Chemical Equilibrium Systems

Brief Revision

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ENERGY CHANGES IN REACTIONS

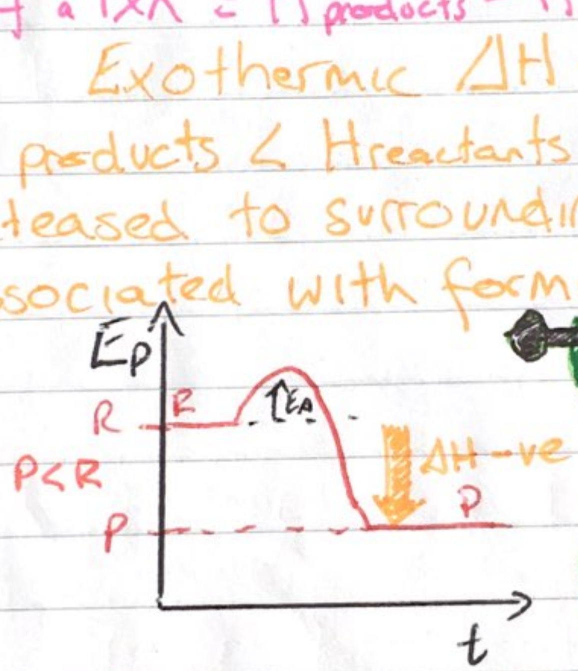
All substances contain chemical potential energy

Chemical E = Heat Content = Enthalpy = ΔH (Change in enthalpy during a rxn)

ΔH of a rxn = $H^{final}_{products} - H^{initial}_{reactants}$

Exothermic ΔH -ve

- H products < Hreactants ∴ energy is released to surroundings → get hot
- associated with forming bonds

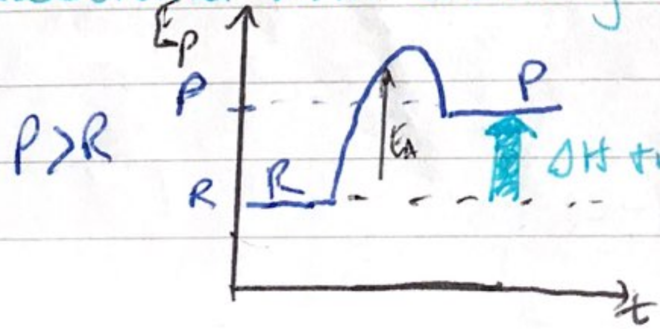


NOTE

ΔH physical changes
^
ΔH chemical changes

Endothermic ΔH +ve

- Hproducts > Hreactants ∴ energy is absorbed from surroundings → get cold
- associated with breaking bonds



COLLISION THEORY + RXN RATES

Collision theory - successful rxn = successful collision → ✓ orientation + sufficient E_A

{Factors affecting rxn rate in terms of collision theory}

{collision theory explains what happens during a rxn on a molecular level.}

1. NATURE OF REACTANTS

If reactant bonds must be broken E_A ↑ and the rxn tends to be slow. ↓ rxn rate

If reactants only need to collide rxn tends to be instantaneous (IONS precipitating in solution)

2. [REACTANTS]

↑[ ] ⇒ ↑ # of particles per unit area ⇒ ↑ frequency of successful collisions ∴ Rxn rate ↑

3. STATE OF SUBDIVISION

little pieces = ↑ S.A. = ↑ particles exposed for collision = ↑ frequency of successful collisions ∴ Rxn rate ↑

4. TEMPERATURE OF SYSTEM

MAJOR - ↑T = ↑$E_{K\,(avg)}$ = ↑ proportion of particles ≥ E_A = ↑ frequency of successful collisions ∴ Rxn rate ↑

MINOR - ↑E_K = faster particles collide more

5. CATALYSTS

Alternative pathway for reactants with ↓er E_A. ↑ proportion of particles $\geq E_A$ = ↑ frequency successful collisions ∴ ↑ Rxn rate.

Rxn rate depends on rate of successful collisions - depends on

- Total frequency of collisions (Change [ ], state subdiv, ↕ temp)
- % successful collisions (Change temp, catalyst)

Chemical System

OPEN CHEMICAL SYSTEM - allows matter AND energy to be exchanged with the surroundings

CLOSED CHEMICAL SYSTEM - allows energy but NOT matter to be exchanged with the surroundings

If matter is escaping (eg gas ~~[illegible]~~ produced in an open beaker) the system is OPEN To establish equilibrium a CLOSED system is needed.

Chemical Equilibrium

IN TERMS OF E_A

The REVERSIBILITY of chemical rxns is related to the E_As of the fwd and rvs rxns.

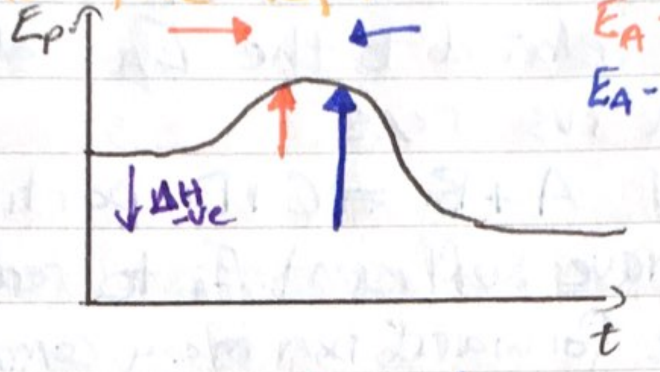
In RXN $A + B \rightleftharpoons C + D$ particles A + B have sufficient E_A to react so the forward rxn may commence. At the same time particles C + D have sufficient E_A to react so the reverse reaction may also commence. The rxn may proceed in BOTH directions so is reversible. If the rates of the forward and reverse reactions are equal (A + B and C + D are colliding at the same rate or frequency) then a CHEMICAL EQUILIBRIUM is reached / established.

Relative E_As of the fwd and rvs rxns can also determine the position of an equilibrium

- Similar E_{AS} => both reactants + products present in significant amounts
- Fwd rxn ↑E_A = endo => equlibrium will tend to the right.

- RVS rxn ↑ E_A = exo ⇒ equilibrium will tend to the left.

EG:



E_A - EXO - FWD
E_A - ENDO - RVS

$$(E_A\text{-exo-fwd}) < (E_A\text{-endo-RVS})$$

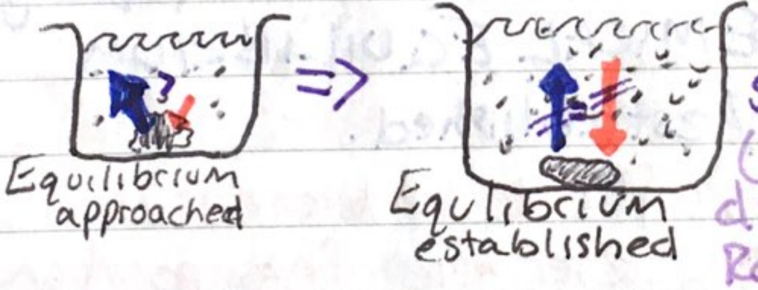
∴ FWD rxn is easier + will be favoured equilibrium will <u>tend</u> right.

Equilibrium - physical systems

Solution Equilibria

when a soluble solid is placed in liquid it may dissolve until saturation is reached.

- SATURATION is a kind of equilibrium.



Dynamic Microscopic processes
(Rate (s) is dissolving = Rate (aq) is solidifying)

Macroscopic Properties: constant (colour/mass)

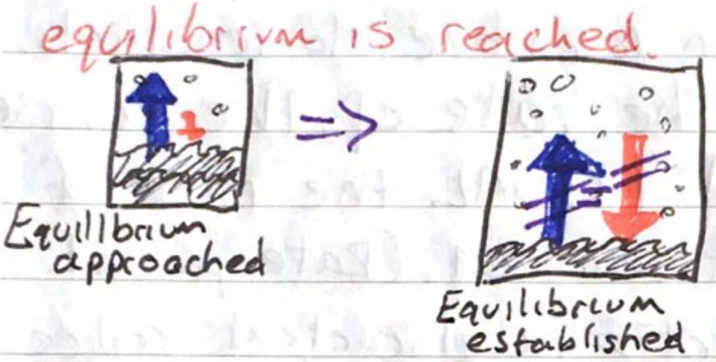
$$I_{2(s)} \rightleftharpoons I_{2(aq)}$$

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

Vapour Pressure Equilibria

Equlibrium reached when (l) in CLOSED container. (l) evaporates until rate of evaporation = rate of condensation and equilibrium is reached.

Dynamic microscopic properties (rate of evap = rate of condens.)



Macroscopic Properties: Constant (vapour pressure, (l) volume)

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$

Dynamic Equilibrium

In most chemical rxns, the reactants collide to form products. The rxn stops when the limiting reagent is completely consumed.

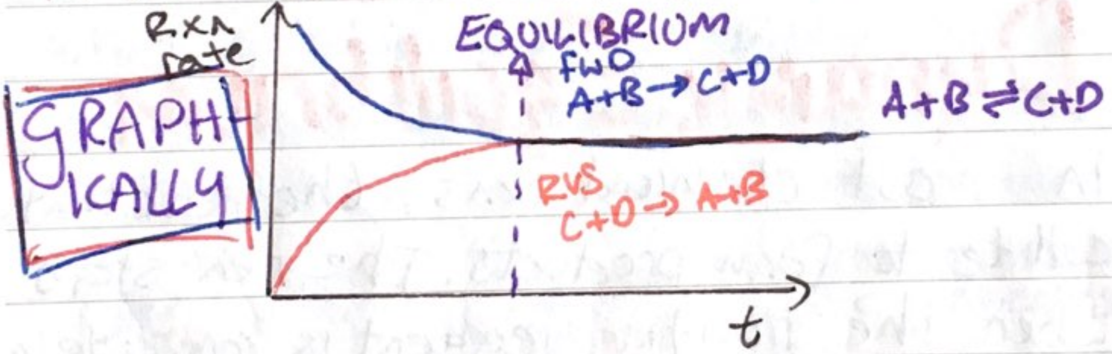
eg $CaCO_{3(s)} + 2H^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + H_2O_{(l)} + CO_{2(g)}$

This rxn stops when all of the acid (H^+) or all of the $CaCO_3$ (s) is consumed. The products can't recombine to form the reactants.

In REVERSIBLE rxns however the products will start to collide and react to form and regenerate the reactants.

eg $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

The products can recombine into reactants. Eventually the rate of the reverse reaction will EQUAL the rate of the forward reaction. (Rate products collide and react = rate reactants collide and react to regenerate eachother) This is when CHEMICAL EQUILIBRIUM is reached / established.



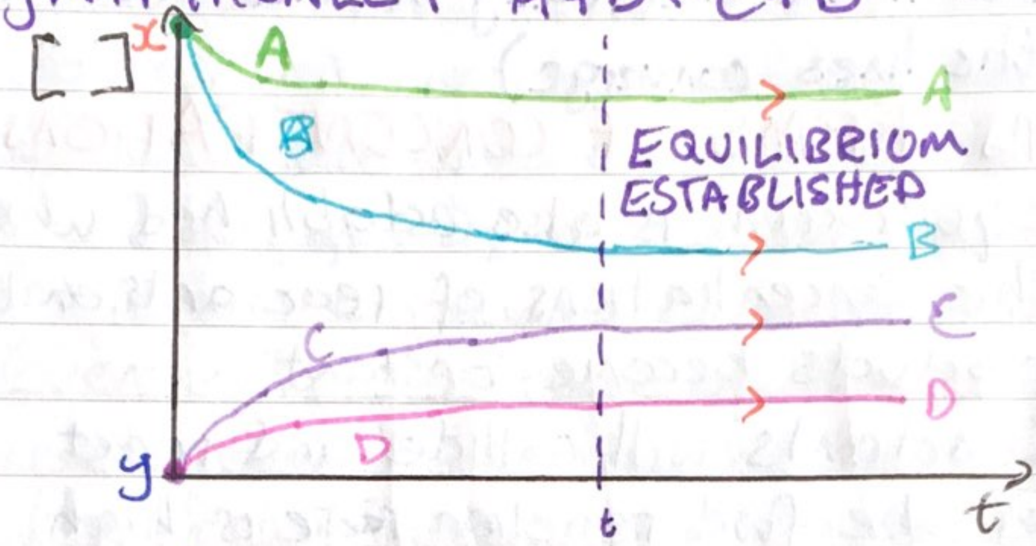
Initially only reactants are present and the FWD rxn rate is ↑. As reactants are consumed the fwd rxn rate slows (curve becomes less steep) and eventually becomes constant. The reverse rxn rate ↑ as products are formed and it too eventually becomes constant (the lines converge)

IN TERMS OF CONCENTRATION

Equilibrium is also established when the concentrations of reactants and products become <u>constant</u>.

Reactants will collide and react as the fwd reaction rate is high. They 'collide off' as they're consumed and their concentrations decrease with the slowing fwd rxn rate. As the reverse reaction commences and the fwd rxn rate is high products are produced rapidly, their concentrations increasing. As the fwd rxn rate slows, less are produced and collide and the rvs rxn rate slows until both fwd and reverse converge. Concentration of products ~~[illegible]~~ over time slows until it and of the reactants become constant and parallel.

GRAPHICALLY $A + B \rightleftharpoons C + D$



$A + 3B \rightleftharpoons 2C + D$

Initially only A and B ate present at a concentration of x. As they collide and react their concentrations decrease. [B] decreases at a rate 3x that of [A], 3 moles of B must collide for every mole (molecule) of A so ultimately more of it must collide and it is 'depleted' 3x quicker. As C and D are produced their concentrations increase. [C] increases at a rate 2x that of [D] as 2 particles of C are produced for each particle of D. [ ]s of A, B, C, D become constant, their lines parallel as EQUILIBRIUM is established.

When a chemical rxn has reached equilibrium:

1) FWD RXN rate = RVS RXN rate
11) [products] and [reactants] = CONSTANT
111) System is <u>DYNAMIC</u> as the fwd and rvs rxns continue to occur.

Chem equilibrium is characterised by:

1) CONSTANT <u>Macroscopic</u> properties
Colour, mass, concentration, vapour pressure
11) EQUAL but OPPOSING rates of rxn
- DYNAMIC microscopic properties

2 methods of Graphical Representation:

1) Reaction rates / time
11) Concentration of involved species / time

EXAMPLES ALL with DYNAMIC FWD and RVS RXNS.

1. Weak acid equilibrium

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

Constant macro properties: pH

11. Precipitate equilibrium

$$Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \rightleftharpoons Ca(OH)_{2\,(s)}$$

Constant macro properties: $m(Ca(OH)_2)$
$[Ca^{2+}]$, $[OH^-]$, pH

iii. Gas equilibrium

colour less → $N_2O_{4\,(g)} \rightleftharpoons 2NO_{2\,(g)}$ ← brown

Constant macro properties: colour
$[N_2O_4]$, $[NO_2]$, pressure.

THE Equilibrium Constant (k)

for the general reversible reaction

$$aA + bB \rightleftharpoons dD + eE$$

$$K = \frac{[D]^d . [E]^e}{[A]^a . [B]^b} \Rightarrow \frac{\text{products}}{\text{reactants}}$$

- k indicates the relative proportions of products : reactants at equilibrium
- Every reaction has its own equilibrium constant at a PARTICULAR TEMPERATURE

IMPORTANT!!! ⇒ Concentrations of SOLIDS and LIQUIDS DO NOT change! ∴ They are NOT included in the expression

Only solutions (aq) and gases (g) are included in K.

eg $H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \Rightarrow K = [H^+][OH^-]$
$= 1.00 \times 10^{-14}$

The Effects of Changes to equilibrium systems

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Certain factors can affect the equilibrium system itself or just the eqilibrium POSITION.

The POSITION of an equilibrium refers to where the equilibrium lies with reference to the equation. This IS DEFINED by the RELATIVE CONCENTRATIONS of products and reactants.

Equilibrium depends on the conditions of a system, changing the conditions impacts reaction rates and species concentration and therefore alters the equilibrium position.

Equilibrium can be described as lying to the left or right.

LEFT: [Reactants] > [products]

RIGHT: [Products] > [reactants]

Factors that affect the equilibrium of a system:

I) Changes in concentration of reactants or products

II) Changes in volume and pressure of a <u>gaseous</u> system

III) Changes in temperature to the system

IV) Catalysts

Understanding how these changes alter FWD and RVS rxns~~rates~~ we can predict the impacts of these changes to the equilibrium and its position

I) Changes in Concentration

Increasing the concentration of a species will move the reaction to the otherside of the equation to use up some of the added chemical and find a new equilibrium position

Reducing the concentration of a species shifts equilibrium position to its side of the equation to regenerate it. Often to reduce chemical concentration and remove it from the system another chemical is added to react with it.

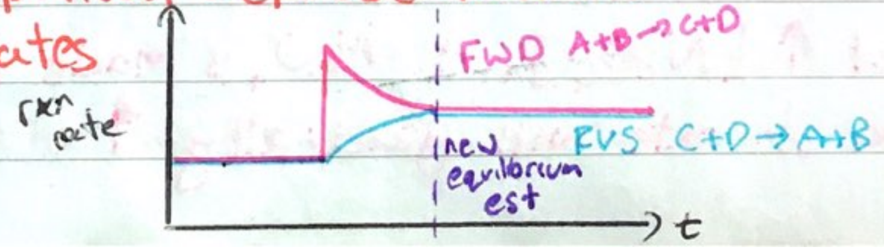
System: $A\uparrow + \overrightarrow{B \rightleftharpoons C} + D$

Imposed Change: Adding more A
ie $\uparrow[A]$

Effects explained using Collision Theory:
More A is available for collision per unit area, increasing the frequency of successful collisions between A and B. The forward reaction rate is increased but will partially decrease as A and B collide and are consumed, decreasing their concentrations, A only partially. The forward reaction is favoured, increasing the concentrations of C and D which increases their frequency of collisions and gradually the reverse reaction rate until equilibrium is established. Equilibrium shifts right

Graphical Representation:

Rxn Rates



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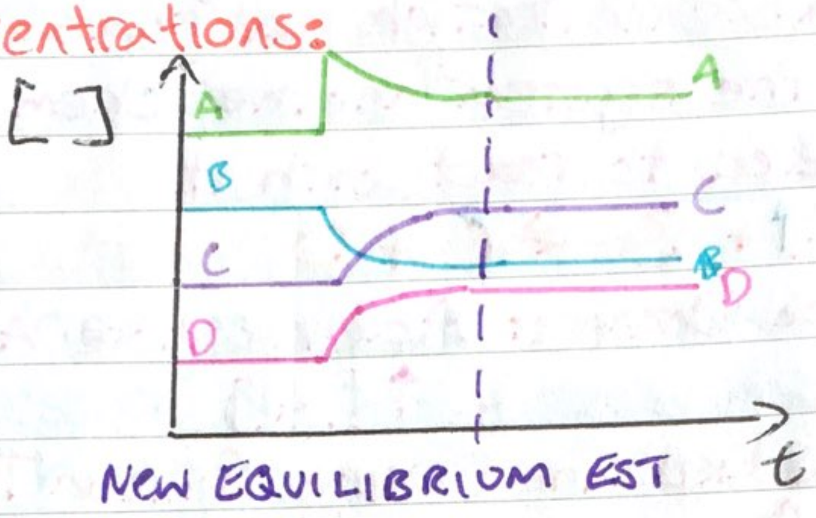
Concentrations:



Summary:

- FWD rxn rate ↑ then partially ↓
- RVS rxn rate gradually ↑
- [A] ↑ then partially ↓
- [B] ↓
- [C] ↑
- [D] ↑
- FWD Rxn favoured, equilibrium →
- Solut^n will be coloured more like C/D

EXAMPLES

1) System: colourless $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ brown

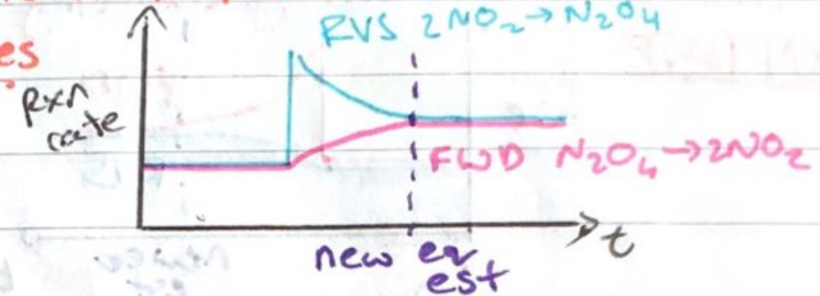
Imposed Change: Add more NO_2 ∴ ↑ $[NO_2]$

Effect on Rxn rate: ↑ $[NO_2]$ → ↑ rate of reverse reaction. As rvs rxn rate ↑ you get ↑ $[N_2O_4]$. As N_2O_4 is made the fwd rxn rate will gradually ↑

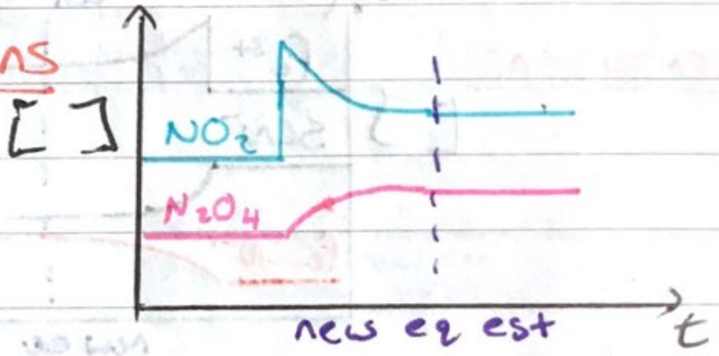
Equilibrium shifs: left
Favouring: Reverse reaction

Graphical Representations:

Rxn Rates



Concentrations



Summary of observations:

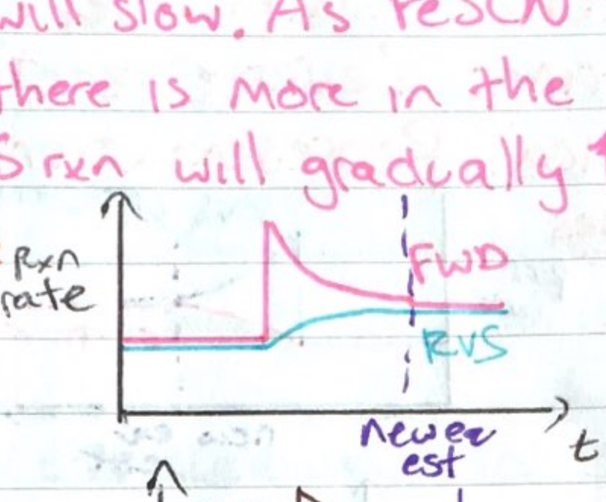
- $[NO_2]\uparrow$ then partially $\downarrow$
- $[N_2O_4]\uparrow$
- Dark brown gas is added to brown gaseous solution, dark brown fades to brown darker than original gas. solutn

2) System: $\overset{\text{Pale Brown}}{Fe^{3+}_{(aq)}} + \overset{\text{colourless}}{SCN^-_{(aq)}} \rightleftharpoons \overset{\text{Red}}{FeSCN^{2+}_{(aq)}}$

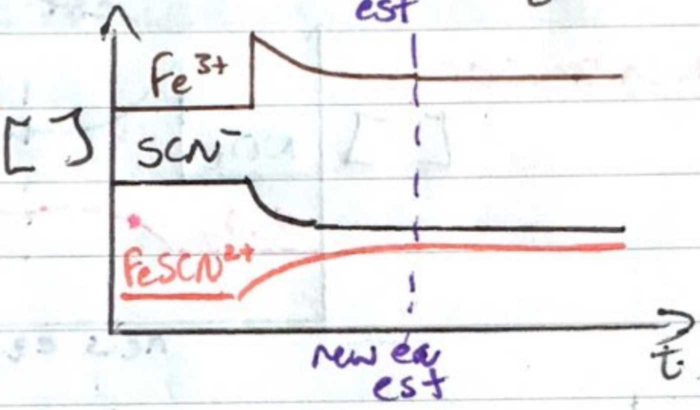
Imposed Charge: Add more Fe^{3+}

Effect on rxn rate: $[Fe^{3+}]\uparrow \rightarrow \uparrow$ rate of FWD rxn as more Fe^{3+} is available for successfl collisions. As the Fe^{3+} is consumed the rxn rate will slow. As $FeSCN^{2+}$ is produced there is more in the system so the RVS rxn will gradually ↑

RXN RATES



Concentrations



Summary of observations

- $[Fe^{3+}]$ ↑ then ↓ slightly
- $[SCN^-]$ ↓
- $[FeSCN^{2+}]$ ↑
- Solut^ becomes a deeper red

Equilibrium shifts: Right

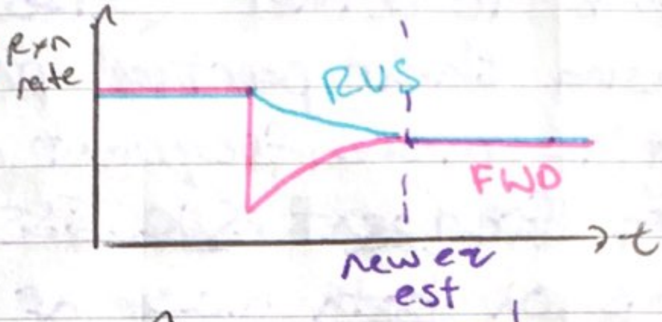
ORANGE

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

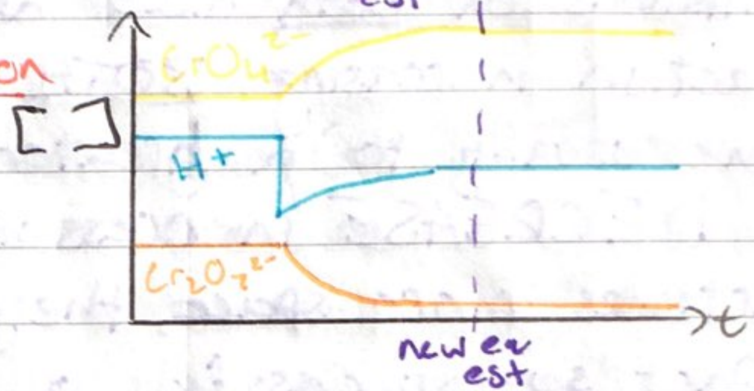
Imposed Change: Add NaOH (OH^-) $(\downarrow [H^+])$

Effect on rxn rate: $[H^+]$ ↓ as $H^+ + OH^- \rightarrow H_2O$ neutralisation. ∴ the rate of the FWD Rxn ↓. As less product is being formed the rate of the RVS rxn also slows but to a lesser extent.

