



# Kinetics of Chemical Reactions – Chem 313

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# References



An Introduction to Chemical Kinetics, **Margaret Robson Wright**, 2004, John Wiley & Sons, Ltd.



Chemical Reaction Kinetics: Concepts, Methods and Case Studies, **Jorge Ancheyta**, 2017, John Wiley & Sons Ltd.



Reaction Kinetics: An Introduction, **Ernő Keszei**, 2021, Springer.



Introduction to Chemical Engineering Kinetics and Reactor Design, **Charles G. Hill, Jr. & Thatcher W. Root**, 2014, John Wiley & Sons, Ltd.



Chem 313 note @ Chem. Dept

# Assessment



~ 20 min 1<sup>st</sup> Quiz (Week 4)

⇒ 10 marks



~ 50 min Midterm examination

⇒ 20 marks



~ 20 min 2<sup>nd</sup> Quiz (Week 10)

⇒ 10 marks



2 h unseen written examination

⇒ 60 marks

## Overall

⇒ 100 marks



Lectures' attendance should exceed 70 %

# Back to Thermodynamics

- Consider a system in a **thermal equilibrium** with its surroundings at a **temperature T**. When a change in the system occurs and there is a transfer of energy as heat between the system and the surroundings, the **Clausius inequality** requires;

$$dS \geq \frac{dq}{T}$$

Or

$$dS - \frac{dq}{T} \geq 0$$

Sys + Surr  
description

**dS**: describes entropy change of system

**dq/T**: describes entropy change of surroundings

- This **inequality** is developed in two ways (**constant volume** or **constant pressure**).

# At constant pressure

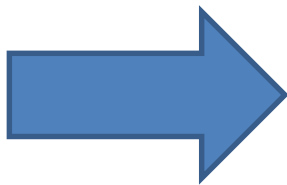
$$dS - \frac{dq}{T} \geq 0$$

Substitute



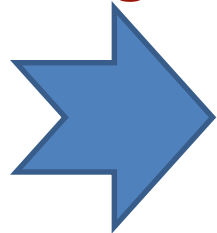
$$dq_p = dH$$

(from surrounding to system notation)

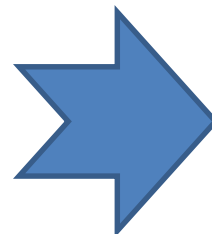


$$dS - \frac{dH}{T} \geq 0$$

Rearrange



$$TdS \geq dH$$



$$dH - TdS \leq 0$$

(constant  $p$ , no additional work other than PV work)

# Gibbs Energy (G)\_At constant P

$$dH - TdS \leq 0$$

✚ For a simple representation, a new property called **Gibbs energy, G**, is defined as

$$G = H - TS$$

**Gibbs energy**

All symbols in this definition refer to the **system**.

▶ When the state of the system changes at constant temperature

$$dG = dH - TdS$$

Employing at constant P that

$$TdS \geq dH$$



$$dG_{T,p} \leq 0$$

# Interpretation

$$dG_{T,p} \leq 0$$

At constant temperature and pressure, chemical reactions are **spontaneous** in the direction of **decreasing Gibbs energy**.

- ▶ The criterion of **equilibrium**, when the rates of forward and reverse process are equal.

$$dG_{T,p} = 0$$

$$\Delta_r G_{T,p}$$

<0, spontaneous

=0, equilibrium

>0, non-spontaneous. Reverse is spontaneous

# $\Delta G$ Interpretation

- ▶ At constant T and p, the **maximum additional (non-expansion) work**,  $w_{add,max}$ , is given by the change in Gibbs energy.

$$dw_{add,max} = fdl + \gamma d\sigma + EdQ$$

$$dw_{add,max} = dG$$

measurable  
change

$$w_{add,max} = \Delta G$$

- ▶ This expression is particularly useful for assessing the **electrical work** that may be produced by fuel cells and electrochemical cells.
- ▶ The free energy is sometimes called “**net work function**”



# Thermodynamics/Kinetics

- ❑ A reaction is characterized by its **stoichiometry**, **energetics**, and **rate**.
- ❑ **Spontaneity** (  $\Delta G = -RT \ln K = -Ve$ , **i. e., high K** ) refers to the inherent tendency of a process to occur; however, it implies nothing about speed (**kinetics**).
- ❑ Thermodynamics or as few named "**thermostatics**" is not about things moving and changing but instead about how stable they are in one state versus another.
  - ❑ The equilibrium constant,  $K$ , is a **thermodynamic** not a kinetic **quantity**.
- ❑ Kinetics is about how quickly or slowly species react.

## Kinetics

Predicts the **rate** of reaching a reaction a given equilibrium

Concerned with actual mechanistic paths.

Concerned with time.

At **equilibrium** the rates of forward and backward reactions are equal but opposite in sign, the net rate is zero, and no spontaneous change is observed.

