CHEMICAL EQUILIBRIUM

Dynamic Equilibrium

- not all reactions proceed to completion
- some end up with a mixture of reactants and products
- this is because **some reactions are reversible**; products revert to reactants

> *'A dynamic equilibrium exists in a closed system when the rate of the forward reaction is equal to the rate of the reverse reaction and the concentrations of the reactants and products do not change.'*

As the rate of reaction is dependant on the concentration of reactants...

- forward reaction starts off fast but slows as the reactants get less concentrated
- initially, there is no backward reaction but, as products form, it will get faster
- provided the temperature remains constant there will come a time when the backward and forward reactions are equal and opposite; the reaction has reached equilibrium

- a reversible chemical reaction is a dynamic process
- everything may appear stationary but the reactions are moving both ways
- the position of equilibrium can be varied by changing certain conditions

Trying to get up a "down" escalator gives an excellent idea of a non-chemical situation involving **dynamic equilibrium**.

Knockhardy Publishing

Q.1 *Write out equations for the reactions between ...*

- *nitrogen and hydrogen*
- *sulphur dioxide and oxygen*
- *ethanol and ethanoic acid*

What, in the equations, shows the reactions are reversible ?

Summary When a chemical equilibrium is established **in a closed system**...

- both the reactants and the products are present at all times
- the equilibrium can be approached from either side
- the reaction is dynamic - it is moving forwards and backwards
- concentrations of reactants and products remain constant

The Equilibrium Law

Simply states “If the concentrations of all the substances present at equilibrium are raised to the power of the number of moles they appear in the equation, the product of the concentrations of the products divided by the product of the concentrations of the reactants is a constant, provided the temperature remains constant”

There are several forms of the constant; all vary with temperature.

- **K_c** the equilibrium values are expressed as concentrations of mol dm^{-3}
- **K_p** the equilibrium values are expressed as partial pressures

The partial pressure expression can be used for reactions involving gases

Calculating K_c for a reaction of the form

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

then (at constant temperature)

$$\frac{[C]^c . [D]^d}{[A]^a . [B]^b} = \text{a constant, } (K_c)$$

[ ] denotes the equilibrium concentration in mol dm^{-3}

K_c is known as the Equilibrium Constant

Value of K_c

- AFFECTED by a change of temperature
- NOT AFFECTED by
  - a change in concentration of reactants
  - a change in concentration of products
  - a change of pressure
  - adding a catalyst

Q.2 *Write expressions for the equilibrium constant, K_c of the following reactions. Remember,* ***equilibrium constants can have units.***

$$Fe^{3+}_{(aq)} + NCS^{-}_{(aq)} \rightleftharpoons FeNCS^{2+}_{(aq)}$$

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^{+}{}_{(aq)} + OH^{-}_{(aq)}$$

$$2Fe^{3+}_{(aq)} + 2I^{-}_{(aq)} \rightleftharpoons 2Fe^{2+}_{(aq)} + I_{2(aq)}$$

FACTORS AFFECTING THE POSITION OF EQUILIBRIUM

Le Chatelier's Principle

Definition *"When a change is applied to a system in dynamic equilibrium, the system reacts in such a way as to oppose the effect of the change."*

Everyday example A rose bush grows with increased vigour after it has been pruned.

Chemistry example If you do something to a reaction that is in a state of equilibrium, the equilibrium position will change to oppose what you have just done

Concentration The equilibrium constant is not affected by a change in concentration at constant temperature. To maintain the constant the composition of the equilibrium mixture changes.

example *Look at the equilibrium in question Q.4. If the concentration of C is increased, the position of equilibrium will move to the LHS to oppose the change. This ensures that the value of the equilibrium constant remains the same.*

Q.3 *In the reaction* $A + 2B \rightleftharpoons C + D$ *predict where the equilibrium will move when ... a) more B is added b) some A is removed c) some D is removed.*

Pressure For a change in pressure, we consider the number of **gaseous molecules only**. The more particles you have in a given volume, the greater the pressure they exert. If you apply a greater pressure they will become more crowded (i.e. they are under a greater stress). If the system can change it will move to the side with fewer gaseous molecules as they will now be in a less crowded environment.

Summary

Pressure Change	***Effect on Equilibrium***
INCREASE	moves to side with FEWER GASEOUS MOLECULES
DECREASE	moves to side with MORE GASEOUS MOLECULES

No change occurs when equal numbers of gaseous molecules appear on both sides

Q.4 *Predict the effect on the equilibrium position of an increase in pressure.*

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

b) $H_{2(g)} + CO_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$

c) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

Temperature The only thing that can change the value of the equilibrium constant.

Altering the temperature affects the rate of both backward and forward reactions but to different extents. The equilibrium moves to produce a new constant.

The direction of movement depends on the sign of the enthalpy change.

Summary of the effect of temperature on the position of equilibrium

Type of reaction	ΔH	***Increase T***	***Decrease T***
EXOTHERMIC	–	moves to LEFT	moves to RIGHT
ENDOTHERMIC	+	moves to RIGHT	moves to LEFT

Q.5 *Predict the effect of a temperature increase on the equilibrium position of,*

a) $H_{2(g)} + CO_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)} \quad \Delta H = +40\ \text{kJ mol}^{-1}$

b) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H = -\text{ive}$

An **increase in temperature** is used to speed up chemical reactions but it **can have an undesired effect when the reaction is reversible and exothermic**. In this case you get to the equilibrium position quicker but with a reduced yield because the increased temperature moves the equilibrium to the left. In many industrial processes a compromise temperature is used (see Haber and Contact Processes). To reduce the problem one must look for a way of increasing the rate of a reaction without decreasing the yield i.e. with a catalyst.

Catalysts Adding a catalyst DOES NOT AFFECT THE POSITION OF EQUILIBRIUM. However, it does increase the rate of attainment of equilibrium. This is especially important in reversible, exothermic industrial reactions such as the Haber or Contact Processes where economic factors are paramount.

Catalysts work by providing an alternative reaction pathway involving a lower activation energy.

INDUSTRIAL APPLICATIONS

The Haber Process

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad : \quad \Delta H = -92 \text{ kJ mol}^{-1}$$

Typical conditions	Pressure	20000 kPa (200 atmospheres)
	Temperature	380-450°C
	Catalyst	iron
Equilibrium theory favours	low temperature	exothermic reaction - higher yield at low temperature
	high pressure	decrease in number of gaseous molecules
Kinetic theory favours	high temperature	greater average energy + more frequent collisions
	high pressure	more frequent collisions for gaseous molecules
	catalyst	lower activation energy
Compromise conditions	Which is better?	A low yield in a shorter time *or* a high yield over a longer period.

The conditions used are a **compromise** with the catalyst enabling th rate to be kept up, even at a lower temperature.