RXN RATE



Concentration



Equilibrium shifts: Left

Summary and Observations:

- $[H^+]$ ↓ then partially ↑
- $[CrO_4^{2-}]$ ↑
- $[Cr_2O_7^{2-}]$ ↓
- Solutⁿ will become more yellow

11) Changes to Volume (Pressure)

The effect of changing the pressure on a gaseous equilibrium system depends on the number of moles of ~~each~~ gases on each side of the eqvation. However, in general an

INCREASE in pressure pushes all particles closer together (also effectively increasing their partial pressure ([])) leading to more frequent collisions ∴ more frequent SUCCESSFUL collisions on both sides of the reaction increasing BOTH rxn rates. (one usually to a greater extent)

A DECREASE in pressure gives particles more space, they're further apart so successful collisions are LESS frequent on both sides of the reaction, decreasing BOTH Rxn rates. (one usually to a greater extent)

If there are more moles on one side of the equation then favouring their production takes up more space in the system, for a decrease in pressure the side with more moles will be favoured to fill the space, for an increase the side with less moles takes up as little space as possible, so is favoured.

Pressure is often changed by ↑ or ↓ container Volume. ↑V → ↓P
↓V → ↑P (Boyle's Law)

GENERAL EXAMPLE

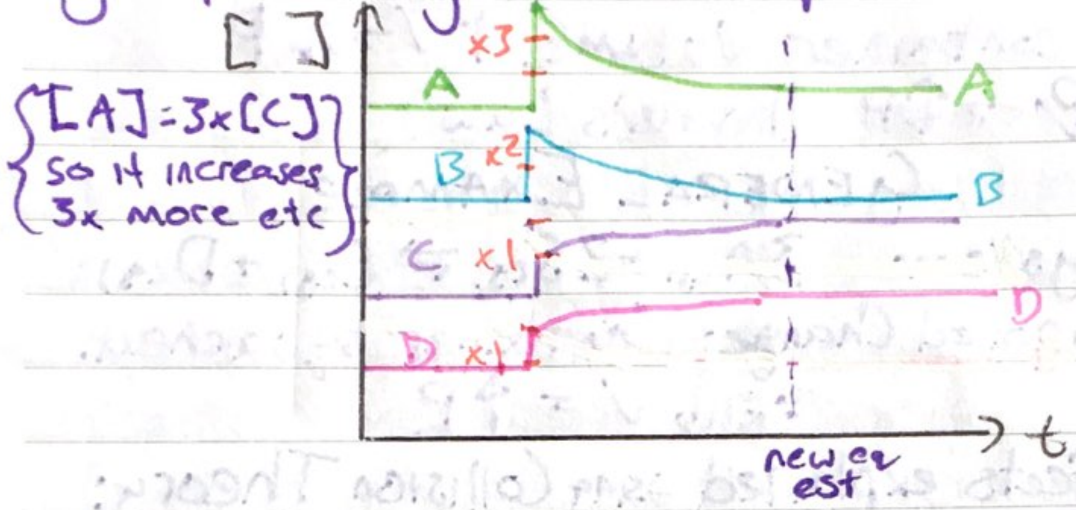
System: $3A_{(g)} + 2B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$

Imposed Change: Container squashed.
∴ ↓V = ↑P

Effects explained using Collision Theory:

↑P → ↑ partial pressure of all gaseous species leading to more frequent successful collisions of reactants and products. The ratio of reactants to products = 5:2, so while both rxn rates increase the forward reaction does so to a greater extent to favour the production of less moles to decrease pressure. As reactants are consumed their partial pressure decreases as does the forward reaction rate. As product is produced and its partial pressure increases the reverse reaction gradually continues to increase. The forward reaction was favoured, equilibrium shifts right.

graphically: Partial pressure



Summary

- [A] ↑ then partially ↓
- [B] ↑ then partially ↓
- [C] ↑
- [D] ↑

EXAMPLE

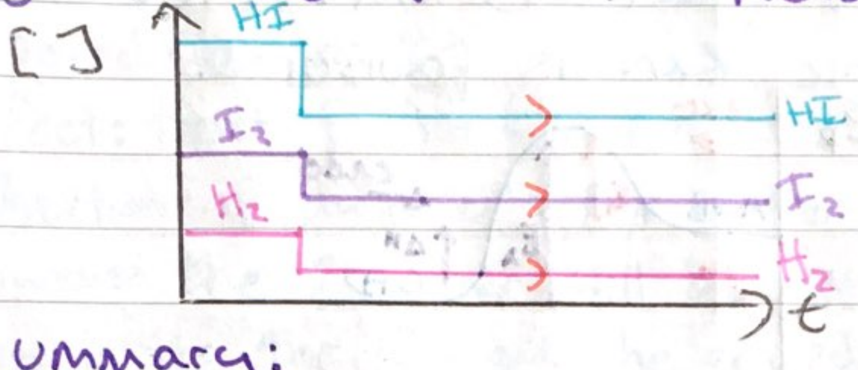
System: $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

Imposed Change: ↑ V ∴ ↓ P

Effect: ↓ P ∴ ↓ [ ] of reactants and products ∴ both the FWD and RVS Rxn rates decrease. As there are equal numbers of moles on both the reactant and product sides the change in reaction rate occurs to the same extent and so EQUILIBRIUM IS

MAINTAINED (but will be reached slower)

GRAPHICALLY: Partial Pressure



Summary:

- ↓[ ] of all species.

(III) Changing Temperature

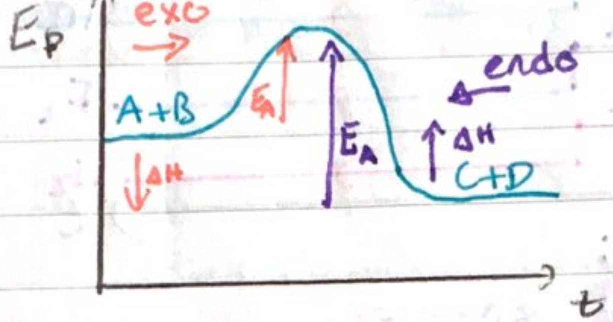
In a reversible reaction the rxn in one direction will be EXOTHERMIC while the rxn in the other direction will be ENDOTHERMIC

$$A + B \overset{\xrightarrow{\text{exo}}}{\underset{\xleftarrow{\text{endo}}}{\rightleftharpoons}} C + D + \text{ENERGY}$$

If the temperature of an equilibrium system ↑ then E is added ∴ there are more particles $\geq E_A$ and so there is an ↑ proportion of successful collisions, ∴ Rxn rates ↑ in BOTH directions.

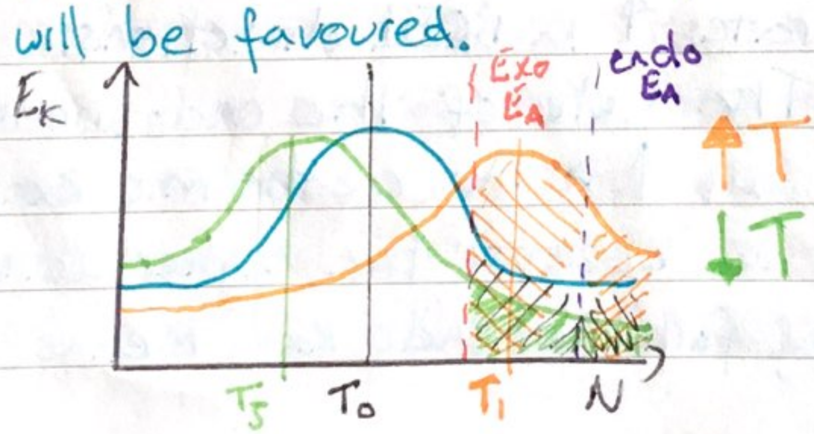
BUT The rate of the endothermic Rxn will ↑ > the exothermic Rxn. This is because the higher activation energy for the endo Rxn means the

$\uparrow T \rightarrow \uparrow_s$ % of particles at or above E_A to a greater extent. ∴ The endothermic Rxn is favoured.



$\uparrow$ E in the system, the system wants to burn it off so the endothermic Rxn is favoured to use up this E.

If the T of the system $\downarrow$ <u>BOTH</u> the rate of the FWD and RVS Rxns will $\downarrow$ as there is a $\downarrow$er portion of particles $\geq E_A$. However the endothermic Rxn will $\downarrow$ more as it has a higher E_A so it will comparatively have less particles $\geq E_A$. ∴ The exothermic Rxn will be faster and so will be favoured.



GENERAL EXAMPLES

System: $A + B \underset{\leftarrow endo}{\overset{\rightarrow exo}{\rightleftharpoons}} C + D + E \; (\Delta H = -ve)$

Imposed Change: ↑T

Effect: Both FWD + RVS Rxn rates ↑ as a ↑portion of particles ≥ E_A on both sides, however the RVS rxn will be favoured due to its ↑er E_A, and the added energy is absorbed by the system.

Imposed Change: ↓T

Effect: Both FWD + RVS Rxn rates ↓ as a ↓er portion of particles ≥ E_A on both sides, however the FWD rxn will be favoured due to its ↓er E_A, and the removed energy is partially regenerated by the system.

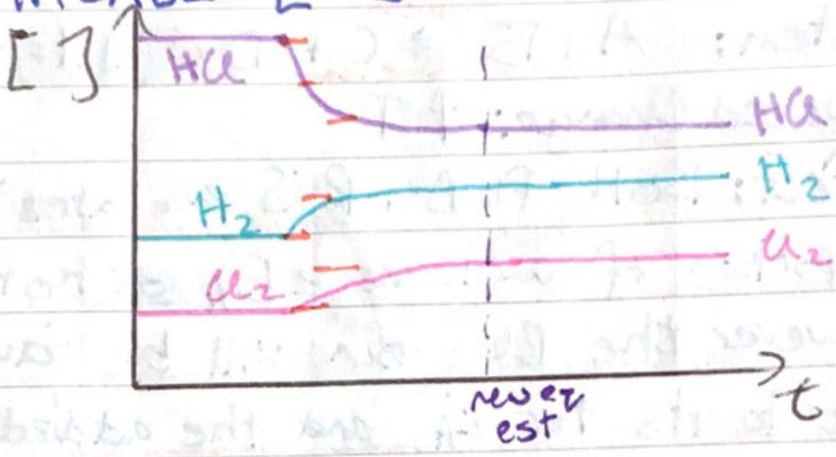
EXAMPLE

System: $H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)} + 44kJ$

Imposed Change: ↑T ∴ $\overset{add}{\uparrow}E$ ∴

Effect: ↑ rate of reaction in both directions but to a greater extent in the endothermic RVS rxn which is favoured. The [reactants] will gradually increase and the [products] will gradually decrease as they're produced, and collided, respectively.

GRAPHICALLY: [ ]

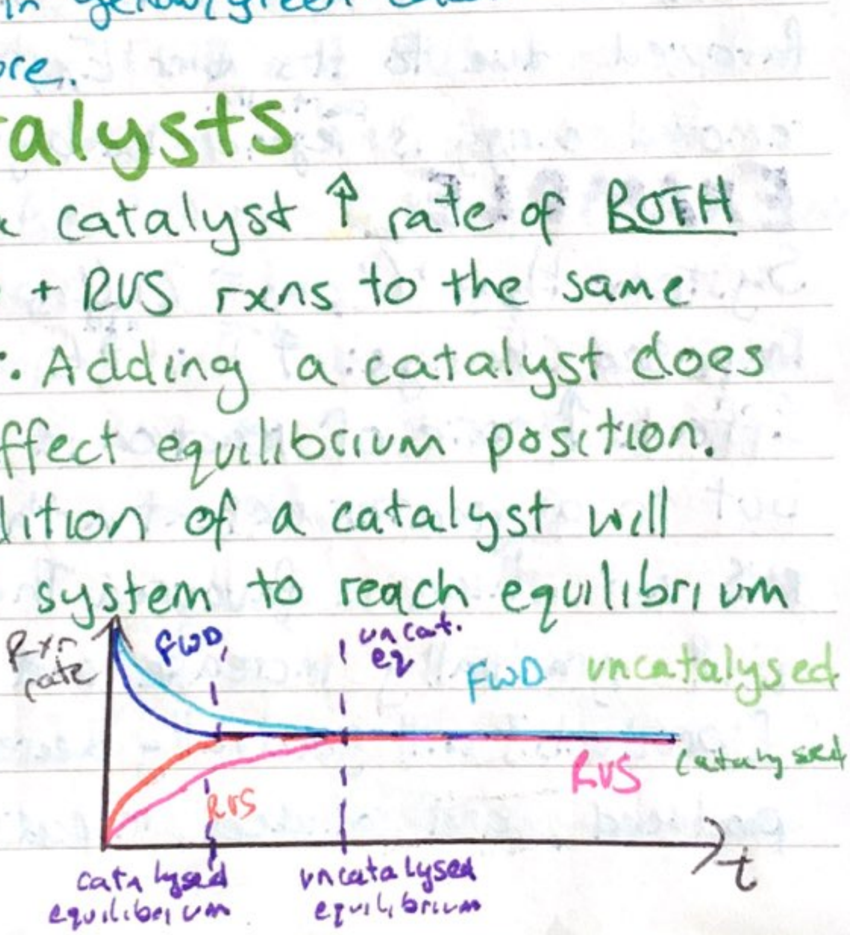


Summary and Observations

- ↑ $[H_2]$
- ↑ $[Cl_2]$
- ↓ $[HCl]$
- Increase in yellow/green color
- ↑ Pressure.

IV) Catalysts

- Adding a catalyst ↑ rate of BOTH the FWD + RVS rxns to the same extent. ∴ Adding a catalyst does NOT affect equilibrium position.
- The addition of a catalyst will enable a system to reach equilibrium Faster.



Changes that DONT Affect Equilibrium Position

I) Addition of a catalyst

BOTH FWD + RVS Rxn rates ↑ EQUALLY

Equilibrium is reached faster.

II) Adding an Inert gas to a gaseous system. (no [ ] change)

or changing V/P to a system with EQUAL Nº of moles on either side.

III) Adding or removing a solid } no Δ[ ]

IV) Adding or removing a liquid }

However adding or removing large amounts of H_2O from an AQUEOUS EQUILIBRIUM system may effect equlibrium [ ] as [all aq species] changes.

V) Changing the state of subdivision of a solid

If a solutn is at saturation no addition of solid or division of solid will cause a higher portion to dissolve.

Le Châtelier's Principle

A more straightforward method of predicting the effets of changes to equilibrium systems, without explanation on a molecular level.

"If a system at equilibrium is subject to a change in conditions, then the system will behave in such a way as to partially counteract the change"

BASICALLY: What is the change?

=> what is the opposite to this change? The system will attempt to do this.

=> ∴ which Rxn is favoured to achieve this opposing change? FWD / RVS

=> Does equilibrium shift left or right?

=> How does this affect the [ ]s of species? (aq / g)

1) Changes to concentration/ partial pressure

If [substance] ↑, system responds to ↓ it. If [substance] ↓, system responds to ↑ it.

Eg ① System: $3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Change: ↑ $[H_2]$

Response: The system tries to ↓ $[H_2]$

∴ the FWD Rxn is favoured to collide off the extra H_2 and the equilibrium shifts right.

∴ [H_2] ↑ initially then partially ↓
[N_2] ↓ [NH_3] ↑

② Change: ↓ [NH_3]
Response: The system tries to ↑ [NH_2]
∴ The RVS Rxn is favoured to partially regenerate lost NH_3 and the equilibrium shifts left.

∴ [NH_3] ↓ initially then partially ↑
[N_2] ↓ [H_2] ↓

II) Changes to Volume/Pressure

- If of a gaseous system V↑ → P↓, the system responds to ↑ P
- If V↓ → P↑, system responds to ↓ P.
- To determine how the system will do this and which Rxn it will favour, the side with the most gaseous moles will ↑ P and the least ↓ P.

Eq. System: $\overset{4mol}{N_{2(g)} + 3H_{2(g)}} \rightleftharpoons \overset{2mol}{2NH_{3(g)}}$
Change: V↓ → P↑
Response: As there are 4 molecules on

the reactant side to 2 on the product side, the FWD Rxn would ↓P to a greater extent ∴ the system shifts right and the FWD Rxn is favoured.

∴ $[NH_3]$ ↑ and continues to ↑ gradually
$[N_2]$ ↑ then partially ↓
$[H_2]$ ↑ then partially ↓

III) Changes to Temperature

- If of a system T ↑ then E is added. System responds to absorb this extra E ∴ endothermic Rxn is favoured.
- If T ↓ then E is removed. System responds to replace lost E ∴ exothermic Rxn is favoured. $\xrightarrow{endo}$ $\xleftarrow{exo}$

Eg System: $^{180}+ N_{2(g)} + 2O_{2(g)} \rightleftharpoons 2NO_{2(g)}$ $\Delta H = +180$
Change: ↓T ∴ ↓E

Response: The system wants to ↑T and ↑E ∴ the exothermic reverse Rxn is favoured. ∴ equilibrium shifts left.

∴ $[N_2]$ ↑ + $[O_2]$ ↑
$[NO_2]$ ↓

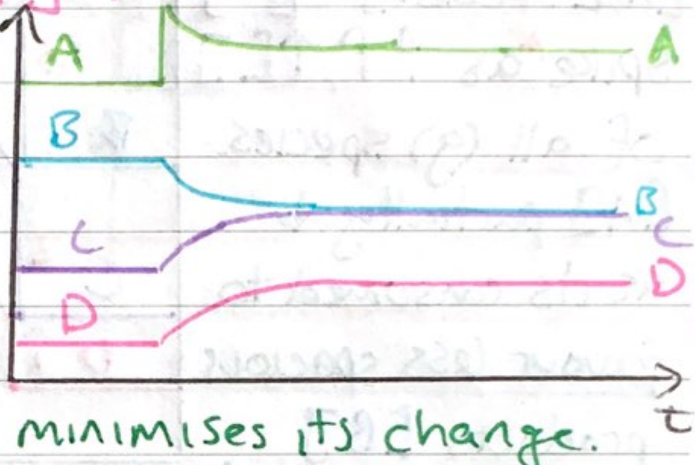
Graphical Representations of changes to Equilibrium

1) Changes to Concentration / partial pressure.

General Equation: $A + 3B \rightleftharpoons 2C + D$

Change: [A] ↑

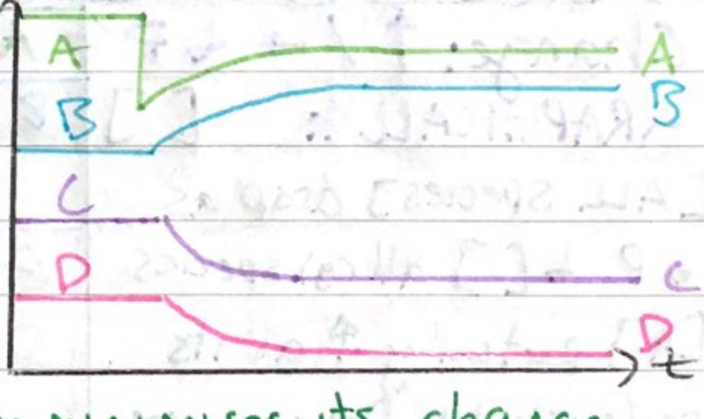
GRAPHICALLY:



[A] spikes [ ] as its added then partially ↓ as its consumed and the system minimises its change. [B] ↓ as its consumed [C] ↑ [D] ↑ as they're produced.

Change: [A] ↓

Graphically:



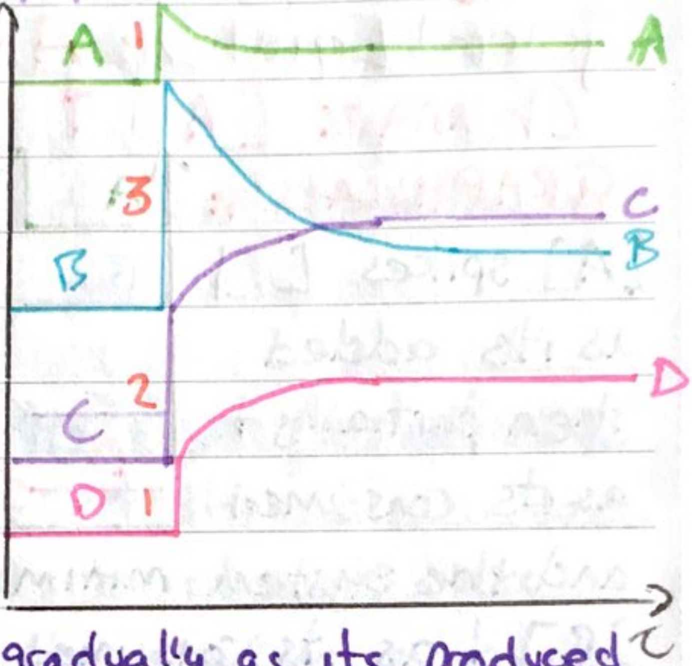
[A] drops [ ] as its removed then partially ↑ as its replenished and the system minimises its change. [B] ↑ as its produced. [C] ↓ [D] ↓ as they're consumed to replenish A.

