:

HCl ***donates a proton*** to water. Therefore, HCl is an ***acid***

H_2O ***accepts a proton*** from HCl. Therefore, H_2O is a ***base***



Ionic Product of Water

In pure water the following equilibrium is established

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

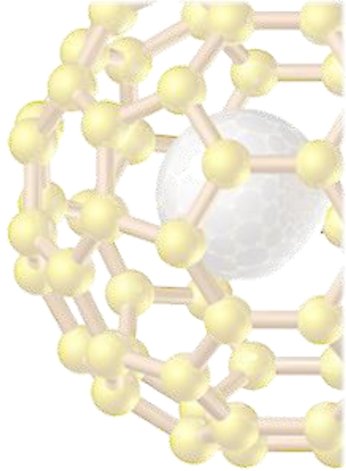
At 25° C (298K)

$$K_c = \frac{[H_3O^+]\,[OH^-]}{[H_2O]^2}$$

$$K_c\,[H_2O]^2 = [H_3O^+]\,[OH^-]$$

$$K_w = [H_3O^+]\,[OH^-] = 1.0 \text{ x } 10^{-14}$$

$$K_w = [H^+]\,[OH^-] = 1.0 \text{ x } 10^{-14}$$



Amphoteric Nature of Water

Amphoteric substances can behave as acids and bases.

Al_2O_3 is an example of an amphoteric substance:

$$Al_2O_{3(l)} + 6HCl_{(aq)} \rightarrow 2AlCl_{3(aq)} + 3H_2O_{(l)}$$

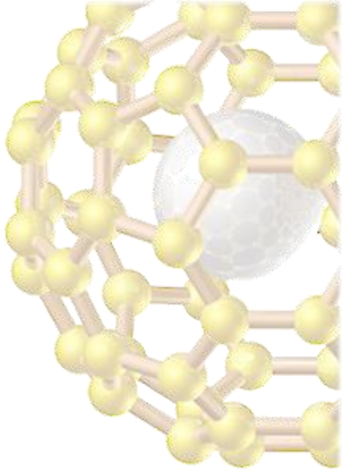
$$Al_2O_{3(l)} + 2NaOH_{(aq)} + 3H_2O_{(l)} \rightarrow 2Na[Al(OH)_4]_{(aq)}$$

Water can behave as either an acid or a base.
Water is ***amphoteric***.

The ionisation of water can be represented by:

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq}$$

Conjugate Acid-Base Pairs



Whatever is left of the acid after the proton is donated is called its ***conjugate base***.

$HCl_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$

acid ***conjugate base***

$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$

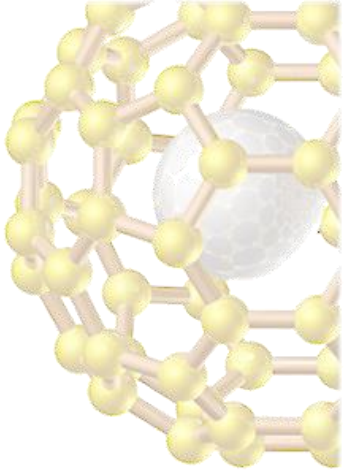
acid ***conjugate base***

$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$

acid ***conjugate base***

Conjugate acid-base ***pairs*** differ by only one proton.

Conjugate Acid-Base Pairs



Similarly, whatever is left of the base after it accepts a proton is called its ***conjugate acid***.

$NH_{3(aq)} + H_3O^+_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + H_2O_{(l)}$

base ***conjugate acid***

$CO_3^{2-}{}_{(aq)} + H_3O^+_{(aq)} \rightleftharpoons HCO_3^-{}_{(aq)} + H_2O_{(l)}$

base ***conjugate acid***

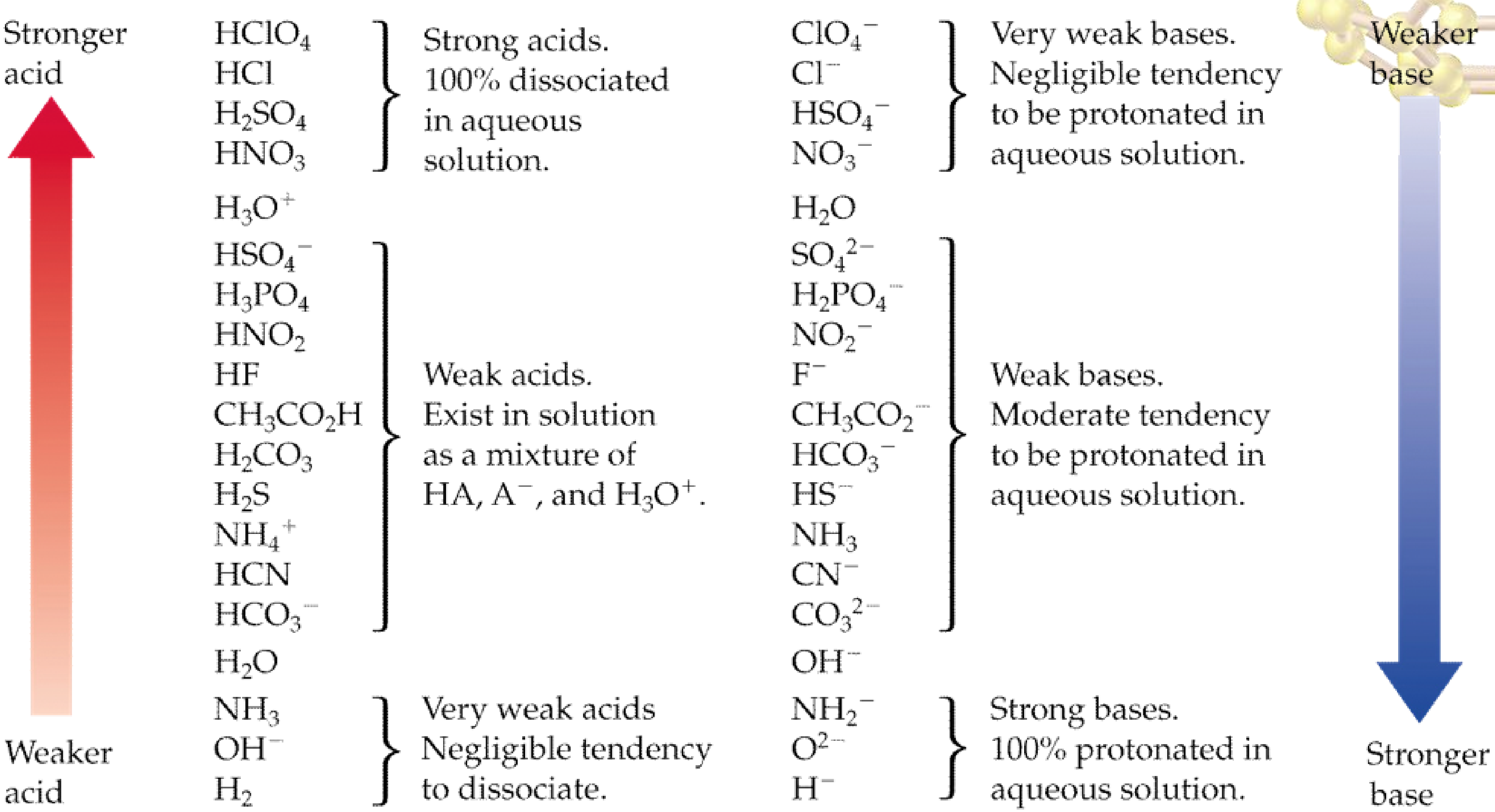
$OH^-_{(aq)} + H_3O^+_{(aq)} \rightleftharpoons H_2O_{(l)} + H_2O_{(l)}$

base ***acid*** ***conjugate acid*** ***conjugate base***

Conjugate acid-base ***pairs*** differ by only one proton.

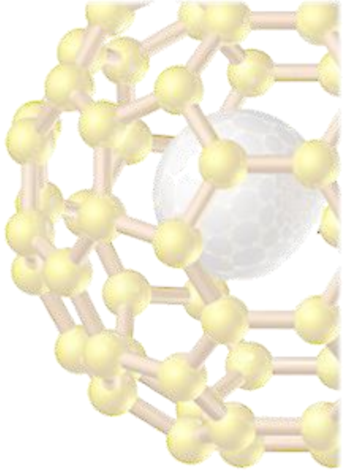
Relative Strengths

The stronger the acid, the weaker the conjugate base.



Acid strength	Acid		Base		Base strength
Stronger acid	$HClO_4$	Strong acids. 100% dissociated in aqueous solution.	ClO_4^-	Very weak bases. Negligible tendency to be protonated in aqueous solution.	Weaker base
	HCl		Cl^-		
	H_2SO_4		HSO_4^-		
	HNO_3		NO_3^-		
	H_3O^+		H_2O		
	HSO_4^-	Weak acids. Exist in solution as a mixture of HA, A^-, and H_3O^+.	SO_4^{2-}	Weak bases. Moderate tendency to be protonated in aqueous solution.	
	H_3PO_4		$H_2PO_4^-$		
	HNO_2		NO_2^-		
	HF		F^-		
	CH_3CO_2H		$CH_3CO_2^-$		
	H_2CO_3		HCO_3^-		
	H_2S		HS^-		
	NH_4^+		NH_3		
	HCN		CN^-		
	HCO_3^-		CO_3^{2-}		
	H_2O		OH^-		
Weaker acid	NH_3	Very weak acids Negligible tendency to dissociate.	NH_2^-	Strong bases. 100% protonated in aqueous solution.	Stronger base
	OH^-		O^{2-}		
	H_2		H^-		

Strong Acids



The strongest common acids are HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$, and H_2SO_4.

All strong acids ***ionise completely*** in solution:

$$HNO_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + NO_3^-{}_{(aq)}$$

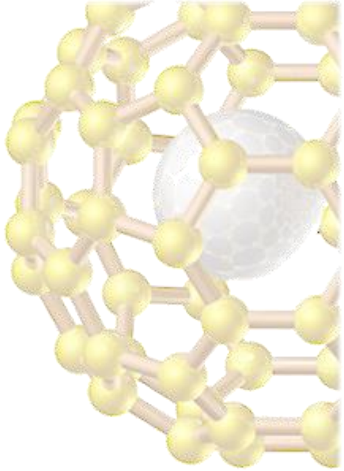
Since H^+ and H_3O^+ are used interchangeably, we write:

$$HNO_{3(aq)} \rightleftharpoons H^+_{(aq)} + NO_3^-{}_{(aq)}$$

The strong acid is usually the only source of H^+. (*If the molarity of the acid is less than 10^{-6} M then the ionisation of water needs to be taken into account*.)

Therefore, the ***pH depends only on the initial molarity*** of the acid.

Strong Bases



The strongest common bases are ***oxides*** and ***hydroxides*** of Group I metals.

