Chapter 3

Rate laws

Basic definitions

1. Homogeneous reaction : one that involves only one phase

2. Heterogeneous reaction : involves more than one phase, reaction usually occurs at the interface.

3. Irreversible reaction : reaction that proceeds only in one direction and continues in that direction until one of the reactants is exhausted

4. Reversible reaction : can proceed in either direction depending on the concentrations of reactant and products. relative to corresponding equilibrium concentration

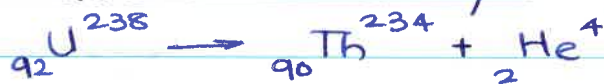⇒ No chemical reaction is completely irreversible

Irreversible reactions → Equilibrium point lies far to the product side.

- **Molecularity of reaction** : is the number of atoms, ions, or molecules involved (colliding) in a reaction step.

→ unimolecular ···one ⎫ molecules
→ bimolecular ··· two ⎬ colliding in
→ termolecular ··· three ⎭ any one
reaction step

⇒ Most common example of unimolecular reaction

— radioactive decay
$$_{92}U^{238} \longrightarrow _{90}Th^{234} + _{2}He^{4}$$

rate of disappearance of U ⇒ $-r_U = kC_U$

⇒ Only true bimolecular reactions are those that involve collision with free radicals

e.g. $Br\cdot + C_2H_6 \longrightarrow HBr + C_2H_5\cdot$

$$-r_{Br\cdot} = kC_{Br\cdot}C_{C_2H_6}$$

⇒ The probability of termolecular reaction (3 molecules collide all at same time) is almost non-existent

— In most instance the reaction pathway follows a series of bimolecular reactions.

Relative rates of reaction

→ Can be obtained from the ratio of stoichiometric coefficients

for reaction

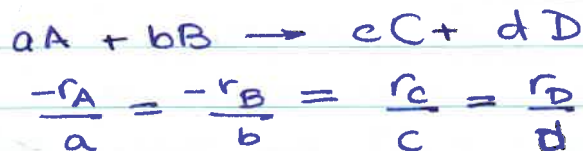$$A + \frac{b}{a} B \longrightarrow \frac{c}{a} C + \frac{d}{a} D$$

→ for every mole of A consumed $\frac{c}{a}$ moles of C appear

Rate of formation of C $= \frac{c}{a}$ rate of disappearance of A

$$r_C = \frac{c}{a}(-r_A) = \frac{-c}{a} r_A$$

Similarly

$$r_C = \frac{c}{d} r_D$$

$$aA + bB \longrightarrow cC + dD$$

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}$$

The reaction order and rate law

- Basis of calculation : Species A
  └ typically limiting reactant

The rate of disappearance of A, $-r_A$
~~depeds~~ depends on
  - Temperature
  - Composition

For many reactions

$$-r_A = k_A(T) \; fn(C_A, C_B, \cdots)$$

k_A : reaction rate constant

algebraic equation that relates $-r_A$
to species concentration
⇕
kinetic expression / rate law

k_A : specific rate of reaction or
rate constant
→ Always refers to a specific species
→ should be subscripted wrt that species

for reactions in which the stoichiometric coefficient is 1 for all species,

e.g.

$$1NaOH + 1HCl \longrightarrow 1NaCl + 1H_2O$$

Subscript can be omitted

$$k = k_{NaOH} = k_{HCl} = k_{NaCl} = k_{H_2O}$$

Power law models and elementary rate laws

→ Dependence of $-r_A$ on concentration of the species present $f(C_j)$ is almost always determined by experimental observations.

→ Functional dependence on concentration may be postulated by theory
↳ experiments are required to confirm the proposed form.

Power law model
⇒ Most common general forms of rate law

$$-r_A = k_A \, C_A^{\alpha} \, C_B^{\beta}$$

→ rate law is the product of concentrations of individual reacting species, each of wich is raised to a power

Order of reaction : refers to the powers to which the concentrations are raised

⇒ the reaction is α order wrt A

β order wrt B

⇒ overall order of reaction n

$$n = \alpha + \beta$$

Strictly : $-r_A = k_A' \, a_A^{\alpha} \, a_B^{\beta}$

a_i : activity = $\Gamma_i C_i$ γ_i : activity coefficient for many reacting systems γ_i does not change appreciably during the course of reaction

$-r_A = k_A' a_A^{\alpha} a_B^{\beta} \Rightarrow k_A' (\gamma_A C_A)^{\alpha} (\gamma_B C_B^{\beta})$