11) Changes to Volume + Pressure

General Equation: $A + 3B \rightleftharpoons 2C + D$ all (g)

Change: ↓V → ↑P

GRAPHICALLY:



[ALL species] spike* as ↑P ↑[ ] of all (g) species.

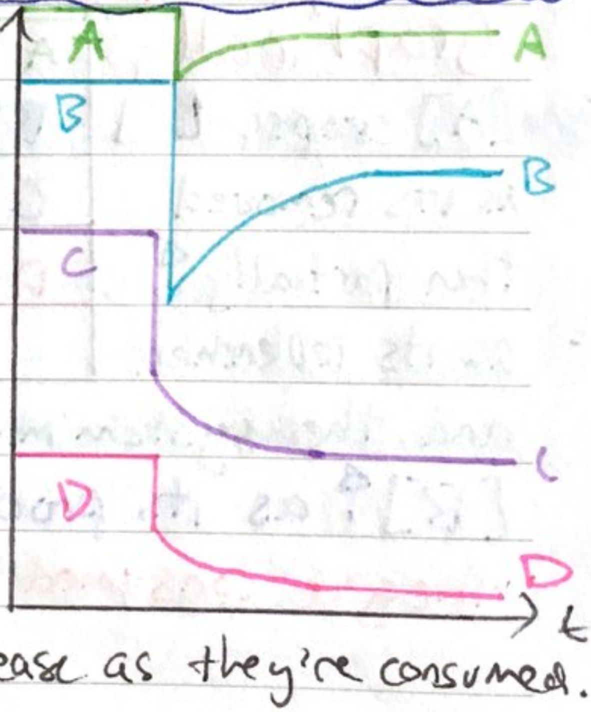
[A] partially ↓ as its consumed to favour less spacious products [B] partially ↓ [C] ↑ gradually as its produced

[D] ↑ gradually as its produced

SPIKE SIZE REFLECTS STOICHIOMETRIC RATIO

Change: ↑V → ↓P

GRAPHICALLY:



[ALL species] drop as ↓P ↓[ ] all (g) species

[A] partially ↑ as its replenished to favour more spacious reactants.

[B] partially ↓ [C] [D] gradually continue to decrease as they're consumed.

III) Changes in Temperature

General Equation:

$$A + 3B \underset{\leftarrow \text{endo}}{\overset{\rightarrow \text{exo}}{\rightleftharpoons}} 2C + D + E_p \; \Delta H = -ve$$

Change: ↑T → ↑E

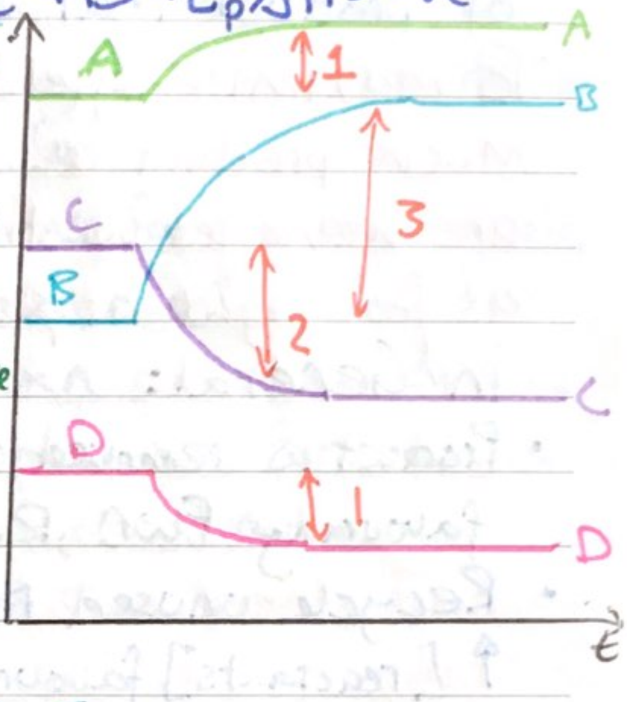
GRAPHICALLY: [ ]

[A] gradually increases factor 1 as endo RVS is favoured to minimise change and ↓T + ↓E

[B] gradually ↑ x 3

[C] gradually ↓ x2

[D] gradually ↓ x 1



Change: ↓T → ↓E

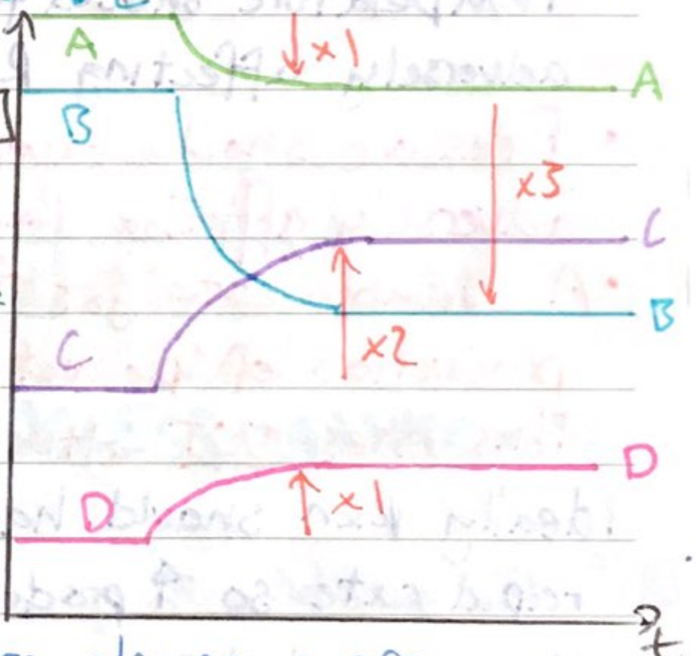
GRAPHICALLY:

[A] gradually ↓ [ ] x1 as exo FWD is favoured to minimise change and ↑T+↑E

[B] gradually ↓ x3

[C] gradually ↑x2

[D] gradually ↑x1



NOTE: Temperature changes are gradual but READ QUESTIONS CAREFULLY A system can be PLUNGED in ice. etc...

Industrial Applications

YIELD - The amount or percentage of product that is actually produced.

To maximise yield and produce as much product as possible conditions are managed so that equilibrium lies as far right as possible.

In General:

- Product is removed as its made. ↓[product] favouring FWD Rxn.
- Recycle unused reactants. ↓ wastage ↑[reactants] favouring FWD Rxn
- Temperature should favour FWD without adversely affecting Rxn rate or ↑$
- Pressure should favour FWD w/o adversely affecting Rxn rate or ↑$
- A suitable catalyst ↑ FWD rxn rate and production of product is in shorter time. This does NOT alter yield.

Ideally Rxn should have ↑ yield at a rapid rate so ↑ product ↓ time. Producing max amount desired product but for a minimum cost.

To be considered:

- Factors affecting Rxn rate - determine how quickly product is produced
- Factors affecting equilibrium to obtain max yield possible
- Sometimes conditions favour max yield of product but at an equilibrium that goes against max Rxn rate. Conditions must reach a compromise for balance of yield and production rate.
- Cost of providing conditions. ↑Ts require energy or fuel. ↑P requires equipment that is costly to build and maintain. If suitable cheap catalysts can be found large savings can be made in production costs.

SYLLABUS EXAMPLES OF INDUSTRIAL PROCESSES

THE HABER PROCESS - AMMONIA

- Fertilisers

$$N_{2\,(g)} + 3H_{2\,(g)} \overset{\text{iron oxide}}{\rightleftharpoons} 2NH_{3\,(g)} \quad \Delta H = -92kJ$$

TEMPERATURE

- ↓T favour exo FWD - max Ammonia production
- ↑T favours max Rxn rate, ↓T slows Rxn

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∴ A compromise is reached, 350-500°C is used to give reasonable yield at a reasonable rate + cost.

PRESSURE

- ↑ P favours FWD → will max NH_3 yield
- ↑ P = ↑ [g] so Rxn rate ↑
- ↑ P → ↑ \$ to maintain and pose ↑ health + safety risk
- compromise P of 100-250 atm. Some high as 350 atm

CATALYSTS

- Equilibrium est faster → ↓ running \$
- ↑ Rxn rate by ↓ E_A
- Porous iron oxide is used.

A modern Ammonia plant produces 30-40% yield ($\frac{\text{actual}}{\text{theory}} \times 100$) which can be ↑ by continually removing NH_3

THE CONTACT PROCESS - SULFURIC ACID

one of the steps: $2SO_{2(g)} + O_{2(g)} \overset{\text{Vanadium pentoxide}}{\rightleftharpoons} 2SO_{3(g)}$ $\Delta H = -196$

TEMPERATURE

- ↓ T favour exo FWD and will max SO_3 at equilibrium
- ↑ T ↑ Rxn rate, ↓ T ↓ Rxn rate ∴

compromise T of 400-500°C used to give reasonable yield at reasonable rate + $

PRESSURE

- ↑P favour FWD + ↑[g] → ↑Rxn rate
- ↑P = ↑$ = ↑ Health + Safety risk
- Due to availability of a v effective catalyst ↑P is not required → ↓$
- Just above 1atm is used.

CATALYSTS

- Equilibrium est faster → ↓ running $
- ↑ Rxn rate by ↓ E_A
- Porous Vanadium Pentoxide V_2O_5

Modern Sulfuric acid plants have a yield of over 99%.

BIODIESEL PRODUCTION

- Produced from fatty plant acids, using waste vegetable oils.
- Triglycerides react w an alcohol (methanol) to produce an ester (the biodiesel) and glycerol.
- 3 main catalysts: Base catalysts, Acid catalysts and enzymes.

- Almost all use Na/K OH - most economical - yields 98% at ↓T.
- However ↑T is produced - safety risk
- Soap also produced. Lipase is an enzyme that breaks down fats → ↑ Rxn rate <u>AND</u> prevents soap formation → ↑ Yield of Biodiesel. But Lipase is ↑$ to produce.
- Another method to max yield is to ensure alcohol is in excess, favouring FWD Rxn.

Summary

CONCENTRATION

↑ [REACTANT]

Equlibrium shift →

<u>NO</u> EFFECT on K, equlibrium constant

Le Châtelier: system responds to ↓ [reactant] favouring FWD Rxn, shifting Equilibrium position right

Collision Theory: ↑ particles per unit area ⇒ ↑ frequency of successful collisions ⇒ FWD Rxn rate ↑ <u>BUT</u> as reactants

Important Notes

- ΔH physical change < ΔH chemical change
- Forming bonds = exothermic
- Breaking bonds = endothermic
- If reactant bonds must break ↑E_A ↓ Rxn rate
- OPEN system allows Matter + E exchange
- CLOSED SYSTEM allows E ONLY
- E_A exothermic < E_A endothermic
- Equilibrium: Dynamic microscopic properties
  CONSTANT macroscopic properties.
- Equilibrium can be physical too:
  solution / vapour pressure equilibrium
- $K = \frac{\text{products}}{\text{reactants}} = \frac{[D]^d \cdot [E]^e}{[A]^a \cdot [B]^b}$
- K only changes with TEMPERATURE
- [s], [e] does NOT change! NOT inc in K
- Equilibrium defined by [react] [prod] relative to one another.
- Equlibrium ~~shift~~ lie right: [R] > [P]
- Equilibrium lie left: [R] < [P]
- Pressure changes ONLY affect GASEOUS species
- ↑ Pressure = ↑ BOTH Rxn rates
- ↑ Temperature = ↑ BOTH Rxn rates

- Catalysts ↑ BOTH Rxn rates
- Catalysts do NOT affect equilibrium position OR yield
- Catalysts make equilibrium reached FASTER
- Equilibrium can ONLY be reached in a CLOSED System
- Changes that do NOT affect equilibrium position: Catalysts
  Adding Inert gases
  +/- solids
  +/- liquids
  State of subdivision of a (s)
- Pressure + Temp changes on graphs
  - spikes + curves reflect stoichiometric ratios!
- Yield = $\frac{\text{actual amount}}{\text{theoretical amount}}$ = Amount % produced
- Rate = Rate of production ($\frac{\text{Production}}{\text{time}}$
- Reversibility: FWD + RVS have sufficient E_A, BOTH commence → Dynamic equilibrium est
- Effects take TIME! Initial effects are usually not reflective of final.

Acids + Bases

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History of

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ANTOINE LAVOISIER

- Carried out experiments on Combostion
- Oxygen involved in combostion
- Acids ∴ contain oxygen

HUMPHRY DAVY

- Acids are substances that contain replaceable hydrogen.
- This hydrogen could be replaced by metals
- Bases are substances that react with acids to form salts and water.

LIMITATIONS

- There are many compounds that contain hydrogen that are not acids

SVANTE ARRHENIUS

- Acids produce hydrogen ions in solution

  eg $HCl \rightarrow H^+ + Cl^-$
- Bases provide hydroxide ions in solution

  eg $NaOH \rightarrow Na^+ + OH^-$
- Neutralisation occurs when H^+

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and OH^- combine to form water.

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

LIMITATIONS

- Only applies to (aq) solutⁿs
- Only accounts for substances that contain H^+ or OH^- in their structure and does not explain why some salts can be basic or acidic
- Doesn't explain how some substances are amphoteric.

BRØNSTED-LOWRY

- Acids are proton donors (donate H^+)
- Bases are proton acceptors (accept H^+)

∴ acid base rxn has two products

BRØNSTED-LOWRY THEORY ON ACIDS & BASES

ACIDS ARE PROTON DONORS

$$\overset{+}{\curvearrowright}\quad\overset{=}{\curvearrowright}$$

$$\textcircled{H}Cl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

HCl has <u>donated a proton</u> to H_2O to produce hydronium (H_3O^+) ∴ acting as an acid.

H_2O has <u>accepted a proton</u> from HCl to produce H_3O^+ ∴ acting as a base.

The above equation shows the HYDROLYSIS of HCl: a reaction that occurs when a molecule or ion in aqueous solution reacts w H_2O to accept or donate a H^+

Dissociation Rxn:

$$HCl_{(g)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

BASES ARE PROTON ACCEPTORS

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

NH_3 has <u>accepted a proton</u> from H_2O to produce NH_4^+ ∴ acting as a base

H_2O has donated a proton to NH_3 to produce OH^- ∴ acting as an acid.

CONJUGATE ACID - BASE PAIRS

$$\begin{tikzcd}[column sep=small] \text{ACID} \arrow[rrrrrr, bend right, "\text{donates } H^+"'] & + & \text{BASE} \arrow[rr, bend left, "\text{accepts } H^+"] & \rightleftharpoons & \text{CONJUGATE ACID} & + & \text{CONJUGATE BASE} \end{tikzcd}$$

Brønsted-Lowry theory recognises REVERSIBILITY of <u>proton transfer</u> reactions (ie equilibrium nature)

Conjugate acid base pairs differ by a proton

Once an ACID has donated a proton it becomes a CONJUGATE BASE which posesses the ability to re-accept a proton → acting as a base

$$H_2SO_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+ + HSO_{3(aq)}^-$$

$$HSO_{3(aq)}^- + H_2O_{(l)} \rightleftharpoons H_2SO_{3(aq)} + OH^-_{(aq)}$$

FWD RXN: H_2SO_3 donates proton ⇒ becomes conjugate base

RVS RXN: HSO_3^- accepts proton acting as base → becomes conjugate acid

Once a BASE has accepted a proton it becomes a CONJUGATE ACID which possesses the ability to donate this proton → acting as an acid.

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_{4(aq)}^+ + OH^-_{(aq)}$$

$$NH_{4(aq)}^+ + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+_{(aq)}$$

Amphiprotic Substances

- Can donate OR accept a proton depending on other reactants ∴ can act as an acid OR a base.

Most commonly: Water

As a base:

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

As an acid:

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

If the solute as an acid: > water, water will act as a base vice versa for stronger bases

DONATES A H^+ to form	Amphiprotic Substance	ACCEPTS A H^+ to form:
OH^-	H_2O	H_3O^+
CO_3^{2-}	HCO_3^-	H_2CO_3
HPO_4^{2-}	H_2PO_4	H_3PO_4
PO_4^{3-}	HPO_4^{2-}	$H_2PO_4^-$
SO_4^{2-}	HSO_4^-	H_2SO_4

IONISATIONS OF POLYPROTIC ACIDS

The first ionisation of a diprotic acid occurs to a greater extent than the second ionisation. In a triprotic acid, the third ionisation occurs to the least extent.

Strength of Acids + Bases

Strong acids: IONISE completely in H_2O

Cats	HCl	hydro Chloric
In	HI	hydro Iodic
Nifty	HNO_3	Nitric
Surfboards	H_2SO_4	Sulphuric
Boop	HBr	hydro Bromic
Penguins	$HClO_4$	Perchloric

Strong bases: DISSOCIATE completely in H_2O

Group 1+2 metal hydroxides + oxides

Most Commonly:

Li	Be	Lithium Berylium
Na	Mg	Sodium Magnesium
K	Ca	Potassium Calcium
	Ba	Barium

RELATIVE STRENGTH OF CONJUGATES

The stronger an acid is, the weaker is its conjugate base.

↑ acid strength

ACID	CONJUGATE BASE
HCl	Cl^-
HF	F^-
H_2O	OH^-

↑ base strength

→ full diagram p95 fig 4.2.3

ACID IONISATION CONSTANTS

SINGLE PROTON TRANSFER

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

$$K_a = \frac{[products]}{[reactants]} = \frac{[A^-][H_3O^+]}{[HA]}$$

The equilibrium constant for an acid base proton transfer reaction is the acidity constant (K_a). It is a numerical measure of the extent to which the Rxn goes to completion ∴ is an indicator of acid strength

A stronger acid ionises more completely ∴ there should be a ↑ [products] than [reactants]

$$\therefore \uparrow K_a = \frac{[products]\uparrow}{[reactants]}$$

∴ K_a will be <u>larger</u>

A weak acid doesn't ionise complety

∴ [Products] < [reactants]

$$\therefore \downarrow K_a = \frac{[products]\downarrow}{[reactants]}$$ ∴ K_a will be smaller

The same principles apply to basicity constants (K_b)

Acid-Base Properties of Salts

SALT: ionic compound containing a cation (other than H^+) and an anion (other than O^{2-} or OH^-)

Salts are formed in neutralisation reactions of acids + bases.

∴ A salt can be thought of as a compound whose cation is derived from a base and anion from an acid.

$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

NaCl: Na^+ derived from base NaOH ∴
Cl^- derived from acid HCl

When such a salt is dissolved, it dissociates into these derived ions. Like conjugates of their original acid/base these ions may react with water and donate/accept a proton, creating H_3O^+ or OH^- in solution and thus changing the acidity of the salt solution. The extent to which this occurs and thus the acidity of the salt solution depends on the strength of the acid and base the salt is derived from. Remember: The stronger an acid, the weaker its conjugate base.

OF A STRONG ACID + STRONG BASE

$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

NaOH is a STRONG base, and HCl is a STRONG Acid. As such they ionise completely and these are <u>NOT</u> reversible.

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

$NaOH_{(aq)} +$ [illegible] $\rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

∴ When NaCl dissociates in water:

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

They (ions) will <u>NOT</u> react with water and the salt solution remains NEUTRAL

∴ A strong acid + strong base makes a NEUTRAL salt whose cations and anions do not undergo proton transfer with water.

OF A STRONG ACID + WEAK BASE

NH_4Cl is the salt of a strong acid (HCl) and a weak base (NH_3)

$HCl_{(aq)} + NH_{3(aq)} \rightarrow NH_4Cl_{(aq)}$

When this salt dissolves in water:

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

As was already shown Cl^- is a very weak conjugate base from a strong acid ∴ doesn't react with water.

However NH_4^+:

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

Will donate a proton to H_2O, acting as an ~~base~~ acid

∴ Solutions of salts of a strong acid and a weak base are acidic because the conjugate acid of the weak base hydrolyses to form H_3O^+

OF A WEAK ACID + STRONG BASE

$NaOH_{(aq)} + CH_3COOH_{(aq)} \rightarrow NaCH_3COO_{(aq)} + H_2O_{(l)}$

$NaCH_3COO_{(s)} \rightarrow Na^+{}_{(aq)} + CH_3COO^-{}_{(aq)}$

Na^+ doesn't react w. water (NaOH) is strong and its dissociation irreversible.

$CH_3COO^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow CH_3COOH_{(aq)} + OH^-{}_{(aq)}$

∴ Solutions of salts of a weak acid and a strong base are basic because the conjugate base of the weak acid hydrolyses to form OH^-.

OF A WEAK ACID + WEAK BASE

A solution of a salt formed from the reaction of a weak acid and a weak base involves two competing hydrolysis reactions:

The conjugate acid of the weak base w water forming H_3O^+

The conjugate base of the weak acid w water forming OH^-

The final pH depends on the extent to which these occur.

$NH_{3(aq)} + HClO_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + ClO^-_{(aq)}$

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

$K_a = 5.6 \times 10^{-10}$

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

$K_b = 3.3 \times 10^{-8}$

$3.3 \times 10^{-8} > 5.6 \times 10^{-10}$

∴ hydrolysis of ClO^- occurs to a greater extent and the solution will be basic

∴ The acidity of salts produced by a weak acid + base depends on the degree of hydrolysis of the anion and cation in the salt.

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IN SUMMARY:

SALT	Strong acid	weak acid
Strong base	Neutral Salts	basic salt
Weak base	acidic salt	Neutral/depends on ion hydrolysis

Solubility of salts:

① $AB_{(s)} \rightarrow A^+_{(aq)} + B^-_{(aq)}$

- Dissociation of a salt
- lattice enthalpy is the E needed to break ionic lattice

Always $+\Delta H$ ENDO

② $A^+ + H_2O_{(l)} \rightarrow A^+_{(aq)}$ $HA_{(aq)} + OH^-_{(aq)}$

- Hydrolysis of an ion
- enthalpy of hydration
- ions surrounded by H_2O molecules
- energy released ∴ Always $-\Delta H$ EXO

Overall ΔH (+ / −) depends on relative magnitude of ① and ②

Buffer Solutions

Buffer solutions are able to resist a change in pH when small amounts of acid or base are added.

A buffer consists of a weak

conjugate acid-base pair:

- A weak acid + its conjugate base
- A weak base + its conjugate acid.

Buffer solutions acidic / basic are made by mixing ≈ equal molar concentrations of a weak acid and one of its salts or a weak base and one of its salts.

The salt (ie extra conjugate) must be added as the weak a/b will not produce much of this in solution by itself, adding extra means both the a/b and its conjugate may be present in ≈ amounts.

Take the ethanoic acid / ethanoate buffer system:

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

where $[CH_3COOH] \approx [CH_3COO^-]$

Adding Acid:

The addition of acid such as HCl to this equilibrium ↑ $[H_3O^+]$, will only decrease its pH a little:

Le Châtelier's Principle: An equilibrium system subject to a change will respond to oppose this change and restore equilibrium.

Thus the buffer system will shift equilibrium left, favouring the consumption of the added H_3O^+. The CH_3COO^- reacts with the H_3O^+ to partially reduce its effect.

∴ $[H_3O^+]$ increases only a fraction of what it would without the buffer and a large drop in pH has been resisted (but still occurs to a SMALL degree)

$[H_3O^+]$ ↑ (<u>PARTIALLY</u>) ∴ pH ↓ (little)
$[CH_3COO^-]$ ↓ (been consumed)
$[CH_3COOH]$ ↑ (been produced)

Adding Base

The addition of base such as NaOH to this equilibrium system ↓ $[H_3O^+]$ by neutralisation:

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

As per Le Châtelier's Principle: The buffer system will shift

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equilibrium right, favouring the production and replenishment of lost H_3O^+. The CH_3COOH reacts with water to partially reduce the effect of $\downarrow[H_3O^+]$ on pH. ∴ $[H_3O^+]$ decreases only a fraction of what it would and a large rise in pH has been resisted (but still occurs to a SMALL degree)

$[H_3O^+]\downarrow$ (PARTIALLY) ∴ pH↑ (a little)
$[CH_3COO^-]\uparrow$ (been produced)
$[CH_3COOH]\downarrow$ (been consumed)

BUFFER CAPACITY

Buffer solutions have a working pH range and capacity to determine how much acid / base can be neutralised before the pH radically changes. A buffer is most effective when both the acid (HA) / base (BOH) and their conjugates (A^-/B^+) are available in large concentrations and many molecules are readily available to react with the strong acid / base.