All strong bases ***ionise completely*** in solution:

$$O^{2-}_{(aq)} + H_2O_{(l)} \rightleftharpoons 2OH^{-}_{(aq)}$$

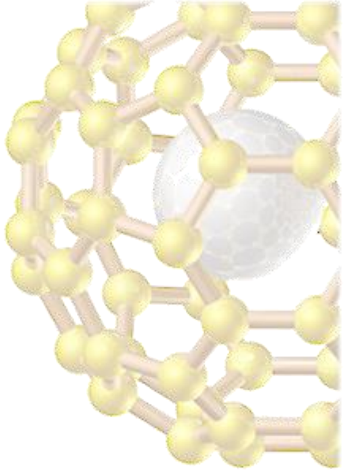
Bases do not need to include OH^- ions:

$$H^{-}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_{2(g)} + OH^{-}_{(aq)}$$

$$N^{3-}_{(aq)} + 3H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + 3OH^{-}_{(aq)}$$

Therefore, the $[OH^-]$, and hence the $[H^+]$ and ***pH, depends only on the initial molarity of the base***.

Weak Acids



Weak acids are only ***partially ionised*** in solution

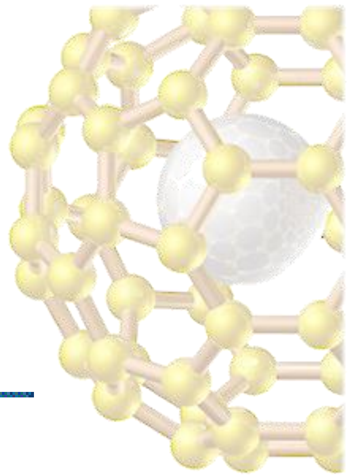
Therefore, weak acids are in equilibrium:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

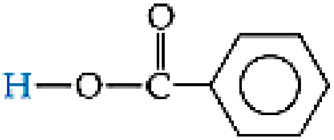
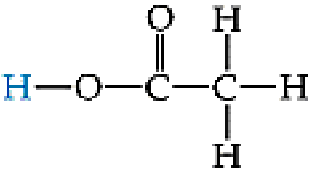
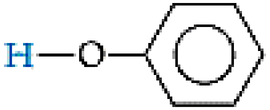
$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

K_a is the ***dissociation constant*** for the weak acid



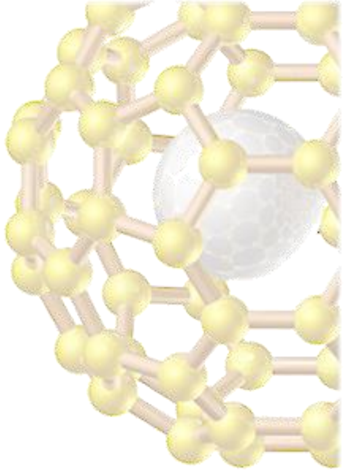
K_a of Weak Acids

SOME WEAK ACIDS IN WATER AT 25°C*

Acid	Molecular Formula	Structural Formula	Conjugate Base	Ka
Hydrofluoric	HF	$H-F$	F^-	6.8×10^{-4}
Nitrous	HNO_2	$H-O-N=O$	NO_2^-	4.5×10^{-4}
Benzoic	$HC_7H_5O_2$		$C_7H_5O_2^-$	6.5×10^{-5}
Acetic	$HC_2H_3O_2$		$C_2H_3O_2^-$	1.8×10^{-5}
Hypochlorous	$HClO$	$H-O-Cl$	ClO^-	3.0×10^{-8}
Hydrocyanic	HCN	$H-C\equiv N$	CN^-	4.9×10^{-10}
Phenol	HOC_6H_5		$C_6H_5O^-$	1.3×10^{-10}

* The proton that ionizes is shown in blue.

Amending K_a



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

The expression for the dissociation constant can be altered as follows:

$$K_a = \frac{[\,H^+\,]^2}{[\,HA\,]}$$

For every H^+ ion produced an A^- ion must be produced:

$$[\,H^+\,] = [\,A^-\,]$$

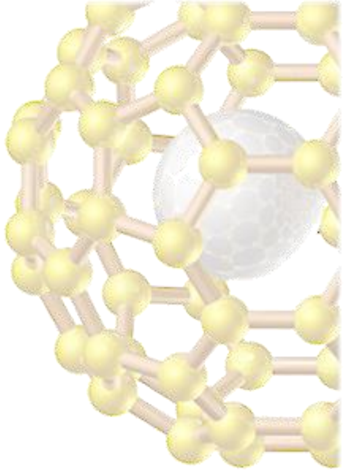
Let, C = ***analytical*** [HA]

If acid is weak, then ***equilibrium*** [HA] is only slightly less than ***analytical*** [HA]

$$C = [\,HA\,]$$

$$K_a = \frac{[\,H^+\,]^2}{C}$$

Using K_a to Calculate pH



$$K_a = \frac{[H^+]^2}{C}$$

Rearranging gives:

$$[H^+] = ¦ \, (K_a . C)$$

For example, calculate the pH of a 0.1 mol l^{-1} solution of ethanoic acid, given that K_a for ethanoic acid is 1.7×10^{-5}.

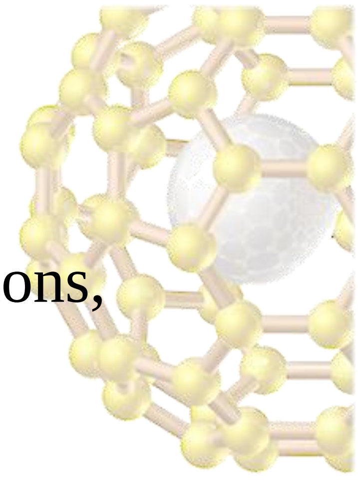
$[H^+] = \sqrt{(1.7 \times 10^{-5} \times 0.1)}$

$[H^+] = \sqrt{(1.7 \times 10^{-6})}$

$[H^+] = 1.304 \times 10^{-3}$ mol l^{-1}

pH = -log[H^+]

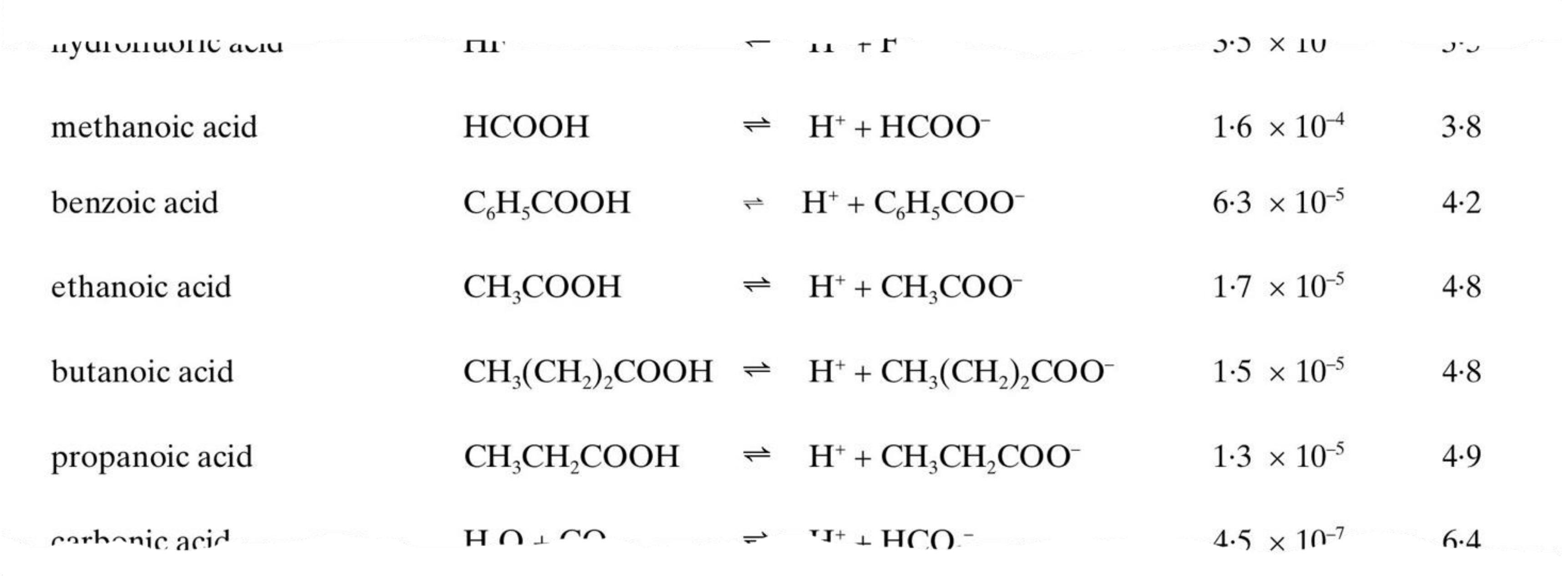
pH = -log(1.304×10^{-3}) = 2.9



pK_a Values

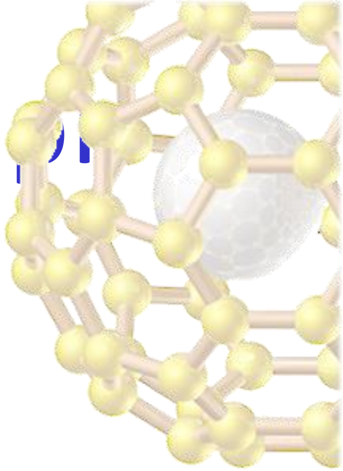
pH was invented to help simplify hydrogen ion concentrations, the large range of K_a values can similarly be simplified.

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



hydrofluoric acid	[illegible]	⇌	[illegible]	[illegible]	[illegible]
methanoic acid	$HCOOH$	⇌	$H^+ + HCOO^-$	$1{\cdot}6 \times 10^{-4}$	3·8
benzoic acid	C_6H_5COOH	⇌	$H^+ + C_6H_5COO^-$	$6{\cdot}3 \times 10^{-5}$	4·2
ethanoic acid	CH_3COOH	⇌	$H^+ + CH_3COO^-$	$1{\cdot}7 \times 10^{-5}$	4·8
butanoic acid	$CH_3(CH_2)_2COOH$	⇌	$H^+ + CH_3(CH_2)_2COO^-$	$1{\cdot}5 \times 10^{-5}$	4·8
propanoic acid	CH_3CH_2COOH	⇌	$H^+ + CH_3CH_2COO^-$	$1{\cdot}3 \times 10^{-5}$	4·9
carbonic acid	[illegible]	⇌	[illegible]	$4{\cdot}5 \times 10^{-7}$	6·4

Using pK$_a$ Values to calculate



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

The ***pH*** of a solution can be calculated from ***pK$_a$*** by converting to ***K$_a$*** and proceeding as before:

$$K_a = \frac{[\,H^+\,]^2}{C}$$

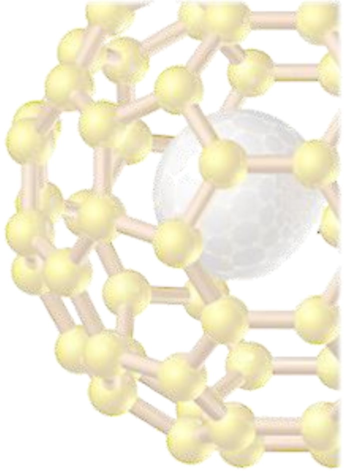
Rearranging gives:

$$[\,H^+\,] = \sqrt{(K_a\,.C\,)}$$

$$pH = -\log[H^+]$$

If preferred, the ***pH*** of a solution can be calculated directly from ***pK$_a$***