$\Rightarrow k_A \, C_A^{\alpha} \, C_B^{\beta}$

$k_A = k_A' \, \Gamma_A^{\alpha} \, \Gamma_B^{\beta}$

The units of $-r_A \Rightarrow$ conc./unit time
units of $k_A \Rightarrow$ vary with reaction order.

$$A \longrightarrow \text{products}$$

Overall reaction order $= n$

$$k = \frac{(conc)^{1-n}}{time}$$

Rate laws:

0th order : $\qquad -r_A = k_A \qquad \{k\} = \dfrac{mol}{dm^3\ s}$

1st order : $-r_A = k_A C_A \qquad \{k\} = \dfrac{1}{s}$

2nd order : $-r_A = k_A C_A{}^2 \qquad \{k\} = \dfrac{dm^3}{mol\ s}$

3rd order : $-r_A = k_A C_A{}^3 \qquad \{k\} = \dfrac{(dm^3/mol)^2}{s}$

<u>Elementary reaction</u> : is the one that
involves a single step.
- The stoichiometric coefficients in
this reaction are equal to the
powers in rate law.

$\Rightarrow$ Sometimes reactions have complex rate expression

$\quad \Rightarrow$ can not be separated into solely temperature-dependent and conc. dependent portions.

e.g. $2N_2O \longrightarrow 2N_2 + O_2$

$$-r_{N_2O} = \frac{k_{N_2O}\, C_{N_2O}}{1 + k'\, C_{O_2}}$$

k_{N_2O}, $k' \Rightarrow$ strongly T dependent

Overall reaction order cannot be stated.

— only under limiting circumstances we can speak of reaction order

e.g. for $1 \gg k'C_{CO}$ ... `apparent` 1st order
for $1 \ll k'C_{CO}$ ... `apparent` 0th order

-1th order with O_2
1st order with N_2O

$\Rightarrow$ Very common rate expression for liquid and gaseous reactions promoted by solid catalysts or homogeneous systems with reactive intermediates

$$H_2 + Br_2 \longrightarrow 2HBr$$

$\longrightarrow$ proceeds by free radical mechanism

$$-r_{Br_2} = \frac{k_{Br_2} C_{H_2} C_{Br_2}^{1/2}}{k' + C_{HBr}/C_{Br_2}}$$
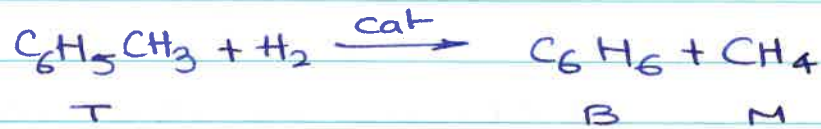
$\longrightarrow$ reaction involves a number of elementary steps and at least one active intermediate.

$\longrightarrow$ high energy molecule that reacts virtually as fast as it is formed

Heterogeneous reactions

- Historically for many gas-solid catalyzed reactions it is customary to write rate laws in terms of partial pressures. rather than conc.
- weight of catalyst is important rather than reactor volume $\Rightarrow -r'_A$

hydro methylation of toluene

$$C_6H_5CH_3 + H_2 \xrightarrow{\text{cat}} C_6H_6 + CH_4$$

$$\quad\quad\quad T \quad\quad\quad\quad\quad\quad\quad\quad B \quad\quad M$$

$$-r'_T = \frac{k\, P_{H_2}\, P_T}{1 + K_B P_B + K_T P_T} \quad \text{... Langmuir Hinshelwood kinetics}$$

' (prime) : Indicates typical units are in /g cat

P : partial pressures (kPa or atm)

K : adsorption const (1/kPa or atm⁻¹)

$$[k] = \frac{\text{mol toluene}}{\text{kg cat} \cdot s \cdot kPa^2}$$

→ To express the reaction in terms of concentration· instead of partial pressure — Use ideal gas law

$$P_i = C_i RT$$

$$-r_A = \rho_b (-r'_A)$$

↑ bulk density of catalyst particles in fluid media

Reaction order cannot be deduced from reaction stoichiometry.
One must determine reaction order from experiments / literature.

Reversible reactions

⇒ all rate laws must reduce to thermodynami relationships relating the reacting species concentrations at equilibrium.