Adding acid to the ethanoic acid / ethanoate buffer consumes ethanoate:

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

Eventually most of the CH_3COO^- will have reacted with enough acid addition, and at this point more acid cannot be reacted with and neutralised. As such the buffer is no longer effective and can no longer resist pH drops.

Adding base to the system consumes CH_3COOH (ethanoic acid):

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

Eventually w enough base there will be negligible CH_3COOH available to neutralise it and the buffer will no longer resist pH spikes.

Buffer capacity summary:

- Buffer capacity is a measure of the effectiveness of a buffer solution to resist a change in pH when either a strong acid or strong base is added.

- A buffer can only resist changes in pH if some of each of its conjugate acid and base pair is present.
- Buffer Capacity is greatest when:

- There is a high concentration of the weak acid and its conjugate base (The more molecules available, the less of an effect a strong acid/base will have on the system pH)
- The concentrations of the acid + its conjugate base are equal (ratio of weak acid to conjugate base within 10:1, 1:10 is effective)

BUFFER EXAMPLES

BLOOD BUFFERING

① $CO_{2(g)} \rightleftharpoons CO_{2(aq)}$ (lungs)

② $CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$

③ $H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons HCO^-_{3(aq)} + H_3O^+_{(aq)}$

Hyperventilation and exercise lower blood pH - alkilosis

OCEAN BUFFERING

$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3(aq)}$

Pollution ↑ CO_2 makes ocean acidic

Indicators
CHARACTERISTICS OF

Acids and bases have the ability to change the colour of plant extracts, such extracts are INDICATORS

They are weak acids/bases. The conjugate acid form of the acid is one colour, the conjugate base form another.

PROPERTIES:

- large organic molecules
- weak acids/bases
- In solution the acidic form is in equilibrium with its conjugate base

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

Equilibrium position depends on the pH

- Acidic form (HIn) and conjugate base form (In^-) are different colours
- Colour is visible at low [In]s
- Changing the pH of an In sol^n changes the [relative]s of the acidic and basic forms, and hence the sol^n colour can change.

COMMON INDICATORS

UNIVERSAL INDICATOR

- Mixture of several indicators, changes through a large colour range from pH 1 → 14

BROMOTHYMOL BLUE

🟨 in acid 🟦 in base 🟩 in neutral

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

acid form 🟨

🟦 conjugate base form

Le Châtelier's Principle can describe pH and [ ] ∴ colour changes.

In Acid: par

$[HBB] > [BB^-]$ ∴ 🟨

In Base: $[HBB] < [BB^-]$ ∴ 🟦

In Neutral: $[HBB] = [BB]$ ∴ 🟩

METHYL ORANGE

🟥 in acid 🟨 in base / neutral

transition point ≈ 4.1 (3.1 → 4.4)

pH RANGE OF AN INDICATOR

The range of pH values over which an indicator changes colour is known as the <u>indicator range</u>.

Indicators are useful at determining the EQUIVALENCE POINT of an acid-base neutralisation reaction.

The EQUIVALENCE POINT of a neutralisation reaction is when the amount of acid and base are in the stoichiometric ratio of their Rxn Eqn.

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

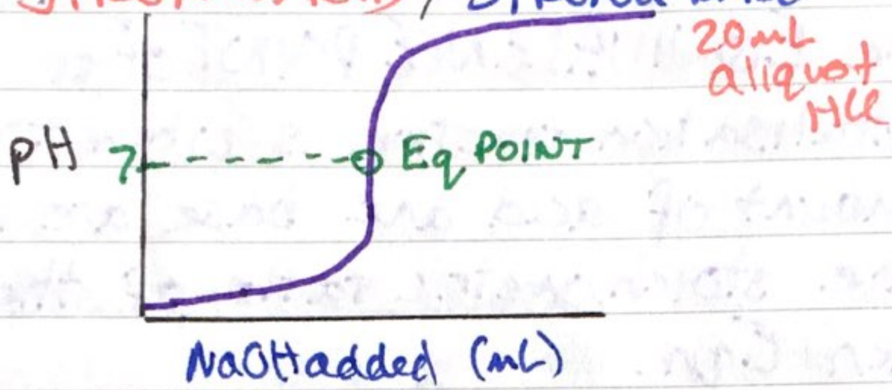
Equivalence point- when n(HCl) and n(NaOH) are 1:1 and have completely neutralised one another as per ↑ Rxns stoich ratio.

In volumetric analysis (quantitative analysis adding v(solution) [known] to v(solution) [unknown]) and titrations (vol-analysis w acids + bases to determine [unknown]) the END POINT of the indicator is the point in a titration when the indicator changes colour.

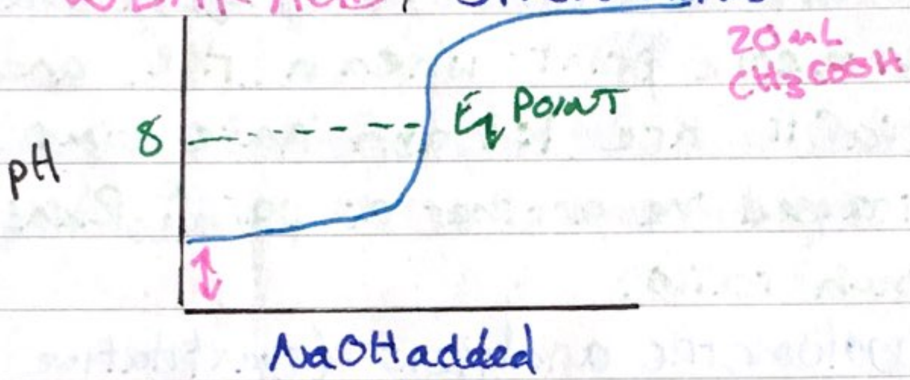
In titrations an end point very similar to the equivalence point is desirable. End point marks the completion of the titration.

Titrations of diff a/b strengths

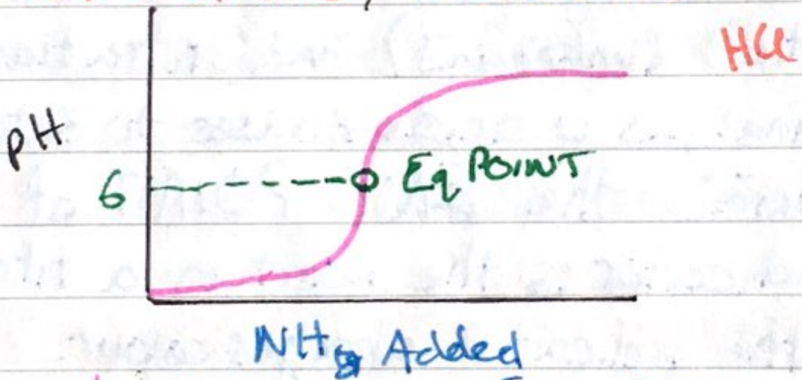
STRONG ACID / STRONG BASE



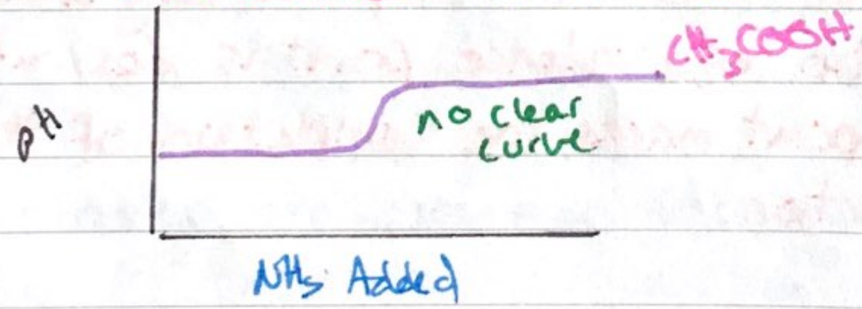
WEAK ACID / STRONG BASE



STRONG ACID / WEAK BASE



WEAK ACID WEAK BASE



Redox

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Redox

Oxidation and Reduction are part of Electrochemistry, they involve the transfer of electrons.

REDUCTION

The gain of electrons in a redox Rxn

OXIDATION

The loss of electrons in a redox Rxn

In a redox Rxn electrons are transferred from one species to another - redox occurs in reduction, oxidation pairs.

Oxidation Is Loss Reduction Is Gain → OILRIG

Red-Ox half equations that show e^- movement come together to form redox Rxns. e^- loss → RHS

Ox: $Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e^-$ × 1

Red: $Cl_{2(g)} + \underset{LHS}{2e^-} \xrightarrow{e^-\text{ gain}} 2Cl^-_{(aq)}$ × 1

OVERALL: Balance e^-s

$Mg_{(s)} + Cl_{2(g)} \rightarrow Mg^{2+}_{(aq)} + 2Cl^-_{(aq)}$

The reactant that causes the reduction of the other reactant is the reductant / reducing agent, it is

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itself oxidised.

The reactant that causes the oxidation of the other reactant is the oxidant/oxidising agent, it is itself reduced.

Conjugate redox pairs are the reactant and its oxidised/reduced product in a ½ eqn.

When a reducing agent loses electrons (oxidation) it becomes an oxidising agent.

Oxidation of Zn ½ eqn:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

$Zn(s)$ - reducing agent

$Zn^{2+}(aq)$ - oxidising agent

Conjugate redox pair: $Zn(s) \underset{\rightarrow}{/} Zn^{2+}(aq)$

In this order they show oxidation.

Oxidation N°s (Not always)

Essentially the charge of a species, but a stricter set of rules apply when determining an ~~spec~~ atom's oxidation Number.

RULES FOR OXIDATION N°s

① The oxidation N° of a free element = 0 (Na, O_2, Cl_2, P_4)

② The oxidation N° of a monoatomic ion = its charge
$Cl^- = -1$ $Mg^{2+} = +2$ $Al^{3+} = +3$

③ In compounds most elements have 'fixed' ONs, exceptions:
H = +1 in compounds w/ non metals
but −1 in metal hydrides (NaH)
O = −2 except w F (⑥) +2
= −1 in peroxides $(H_2\overset{-1}{O}_2)$ $(Ba\overset{-1}{O}_2)$

④ Sum of ONs in a neutral compound = 0
$CO_2 = (+4) + 2(-2) = 0$

⑤ Sum of ONs in a polyatomic ion = its charge
$SO_4^{2-} : (+6) + 4(-2) = -2$

⑥ Most electronegative element is assigned −ve ON:
$^{+2}O\overset{-1}{F_2}$ (F = most e⁻ve, Fr least e⁻ve)

Oxidation: a species' ON will increase across the equation

Reduction: a species' ON will

decrease across the equation.

To find an unknown ON:

$K_2Cr_2O_7$ what is Cr's ON?

$2(+1)+2x+7(-2)=0$

$2x=12 \Rightarrow x=+6$

If there is no change in ONs across an equation the Rxn is NOT redox! No e^- transfer (eg precipitation)

Conjugate redox pairs are elements with changing ONs in a Rxn.

Balancing Redox Eqns

In redox eqns atoms as well as charges must be balanced, especially involving polyatomic ions and acidic conditions (involve H^+)

For $\frac{1}{2}$ eqns:

① Identify reactant + product
② balance atoms (not H or O)
③ Balance O by adding H_2O to opposite side of $\frac{1}{2}$ eqn

④ Balance H from H_2Os by adding H^+ to opposite eqn side

⑤ Balance charges by adding electrons to ONE side

⑥ Add state symbols

⑦ Combine both $\frac{1}{2}$ rxns by balancing e^-s between them, multiplying the whole $\frac{1}{2}$ eqn to make the e^- coefficients =.

⑧ Cancel excess H_2O or H^+ from either side of eqn, only one side of Rxn should contain them.

The Electrochemical Series

From the electrochemical series we can deduce the reactivity of substances (metals), whether a reaction will actually occur, and the standard reduction potentials of $\frac{1}{2}$ Rxns as well as the 'voltage' of a redox Rxn.

IN GENERAL

- Reduction ½ eqns are listed
- Going UP the table: REACTANTS SIDE
  - Strength of oxidising agents INCREASES
  - Species are MORE LIKELY to be <u>reduced</u>
- Going DOWN the table: PRODUCTS SIDE
  - Strength of reducing agents INCREASES
  - Species are MORE LIKELY to be <u>oxidised</u>

In determining if a Rxn will spontaneously occur → CLOCKWISE RULE
The highest ½ Rxn will be reduction →, the lowest will be oxidation ← ↻

METAL REACTIVITY + DISPLACEMENT

Metals have small #s of valence electrons and a relatively small amount of E is required to remove them and ionise the metal. Oxidation is the loss of e^- so metals are easily oxidised (strong reducing agents). Going down the reactivity series are stronger reducing agents, the metals become more likely to lose e^-s and are MORE <u>REACTIVE</u>.

As such going down the side with cations they become harder to reduce - are weak oxidising agents - and less reactive.

The further down the metal from the reduction of:

Oxygen Hydrogen ions Water

The more vigorously it will:

Corrode React to acid react in water (dissolve)

METAL DISPLACEMENT

In metal displacement reactions solid metals <u>displace</u> other metals from their solutions. If a solid metal is more reactive (lower in series) than another, when introduced to a solution of this metal it will oxidise, donating its electrons to the other metal ions and reducing them.

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The stronger reducing agent (more reactive metal) replaces the weaker metal as ions in its solution and precipitates them out.

More reactive metals easily and forcibly donate their electrons.

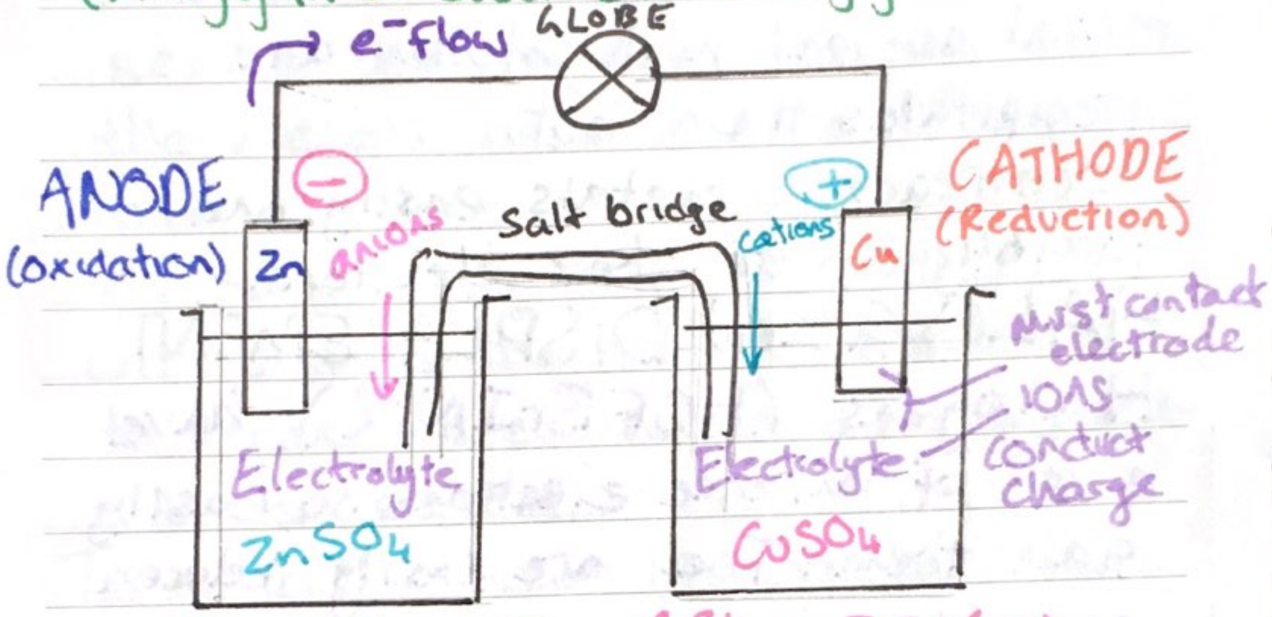
HALOGEN DISPLACEMENT

Halogens (HOFBrINCl) have a lot of valence electrons so easily gain them. They are easily reduced and are strong oxidising agents.

A halogen higher up in series (stronger oxidising agent) than another will displace its halides (ions in solution), stealing its electrons and replacing it in solution as a new halide. It oxidises the halide to a halogen and it itself reduces from a halogen to a halide.

Galvanic Cells

Galvanic cells are electrochemical cells that use electron transfer in redox reactions to convert chemical energy into electrical energy.



$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

As copper is higher in series than zinc (is a stronger oxidising agent) it will be reduced while zinc will be oxidised.

Zinc ions enter solution, the electrons produced flowing through the EXTERNAL circuit to the Copper electrode

Copper ions take up these electrons, becoming copper solid.

Zn^{2+} cause the Zn half cell to gain a net positive charge while the removal of Cu^{2+} causes the Cu half cell to gain a net negative charge. Ions in the salt bridge (NH_4^+ / NO_3^-) are attracted to these charges and flow towards them to counter their build up (internal circuit)

OXIDATION: Occurs at the ANODE (AnOx). Causes it to erode. e^- leave from here making it the -ve terminal.

REDUCTION: Occurs at the CATHODE (RedCat). Causes a build up of solid (metals) e^- enter here making it the +ve terminal.

Rxns are SPONTANEOUS + EXOTHERMIC

Short hand Notation:

ANODE salt bridge CATHODE

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu_{(s)}$$

OXIDATION REDUCTION

If reactants in a galvanic cell Rxn were to come in contact, chem E → Heat E rather than Elec E.

Gases are bubbled into the electrolyte to react while an inert electrode transfers e^-s (Pt or graphite)

Date:

STANDARD REDUCTION POTENTIALS

Current flows in galvanic cells b/c one half cell has a greater tendency to push electrons into the external circuit than the other. An emf exists across the circuit, to find the value of this we use standard reduction potentials.

The Rxn of hydrogen is assigned a PD (E°) of 0V and all other half cell Rxns are relative to this, ie a rxn's E° is the voltage it produces while in a galvanic cell with hydrogen.

STANDARD HYDROGEN $\frac{1}{2}$ CELL

E°s are measured under standard conditions:

- Pressure = 1 bar (100kPa)
- 1molL^{-1} sol^ concentrations
- Temperature: 25°C

Predicting Cell Rxns:

- Reduction occurs in the $\frac{1}{2}$ cell with the higher E° (stronger oxidising agent) This is the cathode and is +ve
- Oxidation occurs in the $\frac{1}{2}$ cell with the lower E° (stronger reducing agent) This is the anode and is -ve

Calculating Voltage across a Cell:

The max potential difference of a cell under standard conditions is the difference of its 2 E° values.

Cell PD: $E^\circ_{(\text{higher } \frac{1}{2} \text{ cell})} - E^\circ_{(\text{lower } \frac{1}{2} \text{ cell})}$
oxidising agent — reducing agent

E° can also be used to predict if a spontaneous redox Rxn will occur when reactants are mixed directly

$$E^\circ_{cell} = E^\circ_{\text{proposed Reduction}} + E^\circ_{\text{proposed oxidation}}$$

If the value is -ve the Rxn will not occur, if +ve it will.

At conditions different to standard this may not be reliable. The larger the difference the more violently/vigorously a Rxn takes place ie the quicker it is.

Corrosion

DRY CORROSION

When metal reacts directly with oxygen to form metal oxide

$$4Na_{(s)} + O_{2(g)} \rightarrow 2Na_2O_{(s)}$$

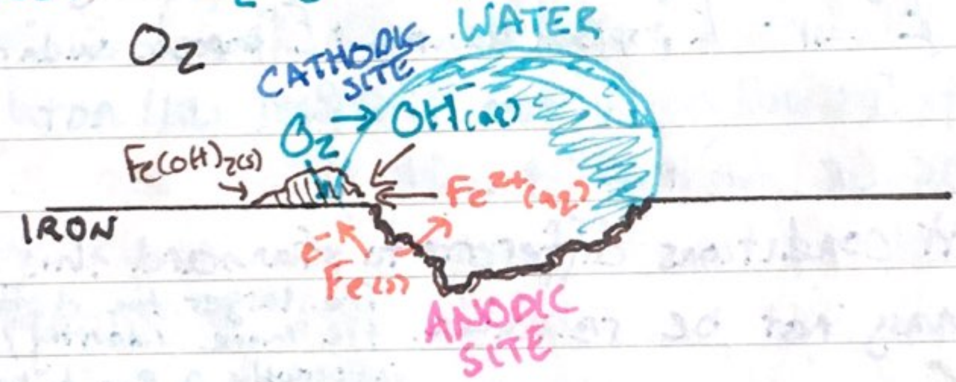
Corrosion of Al forms a tough coating of Al_2O_3 which protects metal underneath from further corrosion

Dry corrosion of Iron is slow but forms coating that flakes off, exposing more iron to corrosion.

WET CORROSION

Moisture accelerates the corrosion of iron, by moist air or contact with water. Impurities in the water (salts/acids) further accelerate the process.

Rust: $Fe_2O_3 . xH_2O$ $1 \leq x \leq 5$



① Iron is oxidised to Fe^{2+}

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$$

e^- are transferred through the conductive iron to the site of reduction of O_2:

$$O_{2(aq)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$$

② In the water $Fe(OH)_2$ (s) precipitates

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2}\ (s)$$

③ $Fe(OH)_2$ is further oxidised in the

prescence of O_2 and H_2O

Red/brown ↓

$4Fe(OH)_{2(s)} + O_{2(aq)} + 2H_2O_{(l)} \rightarrow 4Fe(OH)_{3(s)}$

④ In air $Fe(OH)_3$ loses water to form a hydrate (rust)

$2Fe(OH)_{3(s)} \rightarrow Fe_2O_3.H_2O_{(s)} + 2H_2O_{(l)}$

Electrical contact occurs through the iron itself (electrode)

Water is a conductive medium for ions (electrolyte)

Dissolved salts improve salt bridge effect (ion conductivity) and accelerate.

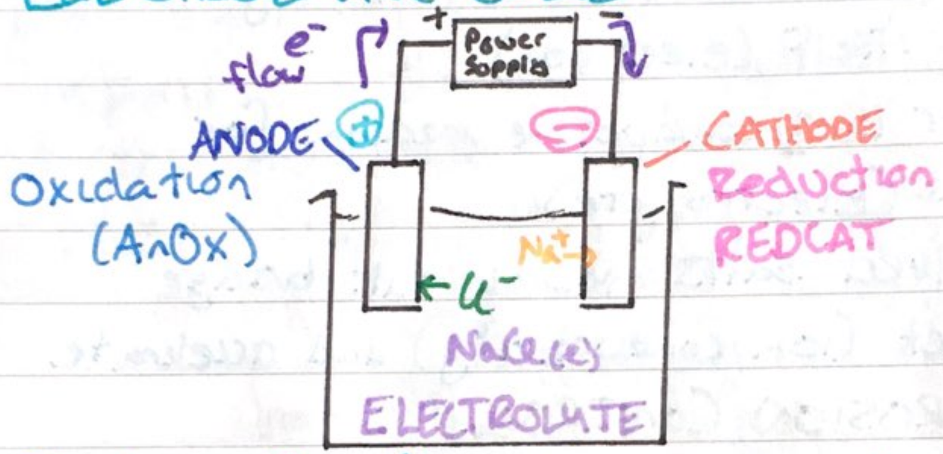
CORROSION CONTROL

- Exclude air/water from metal surface with a coating (paint/plastic) or plating of less reactive metal
- Flowing a current through the metal. For iron to corrode (oxidise) it must lose e^- but the current gives it a negative charge.