Q.6 *List two large-scale uses of ammonia.*

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-

Q.7 *Find details of the **Contact Process**. List the essential features such as temperature, pressure and a named catalyst. Using what you have learned so far, appreciate why the conditions are chosen to satisfy economic principles.*

Equation:

Temperature:

Pressure:

Catalyst:

The Equilibrium Law

States *"If the concentrations of all the substances present at equilibrium are raised to the power of the number of moles they appear in the equation, the product of the concentrations of the products divided by the product of the concentrations of the reactants is a constant, provided the temperature remains constant" ...* ***WOW!***

Calculating Equilibrium Constants

Types

K_c	equilibrium values are **concentrations** **in mol dm^{-3}**
K_p	equilibrium values are **partial pressures** - system at constant temperature

The partial pressure expression can be used for reactions involving gases

Calculating K_c for a reaction of the form

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

then (at constant temperature)

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

[ ] denotes the equilibrium concentration in mol dm^{-3}

K_c is known as the Equilibrium Constant

Value of K_c

- **AFFECTED** by a change of **temperature**
- **NOT AFFECTED** by a change in **concentrations**
  a change of **pressure**
  adding a **catalyst**

Q.1 *What happens to the theoretical yield of a reaction if...*

- *K_c increases*
- *K_c decreases ?*

Q.2 *What happens to the value of K_c if ...*

- *the **temperature is increased** in an **exothermic** reaction*
- *the **temperature is decreased** in an **exothermic** reaction*
- *the **temperature is increased** in an **endothermic** reaction*
- *the **temperature is decreased** in an **endothermic** reaction*

Q.3 *Write expressions for the equilibrium constant, K_c of the following reactions. Remember, equilibrium constants can have units.*

$Fe^{3+}(aq) + NCS^{-}(aq) \rightleftharpoons FeNCS^{2+}_{((aq)}$ **K_c =**

$NH_4OH(aq) \rightleftharpoons NH_4^{+}(aq) + OH^{-}(aq)$ **K_c =**

$2Fe^{3+}(aq) + 2I^{-}(aq) \rightleftharpoons 2Fe^{2+}(aq) + I_2(aq)$ **K_c =**

Calculating value of K_c

- construct the balanced equation, including state symbols (aq), (g) etc.
- determine the number of moles of each species at equilibrium
- divide moles by volume (dm^3) to get the equilibrium concentrations in mol dm^{-3} (If no volume is quoted, use a V; it will probably cancel out)
- from the equation constructed in the first step, write out an expression for K_c.
- substitute values from third step and calculate the value of K_c with any units

Example 1 *Ethanoic acid (1 mol) reacts with ethanol (1 mol) at 298K. When equilibrium is reached, two thirds of the acid has reacted. Calculate the value of K_c.*

	$CH_3COOH_{(l)}$ +	$C_2H_5OH_{(l)}$ $\rightleftharpoons$	$CH_3COOC_2H_{5(l)}$ +	$H_2O_{(l)}$
initial moles	**1**	**1**	**0**	**0**
equilibrium moles	**$1 - {}^2/_3$**	**$1 - {}^2/_3$**	**${}^2/_3$**	**${}^2/_3$**
	If ⅔ mol of the acid has reacted then take the value away from the initial number of moles of acid	If ⅔ mol of the acid has reacted, then ⅔ mol of ethanol will also have reacted. Take ⅔ mol away from the original.	According to the equation, for every mol of acid that reacts you make 1 mol of ester and 1 mol of water. Therefore, if ⅔ mol of acid has reacted, ⅔ mol of ester and ⅔ mol of water are produced.	
equilibrium concs.	**${}^1/_3$ / V**	**${}^1/_3$ / V**	**${}^2/_3$ / V**	**${}^2/_3$ / V**

***V** = volume (dm^3) of the equilibrium mixture*

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]} = \frac{{}^2/_3 / V \;.\; {}^2/_3 / V}{{}^1/_3 / V \;.\; {}^1/_3 / V} = \mathbf{4}$$

Example 2 *Consider the reaction* **$P + 2Q \rightleftharpoons R + S$** *(all are aqueous)*

1 mol of P and 1 mol of Q are mixed. Once equilibrium has been achieved, 0.6 mol of P are present. How many moles of Q, R and S are present at equilibrium ?

	P	**+**	**2Q**	$\rightleftharpoons$	**R**	**+**	**S**
Initial moles	**1**		**1**		**0**		**0**
At equilibrium	**0·6**		**0·2**		**0·4**		**0·4**
	(0·4 reacted)		(2 x 0·4 reacted)		(get 1 R and 1 S for every P that reacts)		
	1- 0·6 remain		1- 0·8 remain				

Explanation

- *if 0.6 moles of P remain of the original 1 mole, 0.4 moles have reacted*
- *the equation states that 2 moles of Q react with every 1 mole of P*
- *this means that 0.8 (2 x 0.4) moles of Q have reacted, leaving 0.2 moles*
- *one mole of R and S are produced from every mole of P that reacts*
- *this means 0.4 moles of R and 0.4 moles of S are present at equilibrium*

Q.4 *The questions refer to the equilibrium* $A + B \rightleftharpoons C + D$ *(all aqueous)*

(a) *If the original number of moles of A and B are both 1 and 0.4 moles of A are present at equilibrium, how many moles of B, C and D are present?*

What will be the value of K_c *?*

(b) *At a higher temperature, the original moles of A and B were 2 and 3 respectively. If 1 mole of A is present at equilibrium, how many moles of B, C and D are present? What else does this tell you about the reaction?*

Calculations involving Gases

Method

- carried out in a similar way to those involving concentrations
- one has the **choice of using K_c or K_p** for the equilibrium constant
- **when using K_p only take into account gaseous species** for the expression
- quotes the partial pressure of the gas in the equilibrium mixture
- pressure is usually quoted in Nm^{-2} or Pa - (atmospheres are sometimes used)
- the **units of the constant K_p depend on the stoichiometry** of the reaction

total pressure = sum of the partial pressures

partial pressure = total pressure x mole fraction

$$\textbf{mole fraction} = \frac{\textbf{number of moles of a substance}}{\textbf{number of moles of all substances present}}$$

Calculating K_p for a reaction of the form $a\ A_{(g)} + b\ B_{(g)} \rightleftharpoons c\ C_{(g)}$

then (at constant temperature)

$$\boxed{\frac{PC^{c}}{PA^{a} \times PB^{b}} = \text{a constant, } (K_p)}$$

P denotes the partial pressure of a gaseous component at equilibrium

K_p is the Equilibrium Constant in terms of partial pressures

Example $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$ $K_p = \frac{(PNO_2)^2}{(PN_2O_4)}$ (units of pressure)

Q.5 *Write expressions for the equilibrium constant, K_p of the following reactions. Remember, equilibrium constants can have units. (assume the pressure is in MPa)*

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_p =$

$PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g)$ $K_p =$

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $K_p =$

$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$ $K_p =$

Example 1 A mixture of 16g of O_2 and 42g of N_2 , exerts a total pressure of 20000 Nm^{-2}.
What is the partial pressure of each gas ?

moles of O_2 = mass / molar mass = 16g / 32g = 0.5 mol
moles of N_2 = mass / molar mass = 42g / 28g = 1.5 mol Total = 2 mol

mole fraction of O_2 = 0.5 / 2 = 0.25
mole fraction of N_2 = 1.5 / 2 = 0.75 sum of mole fractions = 1

partial pressure of O_2 = mole fraction x total pressure
= 0.25 x 20000 Nm^{-2} = **5000 Nm^{-2}**

partial pressure of N_2 = mole fraction x total pressure
= 0.75 x 20000 Nm^{-2} = **15000 Nm^{-2}**

Example 2 Nitrogen (1 mol) and hydrogen (3 mol) react at constant temperature at a pressure of 1MPa. At equilibrium, half the nitrogen has reacted. Calculate K_p .

	$N_{2(g)}$	+	$3H_{2(g)}$	$\rightleftharpoons$	$2NH_{3(g)}$
initial moles	1		3		0
at equilibrium	1 - 0.5 = 0.5 mol		3 - 1.5 = 1.5 mol		2 x 0.5 = 1 mol
mole fractions	0.5 / 3		1.5 / 3		1 / 3
partial pressures	(0.5 / 3) x 1MPa.		1.5 / 3 x 1MPa.		1 / 3 x 1MPa.

applying the equilibrium law

$$K_p = \frac{(PNH_3)^2}{(PN_2)\ .\ (PH_2)^3} = \frac{\tfrac{1}{3} \text{ x } \tfrac{1}{3}}{\tfrac{1}{6} \text{ x } \tfrac{1}{2} \text{ x } \tfrac{1}{2} \text{ x } \tfrac{1}{2}} \text{ MPa}^{-2}$$

therefore **K_p = 5.33 MPa^{-2}**

Example 3 0.102g of solid ammonium sulphide is heated in a closed container at 100°C until equilibrium is reached at a pressure of 0.1MPa. It is found that 75% of the ammonium sulphide has dissociated. Calculate the equilibrium constant K_p for the reaction at 100°C.