↠ At equilibrium the rate of reaction is identically zero for all the species $(-r_A \equiv 0)$
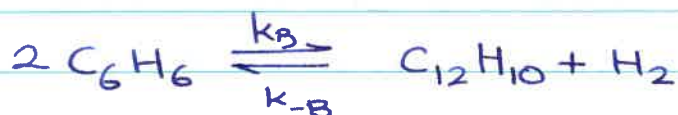
~~Fro~~ For a reaction

$$a A + b B \rightleftharpoons c C + d D$$

$$K_C = \frac{C_{Ce}^c \; C_{De}^d}{C_{Ae}^a \; C_{Be}^b} \qquad \therefore \text{ Units of } K_C$$

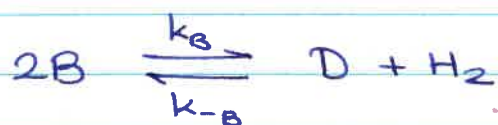$$\Rightarrow \left(\frac{mol}{dm^3}\right)^{(c+d-a-b)}$$

equilibrium constant

rate law for reversible reaction	consider following gas phase reaction — elementary and reversible

$$2 C_6 H_6 \underset{k_{-B}}{\overset{k_B}{\rightleftharpoons}} C_{12} H_{10} + H_2$$

benzene   diphenyl

$$2B \underset{k_{-B}}{\overset{k_B}{\rightleftharpoons}} D + H_2$$

→ forward and reverse rate constants k_B and k_{-B} defined w.r.t. benzene

Forward reaction
$$2B \xrightarrow{k_B} D + H_2$$

$$-r_{B, forward} = k_B C_B^2$$

Rate of formation of B is for the forward reaction
$$r_{B, forward} = -k_B C_B^2$$

Reverse reaction

$$D + H_2 \xrightarrow{\text{wk}_{-B}} B$$

Rate of formation of B

$$r_{B,reverse} = k_{-B} C_D C_{H_2}$$

Net rate

$$r_B \equiv r_{B,net} = r_{B\,forward} + r_{B,reverse}$$

$$r_B = -k_B C_B^2 + k_{-B} C_D C_{H_2}$$

Rate law for disappearance of B

$$-r_B = k_B C_B^2 - k_{-B} C_D C_{H_2}$$

$$= k_B \left(C_B^2 - \frac{k_{-B}}{k_B} C_D C_{H_2} \right)$$

$$K_C = \frac{k_B}{k_{-B}}$$

$$-r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_C} \right)$$

For elementary reaction

$$A \underset{k_{-A}}{\overset{k_A}{\rightleftharpoons}} B$$

$$-r_A = k \left(C_A - \frac{C_B}{K_c} \right)$$

Rate of formation of D

$$r_D = k_D \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$$

relative rates

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}$$

$$\frac{r_D}{1} = \frac{r_B}{-2} = \frac{k_B}{2} \left[C_B^2 - \frac{C_D C_{H_2}}{K_c} \right]$$

$$\Rightarrow \quad k_D = \frac{k_B}{2}$$

↳ We need to define the rate constant with respect to a particular species.

Is the rate law thermodynamically consistent at equilibrium

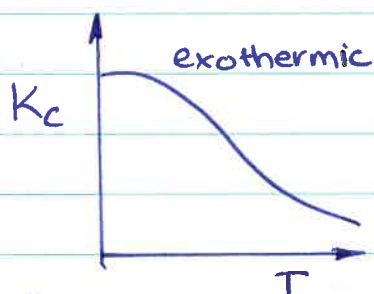$$K_c = \frac{C_{De}C_{H_2e}}{C_{Be}^2} \quad \rightarrow \quad \text{from thermody-namics}$$

at equilibrium $-r_B \equiv 0$

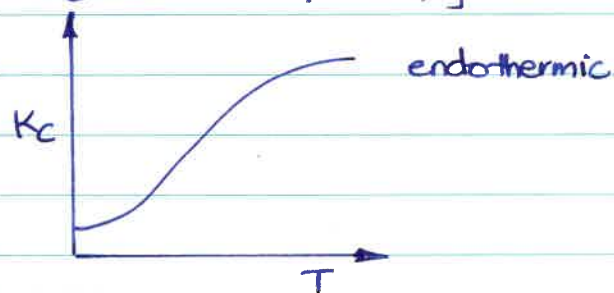$$-r_B \equiv 0 = k_B\left[C_{Be}^2 - \frac{C_{De}C_{H_2e}}{K_c}\right]$$

$$\Rightarrow K_c = \frac{C_{De}C_{H_2e}}{C_{Be}^2}$$

→ When there is no change in number of moles and heat capacity term $\Delta C_p = 0$

$$K_c(T) = K_c(T_1)\exp\left[\frac{\Delta H_{Rx}^0}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

exothermic

K_c

T

K_c decreases with T

endothermic

K_c

T

k_c increases with T

→ Given equilibrium constant at one
temperature, and the heat of reaction
↳ equilibrium constant at any
other temperature can be evaluated.