Calculating pH from pK_a



$$K_a = \frac{[\,H^+\,]^2}{C}$$

Rearranging gives:

$$[\,H^+\,] = ¦\ (K_a\,.C\,)$$

Taking logs of both sides

$$\log[\,H^+\,] = \log\,(¦\ (K_a\,.C\,))$$

simplifying

$\log¦\ A = {}^1/_2\log A$

$$\log[\,H^+\,] = {}^1/_2\,\log\,(K_a\,.C\,)$$

simplifying

$\log AB = \log A + \log B$

$$\log[\,H^+\,] = {}^1/_2\,\log K_a + {}^1/_2 \log C$$

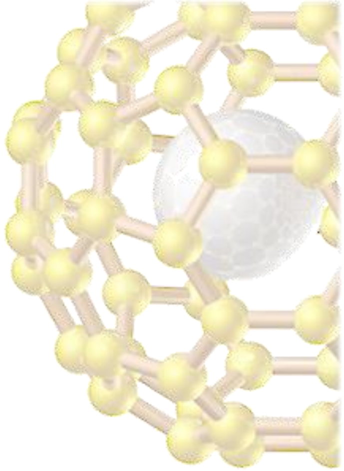
Multiply by -1

$$-\log[\,H^+\,] = -{}^1/_2\,\log K_a - {}^1/_2 \log C$$

Substituting

$$pH = {}^1/_2\,pK_a - {}^1/_2 \log C$$

Diluting Strong Acids



From Standard grade you've been expected to know the effect on pH of diluting a ***strong acid***

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

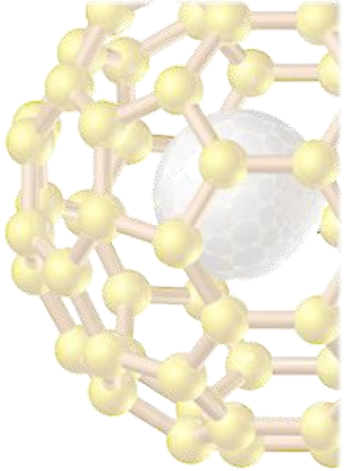
0.1 mol l^{-1} HCl $\quad$ pH = - log (0.1) $\quad$ pH = 1

0.01 mol l^{-1} HCl $\quad$ pH = - log (0.01) $\quad$ pH = 2

Dilute a strong acid by a factor of 10 and the pH will change by 1 unit

Is it the same for a weak acid?

Diluting Weak Acids



This is an ideal application of our pKa formula.

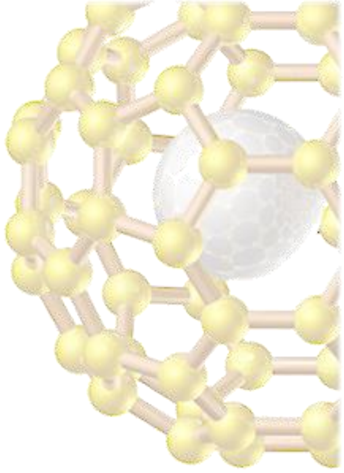
$$\mathbf{pH = {}^{1}/_{2}\,p\mathit{K_a} - {}^{1}/_{2}\mathit{logC}}$$

0.1 mol l^{-1} $\quad$ $pH = {}^{1}/_{2}\,pK_a - {}^{1}/_{2}\log(0.1)$ $\quad$ $pH = {}^{1}/_{2}\,pK_a - 0.5$

0.01 mol l^{-1} $\quad$ $pH = {}^{1}/_{2}\,pK_a - {}^{1}/_{2}\log(0.01)$ $\quad$ $pH = {}^{1}/_{2}\,pK_a - 1.0$

Dilute a weak acid by a factor of 10 and the pH will change by 0.5 unit

Polyprotic Acids



Polyprotic acids have more than one ionisable proton.

The protons are removed in steps not all at once:

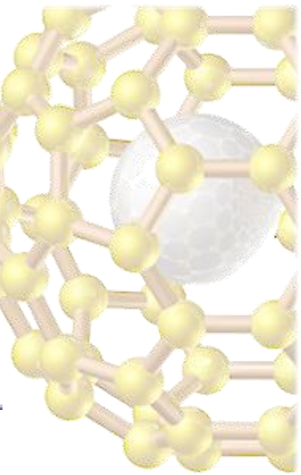
$$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \qquad K_{a1} = 1.7 \times 10^{-2}$$

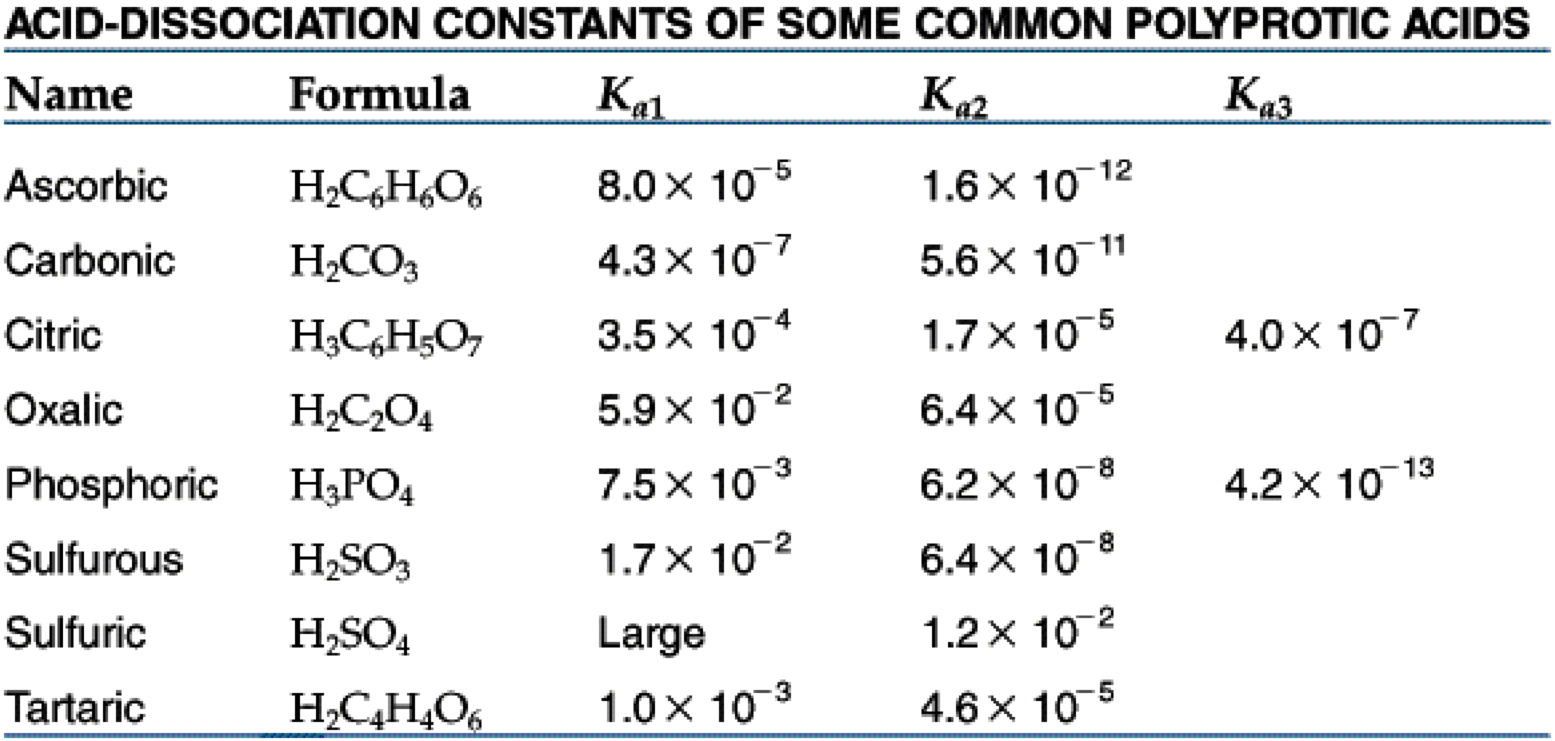
$$HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq) \qquad K_{a2} = 6.4 \times 10^{-8}$$

It is always easier to remove the first proton in a polyprotic acid than the second. Therefore, $K_{a1} > K_{a2} > K_{a3}$ etc.

Most $H^+(aq)$ at equilibrium usually comes from the first ionization (i.e. often only need to consider the K_{a1} equilibrium).

Polyprotic Acids

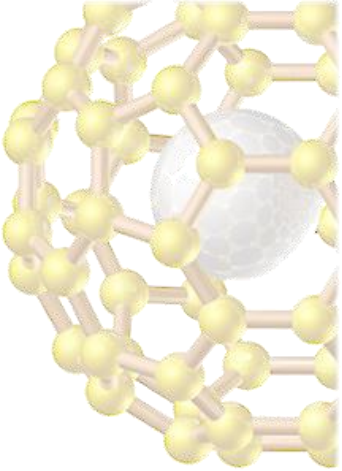




ACID-DISSOCIATION CONSTANTS OF SOME COMMON POLYPROTIC ACIDS

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	3.5×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$H_2C_4H_4O_6$	1.0×10^{-3}	4.6×10^{-5}	

Weak Bases



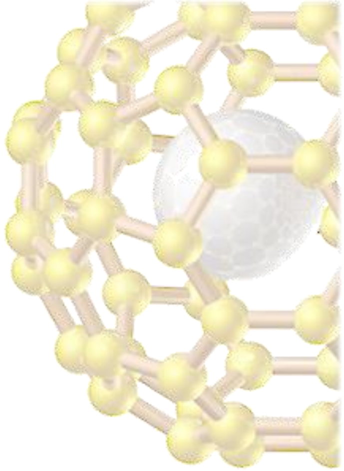
$$\text{Weak base} + H_2O \rightleftharpoons \text{conjugate acid} + OH^-$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