	$NH_4HS_{(s)}$	$\rightleftharpoons$	$NH_{3(g)}$	+	$H_2S_{(g)}$
initial mass (g)	0.102		0		0
initial moles	0.102 / 51 = 2 x 10^{-3}		0		0
moles at equilibrium	0.5 x 10^{-3}		1.5 x 10^{-3}		1.5 x 10^{-3}
	75% has dissociated 1.5 moles have reacted		***1 mole of NH_3 formed***		***1 mole of H_2S formed***

for every 1 mole of NH_4HS reacted

mole fractions	(moles / total moles)	1.5 / 3	1.5 / 3
partial pressures		(1.5 / 3) x 0.1MPa = 0.05 MPa	(1.5 / 3) x 0.1MPa = 0.05 MPa

applying the equilibrium law
(the partial pressure of a solid is
more or less constant so is ignored)

$$K_p = PNH_3 \text{ x } PH_2S = 0.05\text{MPa x } 0.05\text{MPa}$$

K_p = 2.5 x 10^{-3} MPa^2

ACIDS & BASES - IONIC EQUILIBRIA

Acid-base theories

LEWIS

acid	**electron pair acceptor**	H^+ , $AlCl_3$
base	**electron pair donor**	NH_3 , H_2O , C_2H_5OH , OH^-

e.g. $\underset{\text{base}}{\mathbf{H_3N{:}}} \longrightarrow \underset{\text{acid}}{\mathbf{BF_3}} \longrightarrow \mathbf{H_3N^+\!-\!BF_3^-}$ *see co-ordinate bonding*

BRØNSTED - LOWRY

acid	**proton donor**	$\mathbf{HCl} \longrightarrow \mathbf{H^+}(aq) + \mathbf{Cl^-}(aq)$
base	**proton acceptor**	$\mathbf{NH_3}(aq) + \mathbf{H^+}(aq) \longrightarrow \mathbf{NH_4^+}(aq)$

Q.1 *Classify the following according to Lewis theory and Brønsted-Lowry theory.*

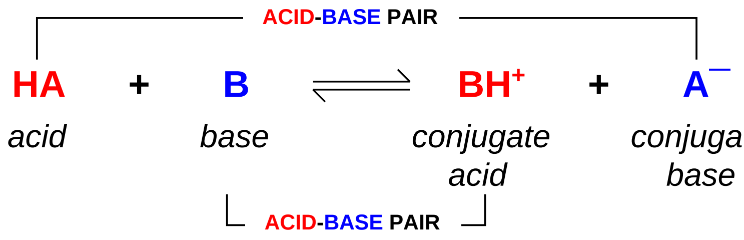
	H_3O^+	BF_3	H_2SO_4	H_2O	NH_4^+	CH_3NH_2
B-L						
Lewis						

Conjugate systems

Acids are related to bases ACID $\rightleftharpoons$ PROTON + CONJUGATE BASE

Bases are related to acids BASE + PROTON $\rightleftharpoons$ CONJUGATE ACID

For an acid to behave as an acid, it must have a base present to accept a proton...



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

Q.2 *Classify all species in the following equations as acids or bases and link the pairs.*

a) $HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$

b) $CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$

c) $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

THE STRENGTH OF ACIDS

Strong acids **completely dissociate** (split up) into ions in aqueous solution

e.g. $\mathbf{HCl} \longrightarrow \mathbf{H^+}(aq) + \mathbf{Cl^-}(aq)$ **MONOPROTIC** *1 replaceable H*

$\mathbf{HNO_3} \longrightarrow \mathbf{H^+}(aq) + \mathbf{NO_3^-}(aq)$

$\mathbf{H_2SO_4} \longrightarrow \mathbf{2H^+}(aq) + \mathbf{SO_4^{2-}}(aq)$ **DIPROTIC** *2 replaceable H's*

Weak acids **partially dissociate** into ions in aqueous solution *eg ethanoic acid* $\mathbf{CH_3COOH} \rightleftharpoons \mathbf{CH_3COO^-}(aq) + \mathbf{H^+}(aq)$

Theory When a weak acid dissolves in water an **equilibrium** is set up $\mathbf{HA}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{A^-}(aq) + \mathbf{H_3O^+}(aq)$

The **water** is essential as it **stabilises the resulting ions**. However to make calculations easier the dissociation is usually written in a shorter way $\mathbf{HA}(aq) \rightleftharpoons \mathbf{A^-}(aq) + \mathbf{H^+}(aq)$

The **weaker** the acid
- the **less it dissociates**
- the **more the equilibrium lies to the left**

The relative strengths of acids can be expressed as K_a or pK_a values (see later).

The **dissociation constant** for weak acid HA is

$$K_a = \frac{[H^+_{(aq)}]\,[A^-_{(aq)}]}{[HA_{(aq)}]} \quad \text{mol dm}^{-3}$$

(see later for a fuller discussion)

THE STRENGTH OF BASES

Strong **completely** dissociate into ions in aqueous solution $\mathbf{NaOH} \longrightarrow \mathbf{Na^+} + \mathbf{OH^-}$

Weak **partially** react to give ions in aqueous solution

When a weak base dissolves in water an equilibrium is set up $\mathbf{NH_3}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{NH_4^+}(aq) + \mathbf{OH^-}(aq)$

as in the case of acids it is more simply written $\mathbf{NH_3}\,(aq) + \mathbf{H^+}(aq) \rightleftharpoons \mathbf{NH_4^+}(aq)$

The **weaker the base**
- the **less it dissociates**
- the **more the equilibrium lies to the left**

HYDROGEN ION CONCENTRATION

Introduction

- hydrogen ion concentration determines the acidity of a solution
- hydroxide ion concentration determines the alkalinity
- for strong acids and bases the concentration of ions is very much larger than their weaker counterparts which only partially dissociate.

pH hydrogen ion concentration can be converted to pH

$$\mathbf{pH = -\log_{10} [\,H^+(aq)\,]}$$

to convert pH into hydrogen ion concentration

$$\mathbf{[\,H^+(aq)\,] = antilog\ (-pH)}$$

or $\mathbf{= 10^{-pH}}$

pOH An equivalent calculation for bases converts the hydroxide ion concentration to pOH

$$\mathbf{pOH = -\log_{10} [\,OH^-(aq)\,]}$$

in the above, **[ ] represents the concentration in mol dm^{-3}**

Ionic Product of Water. . . K_w

Formula Despite being covalent, water conducts electricity to a very small extent.

It is due to the slight ionisation ... $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

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

Applying the Equilibrium Law

$$K_c = \frac{[H^+(aq)]\ [OH^-(aq)]}{[H_2O(l)]}$$

[ ] is the equilibrium concentration in mol dm^{-3}

As the **dissociation is small**, the water concentration is very large compared with the dissociated ions and any changes to its value are insignificant;
its concentration can be regarded as constant.

This “constant” is combined with (K_c) to get a new constant (K_w).

$$K_w = [H^+(aq)]\,[OH^-(aq)]\ \text{mol}^2\ \text{dm}^{-6}$$

$$= 10^{-14}\ \text{mol}^2\ \text{dm}^{-6} \quad \text{(at 25°C)}$$

Variation The value of K_w **varies with temperature** because it is based on an equilibrium.