Electrolysis and Electrolytic Cells

Electrolysis involves the passage of electrical energy from a source through a conductive liquid. The energy causes non spontaneous redox Rxns to occur.

ELECTROLYTIC CELLS



Electrons flow from the supply into the Cathode where REDUCTION takes place. Cations (Na^+) migrate towards the CATHODE and are reduced there.

$$Na^+_{(l)} + e^- \rightarrow Na_{(l)}$$

As cations are attracted to it, it is NEGATIVE.

Anions migrate (Cl^-) towards the anode where they are oxidised:

$$2Cl_{(l)} \rightarrow Cl_{2(g)} + 2e^-$$

Their electrons re-enter the external

circuit to the power pack.
In electrolytic cells the electrodes are often inert, but can be reactive.
Both molten and aqueous solutions can undergo electrolysis

ELECTROLYTIC VS GALVANIC CELLS

GALVANIC	ELECTROLYTIC
• Chemical E → Electrical E	• Electrical E → Chemical E
• Spontaneous Rxns	• Non Spontaneous Rxns
• ANODE -ve	• ANODE +ve
• CATHODE +ve	• CATHODE -ve

• e^- flow from anode to cathode

REDCAT / ANOX

Anions → Anode

Cations → Cathode

• Ions diffuse to balance charges	• Ions attracted to charged electrodes

Require electrolyte

Galvanic Cells + Equilibrium

On the standard reduction potentials table the ½ equations listed are shown as reversible. As a galvanic cell discharges reactants are consumed and the cell voltage eventually drops to 0. The FWD reactions go no faster than their RVS and a state of equilibrium is achieved. e^- don't flow and the cell goes 'flat'.

Organic Chemistry

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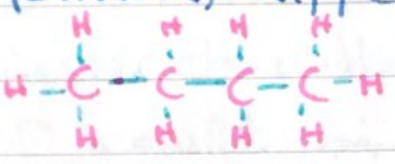
Basics Revision

DEFINITIONS

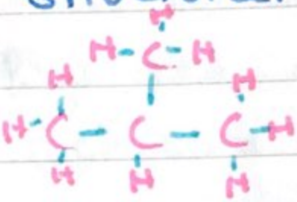
Saturated: Only single bonds

Aliphatic: Compounds with open chains (alkanes) non cyclic.

Isomer, structural: same molecular formula, different structural:

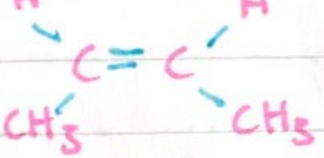


butane

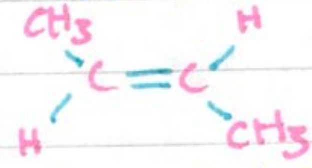


methyl propane

Geometric: Cis or trans isomerism



cis-but-2-ene



trans-but-2-ene

Homologous Series: A series of organic compounds having the same functional group, each subsequent member differs by a CH_2

- Share same general formula
- same functional groups
- similar chemical properties
- show gradual change in physical properties as molar mass increases
- prepared by similar methods

RXNS OF HYDROCARBONS

Combustion: burning in O_2 to produce CO_2 and H_2O (CO in limited O_2).
-exo- Balance C→H→O

Substitution: Halogenation of alkanes + benzene. H steadily replaced with halogens (Cl/Br...) in presence of UV light catalyst.
* OR $AlBr_3$/$AlCl_3$ for benzene.
- SLOW - 2 products.

Addition: Double bond of alkene opens to two singles. HALOGENATION adds halogen, HYDROGENATION adds hydrogen. Pt catalyst, FAST- 1 prod.

BITS + BOBS

-

	Alkanes	Alkenes
(g)	$C_1 \rightarrow C_4$	$C_2 \rightarrow C_4$
(l)	$C_5 \rightarrow C_{17}$	$C_5 \rightarrow C_{16}$
(s)	C_{18}+	C_{17}+

- 2 double bonds - diene → 3 - triene...

Functional Groups (intro)

The presence of functional groups in molecules give substances particular physical and chemical properties.

ALCOHOLS

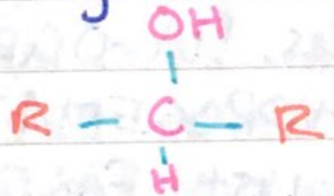
Contain a hydroxyl functional group (-OH) (suffix -ol)

$R-OH$

Primary alcohols (1°)

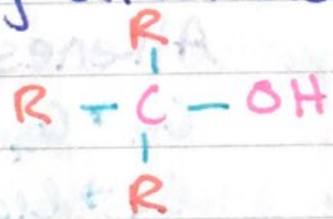
$R-\overset{H}{\underset{H}{C}}-OH$

Secondary alcohols (2°)



$R-\overset{OH}{\underset{H}{C}}-R$

Tertiary alcohols (3°)



$R-\overset{R}{\underset{R}{C}}-OH$

CARBOXYLIC ACIDS

Contain a carboxyl group (-COOH) (suffix -oic acid) Always at one end.

*trigonal planar

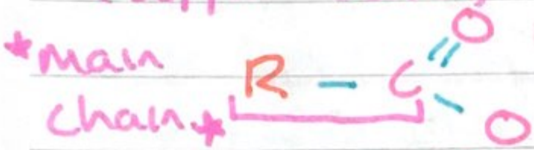
*tetrahedral

* Always has naming preference

ESTERS

Formed by rxn of alcohol + carboxylic acid. (esterification) (−COO−)

(suffix -oate)

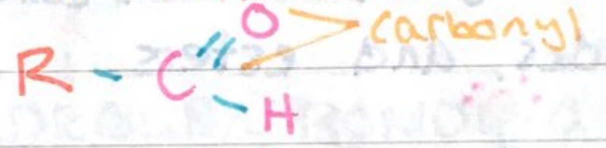


R'- alkyl from alcohol

ALDEHYDES

Contain carbonyl group at end (=O)

(−CHO) (suffix -al)



KETONES

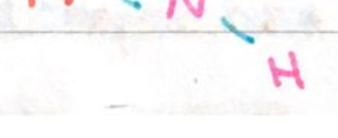
Contain carbonyl group in middle (=O)

(−CO−) (suffix -one)

AMINES

Contain an amino group $(-NH_2)$

(suffix -amine / amino- if not principle)



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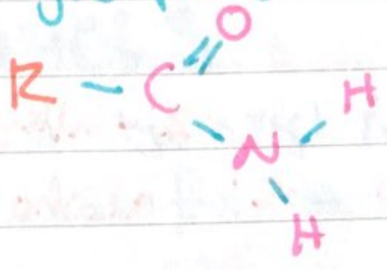
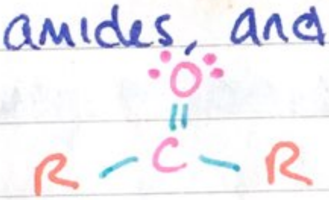
AMIDES

Contain carbonyl group attached to amino group ($-CONH_2$) (-amide)



The Carbonyl Group

Found in aldehydes, ketones, carboxylic acids, amides, and esters.



Physical Properties of Organic Compounds

INTERMOLECULAR FORCES REVISION

(Vaan Der Waal's Forces) Forces b/n molecules in covalent compounds

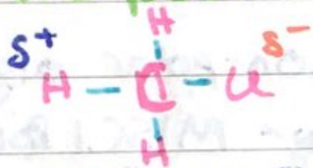
① DISPERSION FORCES

- Present b/n all molecules
- Account for attraction of non-polar molecules
- temporary dipoles due to constant e^- movement
- More atoms → more e^- → stronger disp forces.

- Stronger in molecules w linear shape than branched → larger surface area

(II) DIPOLE-DIPOLE FORCES

- Weak forces of attraction b/n polar molecules
- Slightly ⊕ attracted to slightly ⊖ by UNEVEN CHARGE DIST. (POLAR)
- More polar → stronger di-bonds



$\overset{\delta+}{H}-\underset{H}{\overset{H}{C}}-\overset{\delta-}{Cl}$

(III) HYDROGEN BONDING

- Extreme dipole-dipole
- H-O / H-N / H-F (most electro⊖ atoms)
- O, N, F often have lone pairs the δ+ H is attracted to.

PHYSICAL PROPERTIES OF ALKANES + ALKENES

BOILING POINTS

In general as molecule size increases BPs increase as dispersion forces become more prevalent.

Branched molecules of similar size to straight chains have lower BPs as shape doesn't allow molecules to fit as closely together and their temporary dipoles to interact

SOLUBILITY

- In water - insoluble - as they are non-polar. Weak disp forces canot overcome strong attraction of water molecules so substances remain separated - IMMISCIBLE
- Int-mol forces similar in non-polar organic solvents strength wise so - MISCIBLE

FUNCTIONAL GROUPS

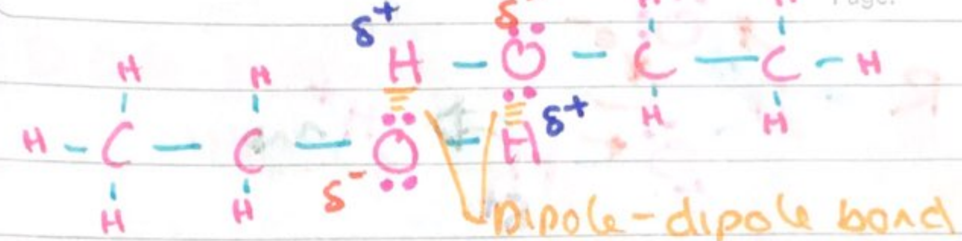
Functional Groups have effects on physical properties of substances (BP/solubility etc) and is linked to intermolecular interactions.

In general polar functional groups increases BPs and solubility in water

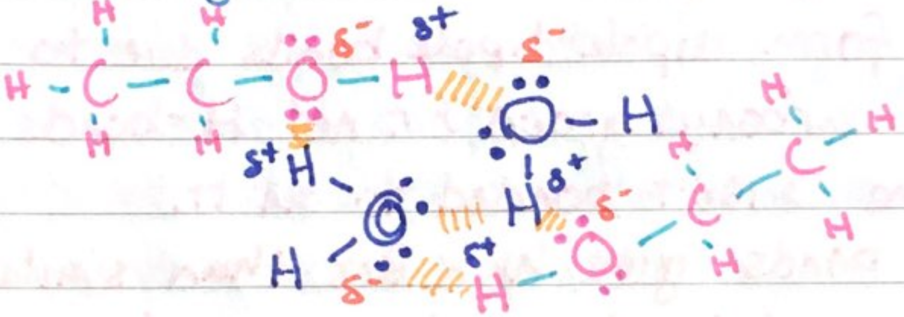
ALCOHOLS

Alcoholes contain DISPERSION - DIPOLE DIPOLE - AND H bonding

Dipole Dipole bonds occur as alcohols are polar. This gives them strong int-mol forces, they are all liquids at room temp and have high BPs. Decrease (1° > 2° > 3°) (crowdedness)



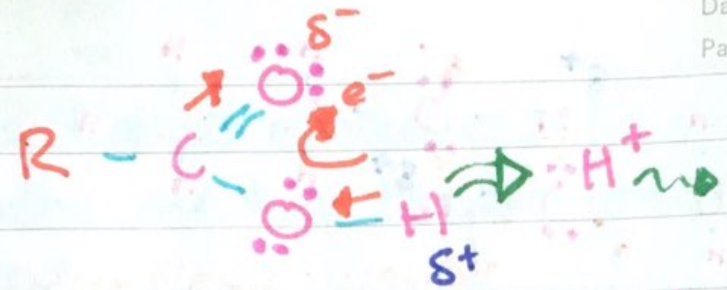
Small alcohols dissolve well in water (as the parent C chain gets longer the forces of the OH get less significant) as they make H-bonds with water:

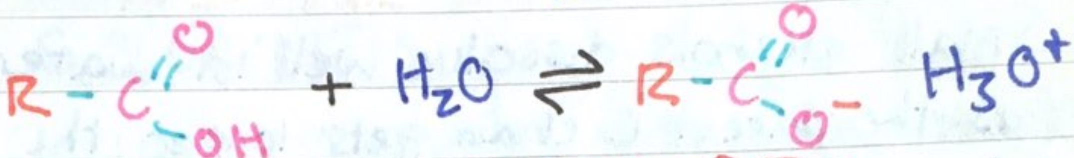


CARBOXYLIC ACIDS

BP > alcohols. Int-mol forces are very strong as carboxyl group can form two H-bonds - DIMERS. They are like a new molecule → ↑ disp forces → ↑ mol mass ⇒ ↑ BPs

Highly soluble, react with water to release H as e^- drawn away from it to the carbonyl group



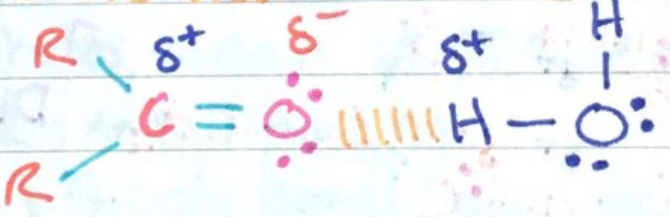


$$R-C(=O)OH + H_2O \rightleftharpoons R-C(=O)O^- \quad H_3O^+$$

ESTERS ALDEHUDES and KETONES

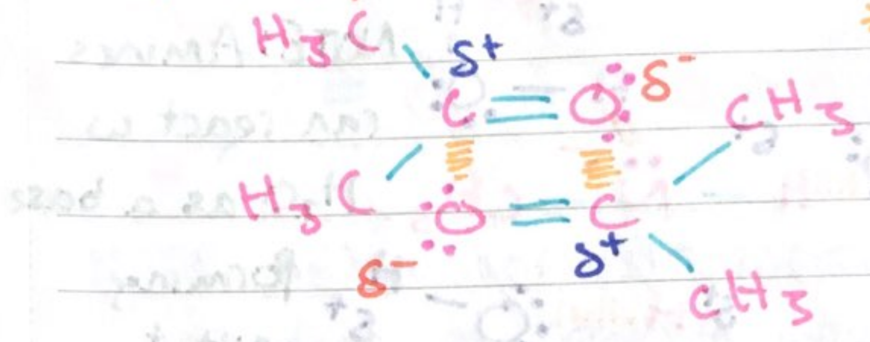
- Can form dipole-dipole bonds due to polar carbonyl group but not H-bonds as the O isn't bonded to an H.
- D-D bonds give high BPs than similar alkanes but less than alcohols + carboxylic acids.
- H-Bonds can occur b/n O lone pairs on carbonyl and δ+ H on water.

∴ Small aldehydes, ketones and (less so) esters are water soluble



- unlike for solubility in polar substances as these molecules get bigger, solubility in non-polar solvents increases

- Dipole-Dipole bond:



* NOT dimer as NOT H BOND

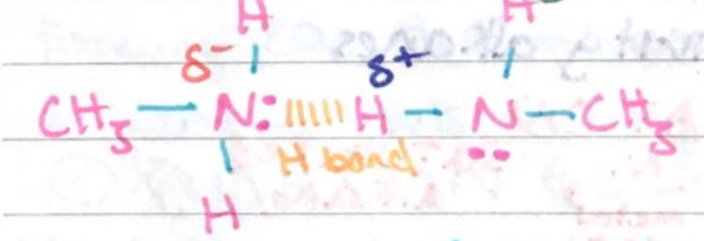
Esters: Often have sweet fruity odours as found in fruit and flowers

∴ used in flavours + scents

- Small esters (l) at room temp and are good organic solvents
- Form large molecules of oils + waxes.

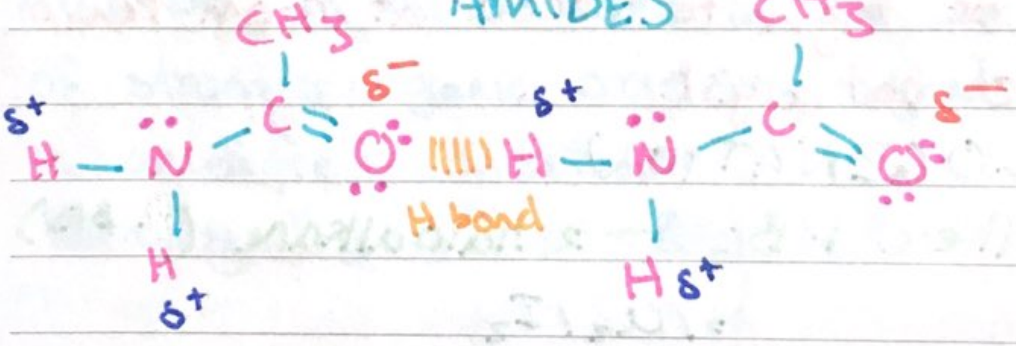
AMINES and AMIDES

- Highly polar (N–H) so form H-bonds ⇒ relatively high BPs

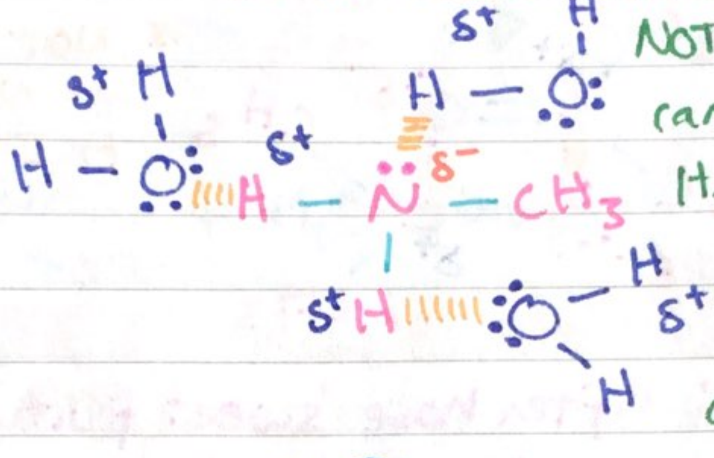


AMINES

AMIDES



- Dissolve well in water amide > amine



NOTE: Amines can react w H_2O as a base forming $-NH_3^+$ and OH^-

Chemical Properties

of organic compounds

As all members of a homologous series have the same functional group they typically undergo the same type of reactions.

ADDITION RXNS OF ALKENES

Alkenes > reactivity alkanes

HYDROGENATION

$\text{Alkene} + H_2 \xrightarrow[\text{metal cat}]{\text{Ni}}$ saturated alkane

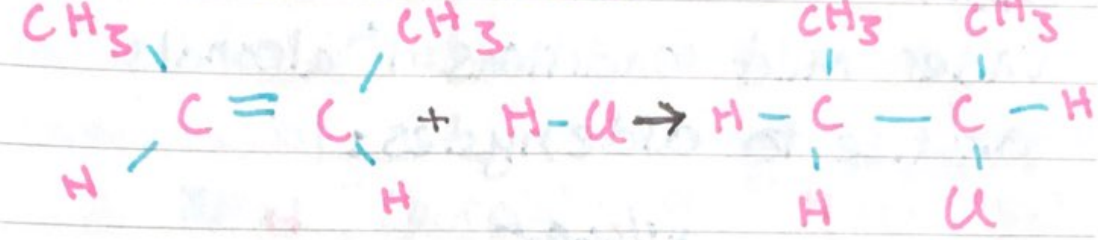
E_a too high to occur at room temp w/o catalyst.

HALOGENATION

Alkene + Br_2 → haloalkane (2 Brs)

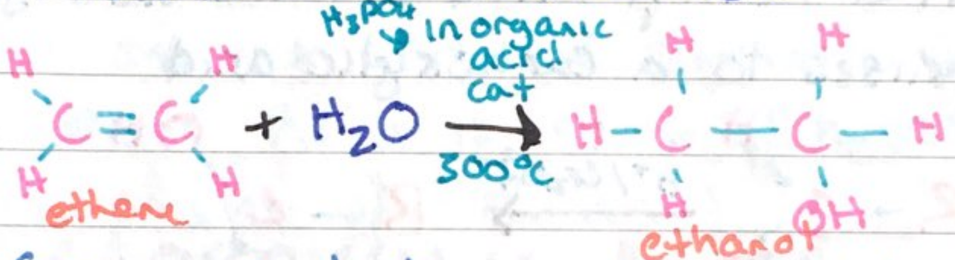
↳ / Cl_2 / I_2

HYDROGEN HALIDES



NOTE: often isomers are possible depending on how the double bond 'opens'.

HYDRATION → ALCOHOL



Gaseous reactants passed over solid catalyst bed at 300°C

ALCOHOLS

- Alcohols combust like other hydrocarbons forming: CO_2, H_2O and energy. They can be used as fuels.

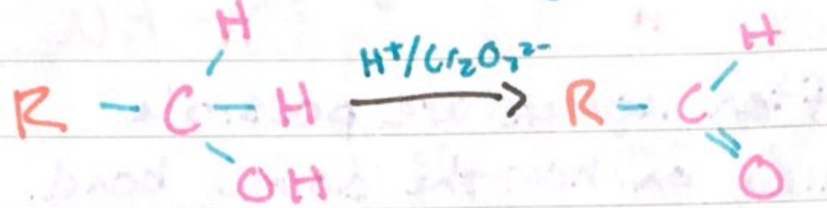
OXIDATION

Alcohols can be oxidised in the presence of strong inorganic oxidising agents in acidified conditions.

Usually $Cr_2O_7^{2-}$ or MnO_4^-

OXIDATION OF PRIMARY ALCOHOLS

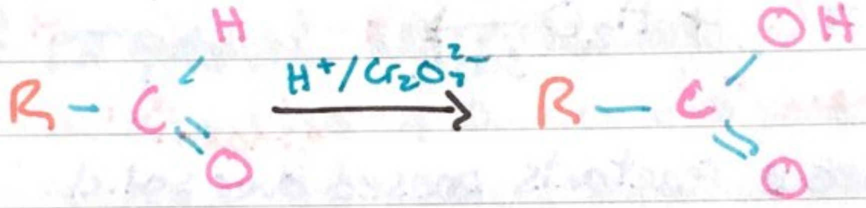
Under mild conditions 1° alcohols oxidise to aldehydes:



$H_{2(g)}$?

$\{RCH_2OH_{(aq)} \rightarrow RCHO_{(aq)} + 2H^+_{(aq)} + 2e^-\}$

Further heating + time and the aldehyde oxidises to a carboxylic acid

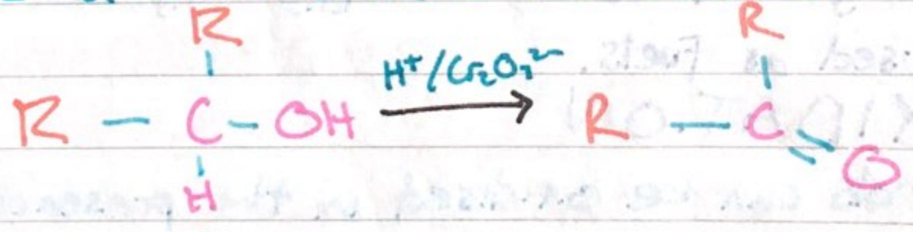


$\{RCHO_{(aq)} + H_2O_{(l)} \rightarrow RCOOH_{(aq)} + 2H^+_{(aq)} + 2e^-\}$

$\Rightarrow RCH_2OH_{(aq)} + H_2O \rightarrow RCOOH_{(aq)} + 4H^+_{(aq)} + 4e^-$

OXIDATION OF SECONDARY ALCOHOLS

2° alcohols oxidise to Ketones:



$RCHOHR_{(aq)} \rightarrow RCOR_{(aq)} + 2H^+_{(aq)} + 2e^-$

TERTIARY ALCOHOLS do not oxidise as a C-H bond must be broken on the OH carbon, in 3° alcohols theres no C-H to break

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1° alcohols usually have a higher Rxn rate than 2° alcohols. The colour changes of $Cr_2O_7^{2-}$ (orange) → Cr^{3+} (green) and MnO_4^- (purple) → $\overset{\text{pale pink}}{Mn^{2+}}$ (colourless) are a qualitative technique to tell the oxidation has taken place and distinguish alcohols as 1°/2° or 3°.