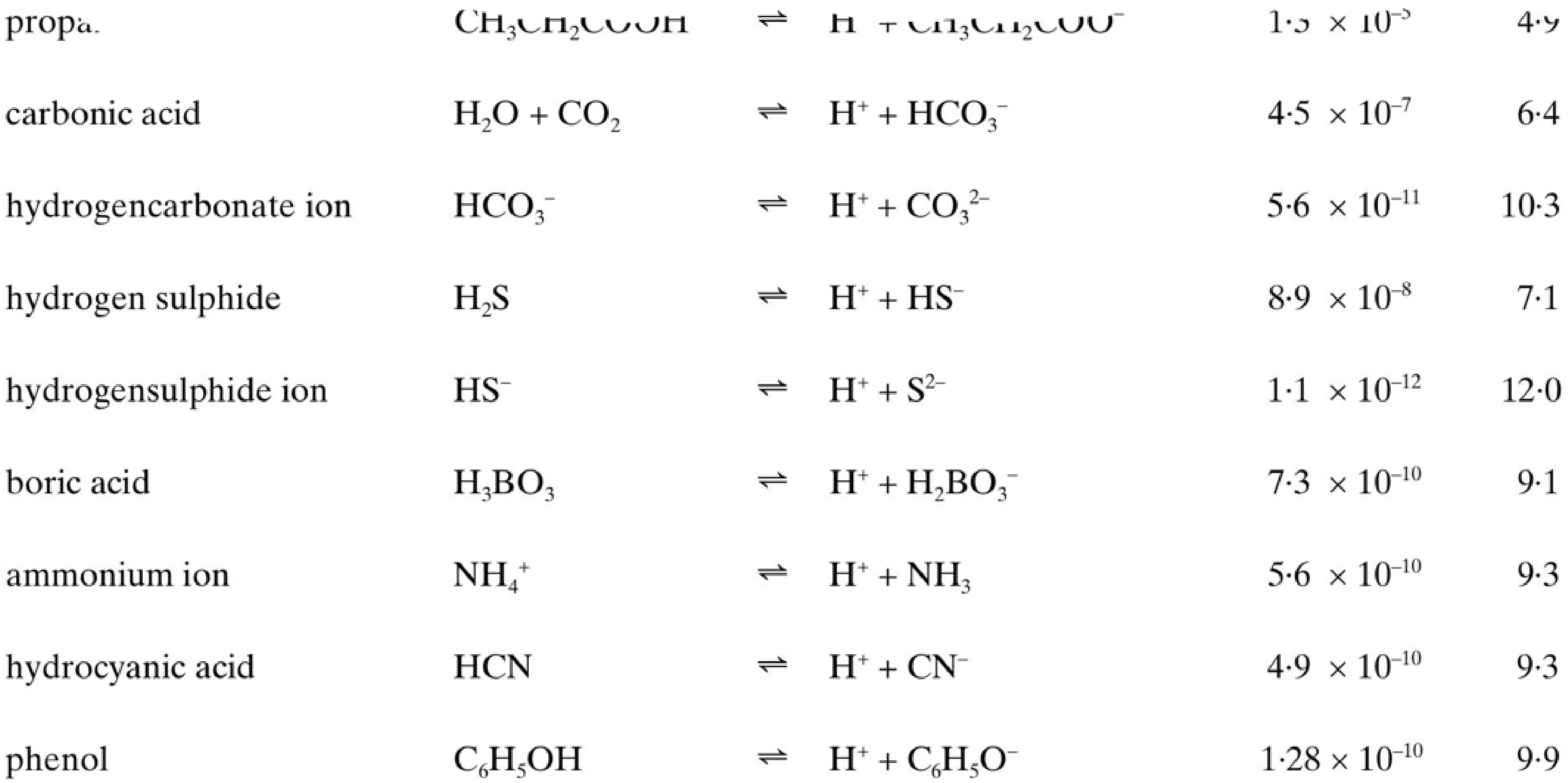
$$\text{conjugate acid} + H_2O \rightleftharpoons \text{base} + H_3O^+$$

Forced to deduce strength of base by looking at ***acid dissociation constant***, ***K_a*** of its ***conjugate acid***

Weak Bases



The ***smaller K_a*** the ***stronger*** the base.



propa	CH_3CH_2COOH	$\rightleftharpoons$	$H^+ + CH_3CH_2COO^-$	$1{\cdot}3 \times 10^{-5}$	4·9
carbonic acid	$H_2O + CO_2$	$\rightleftharpoons$	$H^+ + HCO_3^-$	$4{\cdot}5 \times 10^{-7}$	6·4
hydrogencarbonate ion	HCO_3^-	$\rightleftharpoons$	$H^+ + CO_3^{2-}$	$5{\cdot}6 \times 10^{-11}$	10·3
hydrogen sulphide	H_2S	$\rightleftharpoons$	$H^+ + HS^-$	$8{\cdot}9 \times 10^{-8}$	7·1
hydrogensulphide ion	HS^-	$\rightleftharpoons$	$H^+ + S^{2-}$	$1{\cdot}1 \times 10^{-12}$	12·0
boric acid	H_3BO_3	$\rightleftharpoons$	$H^+ + H_2BO_3^-$	$7{\cdot}3 \times 10^{-10}$	9·1
ammonium ion	NH_4^+	$\rightleftharpoons$	$H^+ + NH_3$	$5{\cdot}6 \times 10^{-10}$	9·3
hydrocyanic acid	HCN	$\rightleftharpoons$	$H^+ + CN^-$	$4{\cdot}9 \times 10^{-10}$	9·3
phenol	C_6H_5OH	$\rightleftharpoons$	$H^+ + C_6H_5O^-$	$1{\cdot}28 \times 10^{-10}$	9·9

Equilibrium in Water

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

- Only a few water molecules dissociate (split up) into ions so equilibrium lies to the left.
- The **concentration of H^+ and OH^- ions** at 25^{oC} is **10^{-7} mol l^{-1}**.
- In pure water:

$$[H^+] \times [OH^-] = (10^{-7}) \times (10^{-7})$$
$$= 10^{-14} \text{ mol}^2 \text{ l}^{-2}$$

- Due to this equilibrium, all solutions will contain some H^+ and OH^- ions and it has been found that, **in all solutions**:

$$[H^+] \times [OH^-] = 10^{-14} \text{ mol}^2 \text{ l}^{-2}$$

- Due to this equilibrium, all solutions will contain some H^+ and OH^- ions and it has been found that, **in all solutions**:

$$[H^+] \times [OH^-] = 10^{-14}\ \mathrm{mol}^2\ \mathrm{l}^{-2}$$

- This is known as the **ionic product of water** and can be used to calculate the $[H^+]$ and thus the pH of any solution.

As $$[H^+]\,[OH^-] = 10^{-14}$$

then $$[H^+] = \frac{10^{-14}}{[OH^-]}$$ for any solution.

Relationship between $[H^+]$, $[OH^-]$ & pH

Concentration of $H^+_{(aq)}$ (mol l^{-1})	$[H^+]$	pH	$[OH^-]$	Concentration of $OH^-_{(aq)}$ (mol l^{-1})
10	1×10^{1}	[redacted]	[redacted]	
1	1×10^{0}	[redacted]	[redacted]	
0.1	1×10^{-1}	[redacted]	[redacted]	
0.01	1×10^{-2}	[redacted]	[redacted]	
0.001	1×10^{-3}	[redacted]	[redacted]	
0.000 1	1×10^{-4}	[redacted]	[redacted]	
0.000 01	1×10^{-5}	[redacted]	[redacted]	
0.000 001	1×10^{-6}	[redacted]	[redacted]	
0.000 000 1	$\mathbf{1 \times 10^{-7}}$	[redacted]	[redacted]	[redacted]
	1×10^{-8}	[redacted]	[redacted]	[redacted]
	1×10^{-9}	[redacted]	[redacted]	[redacted]
	1×10^{-10}	[redacted]	[redacted]	[redacted]
	1×10^{-11}	[redacted]	[redacted]	[redacted]
	1×10^{-12}	[redacted]	[redacted]	[redacted]
	1×10^{-13}	[redacted]	[redacted]	[redacted]
	1×10^{-14}	[redacted]	[redacted]	[redacted]
	1×10^{-15}	[redacted]	[redacted]	[redacted]

NB A change in pH of 1 unit represents a 10 fold change in concentration of $[H^+]$, $[OH^-]$ ions.

2 units = 100 fold change, etc

Strong and Weak Acids

- Acids are classified as either **strong** or **weak** depending on how they dissolve in **water**.

Strong Acids

- Dissolve by **completely dissociating into ions**,

  E.g.

  $$HCl + (aq) \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

  So if the HCl concentration is 0.1 mol l^{-1} then $[H^+]$ is 0.1 mol l^{-1}.

- Examples include:

  Hydrochloric acid (HCl)

  Nitric acid (HNO_3)

  Sulphuric acid (H_2SO_4)

  Hydrofluoric acid (HF)

Weak Acids

- **Do not completely dissociate into ions** in solution,
- E.g.

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

- Ethanoic acid solutions contain molecules of CH_3COOH as well as H^+ and CH_3COO^- ions.
- Examples include:

Ethanoic acid (CH_3COOH)

Methanoic acid ($HCOOH$)

Sulphurous acid (H_2SO_3)

Carbonic acid (H_2CO_3)

Solvents for Acids

- The type of solvent affects **acid properties**:

  E.g. HCl in non –polar solvents **(e.g. CCl_4)**

  - no dissociation therefore only HCl molecules not ions so it is **not an acid**.

- To show **acidic properties**, a **polar solvent**, like water is required.

Strong and Weak Bases

- Again based on how they dissolve in water.

Strong bases/alkalis

- Dissolve by completely dissociating into ions.

  e.g.

  $\mathrm{NaOH(s)} + \mathrm{(aq)} \rightarrow \mathrm{Na^{+}_{(aq)}} + \mathrm{OH^{-}_{(aq)}}$

- Examples include:

  Sodium hydroxide ($NaOH$)

  Potassium hydroxide (KOH)

  Lithium hydroxide ($LiOH$)

Weak bases/alkalis

- **Do not completely dissociate into ions** in solution,
- E.g.

$$NH_{3\,(aq)} + H_2O_{\,(l)} \rightleftharpoons NH_4{}^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$$

- Ammonia solutions contain molecules of NH_3 as well as NH_4^+ and OH^- ions.
- Examples include:

Ammonia (NH_3)

Aminomethane (CH_3NH_2)

Aminoethane ($C_2H_5NH_2$)

Properties of Strong and Weak Acids and Alkalis

- **Equimolar solutions** of strong and weak acids and alkalis **differ** in **conductivity**, **pH** and **speed of reaction.**
- This is due to the different concentrations of H^+ and OH^- ions in solution.

Strong acid vs weak acid

- **Higher conductivity, lower pH, faster reaction**

  …due to higher H^+ ion concentration.

Strong base/alkali vs weak base/alklai

- **Higher conductivity, higher pH**

  …due to higher OH^- ion concentration.

Neutralisation reactions of Acids and Alkalis: Titration

- If you titrate 25 ml of 1.0 mol l^{-1} HCl against 1.0 mol l^{-1} NaOH, what volume of NaOH would you need?

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

$NaOH$	HCl	$NaCl$	H_2O
1 mole	1 mole	1 mole	1 mole

$$P_{acid} \times V_{acid} \times C_{acid} = P_{alk} \times V_{Alk} \times C_{alk}$$

$1 \times 25 \times 1 = 25 \times$ Vol of NaOH **Ans:** **25 ml NaOH**

- What happens if you use 25ml of 1.0 mol l^{-1} ethanoic acid instead?

$$NaOH + CH_3COOH \longrightarrow Na^+CH_3COO^- + H_2O$$

$NaOH$	CH_3COOH	$Na^+CH_3COO^-$	H_2O
1 mole	1 mole	1 mole	1 mole

Ans: **25 ml NaOH**

Why?

- The **stoichiometry** of the reactions (the mole ratio of reactants) is the same in each case therefore the **same volume of alkali is required for neutralisation.**

Definition mix up!