Temperature / °C	**0**	**20**	**25**	**30**	**60**
K_w / 10^{-14} mol^2 dm^{-6}	0.11	0.68	1.0	1.47	5.6

What does the trend tell you about the sign of ΔH for the dissociation of water?

The relationship between pH and pOH

Because H^+ and OH^- ions are produced in equal amounts when water dissociates their concentrations will be the same. $[H^+] = [OH^-] = 10^{-7}$ mol dm^{-3}

- take the equation for K_w $[H^+][OH^-] = 10^{-14}$ mol^2 dm^{-6}
- take logs of both sides $\log[H^+] + \log[OH^-] = -14$
- multiply by minus $-\log[H^+] - \log[OH^-] = 14$
- change to pH and pOH **pH + pOH = 14** (at 25°C)

N.B. As they are based on the position of equilibrium and that varies with temperature, the above values are only true if the temperature is 25°C (298K)

Neutral solutions are best described as those where **$[H^+] = [OH^-]$**
Therefore a neutral solution is pH 7 only at a temperature of 25°C (298K)

The value of K_w is constant for any aqueous solution at the stated temperature

$[H^+]$	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
$[OH^-]$	10^{-14}	10^{-13}	10^{-12}	10^{-11}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1
pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	↔ strongly acidic			↔ weakly acidic				neutral	↔ weakly alkaline				↔ strongly alkaline		

Q.3 *Convert the following pH values to $[H^+]$;* 13 7.5 3.21 – 0.6993

Convert the following $[H^+]$ values to pH ; 0.01 2.5×10^{-4} 1.1×10^{-13}

CALCULATING THE pH AND pOH OF STRONG ACIDS AND BASES

- This is relatively easy because the species have completely dissociated
- Only need to **know the original concentration** of the acid or base

Example 1 *Calculate the pH of 0.1M hydrochloric acid.*

HCl (strong monoprotic acid) is fully dissociated. $HCl \longrightarrow H^+(aq) + Cl^-(aq)$

The [H⁺] is therefore the same as the original concentration of HCl i.e. 0.1M.

$pH = -\log_{10}[H^+] = -\log_{10}(10^{-1}) = 1$ **ANS. 1**

Example 2 *Calculate the pH of 0.001M sodium hydroxide.*

NaOH (a strong base) is fully dissociated. $Na^+OH^- \longrightarrow Na^+(aq) + OH^-(aq)$

$[OH^-]$ is therefore the same as the original concentration of NaOH i.e. 0.001M.

$pOH = -\log_{10}[OH^-] = -\log 10\ (10^{-3}) = 3$

and $pH = 14 - pOH = 14 - 3 = 11$ **ANS. 11**

Q.4 *Calculate the pH and pOH of the following solutions.*

a) HCl; 0.1M, 0.5M

b) H_2SO_4; 0.1M, 0.5M

c) KOH; 0.1M

d) NaOH; 2M, 0.0005M

e) The solution remaining when 30 cm^3 of 0.100M NaOH has been added to 20 cm^3 of 0.200M HCl

f) The solution remaining when 24.9 cm^3 of 0.100M NaOH has been added to 25 cm^3 of 0.100M HCl

CALCULATING THE pH AND pOH OF WEAK ACIDS AND BASES

- can’t be calculated by just knowing the concentration
- need to know... the extent of the ionisation (from K_a) *and*
  the original concentration

The dissociation constant for a weak acid (K_a)

A weak monobasic acid (HA) dissociates in water thus.

$$\mathbf{HA}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{A^-}(aq)$$

Applying the equilibrium law we get

$$K_c = \frac{[H_3O^+(aq)]\,[A^-(aq)]}{[HA(aq)]\,[H_2O(aq)]}$$

[ ] is the equilibrium concentration in mol dm^{-3}

Assumptions For a **weak acid** there is **little dissociation** $[HA(aq)]_{equil} \sim [HA(aq)]_{undisc}$

This assumption becomes less valid for stronger weak acids where there is more dissociation.

In dilute solution, the concentration of water is large compared with the dissociated ions and any changes to its value are insignificant; its concentration can be regarded as ‘constant’. $[H_2O_{(l)}]$ is ‘constant’

Combine this ‘constant’ with (K_c) to get a new one (K_a).

where $K_a = K_c\,[H_2O_{(l)}]$

$$\mathbf{K_a} = \frac{\mathbf{[H_3O^+}(aq)\mathbf{]\,[A^-}(aq)\mathbf{]}}{\mathbf{[HA}(aq)\mathbf{]}} \quad \text{mol dm}^{-3}$$

A **simpler way** to write it all out is

$$\mathbf{HA}(aq) \rightleftharpoons \mathbf{H^+}(aq) + \mathbf{A^-}(aq)$$

The dissociation constant K_a is then

$$\mathbf{K_a} = \frac{\mathbf{[H^+}(aq)\mathbf{]\,[A^-}(aq)\mathbf{]}}{\mathbf{[HA}(aq)\mathbf{]}} \quad \text{mol dm}^{-3}$$

The weaker the acid
- **the less it dissociates**
- **the fewer ions you get**
- **the smaller K_a**

The stronger the acid
- **the more the equilibrium lies to the right**
- **the larger K_a**

pKa
- very weak acids have very small K_a values
- it is easier to compare the strength as pK_a values

The conversion is carried out thus... $\mathbf{pKa = -\log_{10} K_a}$

To convert pK_a into K_a $\mathbf{K_a = antilog\ (-pK_a)}$ or $\mathbf{10^{-Ka}}$

Q.5 *Write out expressions for K_a for the following weak acids . . .*

HF *HCN*

CH_3COOH *C_6H_5COOH*

Calculating the pH of a weak acid

Theory Weak monobasic acid (HA) dissociates in water $\mathbf{HA}(aq) \rightleftharpoons \mathbf{H^+}(aq) + \mathbf{A^-}(aq)$

the dissociation constant (K_a) is

$$K_a = \frac{[H^+(aq)]\,[A^-(aq)]}{[HA(aq)]} \quad \mathbf{mol\ dm^{-3}}$$

Assumptions The equation shows that, on dissociation, ions are formed in equimolar amounts.

$$[H^+(aq)] = [A^-(aq)]$$

$$\therefore \quad K_a = \frac{[H^+(aq)]\,[H^+(aq)]}{[HA(aq)]}$$

The **acid is weak**, so **dissociation is small**. The **equilibrium concentration of HA** can be **approximated to be its original** value.

the equation can be re-written ... $[H^+(aq)]^2 = K_a\,[HA(aq)]$

and $$\mathbf{[H^+(aq)] = \sqrt{K_a\,[HA(aq)]}}$$

The pH can then be calculated ... $\mathbf{pH = -\log_{10}[H^+(aq)]}$

Q.6 *Calculate the pH of the following solutions of weak acids . . .*

a) 0.1M monobasic (monoprotic) acid ($K_a = 2 \times 10^{-4}$ mol dm^{-3})

b) 0.01M monobasic (monoprotic) acid ($K_a = 7.5 \times 10^{-3}$ mol dm^{-3})

ACID - BASE INDICATORS

General

Many indicators are weak acids and partially dissociate in aqueous solution

$$\underset{\text{red}}{\mathrm{HIn(aq)}} \rightleftharpoons \mathrm{H^+(aq)} + \underset{\text{blue}}{\mathrm{In^-(aq)}}$$

The un-ionised form (HIn) is a **different colour** to the anionic form (In^-).

and

$$K_a = \frac{[\mathrm{H^+(aq)}]\,[\mathrm{In^-(aq)}]}{[\mathrm{HIn(aq)}]}$$

Apply Le Chatelier's Principle to predict any colour change

Example

In acid - increases [H^+] - equilibrium moves to the left to give the red form

In alkali - increases [OH^-]
- although OH^- ions don't appear in the equation they remove H^+ ions to form water.
- equilibrium moves to the right giving a blue colour

