

Chapter 3

Rate laws

Notes on
Elements of chemical reaction
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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

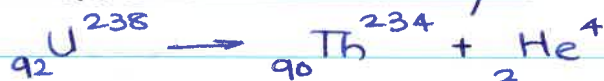
Irreversible reactions ⇒ Equilibrium point lies far to the product side.

• 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



rate of disappearance of U $\Rightarrow -r_{\text{U}} = kC_{\text{U}}$

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



$$-r_{\text{Br}\cdot} = kC_{\text{Br}\cdot}C_{\text{C}_2\text{H}_6}$$

⇒ 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



⇒ 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

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



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

The reaction order and rate law

- Basis of calculation : Species A
↳ typically limiting reactant

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

- Temperature
- Composition

For many reactions

$$-r_A = k_A(T) \text{ fn}(C_A, C_B, \dots)$$

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.



Subscript can be omitted

$$k = k_{\text{NaOH}} = k_{\text{HCl}} = k_{\text{NaCl}} = k_{\text{H}_2\text{O}}$$

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 which 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 $-r_A \Rightarrow \text{conc. / unit time}$
units of $k_A \Rightarrow \text{vary with reaction order.}$

$A \rightarrow \text{products}$
Overall reaction order = n

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

Rate laws:

0th order : $-r_A = k_A \quad \{k\} = \frac{\text{mol}}{\text{dm}^3 \text{ s}}$

1st order : $-r_A = k_A C_A \quad \{k\} = \frac{1}{\text{s}}$

2nd order : $-r_A = k_A C_A^2 \quad \{k\} = \frac{\text{dm}^3}{\text{mol s}}$

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

Elementary reaction : is the one that involves a single step.

→ The stoichiometric coefficients in this reaction are equal to the powers in rate law.

⇒ sometimes reactions have complex rate expression

⇒ can not be separated into solely temperature-dependent and conc. dependent portions.



$$-r_{\text{N}_2\text{O}} = \frac{k_{\text{N}_2\text{O}} C_{\text{N}_2\text{O}}}{1 + k' C_{\text{O}_2}}$$

$k_{\text{N}_2\text{O}}, k' \Rightarrow$ strongly T dependent
Overall reaction order cannot be stated.

— only under limiting circumstances we can speak of reaction order

e.g. for $1 \gg k' C_{\text{O}_2} \dots$ 'apparent' 1st order
for $1 \ll k' C_{\text{O}_2} \dots$ 'apparent' 0th order

— 1th order with O_2
1st order with N_2O

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



↳ proceeds by free radical mechanism

$$-r_{\text{Br}_2} = \frac{k_{\text{Br}_2} C_{\text{H}_2} C_{\text{Br}_2}^{1/2}}{k' + C_{\text{HBr}} / C_{\text{Br}_2}}$$

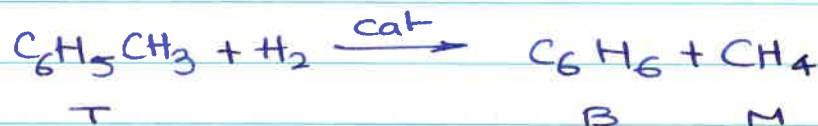
→ reaction involves a number of elementary steps and at least one active intermediate.

↳ 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



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

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

P : partial pressures (kPa or atm)

K : adsorption const (1/kPa or atm⁻¹)

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

⇒ 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 thermodynamic relationships relating the reacting species concentrations at equilibrium.
- ⇒ At equilibrium the rate of reaction is identically zero for all the species ($-r_A \equiv 0$)

