Methanizer

Lecture # 4.2 CHE331A

- **Reaction rate is a function of concentration and temperature**

- **Basic definition about reactions**

- Molecularity, order, elementary and non-elementary reactions

- Irreversible and reversible reactions

- **Rate and Equilibrium constants**

GOUTAM DEO

CHEMICAL ENGINEERING DEPARTMENT

IIT KANPUR

Reaction rate constant, *k*, is often concentration independent

▶ **Also called specific reaction rate or rate constant, units depend on the reaction**

  ○ *for nth order the units of k is* $\dfrac{(concentration)^{1-n}}{time}$

▶ **Strongly dependent on temperature**

▶ **For gaseous system:** $k(T)$ may depend on total pressure

▶ **Liquid systems:** $k(T)$ may depend on ionic strength & choice of solvent

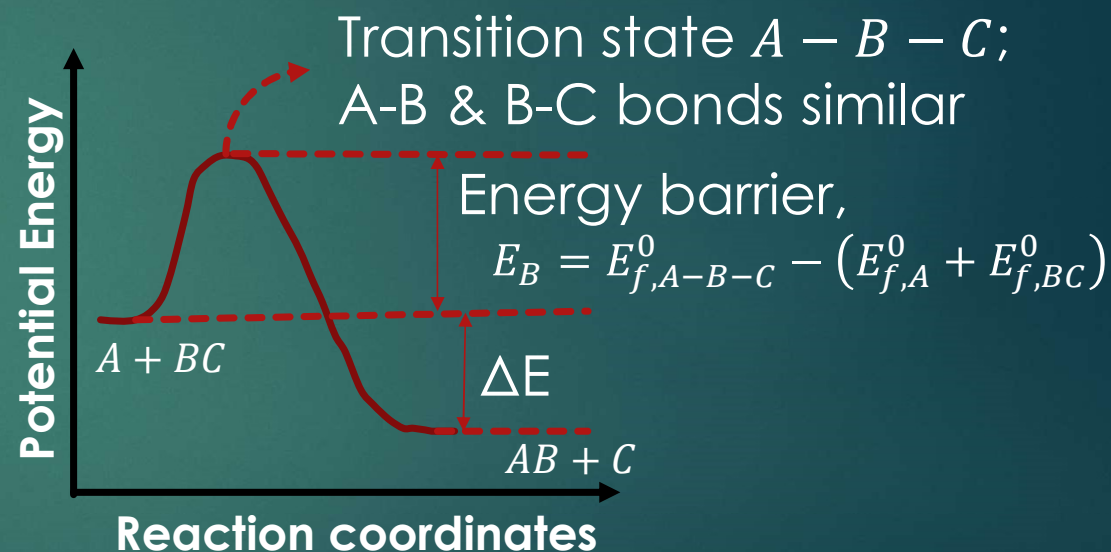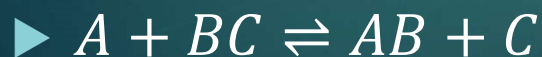# Rate constant is one of the temperature dependent terms, $-r_A = f(T, C_j)$

▶ Strong dependence on temperature given by Arrhenius Equation

▶ $k(T) = A.\,exp(^{-E}/_{RT})$

    ○ A is the pre-exponential factor or frequency factor (order of 10^{13} s^{-1})