Strong acid	**Weak acid**
Fully dissociated in aqueous solution	Not fully dissociated in aqueous solution

Dilute	**Concentrated**
A little solute in a lot of water. e.g. 0.2 mol l^{-1}	A lot of solute in a little of water. e.g. 2.0 mol l^{-1}

pH of Salts

- The **pH of a salt** solution depends on the **strength** of the **acid** and **base** from which it was formed.

Acid	Base	pH of salt
Strong	Weak	Acidic
Strong	Strong	Neutral
Weak	Strong	Alkaline

Examples

1. Reaction of sodium hydroxide with hydrochloric acid

2. Reaction of ethanoic acid with sodium hydroxide

3. Reaction of ammonia with nitric acid

Explanation of Salt pH

- All salts are **strong electrolytes** and completely ionise in solution.
- The ions of a **weak acid** or **base** when dissolved will set up an **equilibrium** the ions in water.

Example 1 – Acidic Salt

In water you have:

$$H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + H^+_{(aq)}$$

Ammonium chloride completely dissociates:

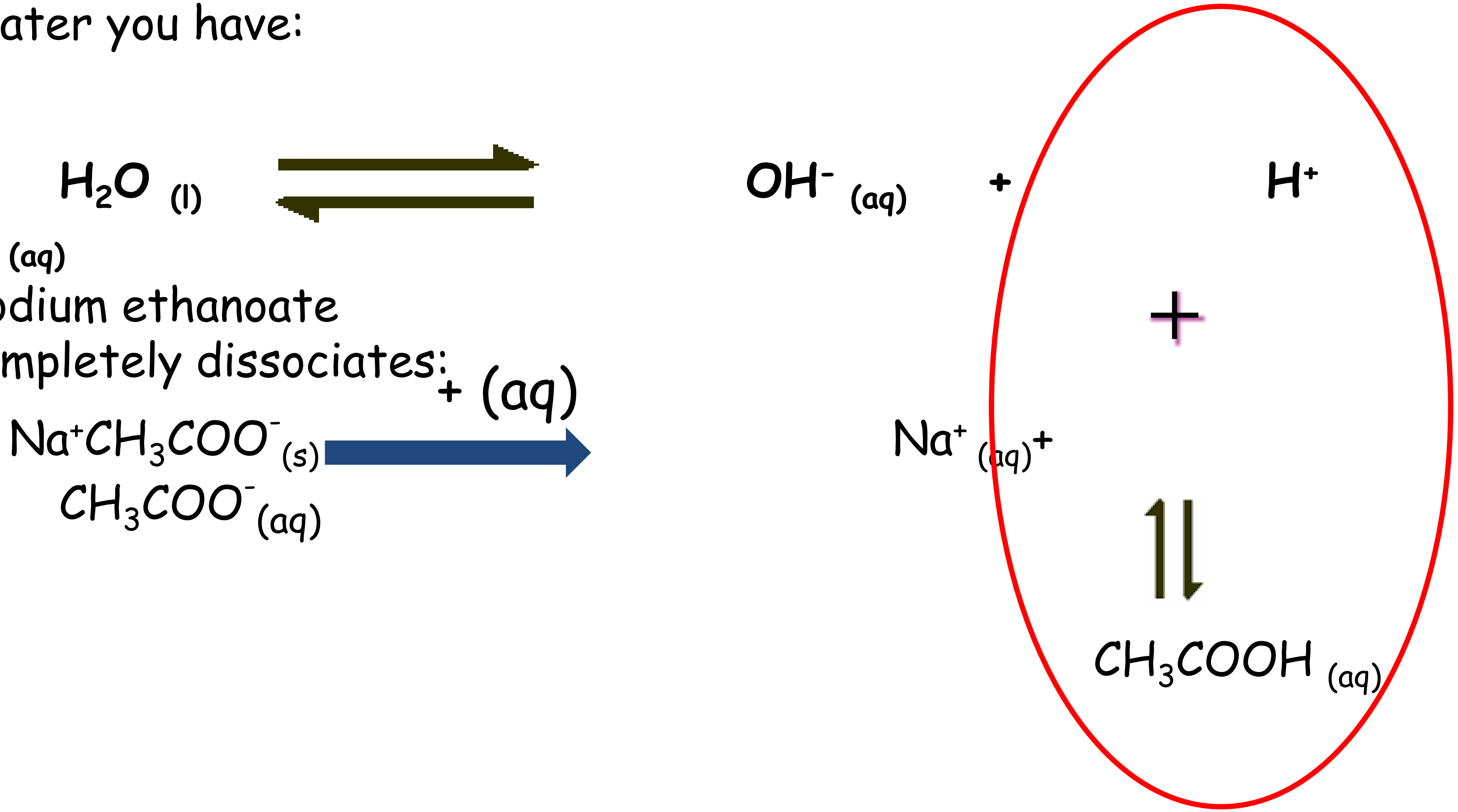
$$NH_4Cl_{(s)} \rightarrow NH_4^+{}_{(aq)} + Cl^-_{(aq)}$$

$$OH^-_{(aq)} + NH_4^+{}_{(aq)} \rightleftharpoons NH_{3(aq)} + H_2O_{(l)}$$

The ammonium ions form an equilibrium with the OH^- ions moving the water equilibrium to the right. Excess H^+ are formed so pH is less than 7.

Example 2 – Alkaline Salt

In water you have:



$H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + H^+$

(aq)

Sodium ethanoate completely dissociates:

+ (aq)

$Na^+CH_3COO^-_{(s)} \rightarrow Na^+_{(aq)} +$

$CH_3COO^-_{(aq)}$

$+$

$\upharpoonleft\downharpoonright$

$CH_3COOH_{(aq)}$

- The ethanoate ions form an equilibrium with the H^+ ions moving the water equilibrium to the right.
- Excess OH^- ions are formed so the pH is greater than 7.

Soaps

- Soap is a salt formed between a fatty acid (weak acid) and sodium or potassium hydroxide.

  e.g. sodium oleate (from oleic acid)

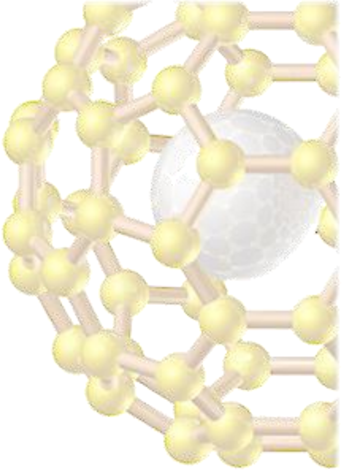
  sodium stearate (from stearic acid)

∴ **Soap solutions are alkaline.**

Summary of Salts

- In all solutions of salts formed from weak acid or base ions:
  - an equilibrium is established
  - the balance of H^+ and OH^- ions in water is changed
  - water molecules split up to oppose this change
  - excess H^+ and OH^- ions then alter the pH
- This is sometimes called **salt hydrolysis** as the break up of water molecules is caused by the salt dissolving.

Buffer Solutions



A buffer consists of a mixture of a ***weak acid*** (HX) and its ***conjugate base*** (i.e. ***salt***) (X^-):

$$\mathbf{HX}(aq) \rightleftharpoons \mathbf{H}^+(aq) + \mathbf{X}^-(aq)$$

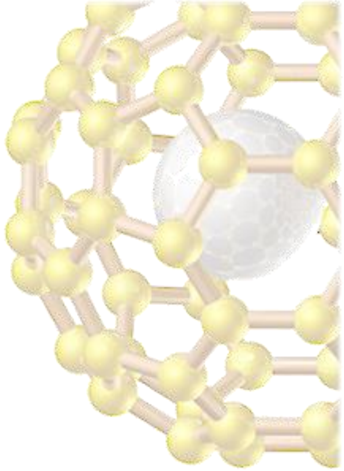
The K_a expression is

$$K_a = \frac{[\mathrm{H}^+][\mathrm{X}^-]}{[\mathrm{HX}]}.$$

$$\therefore [\mathrm{H}^+] = K_a \frac{[\mathrm{HX}]}{[\mathrm{X}^-]}.$$

The pH of a buffer depends on the weak acid chosen (K_a)and the ratio of [HX] to $[A^-]$.

Buffer Solutions



$$K_a = \frac{[H^+][X^-]}{[HX]}.$$

$$\therefore [H^+] = K_a \frac{[HX]}{[X^-]}.$$

In a solution of a weak acid alone, [HX] is ***large*** but [X^-] is ***small***.

The addition of the ***salt*** of the acid means that [X^-] is also ***large***.

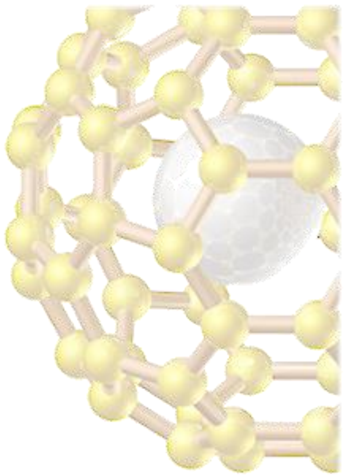
This gives the Buffer the ability to maintain a ***'constant' pH*** even when:

an acid is added - more H^+ ions

an alkali is added - more OH^- ions

the buffer is diluted - more H_2O

Buffer Solutions - more H^+



$$[\,H^+\,] = K_a \frac{[\,HX\,]}{[\,X^-\,]} \qquad pH = pK_a - \log\left(\frac{[\,HX\,]}{[\,X^-\,]}\right)$$

$$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$$

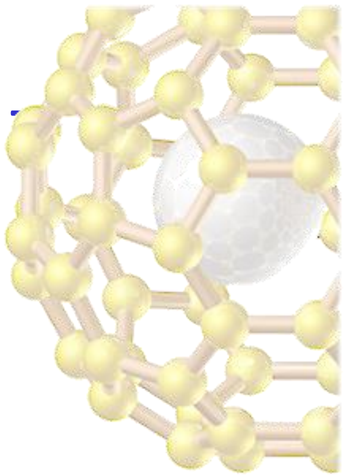
If a small amount of acid is added to a buffer the H^+ ions will react with X^- to form HX.

The $[X^-]$ was so high to begin with that the ***decrease*** is negligible

The [HX] was so high to begin with that the ***increase*** is negligible

The ratio of [HX] to $[X^-]$ remains unchanged so ***pH stays the same***

Buffer Solutions - more OH^-



$$[\,H^+\,] = K_a \frac{[\,HX\,]}{[\,X^-\,]} \qquad pH = pK_a - \log\left(\frac{[\,HX\,]}{[\,X^-\,]}\right)$$

$$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$$

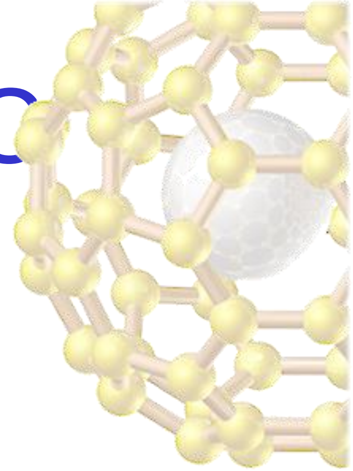
If a small amount of alkali is added to a buffer the OH^- ions will react with H^+ to form H_2O.