~~For~~ For a reaction

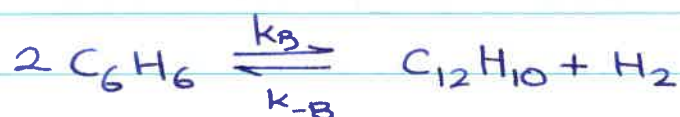


$$K_c = \frac{C_{Ce}^c C_{De}^d}{C_{Ae}^a C_{Be}^b} \quad \text{Units of } K_c \Rightarrow \left(\frac{\text{mol}}{\text{dm}^3} \right)^{(c+d-a-b)}$$

equilibrium constant

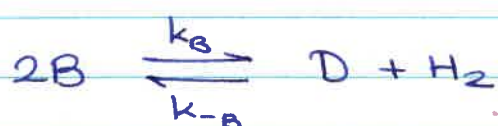
rate law
for
reversible
reaction

consider following gas phase reaction
- elementary and reversible



benzene

diphenyl



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

Forward reaction



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

Rate of formation of B is for the
forward reaction

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

Reverse reaction



Rate of formation of B

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

Net rate

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

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

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



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

Rate of formation of D

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

relative rates

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

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

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

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

Is the rate law thermodynamically consistent at equilibrium

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

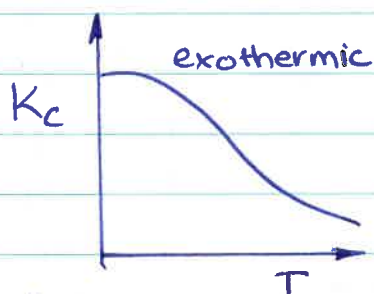
at equilibrium $-r_B \equiv 0$

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

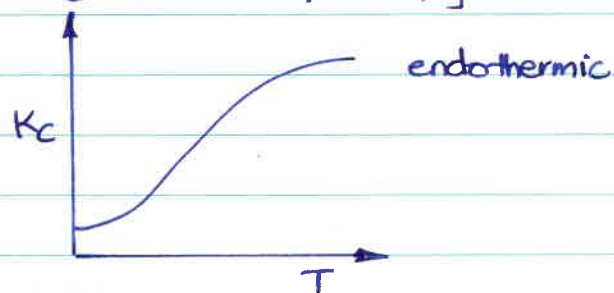
$$\Rightarrow K_c = \frac{C_{De} C_{H_2e}}{C_{Be}^2}$$

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

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



K_c decreases with 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 X_e decrease) as temperature increases for exothermic reactions ⇒ Le Chatelier's principle.

The reaction rate constant

⇒ Not a constant
just independent of concentration

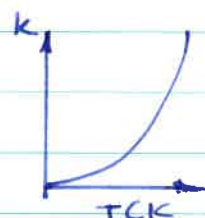
k : Specific reaction rate
: rate constant

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

⇒ 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 : Preexponential factor / frequency factor

E : Activation energy J/mol or cal/mol

R : Gas constant = 8.314 J/mol K

= 1.987 cal/mol K

T : Absolute temperature K

⇒ Empirically verified over a large ~~no.~~ ^{temp range} of

why
there is
activation
energy?

⇒ IF reactants are free radicals
 ↳ react immediately on collision
 ↳ there is no activation energy.

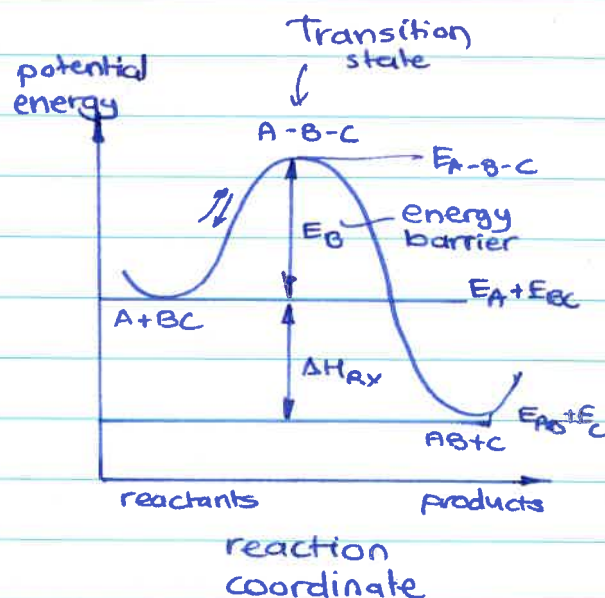
For most molecules and atoms there is activation energy.