Choice

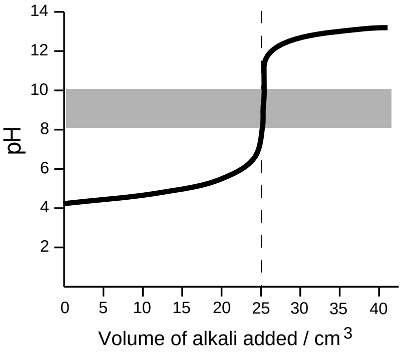
- Must have an easily observed colour change.
- Must change quickly in the required pH range on addition of 'half' a drop of reagent

examples

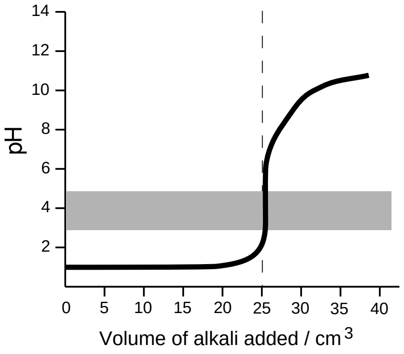
pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Methyl Orange	pink			change					yellow						
Litmus			red				change				blue				
Phenolphthalein			colourless						change			red			

A suitable indicator must... **change over the "vertical" section of the curve** where there is a **large change in pH** for the **addition of a very small volume**.

The indicator used depends on the pH changes around the end point
- the indicator must change during the 'vertical' portion of the curve -



phenolphthalein

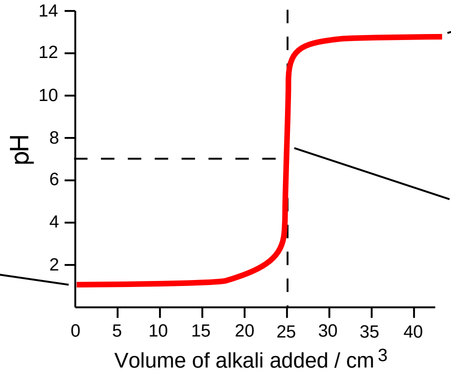


methyl orange

pH Curves

All solutions are 0.1 mol dm^{-3}

1 Strong acid (HCl) v strong base (NaOH)

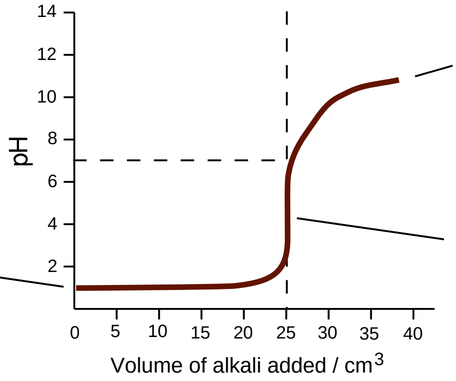


Excess 0.1 mol dm^{-3} NaOH (a strong alkali) is being added so the pH will tend towards 13.

Large pH change (4-10) at the end point.

HCl is a strong acid so is **fully dissociated**. [H$^+$] is 0.1 mol dm^{-3} so pH = 1.

2 Strong acid (HCl) v weak base (NH$_3$)

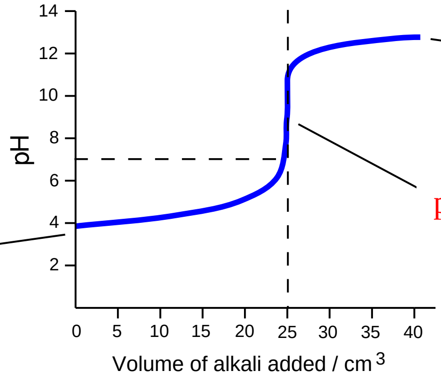


Excess 0.1 mol dm^{-3} NH$_3$ (a weak alkali) is being added so the pH will rise slowly.

pH change (4-6) at the end point.

HCl is a strong acid so is **fully dissociated**. [H$^+$] is 0.1 mol dm^{-3} so pH = 1.

3 Weak acid (CH$_3$COOH) v strong base (NaOH)

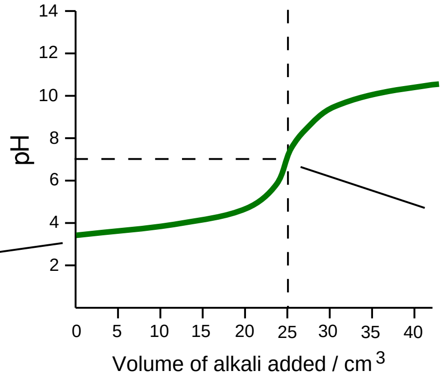


Excess 0.1 mol dm^{-3} NaOH (a strong alkali) is being added so the pH will tend towards 13.

pH change (8-10) at the end point.

CH$_3$COOH is a weak acid so is **not fully dissociated**. The pH will be around 3-4.

4 Weak acid (CH$_3$COOH) v weak base (NH$_3$)



Excess 0.1 mol dm^{-3} NH$_3$ (a weak alkali) is being added so the pH will rise slowly.

No ‘vertical’ pH change at the end point.

NO SUITABLE INDICATOR

CH$_3$COOH is a weak acid so is **not fully dissociated**. The pH will be around 3-4.

Q.7

- *Why can't indicators be used for a weak acid - weak base titration?*

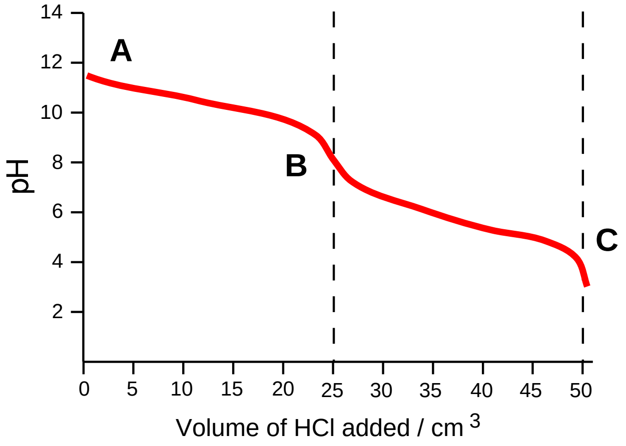
- *What alternative methods can be used?*

Other pH curves

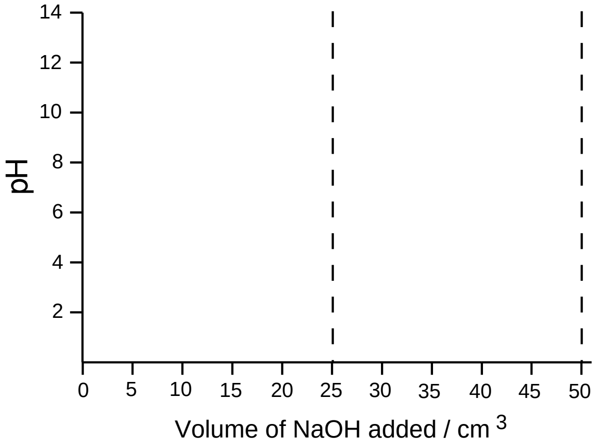
Some titrations have more than one 'vertical' portion

- acid *v.* carbonate
- NaOH *v.* diprotic acids

Q.8 *Explain the pH curve obtained when 0.1M HCl is added to 25 cm³ 0.1M Na_2CO_3*



Sketch the pH curve obtained when 0.1M NaOH is added to 25cm³ 0.1M ethanedioc acid



BUFFER SOLUTIONS - INTRODUCTION AND USES

Definition “Solutions which **resist** changes in pH when **small quantities** of acid or alkali are added.”