⇒ Equilibrium shifts to the left (i.e. K and
Xe decrease) as temperature increases
for exothermic reactions ⇒ Le Chatelier's
~~principle~~ principle.

The reaction rate constant

⇒ Not a constant
just independent of concentration

k : Specific reaction rate
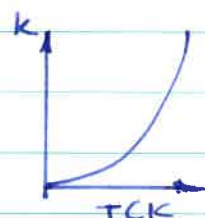: rate constant

- strongly dependent on temperature
- catalyst presence / activity
- may depend on total pressure in
gas systems.
- Liquid systems   } much weaker
  - ionic strength   dependence
  - choice of solvent   compared to T
                                     (erept for supercritical
                                       solvents)

$\Rightarrow$ for practical purposes
$$k = f(T)$$

Arrhenius equation

$$k_A(T) = A e^{-\frac{E}{RT}} \Rightarrow k_0 e^{-E/RT}$$

k_0, A : Pre exponential factor / frequency factor

E : Activation energy   J/mol   or   cal/mol

R : Gas constant $= 8.314$ J/mol k

$\qquad\qquad\qquad\qquad = 1.987$ cal/mo k

T : Absolute temperature   K

$\Rightarrow$ Emperically varified over a large ~~no. of~~ temp range

why there is activation energy?

$\rightarrow$ If reactants are free radicals

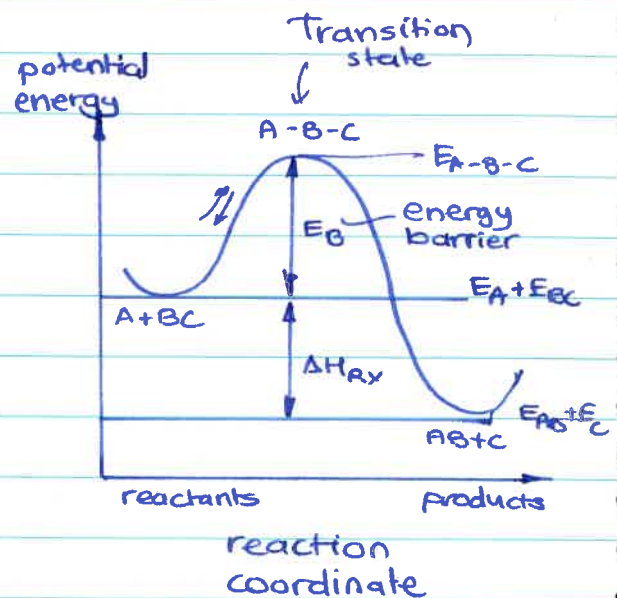⌐ react immediately on collision

⌐ there is no activation energy.

For most molecules and atoms there is activation energy.

$\rightarrow$ Molecules need energy to overcome the steric ~~static~~ and electron repulsive forces

$\hookrightarrow$ related to shape

→ molecules need energy to distort
• /and stretch their bonds so that they
~~brat~~ break and now can form new
bonds.

Activation energy
→ barrier to energy
transfer (from
kinetic energy to
potential energy)
between reacting
molecules that must
be overcome.

→ minimum increase in potential energy
of the reactants that must be
provided to transform the reactants
into products.
↳ can be provided by kinetic energy
of colliding molecules.

Reaction coordinates: denote minimum potential
energy of the system as a function of
the progress along reaction path

consider : $A + BC \rightleftharpoons A\text{-}B\text{-}C \rightleftharpoons AB + C$
fig (previous page) shows potential
energy of a three atom system.

Law of mass action:
- Rate of chemical reaction is proportional
  to the product of activities / conc.
  of the reactants.

- rate increases with increasing conc. of
  reactants owing to the corresponding
  increase in the number of molecular
  collisions.

Collision theory.

