Chapter 6 - Kinetics

### Rate of Reaction [must be +ve]

Def: change in concentration of products/reactants per unit time [$moldm^{-3}s^{-1}$]

o can be monitered through vol of gas evolved, mass change, colour change (clock experiment), pH changes, colour change (use of spectromeder to measure colour absorption)

Finding Rate of Reaction at given points on a graph

1) plot data onto graph
2) $\frac{dy}{dx}$ of graph = to rate of reaction
3) Draw tangent to curve at given point (e.g A)
4) $\frac{\Delta C}{\Delta T}$ = Rate at g A (instaneous RofR)

Note: initial RofR is at $x=0$

E_A = minimum amount of energy that particles need to collide successfully leading to reaction

Note that K.E (kinetic energy) of particles is directly proportional to temperature (Kelvin)

Collision Theory
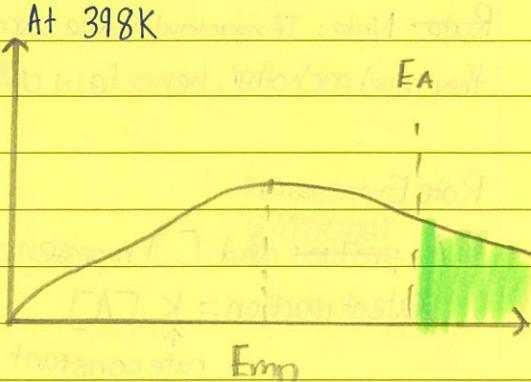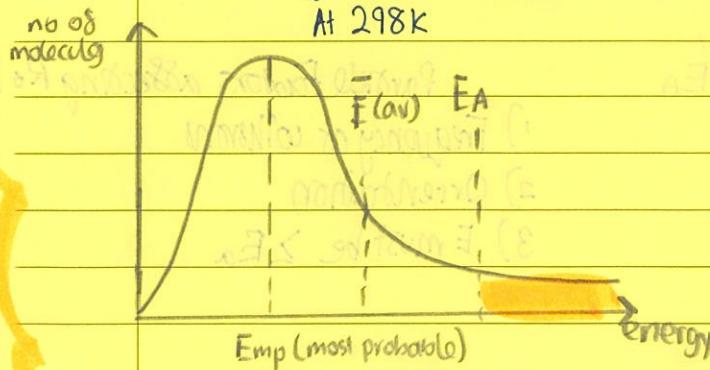
● For reaction to occur
→ Particles must collide
→ must collide with $E \geq E_A$
→ must collide with appropriate geometry

Factors Affecting Rate of Reaction

1) Temperature
2) Pressure
3) Concentration
4) Catalyst Usage
5) Surface Area

Maxwell-Boltzmann Distribution (MBDs)

→ representation of distribution of energy amongst reactant particles
→ Area under graph ($\int y\,dx$) = total number of particles [never changes]

$\int y\,dx$ is the same for both but Emp # is higher at 398 and more particles have $E \geq E_A$

All MBDs have horizontal asymptote = 0

All have no particles at 0 energy hence moves through orgin

No of particles at Emp (398k) lower to accomade more particles at $E \geq E_A$

Explanation Method → more collisions → more successful collisions → ↑ R of R

Collisions Per Unit Time!

Temperature

- ↑T, ↑R of R (↑$\frac{dy}{dx}$), reaches end faster
- More important reason → ↑ K.E of particles, more successful collisions, ↑R of R   [more particles with E ≥ EA]
- Other → as particles move faster → more collisions, more successful collisions, ↑ R of R