→ Molecules need energy to overcome the
steric static and electron repulsive forces
 ↳ related to shape

→ molecules need energy to distort
 • /and stretch their bonds so that they
~~break~~ 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 : $A + BC \rightleftharpoons A-B-C \rightleftharpoons AB + C$
fig (previous page) shows potential energy of a three atom system.

Law of mass action.

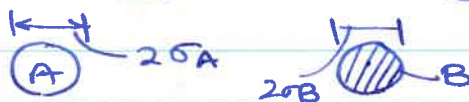
- Rate of chemical reaction is proportional to the product of activities / conc. of the reactants.
- rate increases with increasing conc. of reactants owing to the corresponding increase in the number of molecular collisions.

Collision theory.

objective: Give insight as to why rate depends on concentration

consider : $A + B \rightarrow C + D$

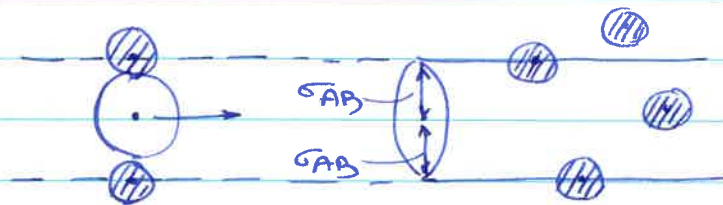
we model the molecules as rigid spheres. S_A and S_B



→ 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
 $S_r = \pi \sigma_{AB}^2$ - const. (Approximation)

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

U_R : relative velocity between two gas molecules.

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

m_A : mass of mol. A (g)

m_B : mass of mol. B (g)

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

M_A : mol. wt. of A (dalton)

M_B : mol wt of B

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

R : gas const. 8.314 J/mol K

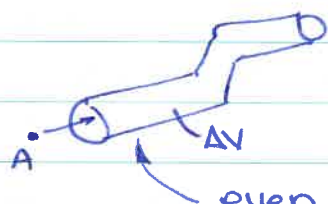
$$R = N_{Avo} K_B$$

$$M_A = N_{Avo} m_A$$

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

$$U \approx 5000 \text{ km/hr @ } 300 \text{ K}$$

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 = $\Delta v \bar{C}_B$

$$\text{place} = \Delta V \bar{C}_B$$

\nwarrow molecules
 dm^3

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

$$\sum_{A \cdot B} = \pi \sigma_{AB}^2 \tilde{C}_B U_R$$

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

Adding up collisions of all molecules

$$\tilde{Z}_{AB} = \underbrace{\pi \sigma_{AB}^2}_{S_B} \tilde{C}_A \tilde{C}_B$$

SR
No. of collisions of all molecules

$$\tilde{Z}_{AB} = \pi \sigma_{AB}^2 \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2} \tilde{C}_A \tilde{C}_B$$

If collisions result in reaction

$$-\bar{\Gamma}_A = \bar{Z}_{AB} = \pi \sigma_{AB}^2 \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2} \bar{C}_A \bar{C}_B$$