DEHYDRATION

Alcohols can have H_2O removed to form alkenes, this is the reverse of hydration (in presence of conc. acid).

CARBOXYLIC ACIDS

Carboxylic acids undergo typical acid Rxns

- CA + $\underbrace{\text{Metal } \overset{\text{oxide}}{\text{hydroxide}}}_{}$ → $\overset{\text{metal}}{\text{salt}}$ + H_2O (BASE)

$CH_3COOH_{(aq)} + NaOH_{(aq)} \rightarrow CH_3COONa_{(aq)} + H_2O_{(l)}$

$CH_3COOH_{(aq)} + OH^-_{(aq)} \rightarrow CH_3COO^-_{(aq)} + H_2O_{(l)}$

- CA + Metal $\overset{CO_3}{HCO_3}$ → salt + H_2O + CO_2

$Na_2CO_{3(s)} + 2CH_3COOH_{(aq)} \rightarrow 2CH_3COO^-_{(aq)} + 2Na^+_{(aq)}$
$+ H_2O_{(l)} + CO_{2(g)}$

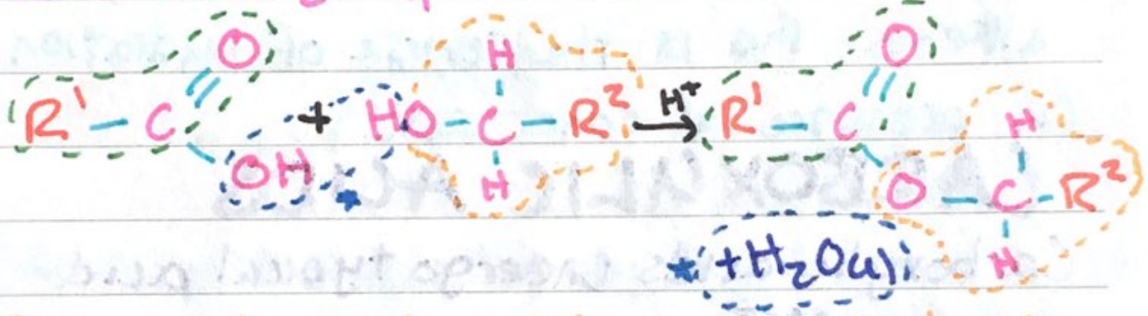
- CA + $\overset{\text{reactive}}{\text{metal}}$ → salt + H_2

$2CH_3COOH_{(aq)} + Mg_{(s)} \rightarrow 2CH_3COO^-_{(aq)} + Mg^{2+}_{(aq)} + H_{2(g)}$

ESTERIFICATION

Rxns that involve the combination of two reactants and the production elimination of a small molecule (H_2O) are called condensation reactions

Alcohol + carboxylic acid synthesises an ester. Naturally this is slow (ripening of fruit) so the Rxn is heated and a conc H_2SO_4 cat is used.



The part of the ester denoted the ALKYL group comes from the ALCOHOL and is on the single bonded O side

The part of the ester that forms the -oate and is the MAIN chain comes from the CARBOXYLIC ACID and is on the double bonded O side.

The carboxylic acid's hydroxyl group and the alcohol's H form water.

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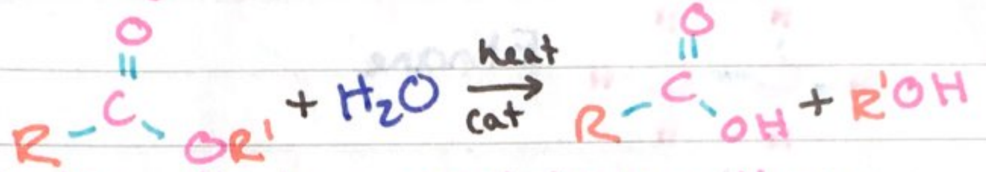
ESTER HYDROLYSIS

Esterification may be reversed with heat under acidic conditions



$$R-C(=O)-OR' + H_2O \xrightarrow[cat]{heat} R-C(=O)-OH + R'OH$$

Under alkaline conditions - alkaline hydrolysis/saponification occurs. A salt of the carboxylic acid forms. ($-COO^- + Na^+$ $\rightarrow$ $-COONa$)

Chemical Synthesis

A Rxn pathway is a series of one or more steps, or Rxns, that can be used to convert a reactant to a desired product with different funct. groups.

PRODUCTION OF ETHYL ETHANOATE

① Ethanol is synthesised by the hydration of ethene in presence of H_3PO_4 cat.

$$CH_2=CH_{2(g)} \xrightarrow[H_2O]{H_3PO_4} CH_3CH_2OH_{(l)}$$

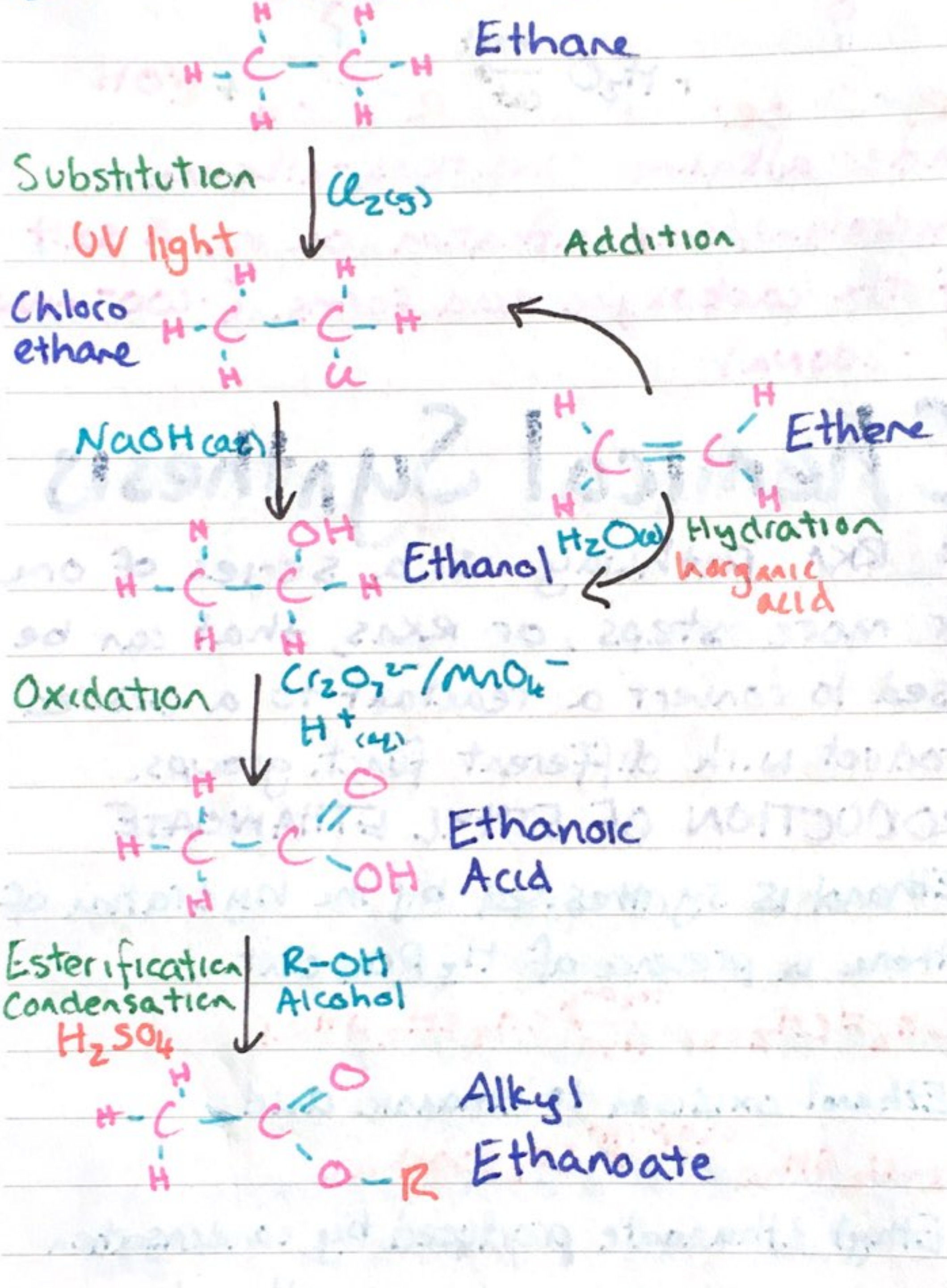
(II) Ethanol oxidised to ethanoic acid

$$CH_3CH_2OH_{(l)} \xrightarrow{Cr_2O_7^{2-}/H^+} CH_3COOH_{(l)}$$

(III) Ethyl ethanoate produced by condensation Rxn b/n ethanoic acid and ethanol in presence of H_2SO_4 cat.

$CH_3CH_2OH_{(l)} + CH_3COOH_{(l)} \xrightarrow{H_2SO_4} CH_3COOCH_2CH_3\,(l)$

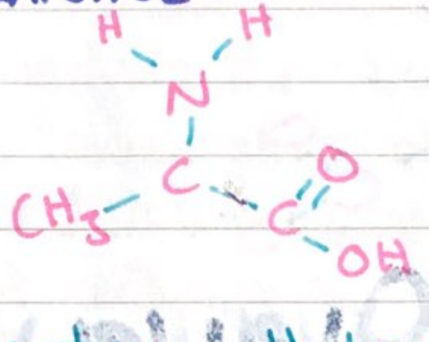
ETHANE/ENE TO ESTER



'Zwitterions'

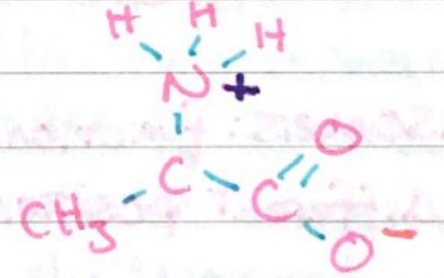
Amino acids contain both a carboxyl and an amino group.

Eg: ALANINE:

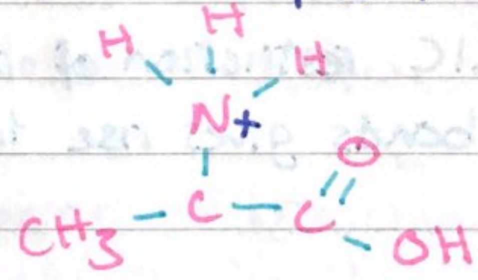


By donating a H to itself elsewhere it becomes a zwitterion having separately ⊕ and ⊖ charged groups

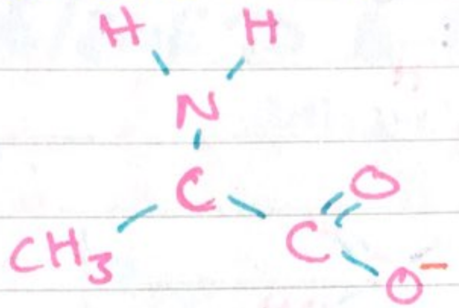
In Sol^: Zwitterion:



In acid: cationic form (weakly basic -COO$^-$ accepts H$^+$:



In base: Anionic form: (weakly acidic $-NH_3^+$ donates H^+)



Isomers Overview

STRUCTURAL: same molecular formula bonded together in different arrangements

CHAIN isomers: different branching of C chain

POSITIONAL isomers: functional group(s) on different positions on chain

Structural isomers can be both chain and positional

GEOMETRIC restriction of rotation about double bonds gives rise to cis-trans isomerism

IUPAC NOMENCLATURE

SUMMARY

(I) The longest C chain is used to derive the parent ~~chain~~ name. The longest chain MUST include the functional groups

(II) The names and locations of branches and additional functional groups are added to this parent name.

(III) Numbers are used to identify the C atom that groups are attached to

(IV) Numbers and letters are separated by hyphens

(V) Numbers are separated from other numbers by commas

(VI) There are no spaces in a name, apart from the two-word names of acids and esters

(VII) If there is more than 1 type of funct. group to be listed, they are in alphabetical order.

(VIII) The names of branching alkyl groups are added before the parent name

(IX) If there is more than one of the same functional group prefixes 'di', 'tri', 'tetra' are used

HOMOLOGOUS SERIES'

HS	Funct. group	Formula	naming convention
Alkane	alkane	C_nH_{2n+2}	-ane
Alkene	C=C	-C=C-	-ene
Haloalkane	Halo	-F, -Cl, -Br, -I	fluoro chloro bromo iodo
Alcohol	Hydroxyl	-OH	-ol / hydroxy-
Amine	Amino	$-NH_2$	-amine / amino-
Carboxylic Acid	Carboxyl	-COOH	-oic acid
Ester	Ester	-COO-	-yl -oate
Aldehyde	Carbonyl	-CHO	-al
Ketone	Carbonyl	-CO-	-one
Amide	Amide	$-CONH_2-$	-amide

FUNCTIONAL GROUP PRIORITIES

	FG	Suffix	Alt name
Highest priority	Carboxyl	-oic acid	—
↓	Hydroxyl	-ol	hydroxy-
	Amino	-amine	amino-
	Alkene	-ene	-ane → -en-
lowest	Halo	–	halo-

Empirical Formula Calcs

① From $m(CO_2)$ find $m(C)$
($n(C) = n(CO_2)$

② From $m(H_2O)$ find $m(H)$
($n(H) = 2 \times n(H_2O)$)

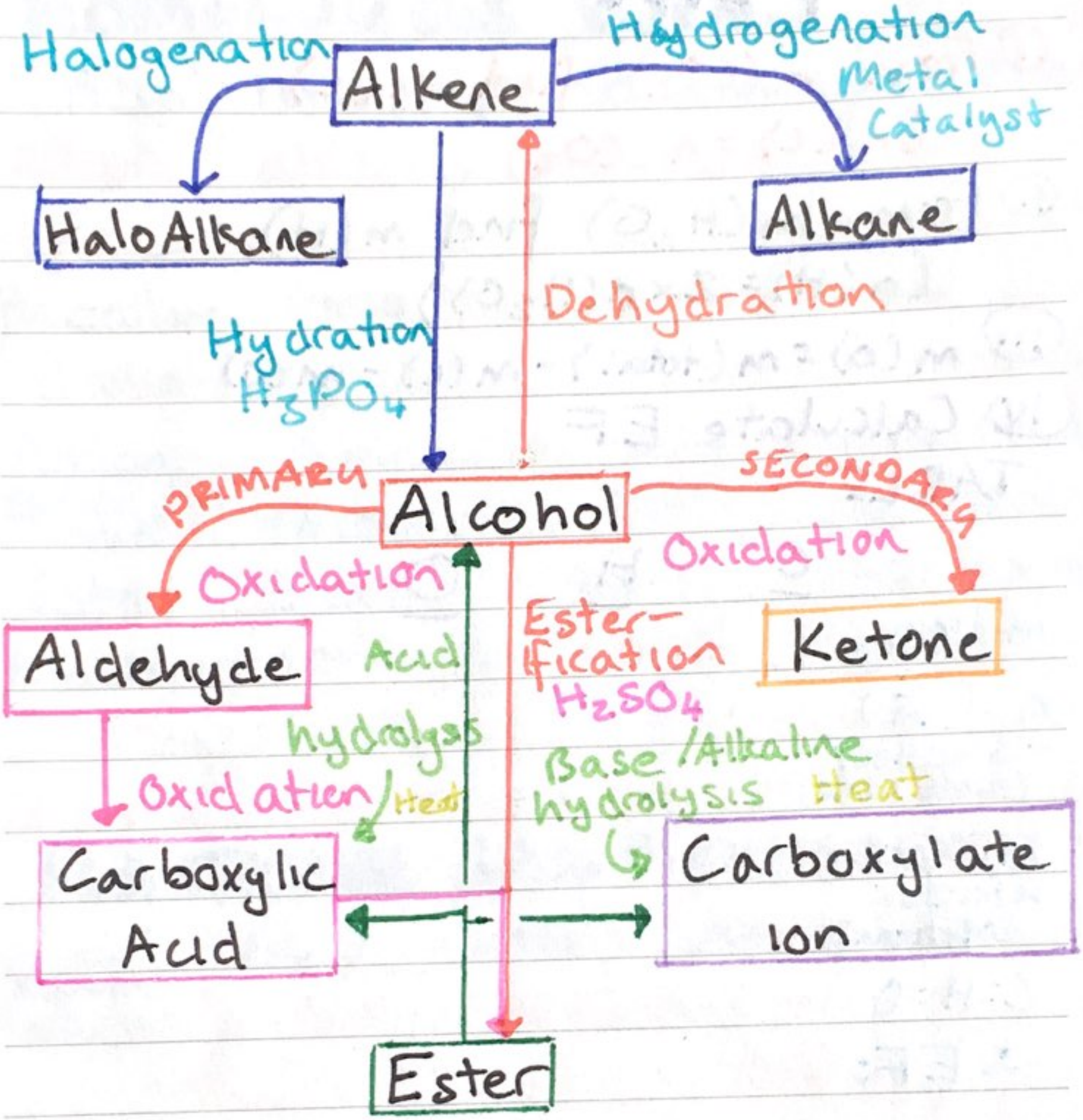
③ $m(O) = m(\text{total}) - m(C) - m(O)$

④ Calculate EF

TABLE

	C	H	O
m/100g			
n ($\frac{m}{M}$)			
÷ smallest (mole ratio)			
integers → ×factor (optional)			
C:H:O			
∴ EF:			

Rxns Flow Chart



~Organic~
Bio Chemistry
+ Chemical
Synthesis

Polymers

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Polymers are COVALENT MOLECULAR substances composed of many smaller molecules (MONOMERS) joined together.

POLY = MANY MER = PART

Monomers are joined through POLYMERISATION forming long chains of identical segments

⇒ repeating units.

STRUCTURAL PROPERTIES

- Determined primarily by the monomers
- However structural factors affect int.mol. forces b/n polymer chains:

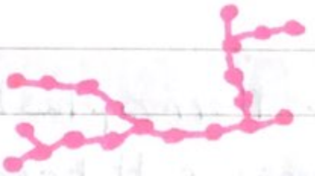
POLYMER MOLECULE CHAIN LENGTH

- As length ↑, dispersion force strength b/n neighbouring polymer chains ↑
  - ⇒ polymer forms hard, rigid material
  - ⇒ HIGH mol. weight = long polymer chains = tougher material.

BRANCHING OF POLYMER CHAINS

- Branched polymers form when monomers react w the SIDE of a polymer chain, instead of end.

⇒ new chain begins as a branch



· Branching → spaced apart chains → ↓ density → int.mol. attraction is weakened ⇒ flexibility

CROSS-LINKING OF POLYMER CHAINS

· Polymer branches are covalently bonded to neighbouring polymer chains
⇒ cannot exist as (l) as chains held in place by links and cannot flow.

strong covalent bonds ⇒ hard, rigid material

- Elastomers: formed when only occasional cross links are present ⇒ chains may still move past one another when stretched, but cross links return them to original position once released ⇒ Rubber bands.

THERMOPLASTICITY

In chem 'plastic' = property NOT material

Thermoplastic – can be heated + remoulded

Straight chain + branched chain can be thermoplastic → as long as NO covalent cross links

Polymer only = thermoplastic if bonds b/n polymer chains = H-bond, dipole-dipole, OR WEAK dispersion NOT covalent.

When heated thermoplastics molecules have enough E to overcome int. mol. forces ⇒ become free to move + slip past one another

⇒ usually recyclable = desirable property!

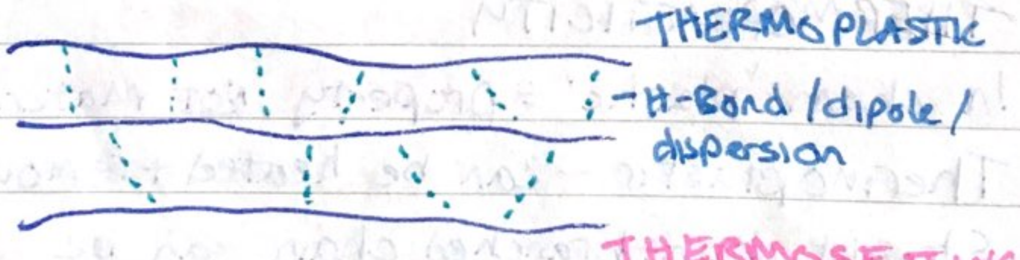
Thermosetting - polymers decompose or burn when heated. ≠ melt.

∴ Don't 'soften' as bonds b/n chains are so strong ⇒ COVALENT

If T ↑ enough to break covalent bonds, not just the crosslinks break; the whole molecule will decompose ∴

⇒ pot handles, bowling balls

⇒ usually non-recyclable



ADDITION POLYMERISATION

ADDITION ⇒ Alkene + X → X-Alkane

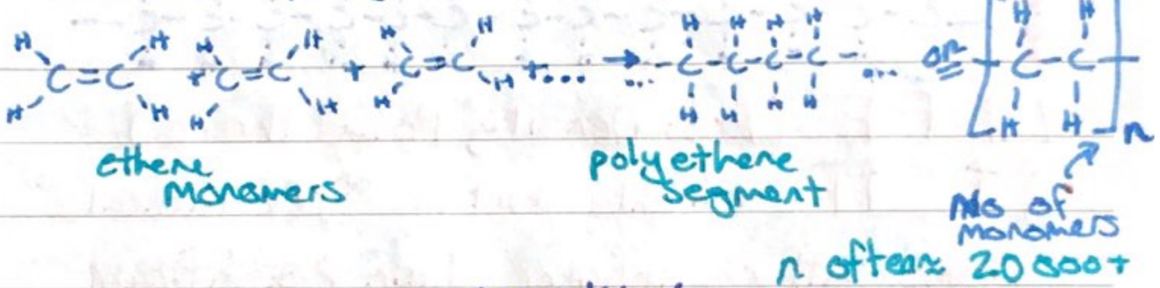
ADDITION POLYMERISATION:

Alkene + Alkene → ... Alkane-Alkane-Alkane ....

or "Poly-alkene"

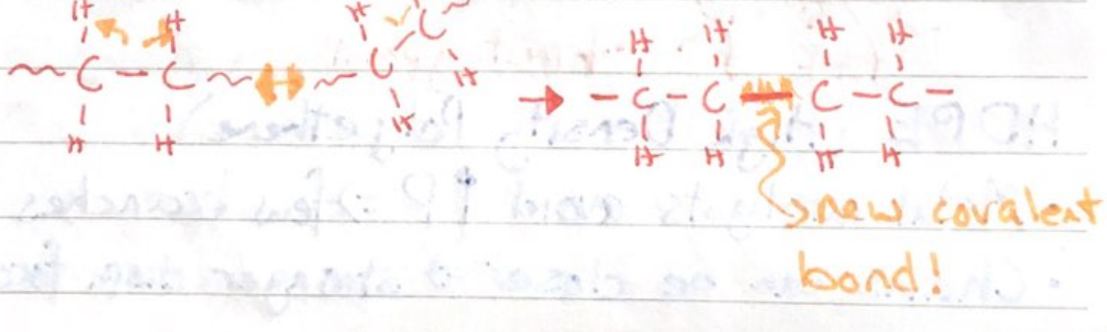
When alkenes undergo addition with themselves they can form long chains ⇒

⇒ 'addition polymers'



An unsaturated (has dble/ triple bonds) molecule polymerises → dble bond breaks

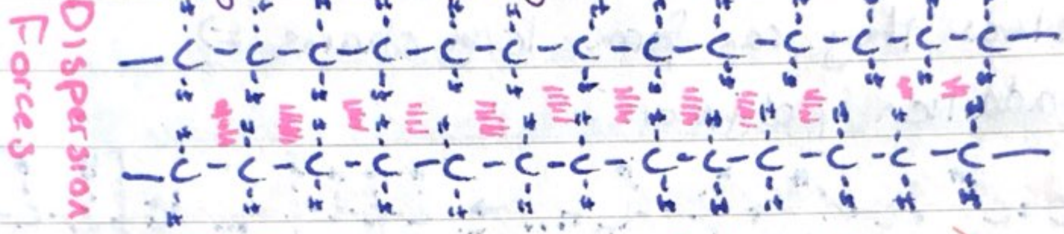
New covalent bonds are formed between C on nearby monomers ⇒ form SATURATED (single bond ONLY) molecules



- Often the name of a polymer includes the monomer that made it.