Surface Area Note
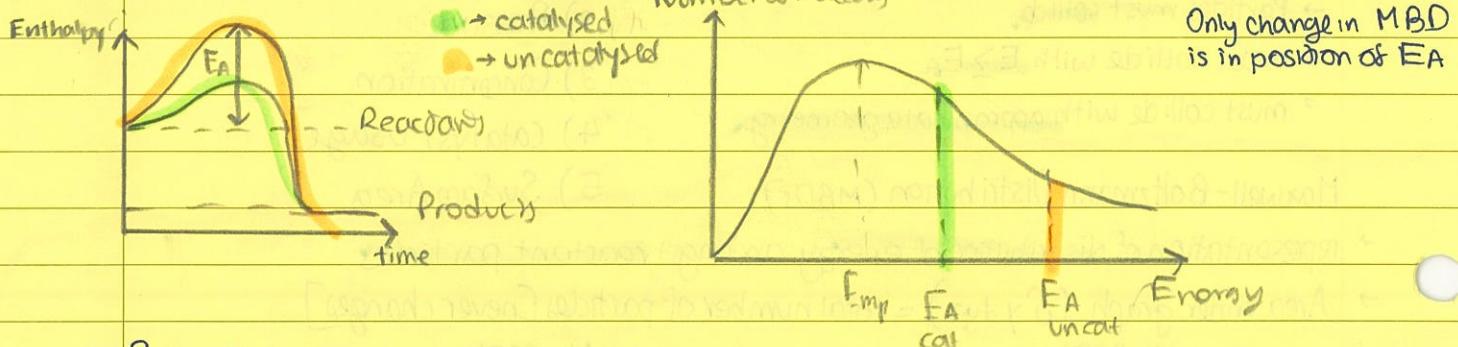
- More S.A, more particles that can come into contact with surrounding reagctant
- more collisions → more successful collisions → ↑R of R

Pressure / Concentration

- ↑ conc / pressure, more collisions per unit time, per unit vol
- more successful collisions, ↑ R of R
- However R of R gets slower as reaction proceeds as ↓ conc od reactants, hence ↓ collisions

Catalysts

- → substances that ↑ R of R while without being chemically changed
- → bring reactant molecules closer together, hence reducing E_A, by providing alternative reaction pathway
- → More particles with $E > E_A$ ∴ ↑ rate because ↑ successful collisions

→ catalysed
→ uncatalysed

Only change in MBD is in position of E_A

Rate Note: If reactant have same charge, they repel each other, hence few collisions, ↑ E_A

Particle Factors affecting R of R
1) Frequency of collisions
2) Orrientation
3) E must be ≥ E_a

Rate Expressions

If A = reactants ~~products~~ and [ ] represents conc

   rate of reaction = k [A]
                       ↑
                  rate constant

If you double the [A], and the rate doubles → R = k[A]

If you double the [A], and rate × 4 → R = k [A]^2

   You can have [B] influencing reaction as well.
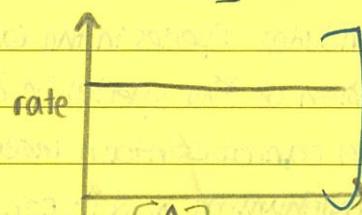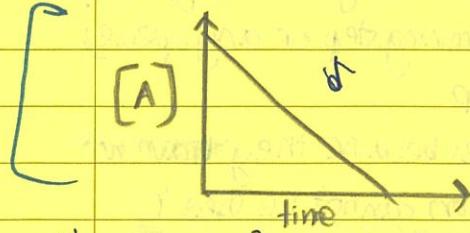
If no change in R when [A] is doubled, R = k[A]^0 = R = k

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Orders [= sum of exponents]
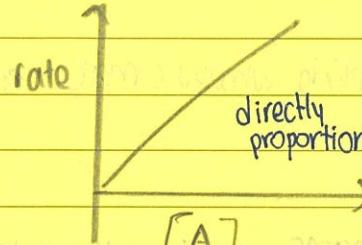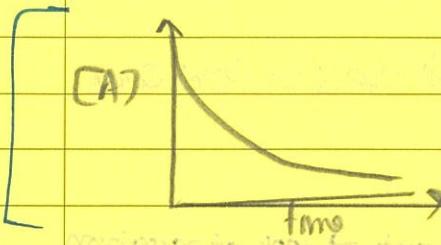
$1^{st} \rightarrow R = k[A]$ where $k = s^{-1}$ [sum of exponents = 1]
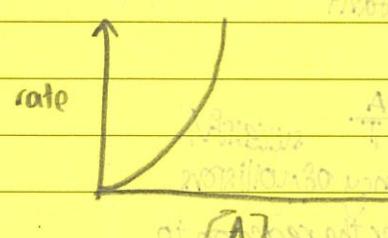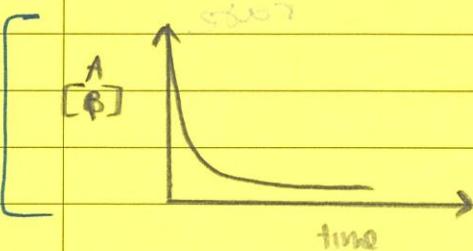
→ graphs here pertain to order 0