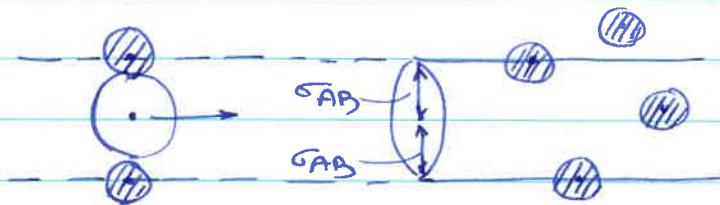objective: Give insight as to why rate
depends on concentration

consider : $A + B \longrightarrow C + D$
we model the molecules as rigid
spheres. S_A and S_B

→ Molecule B is stationary w.r.t. A

→ A moves towards B with a relative velocity U_R

→ A moves through a space to sweep out a collision volume with a collision cross section $\pi \sigma_{AB}^2$

σ_{AB} : collision radius

$\sigma_{AB} = \sigma_A + \sigma_B$

⇒ If the center of mol. B comes within a distance of σ_{AB} of the center of 'A', they will collide.

⇒ Collision cross section of rigid sphere

$$S_r = \pi \sigma_{AB}^2 \quad \text{~ const. (Approximation)}$$

$$U_R = \left(\frac{8 k_B T}{\pi \mu_{AB}} \right)^{1/2}$$

U_R : relative velocity between two gas
molecules.

K_B : Boltzmann constant $= 1.381 \times 10^{-23}$ J/k mol

m_A : mass of mol. A (g)

m_B : mass of mol. B (g)

M_{AB} : reduced mass $= \dfrac{m_A m_B}{m_A + m_B}$ $[= \mu]$

M_A : mol. wt. of A (dalton)

M_B : mol wt of B

N_{AVO} : Avogadro's no. 6.022 mo/mol

R : gas const. 8.314 J/mol K

$R := N_{AVO} \, K_B$

$M_A = N_{AVO} \, m_A$

$\therefore \dfrac{K_B}{M_{AB}} = \left(\dfrac{R}{\dfrac{M_A M_B}{M_A + M_B}} \right)$

$U \cong 5000$ km/hr @ 300 K

consider molecule A moving in space

$$\Delta V = (U_R \Delta t) \, \pi \sigma_{AB}^2$$

even though A may change directions
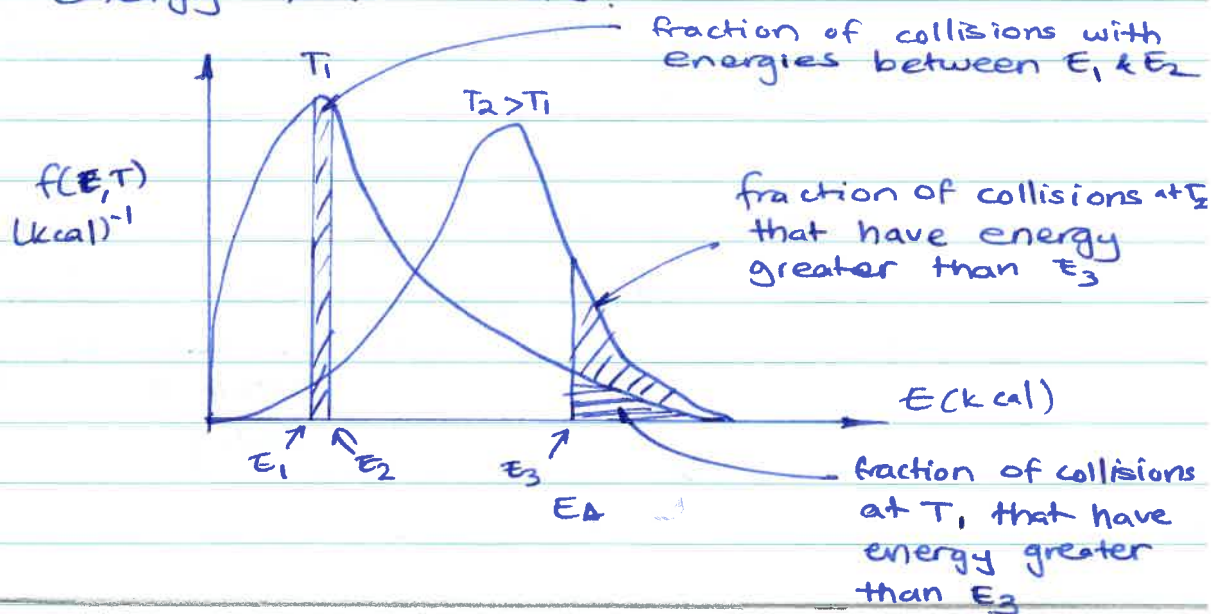upon collision, the volume sweep out is
same

No. of collisions that will take place $= \Delta V \, \bar{c}_B$

$\underbrace{\qquad}$ $\dfrac{molecules}{dm^3}$

No. of collisions in time Δt by this 1 mol. of A with many B

$$\check{Z}_{1A \cdot B} = \pi \sigma^2_{AB} \, \bar{c}_B \, U_R$$

→ We have many molecules of A present. at conc. $\bar{c}_A$ (molecules/dm³)