Types

Acidic Buffer (pH < 7)	**weak acid** *ethanoic acid*	**+**	**its sodium or potassium salt** *sodium ethanoate*
Alkaline Buffer (pH > 7)	**weak base** *ammonia*	**+**	**its chloride** *ammonium chloride*

Biological Uses

In biological systems (saliva, stomach, and blood) it is essential that the pH stays ‘constant’ in order for any processes to work properly. Most enzymes work best at particular pH values.

Blood

- the pH of blood is normally about 7.4
- If the pH varies by 0.5 it can lead to unconsciousness and coma
- carbon dioxide produced by respiration can increase the acidity of blood by forming H+ ions in aqueous solution

$$\mathbf{CO_2}(aq) + \mathbf{H_2O}(aq) \rightleftharpoons \mathbf{H^+}(aq) + \mathbf{HCO_3^-}(aq)$$

- the presence of hydrogencarbonate ions in blood removes excess H^+

$$\mathbf{H^+}(aq) + \mathbf{HCO_3^-}(aq) \rightleftharpoons \mathbf{H_2CO_3}(aq) \quad \text{(equivalent to } CO_2 \text{ in water)}$$

Other Uses

Many household and cosmetic products need to control their pH values.

Shampoo	Counteract the alkalinity of the soap and prevent irritation
Baby lotion	Maintain a pH of about 6 to prevent bacteria multiplying
Others	Washing powder
	Eye drops
	Fizzy lemonade

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BUFFER SOLUTIONS - ACTION

Acid buffer It is **essential to have a weak acid** for an equilibrium to be present so that ions can be removed and produced. The dissociation is small and there are few ions.

$$\mathbf{CH_3COOH}\text{(aq)} \rightleftharpoons \mathbf{CH_3COO^-}\text{(aq)} + \mathbf{H^+}\text{(aq)}$$

relative concs.	*HIGH*	*LOW*	*LOW*

A strong acid can't be used as **it is fully dissociated and cannot remove H^+**(aq)

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

Adding acid Any H^+ **is removed by reacting with CH_3COO^-** ions to form CH_3COOH via the equilibrium. Unfortunately, the concentration of CH_3COO^- is small and only a few H^+ can be "mopped up". A much larger concentration of CH_3COO^- is required.

To build up the concentration of CH_3COO^- ions, sodium ethanoate is added.

Adding alkali Adds OH^- ions. Although they do not appear in the equation, they react with H^+

$$\mathbf{H^+}\text{(aq)} + \mathbf{OH^-}\text{(aq)} \rightleftharpoons \mathbf{H_2O}\text{(aq)}$$

Removal of H^+ from the weak acid equilibrium means that, according to Le Chatelier's Principle, more CH_3COOH will dissociate to form ions to replace those being removed.

$$\mathbf{CH_3COOH}\text{(aq)} \rightleftharpoons \mathbf{CH_3COO^-}\text{(aq)} + \mathbf{H^+}\text{(aq)}$$

As the added OH^- ions remove the H^+ from the weak acid system, the equilibrium moves to the right to produce more H^+ ions. Obviously, there must be a large concentration of undissociated acid molecules to be available.

Other The concentration of a buffer solution is also important

If the concentration is too low, there won't be enough CH_3COOH and CH_3COO^- to cope with the ions added.

Summary For an acidic buffer solution one needs ...

large [CH_3COOH(aq)] - for dissociating into H^+(aq) when alkali is added

large [CH_3COO^-(aq)] - for removing H^+(aq) as it is added

This can't exist if only acid is present so a mixture of the acid and salt is used.

The weak acid provides the equilibrium and the large CH_3COOH(aq) concentration. The sodium salt provides the large CH_3COO^-(aq) concentration.

$\therefore$ **One uses a WEAK ACID + its SODIUM OR POTASSIUM SALT**

CALCULATING THE pH OF AN ACIDIC BUFFER SOLUTION

Example 1 *Calculate the pH of a buffer solution whose [HA] is 0.1 mol dm^{-3} and [A$^-$] of 0.1 mol dm^{-3}. Assume the K_a of the weak acid HA is 2 x 10^{-4} mol dm^{-3}.*

$$K_a = \frac{[H^+_{(aq)}]\,[A^-_{(aq)}]}{[HA_{(aq)}]}$$

re-arranging

$$[H^+_{(aq)}] = \frac{[HA_{(aq)}]\ K_a}{[A^-_{(aq)}]} = \frac{0.1 \times 2 \times 10^{-4}}{0.1} = \mathbf{2 \times 10^{-4}\ mol\ dm^{-3}}$$

$$\therefore \quad \mathbf{pH} = \mathbf{-\log_{10} [H^+_{(aq)}]} = \mathbf{3.699} \quad (3.7)$$

Example 2 *Calculate the pH when 500cm^3 of 0.10 mol dm^{-3} of weak acid HX is mixed with 500cm^3 of a 0.20 mol dm^{-3} solution of its salt NaX. K_a = 4.0 x 10^{-5} mol dm^{-3}.*

$$K_a = \frac{[H^+_{(aq)}]\,[X^-_{(aq)}]}{[HX_{(aq)}]}$$

re-arranging

$$[H^+_{(aq)}] = \frac{[HX_{(aq)}]\ K_a}{[X^-_{(aq)}]}$$

The solutions have been mixed*; volume is now 1 dm^3* *[HX] = 0.05 mol dm^{-3}*

[X$^-$] = 0.10 mol dm^{-3}

$$\therefore \quad [H^+_{(aq)}] = \frac{0.05 \times 4.0 \times 10^{-5}}{0.1} = \mathbf{2.0 \times 10^{-5}\ mol\ dm^{-3}}$$

$$\therefore \quad \mathbf{pH} = \mathbf{-\log_{10} [H^+(aq)]} = \mathbf{4.699} \quad (4.7)$$

Alkaline buffer Similar but is based on the equilibrium surrounding a weak base.

	$\mathbf{NH_3}$(aq)	+	$\mathbf{H_2O_{(l)}}$(aq)	$\rightleftharpoons$	$\mathbf{OH^-}$(aq)	+	$\mathbf{NH_4^+}$(aq)
relative concs.	*HIGH*				*LOW*		*LOW*

but one needs ; **a large conc. of OH$^-$(aq)** to react with any H$^+$(aq) added
a large conc of NH$_4^+$(aq) to react with any OH$^-$(aq) added

There is enough NH$_3$ to act as a source of OH$^-$ but one needs to increase the concentration of ammonium ions by adding an ammonium salt.

Use **AMMONIA (a weak base) + AMMONIUM CHLORIDE (one of its salts)**

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PARTITION COEFFICIENT

Chromatographic techniques can be classified (Table 21.8) according to whether the separation takes place on a flat surface (planar) or in a column. They can be further sub-divided into gas and liquid chromatography, and whether the stationary phase is a solid or liquid.

Technique	Stationary phase	Mobile phase	Format	Mechanism of separation
Paper chromatography	Paper (cellulose)	Liquid	Flat	Partition
Thin layer chromatography (TLC)	Silica, cellulose	Liquid	Flat	Adsorption or partition
Gas–liquid chromatography (GLC)	Liquid	Gas	Column	Partition
High-performance liquid chromatography (HPLC)	Solid	Liquid	Column	Modified partition

Table 21.8 A classification of chromatographic techniques

A further very important classification involves the nature of the interactions between the mobile and stationary phases. The two main forms of interaction between the analyte and the stationary and mobile phases are **adsorption** and **partition** (Figure 21.78).