$2^{nd} \rightarrow R = k[A]^2$ or $k[A][B]$, where $k =$ ~~mol dm^{-3}~~ $dm^3 \, mol^{-1} s^{-1}$

→ 1st Order Graphs

directly proportional

$3^{rd} \rightarrow R = k[A]^2[B]$ or $k[B]^2[A]$ or $k[B][A][C]$, where $k = dm^6 mol^{-2} s^{-1}$

→ 2nd Order graphs

Reaction Mechanisms (construct of how overall reaction occurs)

→ comprise of all the elementary steps that ~~lead to the~~ occur in the reaction
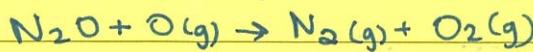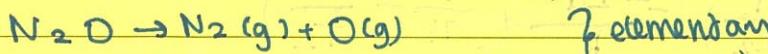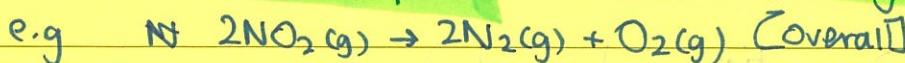
→ Elementary steps outline overall reaction mechanism

Molecularity
                    reactant particles   in that step
o Number of species (inclusive of ios molecules) involved ∧ uni, bi and termolecular process.

o Uni → 1 reactant, Bi, 2x, Ter, 3.

o Termolecular reactions are rare and unlikely because of 3 molecules are needed to collide with sufficient energy and correct orientation, Very unlikely for this to occur.
[statistically unlikely]

Note: Rate equations can only be determined experimentally

Intermediate - substance produced and consumed during elementary steps

e.g   ~~N~~ $2NO_2 (g) \rightarrow 2N_2(g) + O_2(g)$ [overall]

$N_2O \rightarrow N_2 (g) + O(g)$ ⎫ elementary
$N_2O + O(g) \rightarrow N_2 (g) + O_2(g)$ ⎬

        O is an intermediate, as it is produced and consumed.

Determining the expression → by number of molecules involved in the step → coefficient
    State what are the reactants in rate determining step.
    Say if overall equation matches stoichiometric too. Rate of slow step with
    respect to intermediates, then replace

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The rate determining step is the slowest elementary step (usually has v. high Ea)
∴ the rate expression includes species in the rate determining step or any species
that lead to the formation of the species in the step

    Note: Rate expression cannot contain intermediates because they have no
role in overall reaction mechanism and its concentration cannot be used to
assess change in rate because it is produced and consumed in elementary step

Rate expression would include whatever makes compounds used in slow step

Arrhenius
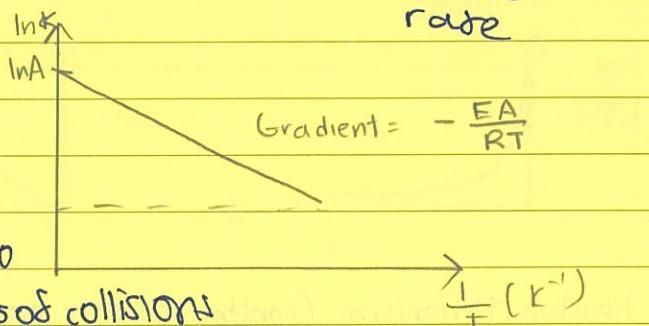
As the temperature increases, so does the rate constant. → look at equation,
explain how k must increase to increase rate

$$k = Ae^{-\frac{EA}{RT}}$$

← activation energy
← 8.31 and Temp
↑ Arrhenius constant

rate constant

$$\ln k = \ln A - \frac{EA}{RT}$$ successful

A also represents the frequency of collisions
with correct orientation for the reaction to
occur and relates to energy requirements of collisions

ln k
ln A

Gradient = $-\frac{EA}{RT}$

$\frac{1}{T}$ (k^{-1})

$\ln A = $ y intercept
$-\frac{EA}{RT} = $ gradient

Dependence of temperature

• If Ea low, then ↑ temp would have a small increase on k as less small increase
in particles with $E \geq Ea$, small change in rate
• If Ea is high, ↑ temp, big ↑ k because large increase in particles with $E \geq Ea$,
hence large change in rate

Simultaneous Arrhenius

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{-Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Ea is in $J\,mol^{-1}$