POLYETHENE

Essentially an extremely long alkane ⇒ non-polar ⇒ disp. forces only ⇒ strong enough that polyethene = (s) at room Temp



LDPE (Low Density Polyethene)

- ↑T, ↑P → highly reactive 'free radicals' atoms attack polymer chain ⇒ significant branching (free-radical polymerisation)
- Branching ⇒ chains can't pack closely together ⇒ weaker dispersion forces ∴ low density, soft, flexible
- Plastic bags ... etc

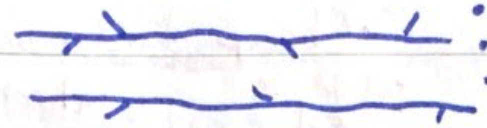
- ↓density
- soft
- ↓melting point
- doesn't conduct e
- non-crystalline

HDPE (High Density Polyethene)

- Metal catalysts avoid ↑P ⇒ few branches
- Chains can be closer ⇒ stronger disp. forces

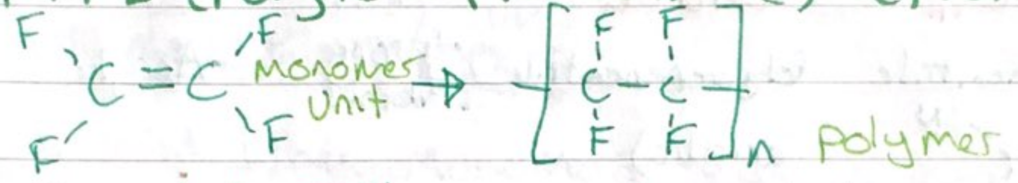
: arrangement = more ordered

- Plastic bottles, water pipes, containers



- ↑ Density
- Hard
- ↑ melting point
- crystalline sections

PTFE (Polytetrafluorcethene) - Teflon -

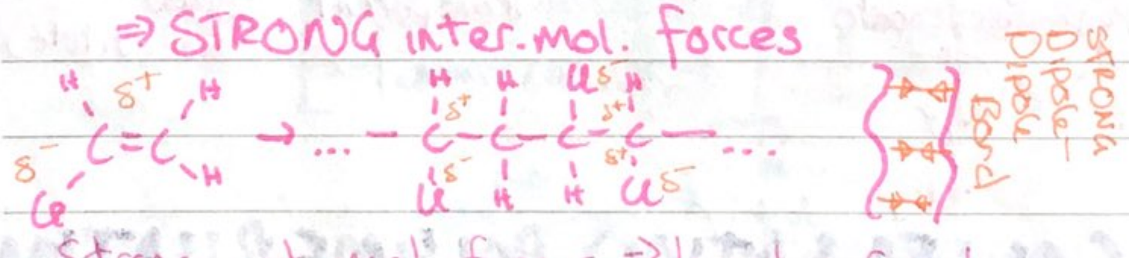


- Non-stick - Teflon repels - hydrophobic AND hydrophillic substances
- Heat-Resistance - ↑ melting point - 335°C
- Chem-Resistance - As F is very electro ⊖ve and reactive, C-F bonds are VERY strong ⇒ difficult to overcome with other chemicals

PVC (Polyvinyl chloride)

Polar monomer ⇒ Polar polymer

⇒ STRONG inter. mol. forces



- Strong int-mol forces ⇒ hard + rigid

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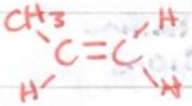
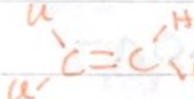
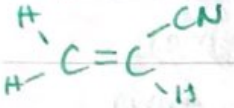
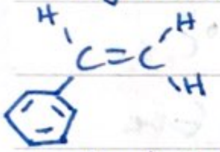
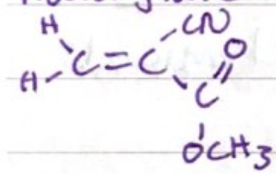
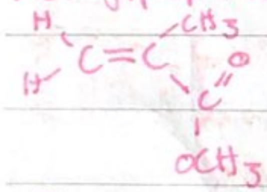
ADDITION POLYMERS:

Monomer	Polymer	Properties	Eg:
Propene 	Polypropene	·Durable ·Cheap	Ice-cream containers
Dichloroethene 	PVDC polyvinyl-idene chloride	·sticks to self ·stretchy	Glad Wrap
Propenenitrile 	Polypropenenitrile (acrylic)	·Strong ·Fibrous	·Acrylic
Phenylethene (styrene) 	Polystyrene	·Brittle ·low MP	Packing peanuts 
Methyl cyanoacrylate 	Polymethyl cyanoacrylate	·Polymerises on contact with water	Super Glue
Methyl 2-methylpropenoate 	Perspex	·strong ·Transparent	Perspex (glass substitute)

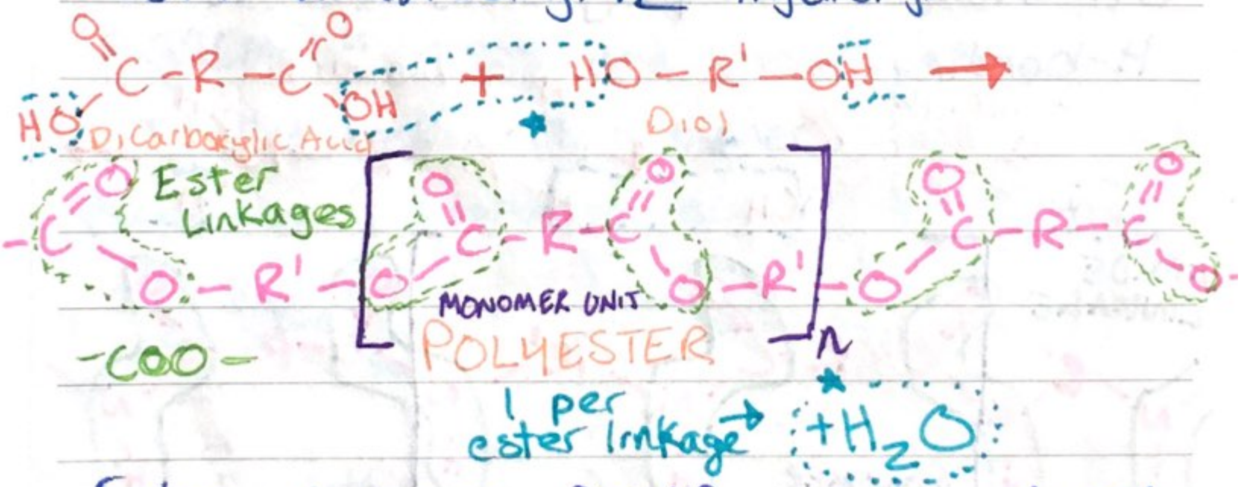
CONDENSATION POLYMERISATION

Addition polymerisation = limited to unsaturated (dble bond) molecules + monomers Condensation polymerisation occurs between two monomers with two functional groups on either end that react chemically to link together. 'Condensation' implies a smaller byproduct molecule is produced - usually a water molecule.

POLYESTERS

formed when monomers that contain carboxyl and hydroxyl funct. groups react.

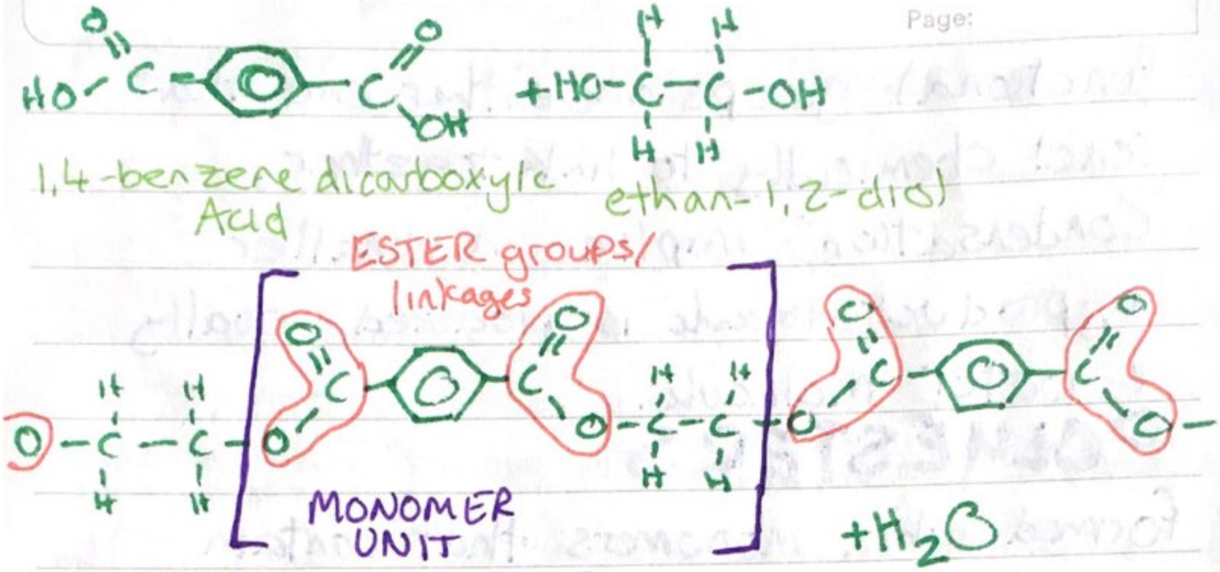
=> Typically dicarboxylic acid + diol monomers or monomers that contain both a carboxyl AND hydroxyl



Ester groups are POLAR ∴ strong int.mol forces exist b/n polyesters.

PET (Polyethylene Te~~r~~aphthalate)

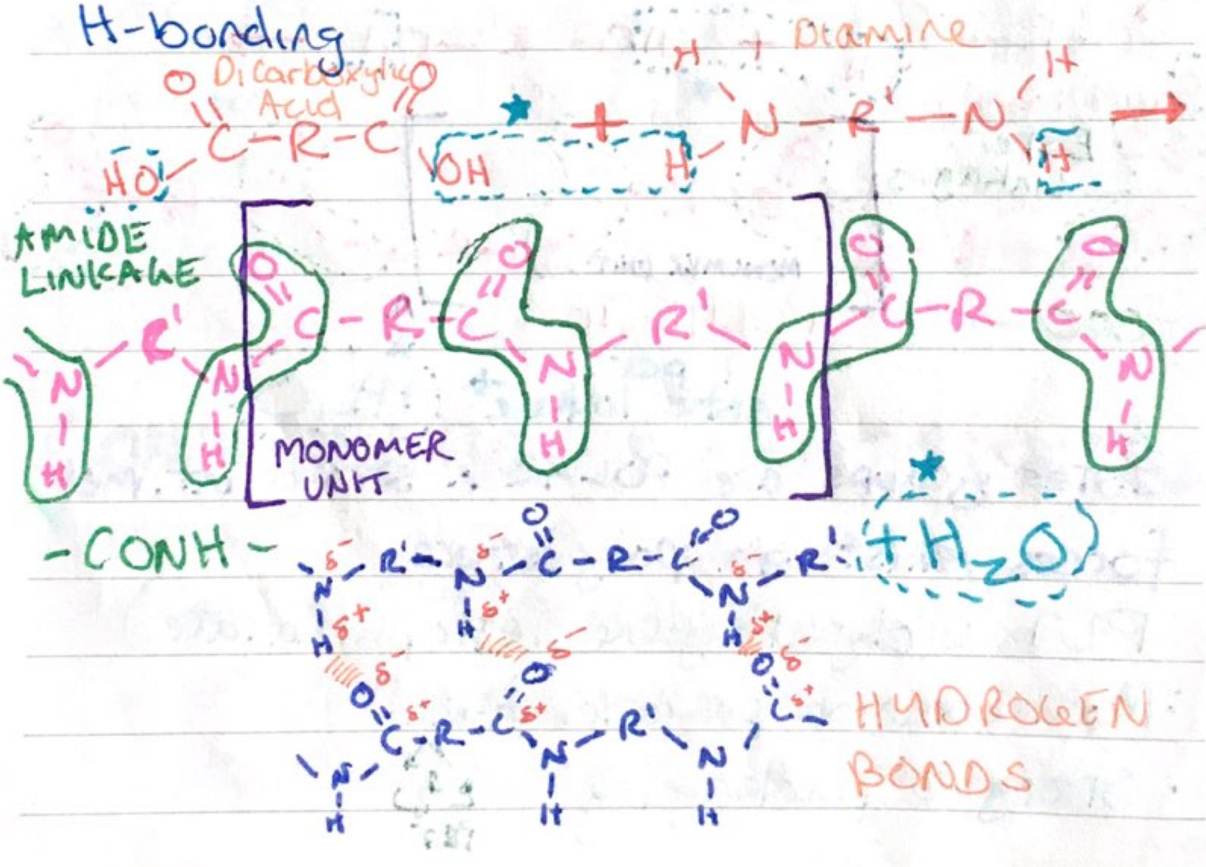
- Most common polyester fabric
- Strong → packaging



POLYAMIDES

Typically form when dicarboxylic acid molecules and diamine molecules react (or 1 monomer containing both)

STRONGER than polyesters due to H-bonding



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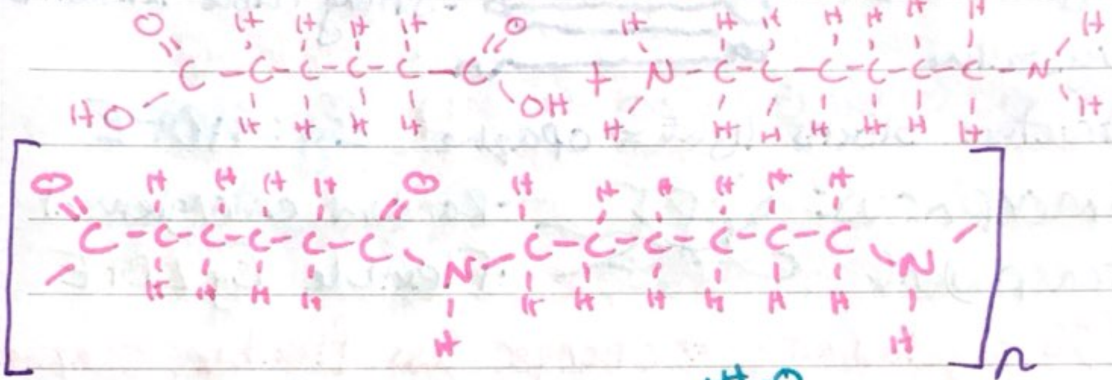
NYLON

- High tensile strength fibers → ropes + parachutes
- 'Nylon' = polyamide monomers contain LINEAR C chains

NYLON-6,6: hexane-1,6-dioc acid
+ 1,6-diaminohexane

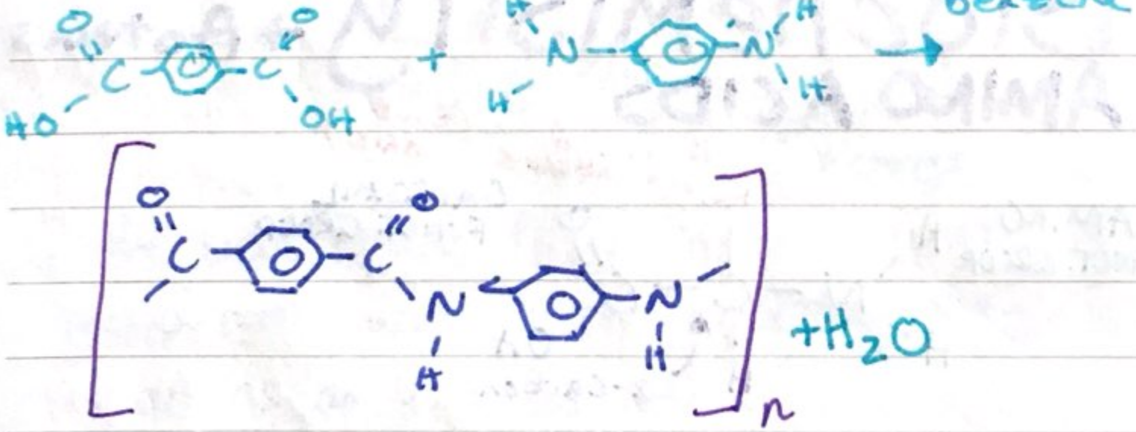


$+H_2O$

KEVLAR

EXTREMELY strong and lightweight
⇒ bullet proof vests + anchor cables

Benzene-1,4-dicarboxylic acid + 1,4-diamino benzene



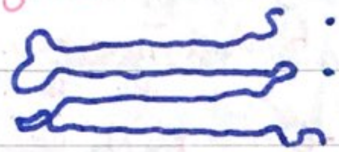
benzene rings → RIGID → strength
Close molecular alignment → strong H-bonds

DESIGNING POLYMERS

CRYSTALLINITY

Polymer chains twist around each other, int. mol. forces create CRYSTALLINE and AMORPHOUS Regions

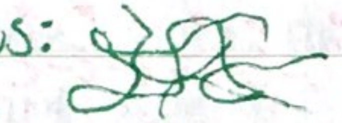
Crystalline:



- Regular
- Strong (close int. mol. forces)

·Crystalline structure blocks light ⇒ opaque Eg: HDPE

Amorphous:



- Random entanglement
- Flexible Eg LDPE

-Transparent

↑ % crystallinity ⇒ stronger, less flexible, opaque

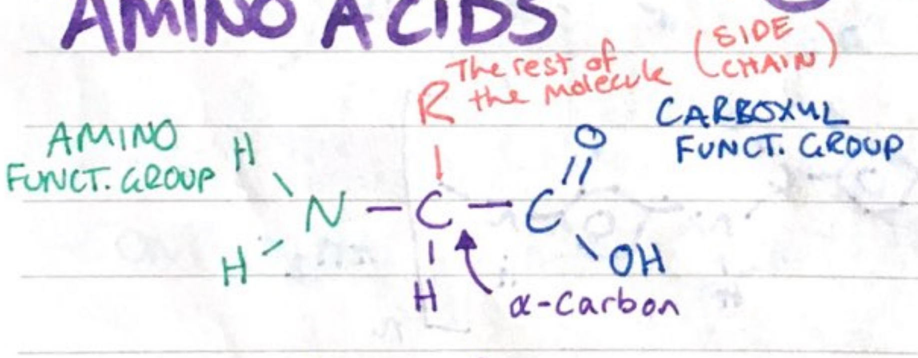
ADDITIVES: additives include pigments, UV stabilisers, flame retardants...

PLASTICISERS: Make softer + more flexible

Biochemistry

Amino acids → Proteins

AMINO ACIDS



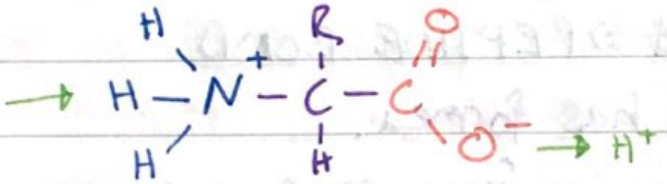
General form of an α-amino acid

α amino acids as Zwitterions:

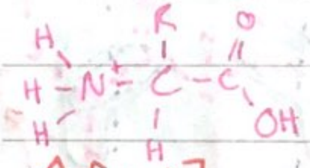
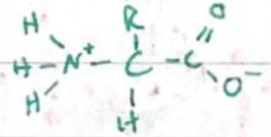
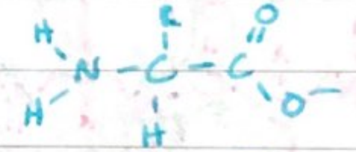
As NH_2 and COOH are polar groups, α amino acids are water soluble

- NH_2 can act as a base (proton acceptor)
    - $-NH_3^+$
- COOH can act as an acid (proton donor)
    - $-COO^-$

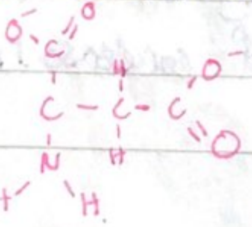
A Zwitterion contains both ⊕ AND ⊖ charges



↑ melting points of pure crystalline amino acids ⇒ zwitterion in (s) state ⇒ <u>IONIC</u> bonds

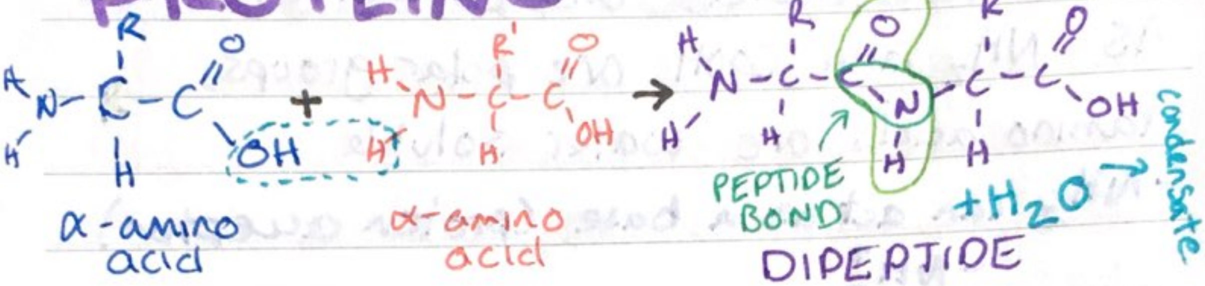
LOW PH (ACIDIC CONDITIONS)	pH 7	HIGH PH (basic cond.)
		
↑ $[H^+]$	$[OH^-] = [H^+]$	↓ $[H^+]$
CATION ⊕ charge	ZWITTERION NO overall charge	ANION ⊖ charge

If the side chain 'R' contains a funct. group with acid-base properties, they may act as an a/b as well



OVERALL
-2 charge

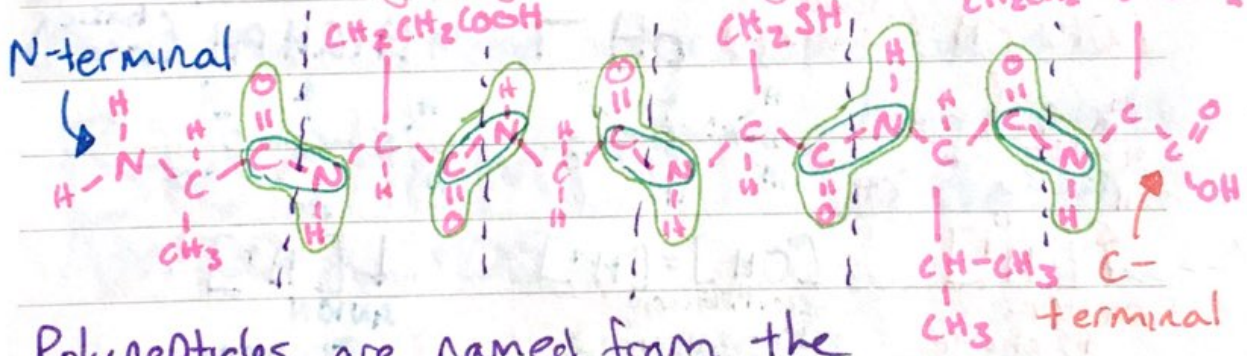
PROTEINS



- When two α-amino acids react undergoing a condensation reaction the amide link between them ⇒ PEPTIDE LINK
  The C-N bond ⇒ PEPTIDE BOND
  A DIPEPTIDE has formed.