HX molecules will dissociate to replace the H^+ ions but [HX] was so high to begin with that the ***decrease*** is negligible

More X^- will be formed but the [X^-] was so high to begin with that the ***increase*** is negligible

The ratio of [HX] to [X^-] remains unchanged so ***pH stays the same***

Buffer Solutions - more H_2O



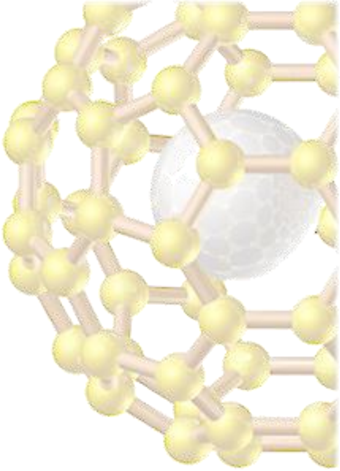
$$[\,H^+\,] = K_a \frac{[\,HX\,]}{[\,X^-\,]} \qquad pH = pK_a - \log\left(\frac{[\,HX\,]}{[\,X^-\,]}\right)$$

If water is added to a buffer the [HX] will ***decrease*** and the [X$^-$] will ***decrease***.

The decrease will be ***the same*** for both substances.

The ratio of [HX] to [X$^-$] remains unchanged so ***pH stays the same***

Buffer Solutions - calculating pH



$$\mathbf{pH} = \mathbf{p}K_a \ \mathbf{-log}\left(\frac{[\,\mathbf{HX}\,]}{[\,\mathbf{X}^-\,]}\right)$$

normally represented as:

$$\mathbf{pH} = \mathbf{p}K_a \ \mathbf{-log}\left(\frac{\mathbf{Acid}}{\mathbf{Salt}}\right)$$

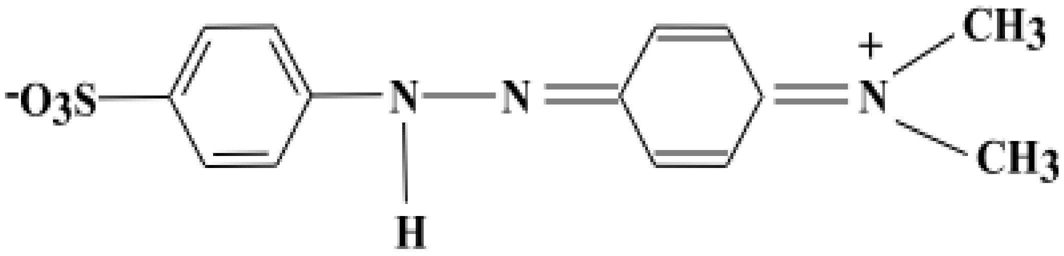
and ‘tidied up’ to give:

$$\mathbf{pH} = \mathbf{p}K_a \ \mathbf{+log}\left(\frac{\mathbf{Salt}}{\mathbf{Acid}}\right)$$

Indicators - weak acids

Indicators are ***weak acids*** that change ***colour*** when they are converted into their ***conjugate base***.

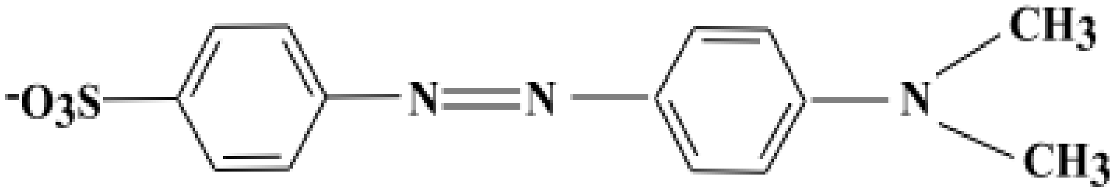
e.g Methyl Red



Acid

HIn

Present at ***low pH's***

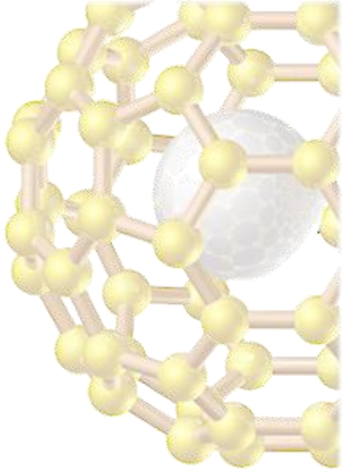


Conjugate Base

In^-

Present at ***high pH's***

Indicators K_{In}



$$HIn_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + In^-_{(aq)}$$

The ***dissociation constant*** is relabelled as K_{In} but is still:

$$K_{In} = \frac{[\,H_3O^+\,]\,[\,In^-\,]}{[\,H_2O\,]\,[\,HIn\,]}$$

which simplifies to

$$K_{In} = \frac{[\,H^+\,]\,[\,In^-\,]}{[\,HIn\,]}$$

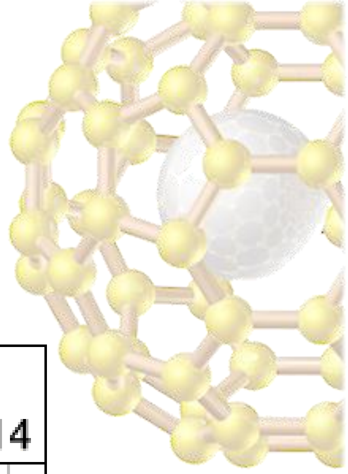
Rearranging gives:

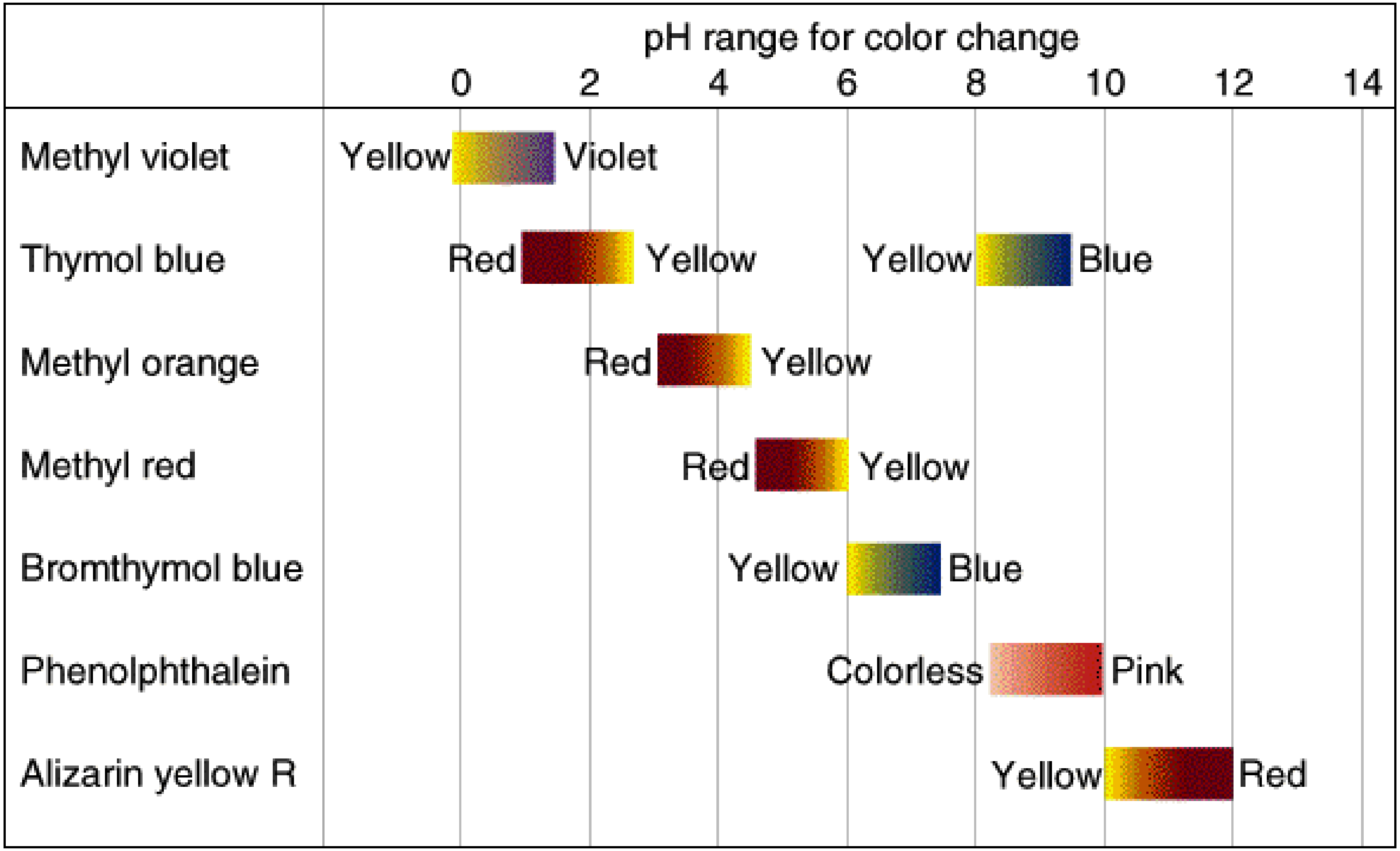
$$\frac{K_{In}}{[\,H^+\,]} = \frac{[\,In^-\,]}{[\,HIn\,]}$$

The ratio of $[In^-]/[HIn]$ represents the ***colour*** that would be observed.