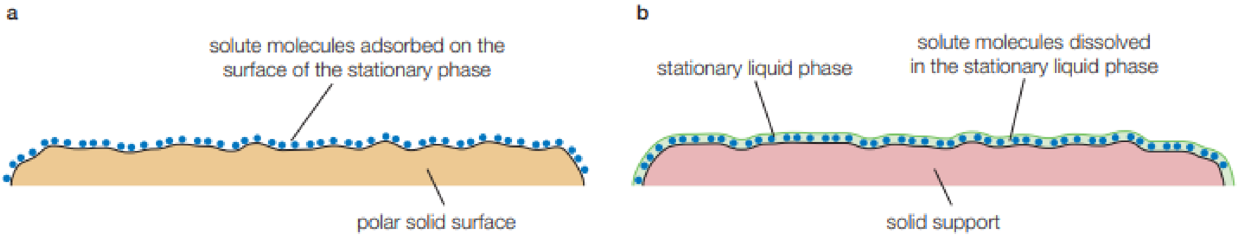


Figure 21.78 The two mechanisms of separation: **a** adsorption chromatography and **b** partition chromatography

Adsorption (Figure 21.78a) involves the electrostatic interactions between chemical species and a surface. In adsorption chromatography, the solute molecules are held on the surface of the stationary phase. Generally, the stationary phase is a polar solid and the solutes are polar molecules. Strongly polar stationary phases attract and retain the polar solutes. Hence the separation of the solutes depends on their difference in polarity: the more polar solutes are more readily adsorbed than less polar solutes.

Partition (Chapter 17) can be demonstrated by adding bromine to a mixture of water and tribromoethane (Figure 21.79). These two liquids are immiscible and do not mix, but the bromine distributes itself in both liquids. Equilibrium is reached when the rates of movement of bromine up and down between the two liquids are equal. At equilibrium the solute molecules are distributed between the two liquids in a definite ratio (for a specific temperature); the solute has been partitioned between the two liquids. The bromine equilibrium favours the tribromomethane: the 'like dissolves like' principle (Chapter 4).

During the separation process in forms of partition chromatography, the solutes move between the stationary phase and the mobile phase and are partitioned between them (Figure 21.78b). Solutes in the mobile phase move forward with it. When the mobile phase is a gas, the rate of movement of solutes depends on their *volatility* and their *relative solubility*.

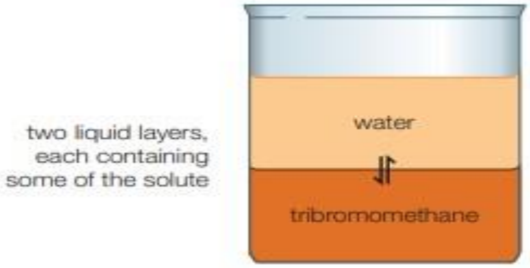
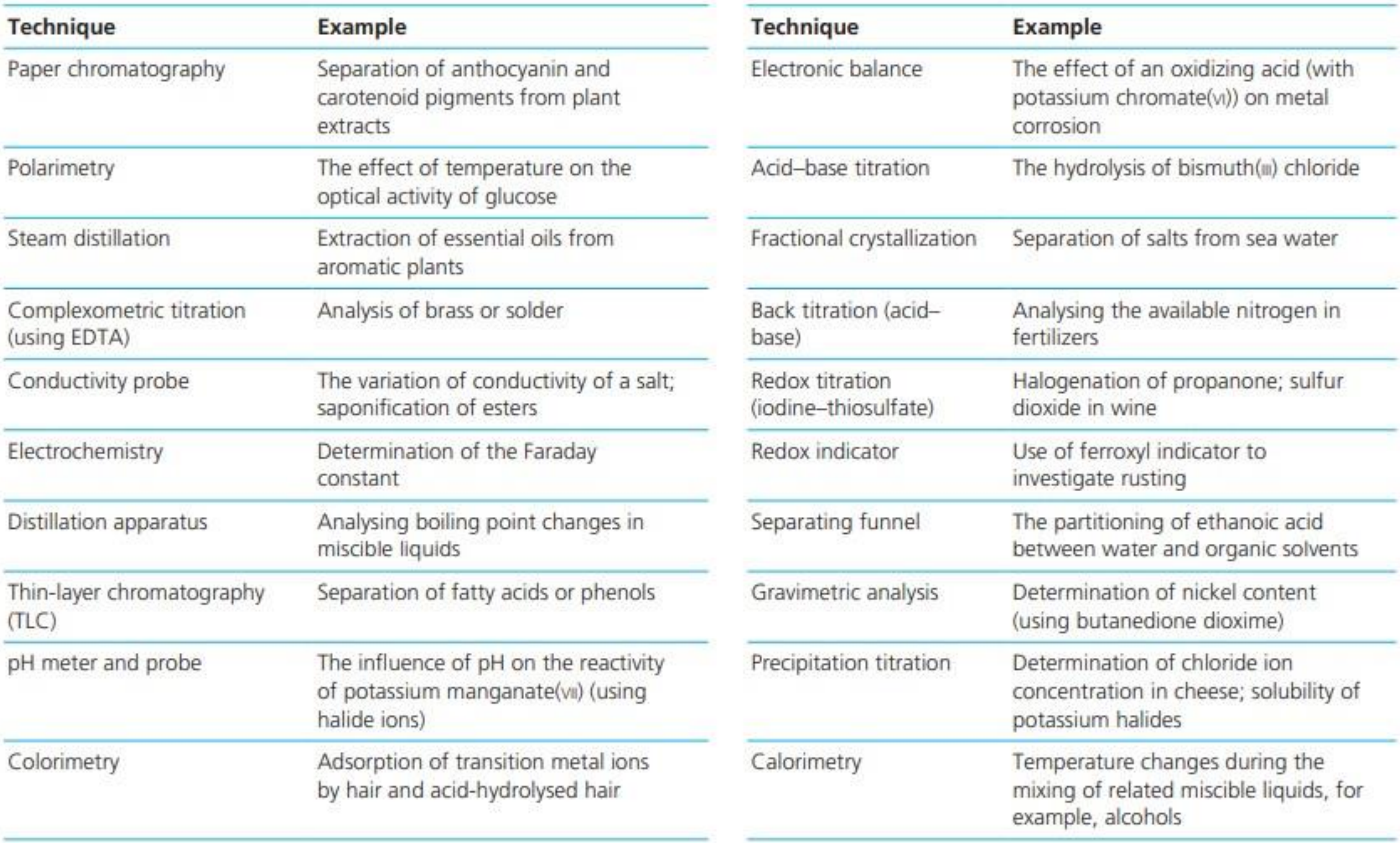
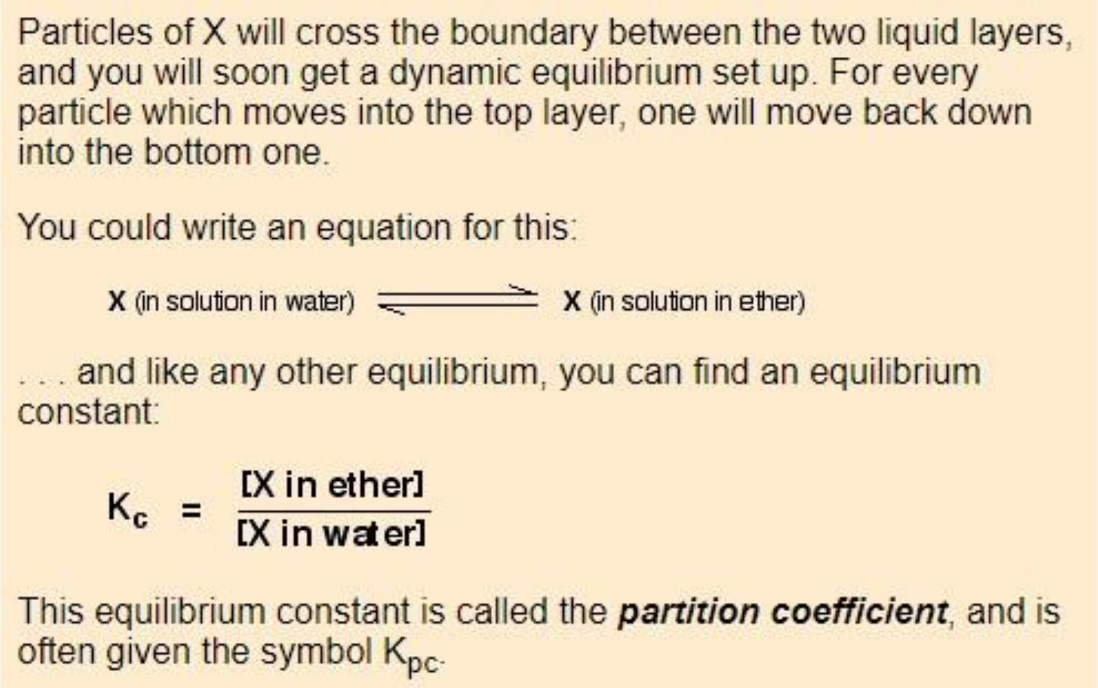