multiplying by Avogadro number

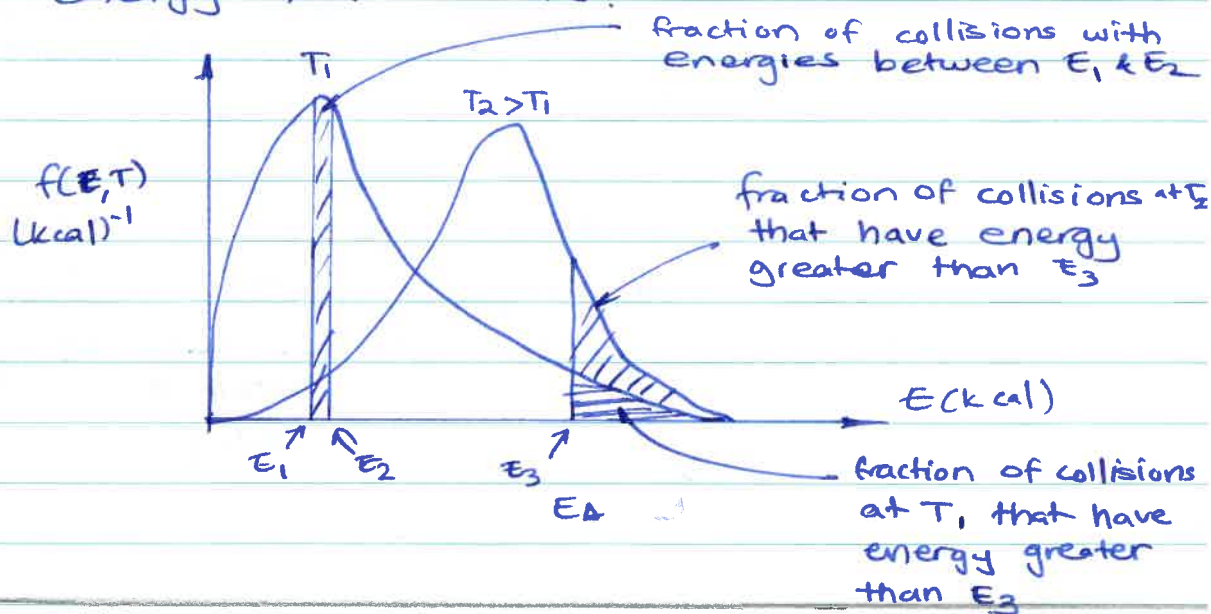
$$\left(\frac{\bar{r}_A}{N_{AVO}} \right) N_{AVO} = \pi \sigma_{AB}^2 \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} \frac{\bar{C}_A}{N_{AVO}} \frac{\bar{C}_B}{N_{AVO}} N_{AVO}^2$$

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

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

$$-r_A = A C_A C_B$$

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



$f(E, T)$

⇒ 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.

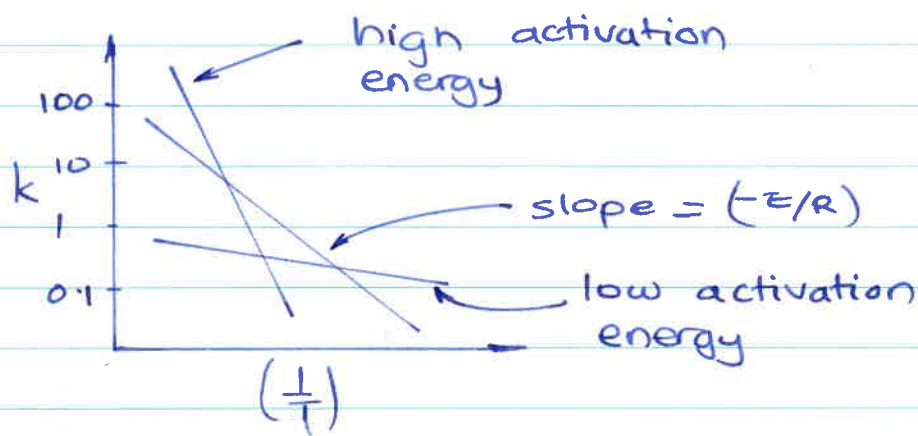
⇒ Postulation of the Arrhenius equation remains the greatest single step in chemical kinetics and retains its usefulness even today.

⇒ Determining activation energy
→ Experimentally measuring reaction rate at various temperatures different

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

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

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

at T

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

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