A POLYMER made from many amino acids ⇒ POLYPEPTIDE

Ala + Glu + Gly + Cys + Val + Lys →



Polypeptides are named from the N-terminal to the C-terminal

A polypeptide of ≥ 50 α-amino acids ⇒ PROTEIN The body can break down proteins using water, the reverse of condensation ⇒ HYDROLYSIS

1°, 2°, 3°, 4° STRUCTURE OF PROTEINS

Proteins differ by N°, type, and sequence of their constituent amino acids.

⇒ precise chem. composition + sequence

⇒ unique 3-D shape ⇒ role depends on shape

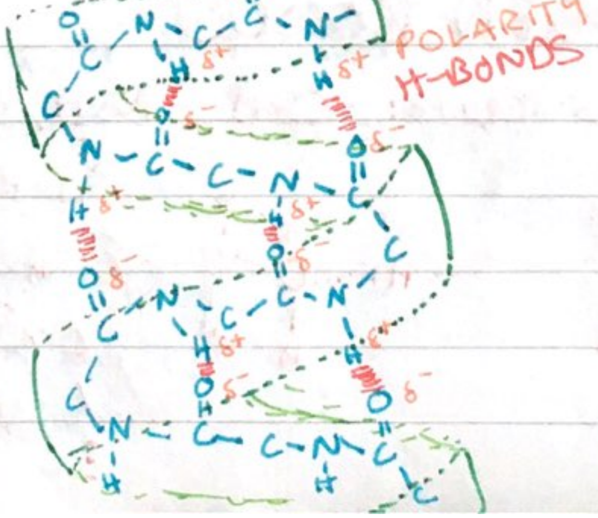
PRIMARY STRUCTURE - 1°

- N°, type, sequence of amino acid units
- 1° structure is named by abbreviations of amino acids from N-C terminal
- small error in sequence ⇒ BIG impact on funct. (shape, chem. properties, hydrophobia/phillia etc...)

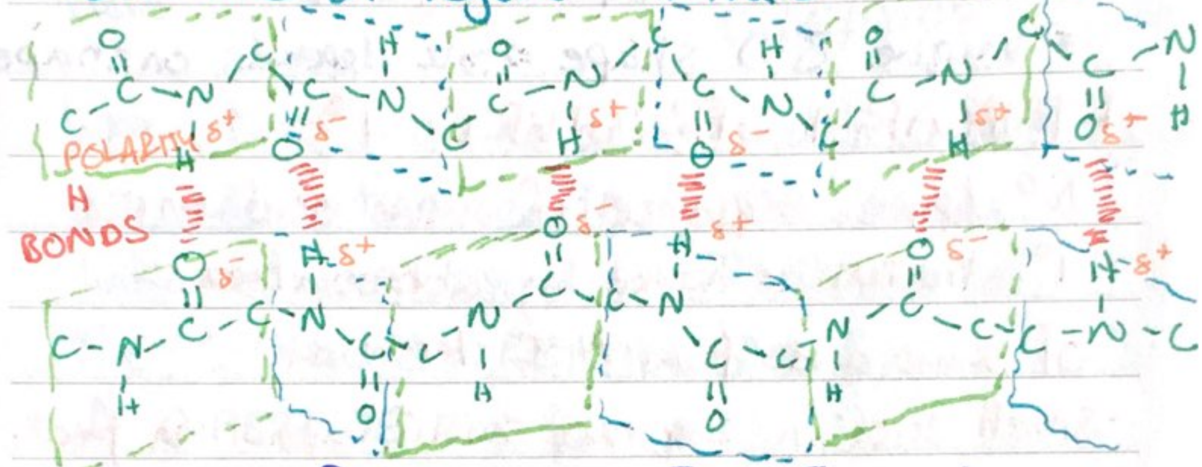
SECONDARY STRUCTURE - 2°

As molecules form their shape, regions that are regular and stabilised by H-bonds appear as secondary structure $\overset{\delta+}{C}\overset{\delta-}{O}\cdots\overset{\delta+}{H}-N^{\delta-}$

α Helices - H-bonds occur regularly, pulling a molecule into a spiral - a helix



β-Pleated Sheets - when two+ polypeptide chans line up parallel, H-bonds can form along the repeating N-C-C-N backbone at regulas intervals



TERTIARY STRUCTURE - 3°

Different types of bonds cause proteins to adopt different shapes and overall 3-D structure

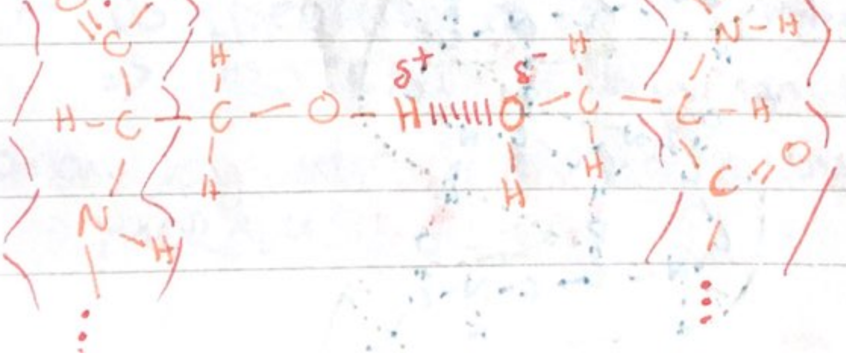
$3°$ structure = result of folding of $2°$ structures

Side chains of amino acid units influence $3°$ structure by interacting

$3°$ structure is critical to function

HYDROGEN BONDS

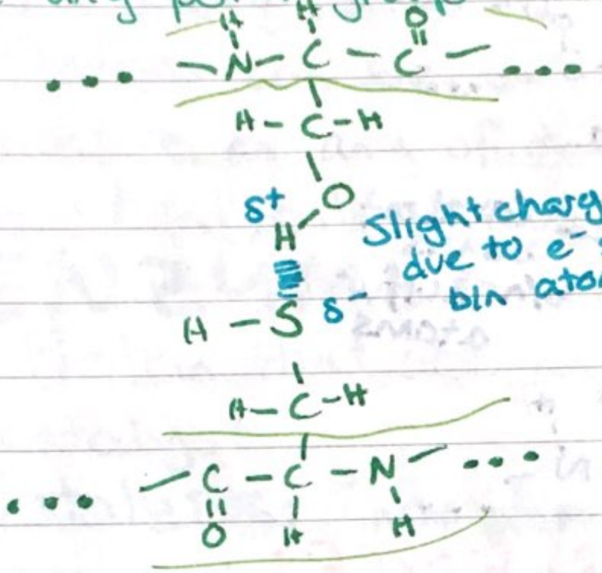
Side chains require: -O-H, -N-H, -C=O



DIPOLE-DIPOLE INTERACTIONS

Side chains require: -S-H, -O-H, -N-H,

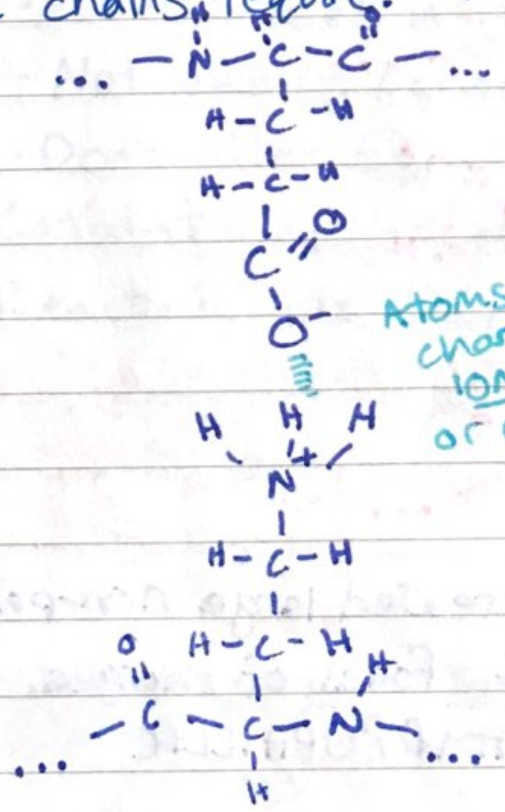
ie any polar group



Slight charge due to e^- share b/n atoms

IONIC INTERACTIONS

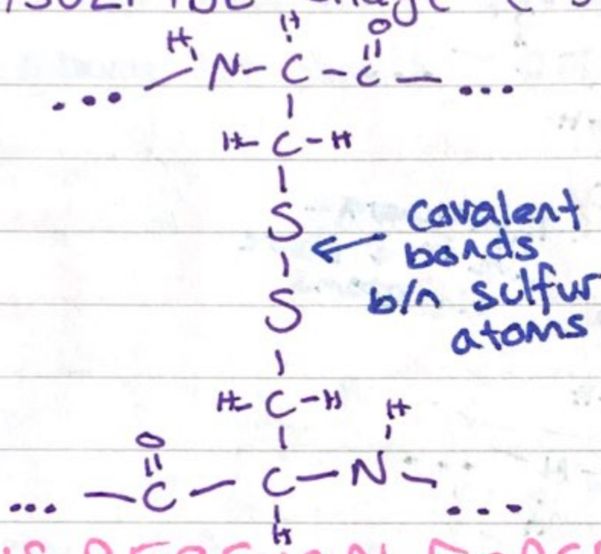
Side chains require: $-NH^+$, $-COO^-$



Atoms are charged and IONIC, missing or extra e^-'s...

COVALENT CROSS-LINKS

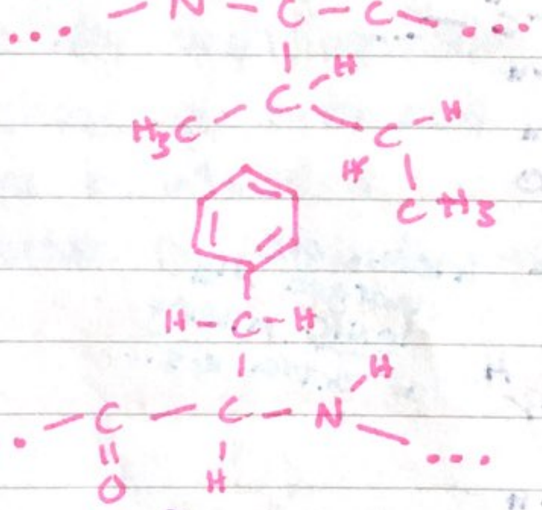
Cysteine side groups react to form a DISULFIDE bridge (-S-S-)



covalent bonds b/n sulfur atoms

DISPERSION FORCES

Side chains require: Any large non-polar group



Dispersion forces create large non-polar areas ⇒ HYDROPHOBIC Forces of charges create polar areas ⇒ HYDROPHILLIC

- When two+ polypeptide chains interact to form larger, more complex unit ⇒ quartenary structure - 4°.
- Proteins can be denatured by disrupting structure on any of the structural levels by heat, pH, chemical means... etc

ENZYMES

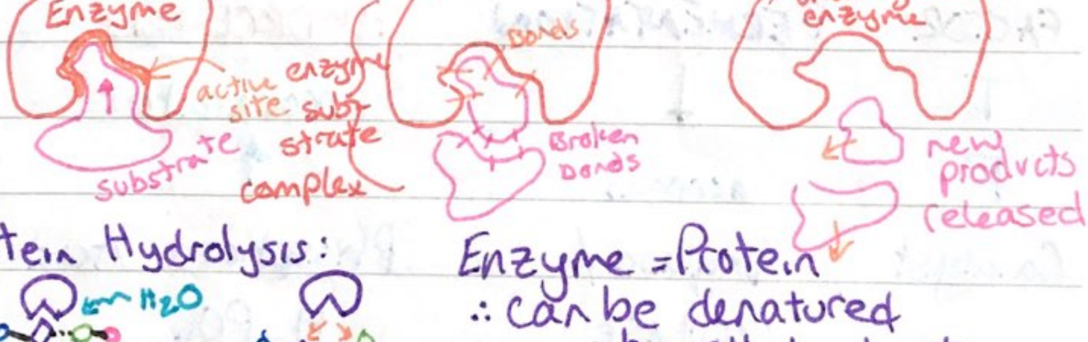
- Protein that acts as a biological catalyst.

Catalysts: ↑ rate of rxn by alternat Rxn pathway of ↓-er E_A ⇒ proportion of particles w $E \geq E_A$ ↑

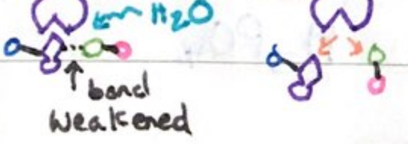
- Only needed in rel. small amounts
- Not used up / changed at end of Rxn
- Don't alter Eqm position

- Catalytic action of enzymes is Reaction specific.

LOCK + KEY MODEL:



Protein Hydrolysis:



Enzyme = Protein
∴ can be denatured by pH, heat, etc

ENZYMES AS INDUSTRIAL CATALYSTS

ADVANTAGES

- are specific, only catalyse a particular [Kind] of] reaction
- In general effective at biological Ts and pH → saves E and $ as ↑T/P is not required.
- Not consumed in Rxn, so can be used for a long time.
- Biodegradeable ∴ ↓ pollution

DISADVANTAGES

- Sensitive to pH / T change
- Certain chemicals may denature them
- Can be $$$ to produce
- Enzyme-catalysed Rxn generally (aq), product separation may be difficult

FERMENTATION VS HYDROLYSIS OF ETHENE ⇒ ETHANOL

FACTOR	FERMENTATION	HYDROLYSIS
T	↓	Moderate
P	normal	↑
Catalyst	Amylase / cellulase yeast enzymes	Phosphoric Acid H_3PO_4

Purification	Many distill.	Limited distill.
Raw Materials	Monosaccharides from grains..	Ethene => crude oil
Renewable	Yes	No
cost	↓	↑

Fats and Oils

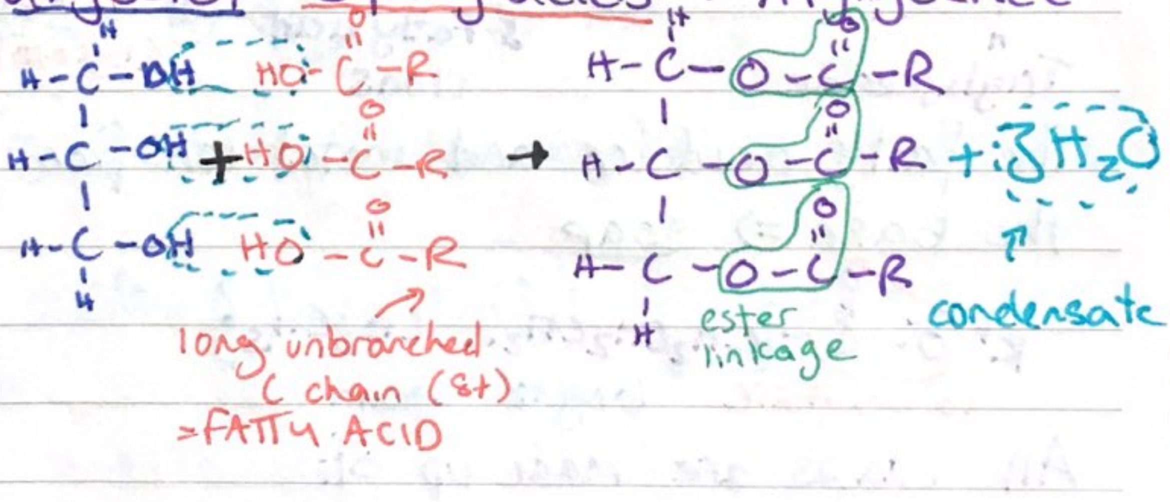
'Fat' = organic compound class of biological molecules - LIPIDS

Animal fats - (s) at room Temp
- Saturated fats (single C bonds)

Plant Oils - (l) at room Temp
- unsaturated fats

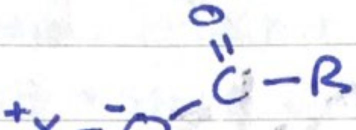
Contain triglycerides (tri-esters)
=> large + non-polar

Glycerol + 3 fatty acids → Triglyceride



Soaps

Soap molecules contain a long HC chain attached to a charged end

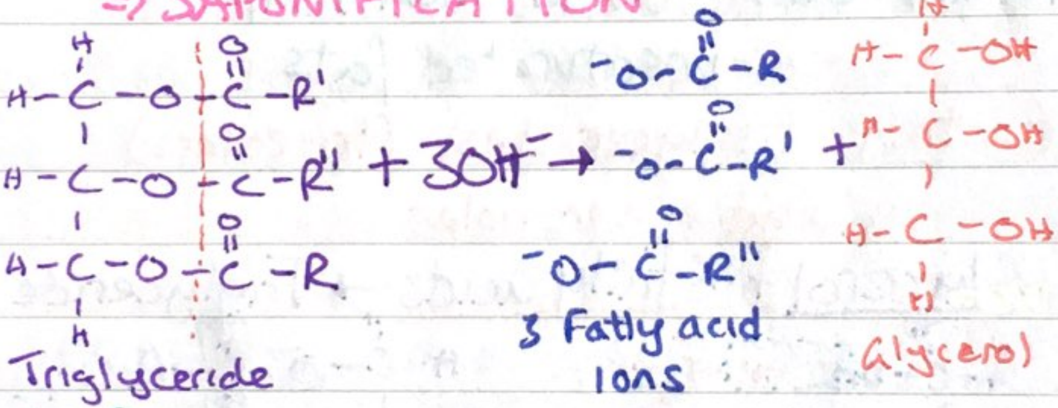


Soap is synthesised from triglyceride, hydrolysis is slow

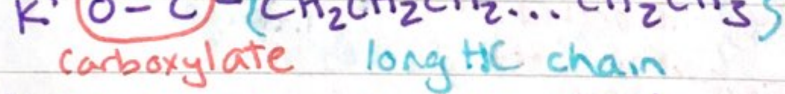
=> BASE-HYDROLYSIS (NaOH / KOH)

When base hydrolysis is applied to esters

=> SAPONIFICATION



The fatty acid ion and metal ion from the base => soap

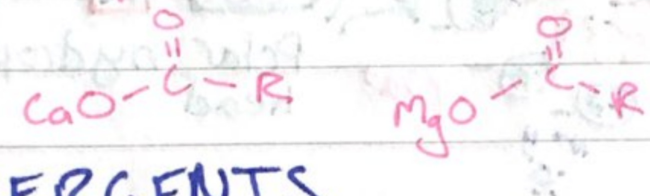

$K^+ \boxed{O^- - \overset{O}{\overset{\|}{C}}} - \{CH_2CH_2CH_2 \ldots CH_2CH_3\}$

All soaps are made up of:

- Long NON-POLAR HC chain

- POLAR carboxylate ion ($-COO^-$) conjugate bases of carboxylic acids
- Metal ion (Na^+ / K^+)

Water with significant $[Ca^{2+}]$ or $[Mg^{2+}]$ ⇒ HARD WATER these ions react w soap to form insoluble 'soap scum'.



$$CaO-\overset{O}{\overset{\|}{C}}-R \qquad MgO-\overset{O}{\overset{\|}{C}}-R$$

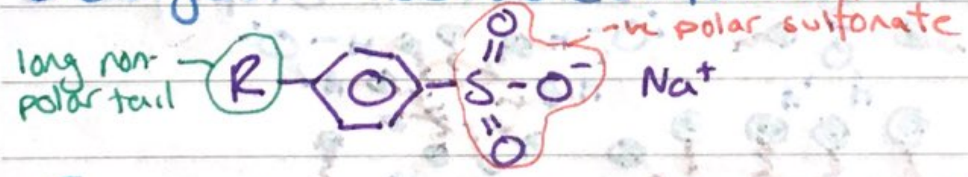
DETERGENTS

Contain long HC chain sourced from petroleum products

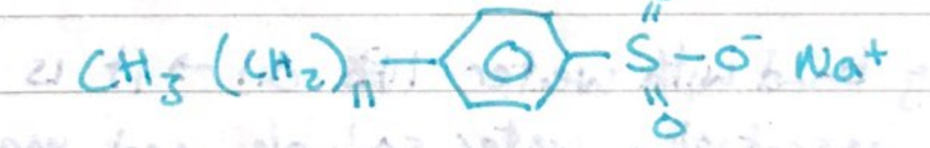
- Don't form soap scum with Ca^{2+}/Mg^{2+}

Anionic detergents ⇒ active constituent = ⊖ charged species

Detergent: -benzenesulfonate

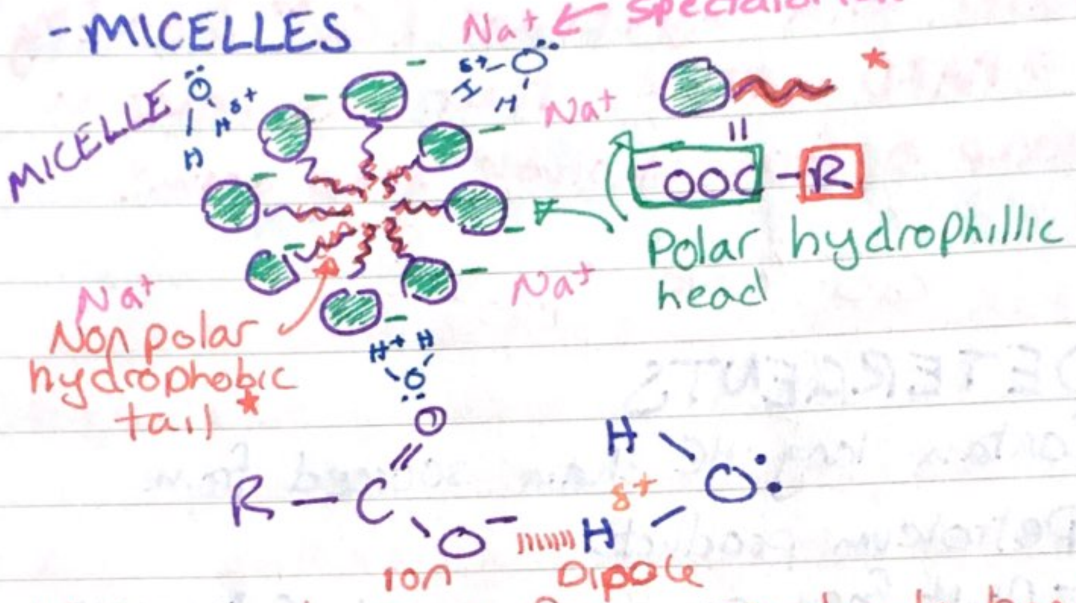


Eg sodium p-dodecylbenzenesulfonate



CLEANING ACTION OF SOAPS + DETERGENTS

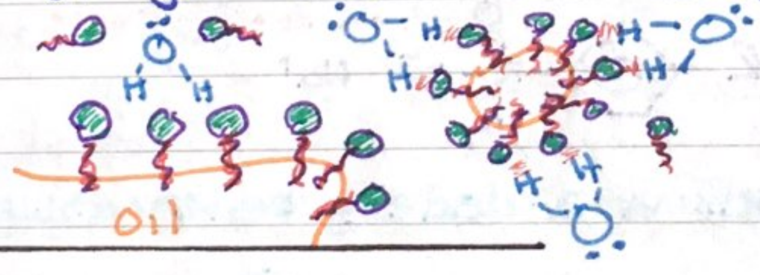
In water soap molecules form clumps - MICELLES



Water and soap form ion-dipole bonds

Agitation breaks up micelles

⇒ non polar ends then bond to oil or grease via mutual Disp. forces



Strong bond with water lifts oil →, it is now essentially water soluble and may be washed away Soaps = surface active agent ⇒ surfactant