Figure 21.79 Bromine partitioned between water and tribromomethane



Technique	Example	Technique	Example
Paper chromatography	Separation of anthocyanin and carotenoid pigments from plant extracts	Electronic balance	The effect of an oxidizing acid (with potassium chromate(VI)) on metal corrosion
Polarimetry	The effect of temperature on the optical activity of glucose	Acid–base titration	The hydrolysis of bismuth(III) chloride
Steam distillation	Extraction of essential oils from aromatic plants	Fractional crystallization	Separation of salts from sea water
Complexometric titration (using EDTA)	Analysis of brass or solder	Back titration (acid–base)	Analysing the available nitrogen in fertilizers
Conductivity probe	The variation of conductivity of a salt; saponification of esters	Redox titration (iodine–thiosulfate)	Halogenation of propanone; sulfur dioxide in wine
Electrochemistry	Determination of the Faraday constant	Redox indicator	Use of ferroxyl indicator to investigate rusting
Distillation apparatus	Analysing boiling point changes in miscible liquids	Separating funnel	The partitioning of ethanoic acid between water and organic solvents
Thin-layer chromatography (TLC)	Separation of fatty acids or phenols	Gravimetric analysis	Determination of nickel content (using butanedione dioxime)
pH meter and probe	The influence of pH on the reactivity of potassium manganate(VII) (using halide ions)	Precipitation titration	Determination of chloride ion concentration in cheese; solubility of potassium halides
Colorimetry	Adsorption of transition metal ions by hair and acid-hydrolysed hair	Calorimetry	Temperature changes during the mixing of related miscible liquids, for example, alcohols

Table 29.2 A sample of laboratory techniques and possible areas of investigation suitable for the extended essay



Particles of X will cross the boundary between the two liquid layers, and you will soon get a dynamic equilibrium set up. For every particle which moves into the top layer, one will move back down into the bottom one.

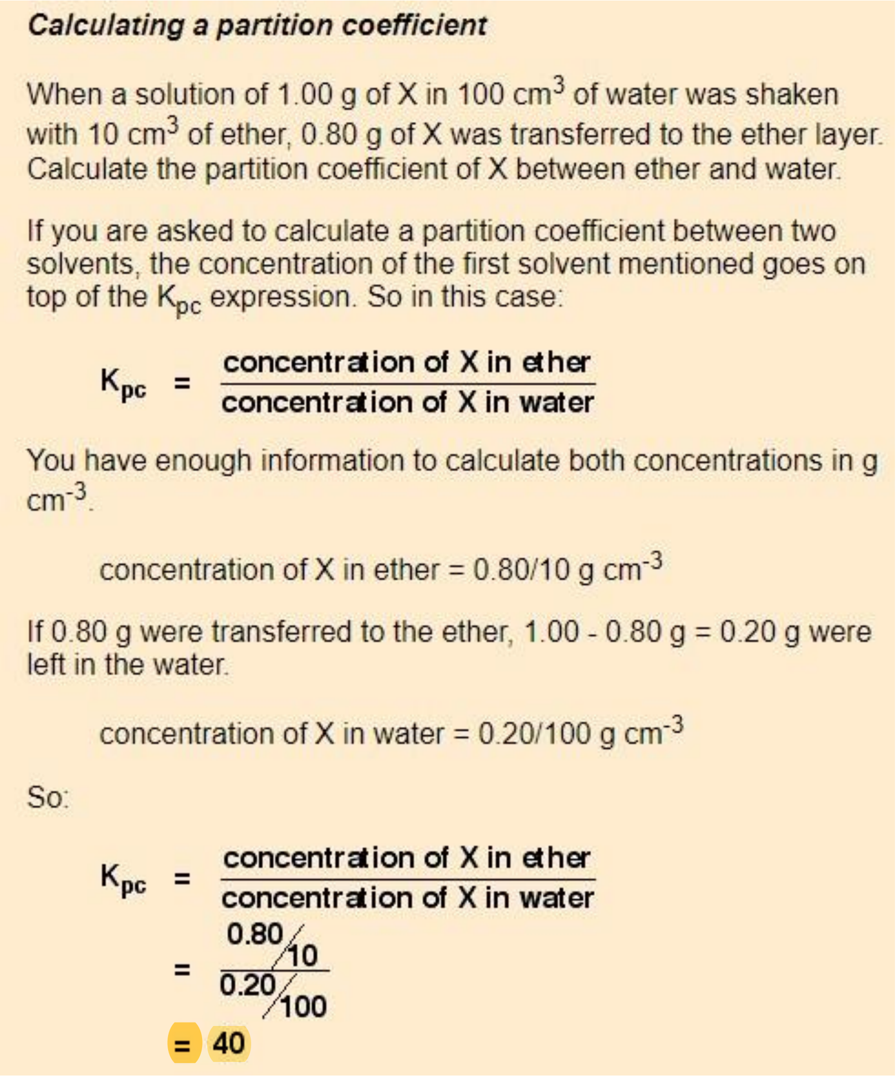
You could write an equation for this:

$$\textbf{X} \text{ (in solution in water)} \rightleftharpoons \textbf{X} \text{ (in solution in ether)}$$

. . . and like any other equilibrium, you can find an equilibrium constant:

$$K_c = \frac{[\text{X in ether}]}{[\text{X in water}]}$$

This equilibrium constant is called the ***partition coefficient***, and is often given the symbol K_{pc}.



Calculating a partition coefficient

When a solution of 1.00 g of X in 100 cm^3 of water was shaken with 10 cm^3 of ether, 0.80 g of X was transferred to the ether layer. Calculate the partition coefficient of X between ether and water.

If you are asked to calculate a partition coefficient between two solvents, the concentration of the first solvent mentioned goes on top of the K_{pc} expression. So in this case:

$$K_{pc} = \frac{\text{concentration of X in ether}}{\text{concentration of X in water}}$$

You have enough information to calculate both concentrations in g cm^{-3}.

concentration of X in ether = 0.80/10 g cm^{-3}

If 0.80 g were transferred to the ether, 1.00 - 0.80 g = 0.20 g were left in the water.

concentration of X in water = 0.20/100 g cm^{-3}

So:

$$K_{pc} = \frac{\text{concentration of X in ether}}{\text{concentration of X in water}}$$

$$= \frac{0.80/10}{0.20/100}$$

$$= 40$$