    ○ E is the activation energy of the reaction

    ○ T is the temperature and R the universal gas constant

▶ **Exceptions are free radicals that react immediately on collisions**

▶ **Depends on the presence of catalyst**
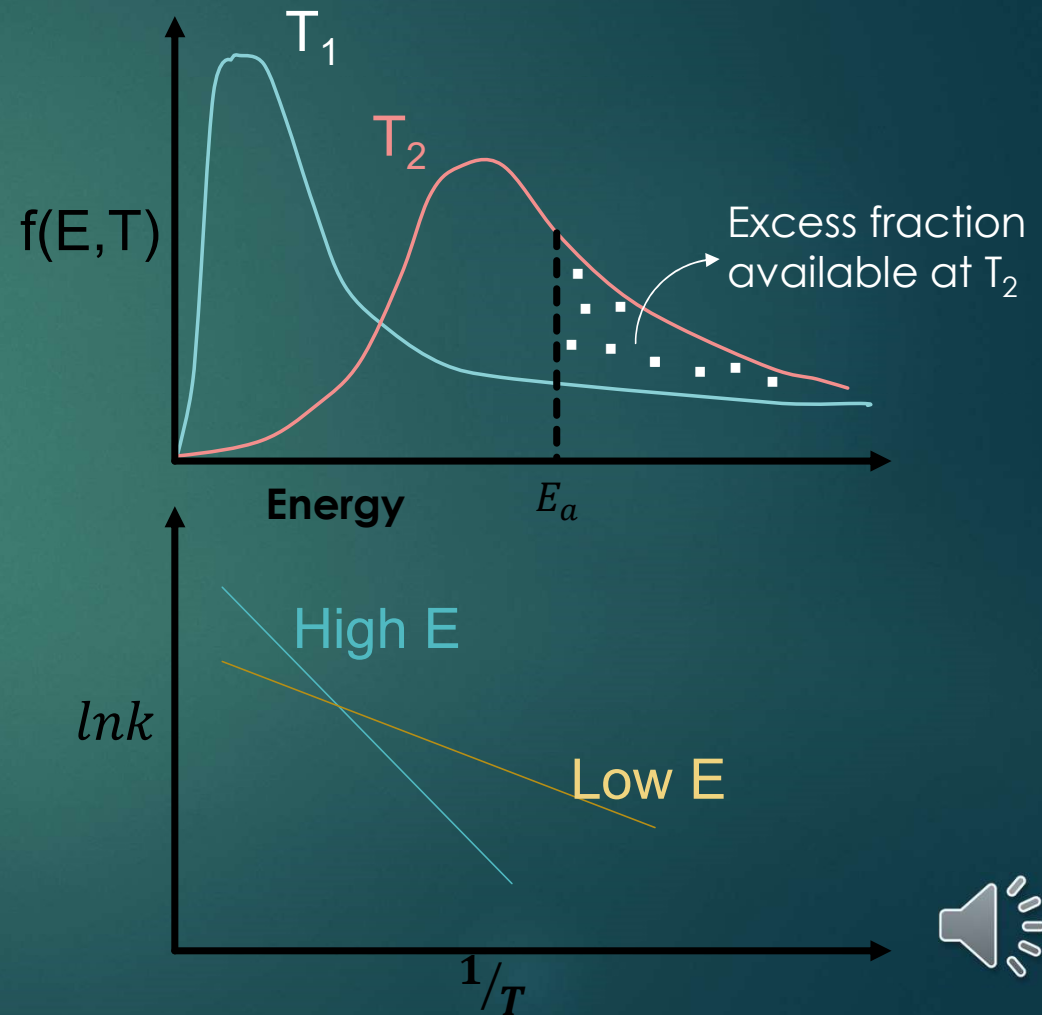
Activation energy is required by most reactions

▶ **Activation energy is required (some reasons)**

- ○ Molecules need energy to distort or stretch bonds so that bonds break and/or new bonds are formed

- ○ Overcome stearic and electronic repulsion forces as the reacting molecules come close together

▶ $A + BC \rightleftharpoons AB + C$

▶ Transition state, $A - B - C$

Transition state $A - B - C$; A-B & B-C bonds similar

Energy barrier, $E_B = E^0_{f,A-B-C} - \left(E^0_{f,A} + E^0_{f,BC}\right)$

$A + BC$

ΔE

$AB + C$

Potential Energy

Reaction coordinates

Energy of molecules are distributed at temperature T

▶ At T_2, the fraction of molecules having energy is larger at E_a
$\quad\rightarrow$ the rate $(-r_A)$ increases

▶ The activation energy is determined experimentally by carrying out the reaction at different temperatures

$$lnk = lnA - \frac{E}{R}\left(\frac{1}{T}\right)$$

▶ $\rightarrow plot\ lnk\ versus\ \frac{1}{T}$ to determine $\frac{E}{R}$

T₁

T₂

f(E,T)

Excess fraction available at T₂

Energy $\quad E_a$

lnk

High E

Low E

$\frac{1}{T}$

Equilibrium constant is also temperature dependent

▶ $\Delta G = -RT ln(K_a)$, where K_a is the true equilibrium constant in terms of activity, a_i, and is dimensionless

▶ $a_i = \dfrac{f_i}{f_i^0}$ where f_i is the fugacity of the species i in the mixture and

f_i^0 is the fugacity of i in the standard state

▶ **The temperature dependency of the equilibrium constant is given by van't Hoff equation**

$$\frac{\partial ln K_a}{\partial T} = \frac{\Delta H_{Rxn}}{RT^2}$$

▶ **Change in $K_a(T)$ with temperature depends ΔH_{Rxn}**

○ Decreases with increasing temperature for exothermic reactions

○ Increases with increasing temperature for endothermic reactions

Other equilibrium constants defined from K_a

▶ Reaction given by: $\quad A + \dfrac{b}{a}B \rightleftharpoons \dfrac{c}{a}C + \dfrac{d}{a}D$

▶ For liquid systems: $\quad K_a = K_\gamma K_x \quad$ correction factor $\rightarrow \quad 1$

▶ For gaseous systems: $\quad K_a = K_\varphi K_y P^\delta = K_\varphi K_{P_i}$ with P or P_i in atm.

▶ Further, for ideal gas systems: $\quad P_i = C_i R T$ and $K_P = K_C (RT)^\delta$

   ○ with $\boldsymbol{\delta = \dfrac{d}{a} + \dfrac{c}{a} - \dfrac{b}{a} - 1}$

▶ If $k(T)$ and $K_C(T)$ are known at a particular temperature, T_0, they can be determined at another temperature, T, if E and ΔH_{Rxn} are known

▶ $k(T) = k(T_0) exp\left[\dfrac{E}{R}\left(\dfrac{1}{T_0} - \dfrac{1}{T}\right)\right] \quad$ and $\quad K_e(T) = K_e(T_0) exp\left[\dfrac{\Delta H_{Rxn}}{R}\left(\dfrac{1}{T_0} - \dfrac{1}{T}\right)\right]$