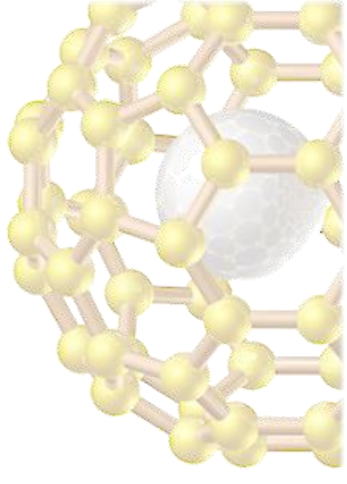
Since K_{In} is a constant, ***the colour of an indicator depends on*** $[H^+]$, i.e. pH

Indicators - pH ranges





Indicators - pK_{In}



For indicators, ***pK_{In}*** is more useful than ***K_{In}***:

The midpoint of any indicators colour change is when

$$[HIn] = [In^-]$$

$$\frac{K_{In}}{[H^+]} = \frac{[In^-]}{[HIn]}$$

so $$\frac{K_{In}}{[H^+]} = 1$$

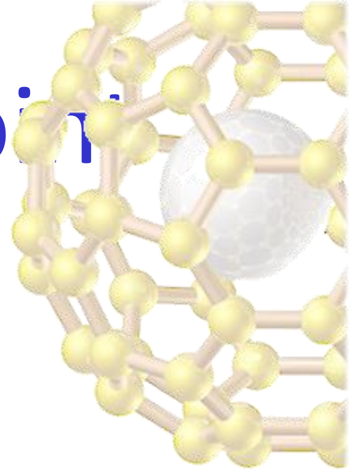
$$K_{In} = [H^+] \quad pK_{In} = pH$$

In other words the pH at which an indicator is midway through its colour change can be calculated easily from K_{In} ……..

and *vice versa*

the pK_a of an indicator is the same as the pH of its midpoint

Indicators - detecting end-poin



For only ***one particular colour*** to be observed, that form must be ***10 times more concentrated*** than the other.

$$\frac{[\,\mathrm{HIn}\,]}{[\,\mathrm{In}\,]} = 10 \qquad \text{or} \qquad \frac{[\,\mathrm{HIn}\,]}{[\,\mathrm{In}\,]} = 0.1$$

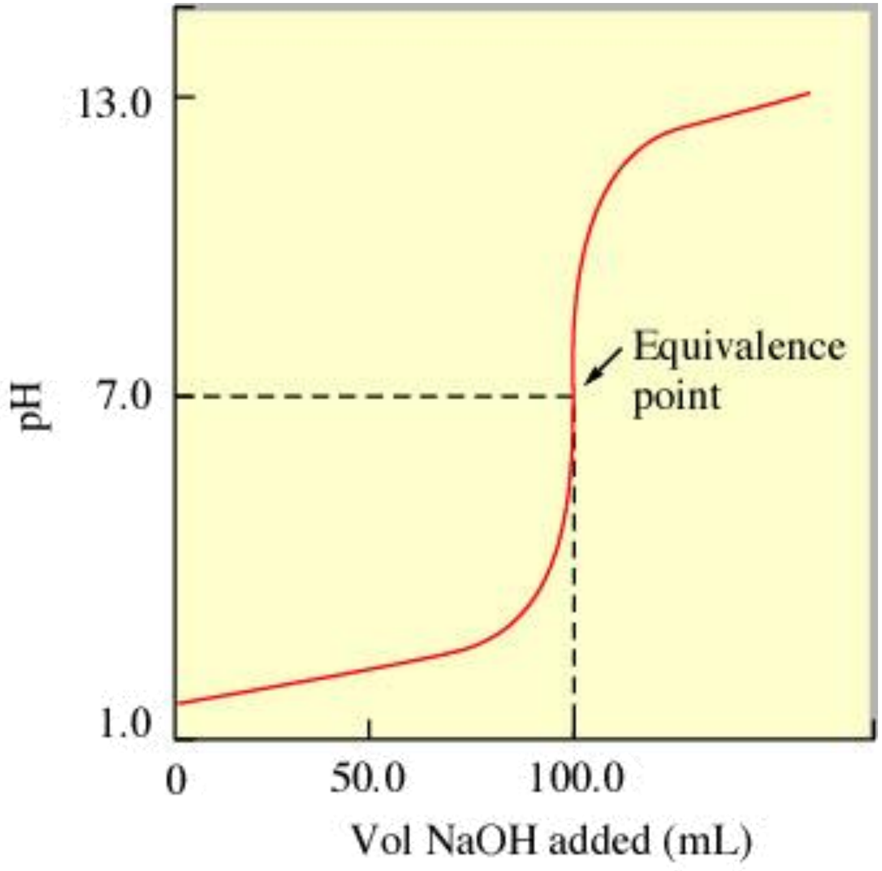
Rearranging

$$K_{In} = \frac{[\,\mathrm{H}^{+}\,][\,\mathrm{In}^{-}\,]}{[\,\mathrm{HIn}\,]} \Rightarrow -\log[\,\mathrm{H}^{+}\,] = -\log\left(K_{In}\frac{[\,\mathrm{HIn}\,]}{[\,\mathrm{In}^{-}\,]}\right)$$

$$\mathrm{pH} = \mathrm{p}K_{In} \pm 1 \Leftarrow \mathrm{pH} = \mathrm{p}K_{In} - \log\left(\frac{[\,\mathrm{HIn}\,]}{[\,\mathrm{In}^{-}\,]}\right)$$

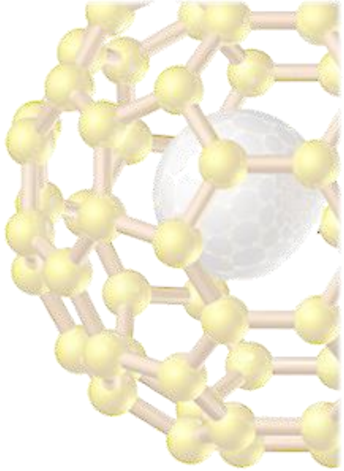
Equivalence point

The ***equivalence point*** is when the reaction is just completed

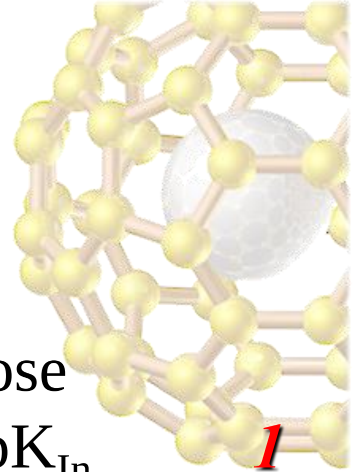


For a titration between a ***strong acid*** (e.g HCl) and a ***strong base*** (e.g NaOH) the ***equivalence point*** will be when pH = 7.

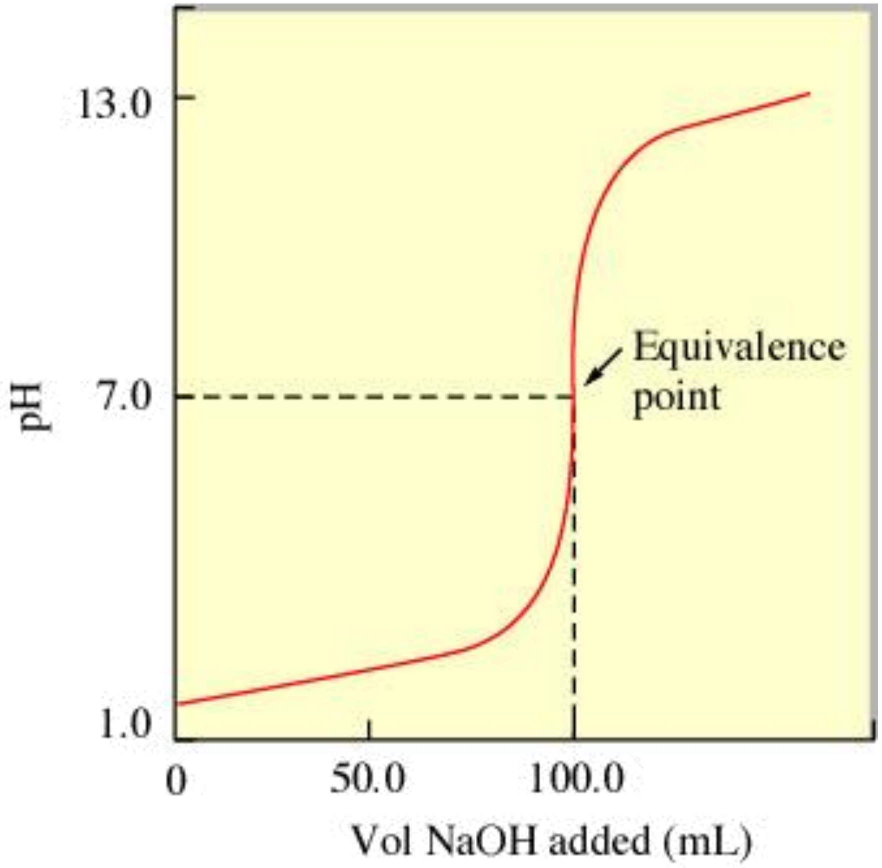
However, not all indicators will complete their colour change at this point so ***end-point observed*** may be different.



Choosing an Indicator



$$\mathrm{pH} = \mathrm{p}K_{In} \pm 1$$



Strong Acid / Strong Base

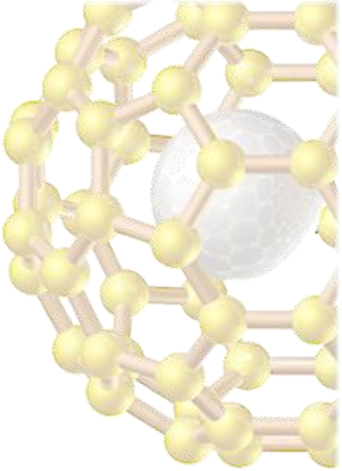
If titrating with a base, you should ideally choose an indicator that has a pK$_{In}$ ***1 less*** than the pH at the equivalence point, i.e. ***pK$_{In}$ = 6***

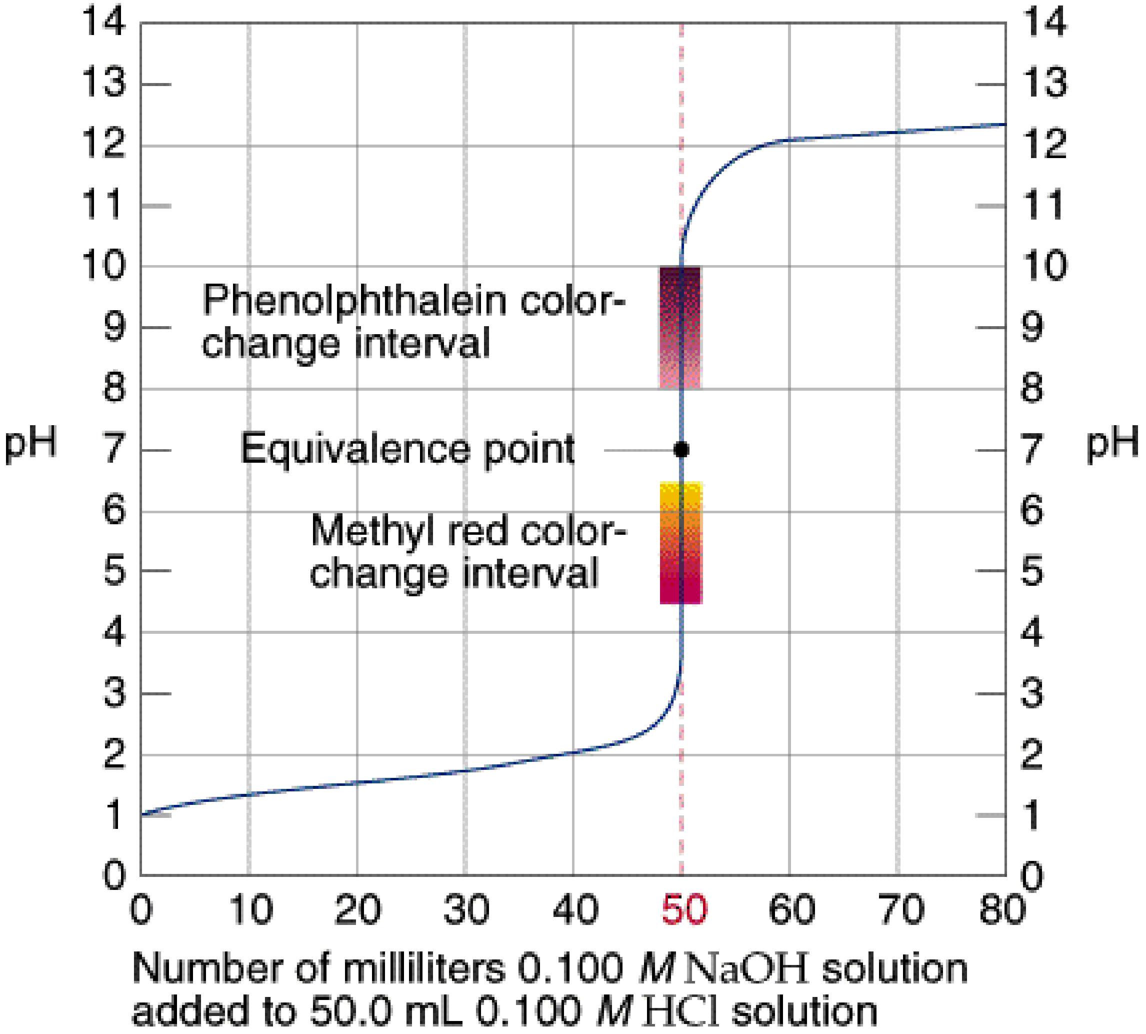
At pH = 5 colour change starts

By pH = 7 colour change ***visible***

If titrating with an acid, you should ideally choose an indicator that has a pK$_{In}$ ***1 more*** than the pH at the equivalence point.