Adding up collisions of all molecules

$$\check{Z}_{AB} = \underbrace{\pi \sigma^2_{AB} \, U_R}_{SR} \, \bar{c}_A \, \check{c}_B$$

No. of collisions of all molecules

$$\check{Z}_{AB} = \pi \sigma^2_{AB} \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2} \bar{c}_A \, \check{c}_B$$

If collisions result in reaction

$$- \bar{r}_A = \check{Z}_{AB} = \pi \sigma^2_{AB} \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2} \bar{c}_A \, \bar{c}_B$$

multiplying by Avogadro number

$$\left(\frac{-\tilde{r}_A}{N_{AVO}} \right) N_{AVO} = \pi \sigma_{AB}^2 \left(\frac{8 k_B T}{\pi M} \right)^{1/2} \frac{\breve{C}_A}{N_{AVO}} \frac{\tilde{C}_B}{N_{AVO}} \hat{N}_{AVO}^2$$

$$-r_A = \sigma_{AB}^2 \left(\frac{8 \pi k_B T}{M} \right)^{1/2} C_A C_B N_{AVO}$$

Let $\quad A = \sigma_{AB}^2 \left(\frac{8 \pi k_B T}{M} \right)^{1/2} N_{AVO}$: Frequency factor

$$-r_A = A C_A C_B$$

The energy of the individual molecules
falls within a distribution of energies
where some molecules have more
energy than others.

fraction of collisions with
energies between E_1 & E_2

fraction of collisions at E_2
that have energy
greater than E_3

fraction of collisions
at T_1 that have
energy greater
than E_3

$f(E, T)$

$\Rightarrow$ energy distribution function for the kinetic energies of reacting molecules

$(f \cdot dE)$ = fraction of molecular collisions that have an energy between E and $E + dE$

Activation energy = minimum energy that must be possessed by reacting molecules before reaction will occur.
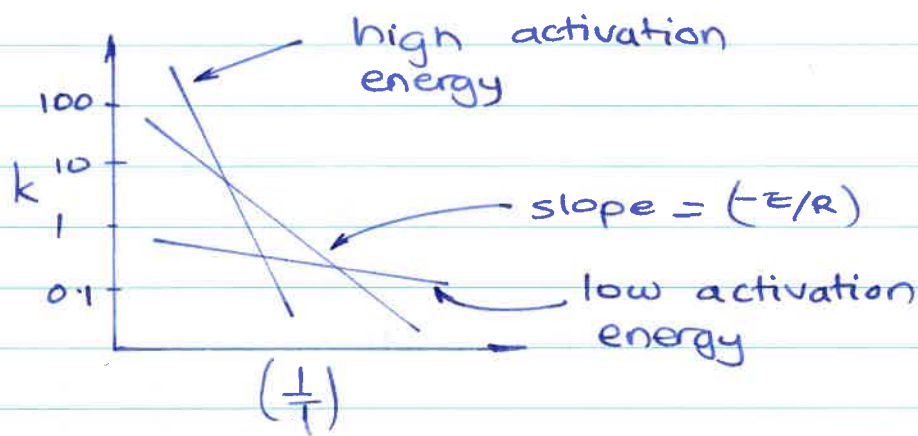
$\nearrow$ Postulation of the Arrhenius equation remains the greatest single step in chemical kinetics and retains its usefulness even today.

$\Rightarrow$ Determining activation energy
$\rightarrow$ Experimentally measuring reaction rate at ~~various~~ temperatures
different

$\hookrightarrow k_A(T) = A e^{-E/RT}$

taking natural log

$$\ln k_A = \ln A - \frac{E}{R}\left(\frac{1}{T}\right)$$

- Arrhenius plot -

Larger activation energy:
→ More temperature sensitive reaction
→ Just a few degrees in temperature increase can greatly increase k and the rate of reaction.

⇒ Rule of thumb. Reaction rate doubles every 10°C increase in temperature.

Specific reaction rate at T_0

$$k(T_0) = A e^{-E/RT_0}$$

at T

$$k(T) = A e^{-E/RT}$$

Taking ratio

$$k(T) = k(T_0) e^{\frac{-E}{R}\left(\frac{1}{T_0} - \frac{1}{T_1}\right)}$$

$\Rightarrow$ If we know sp. reaction rate
at temperature T_0, and we know
E, we can find k @ T