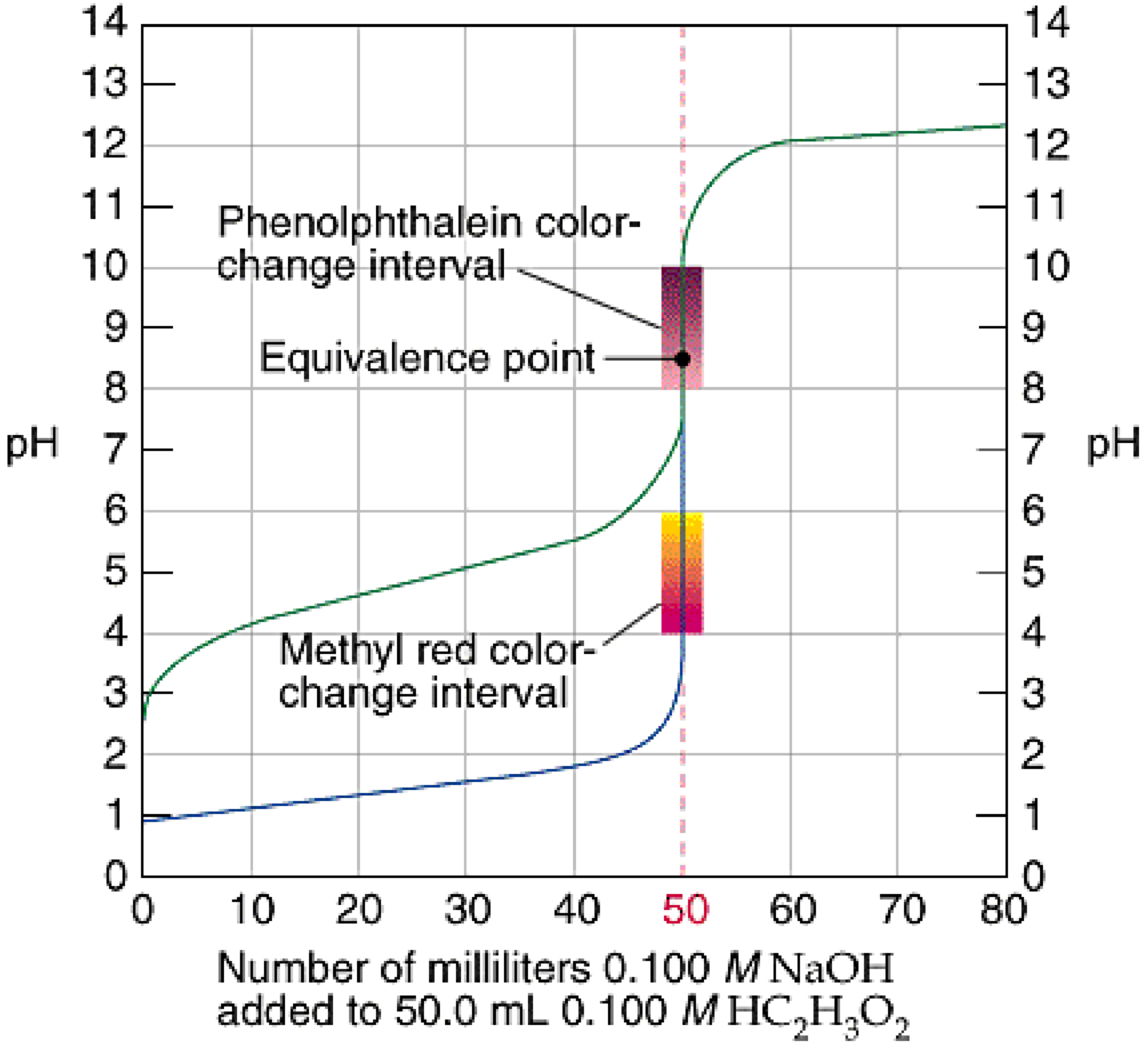
Choosing an Indicator

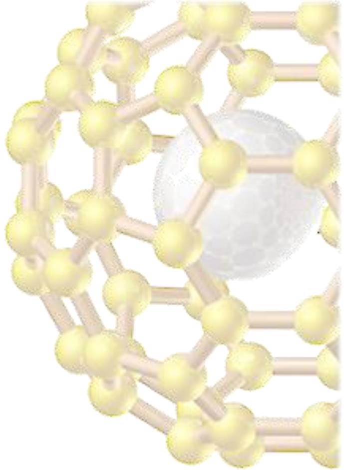




Choosing an Indicator

Weak Acid / Strong Base

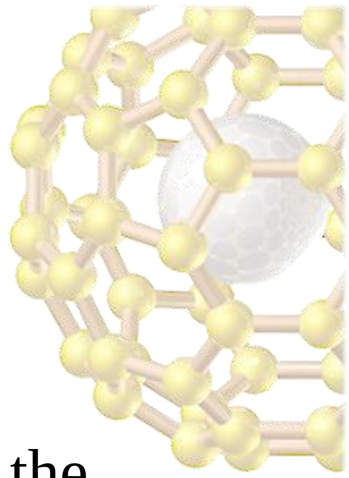




The equivalence point has moved to a higher pH ~ 8.5

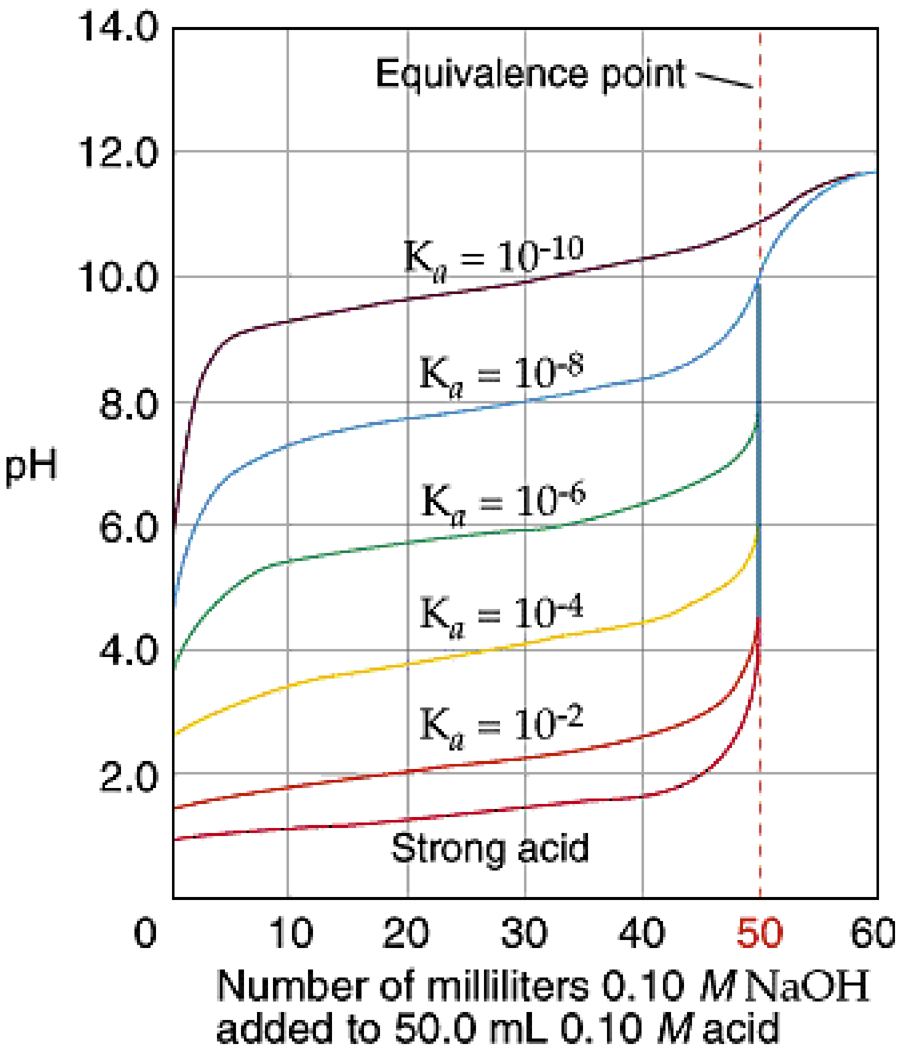
$pH = pK_{In} \pm 1$

Use an indicator with a pK_{In} as close to 7.5 as possible.



Choosing an Indicator

Weak Acid / Strong Base

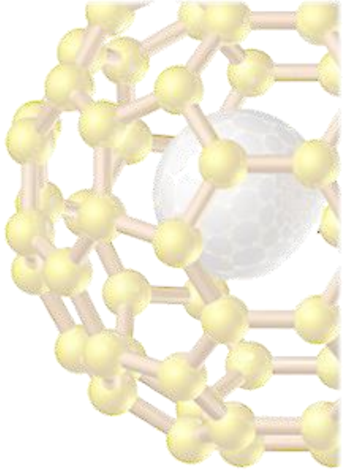


The weaker the acid, the higher the equivalence point

The change in pH becomes ***less dramatic***.

Eventually, ***no indicator will be suitable*** as you need at least a change of 2 pH units.

Important Formulae



$pH = -\log[H^+]$

$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{[H^+]^2}{C}$$

$$pH = {}^1/_2\, pK_a - {}^1/_2 \log C$$

$$\frac{K_{In}}{[H^+]} = \frac{[In^-]}{[HIn]}$$

$$pH = pK_{In} \pm 1$$

$$pH = pK_a + \log\left(\frac{\text{Salt}}{\text{Acid}}\right)$$