## Thermodynamics

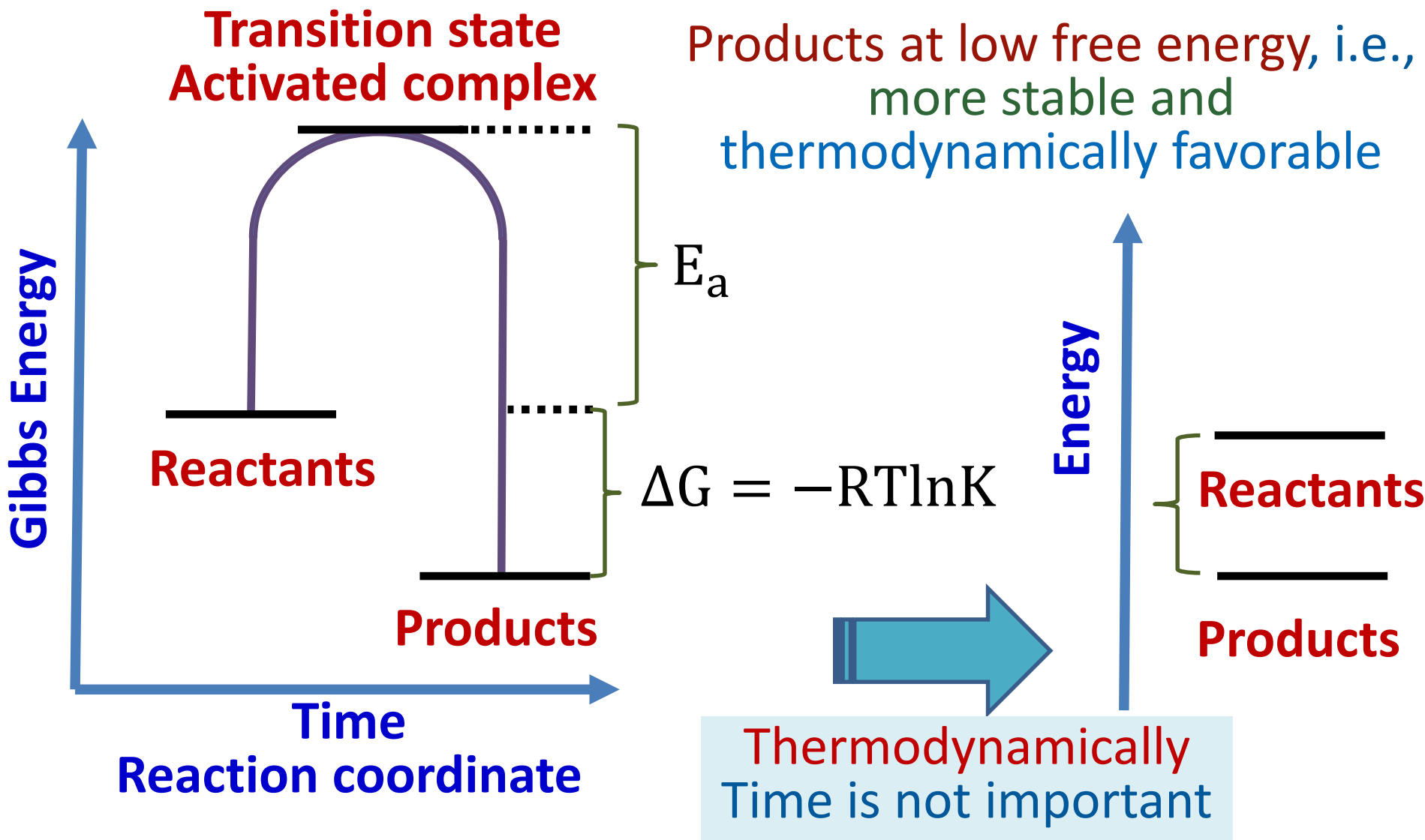
Predicts whether reactants or products are favored at equilibrium

Path independent.

Time independent.

At **equilibrium**, the forces driving the forward and backward reactions are equal but opposite in sign, ( $\Delta G = 0$ ), and no spontaneous change is observed.

# Reaction diagrams



Large  $E_a$ , i.e., Kinetically not favored  
**Kinetically controlled**

# Reaction diagrams

- ❑ The "**reaction coordinate**" is a measure of how far the reaction has progressed.
- ❑ It is often more convenient to assume the reaction is "going" at a somewhat constant rate and think of the x-axis simply as **time**.
- ❑ As products are at a **lower free energy**, i.e., more stable than the reactants, reactants "want" to be converted into the products.

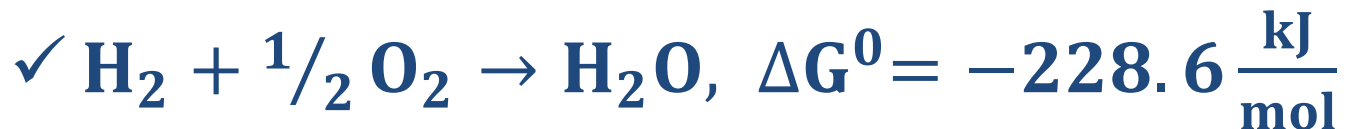
# Spontaneous does not mean fast

- ❑ **For example**, graphite and diamond are both forms of carbon, but graphite has a lower free energy. Therefore, diamond wants to convert into graphite.



Very Slow at RT- Not detectable

- ❑ **Similarly,**



Very Slow at RT- Not detectable

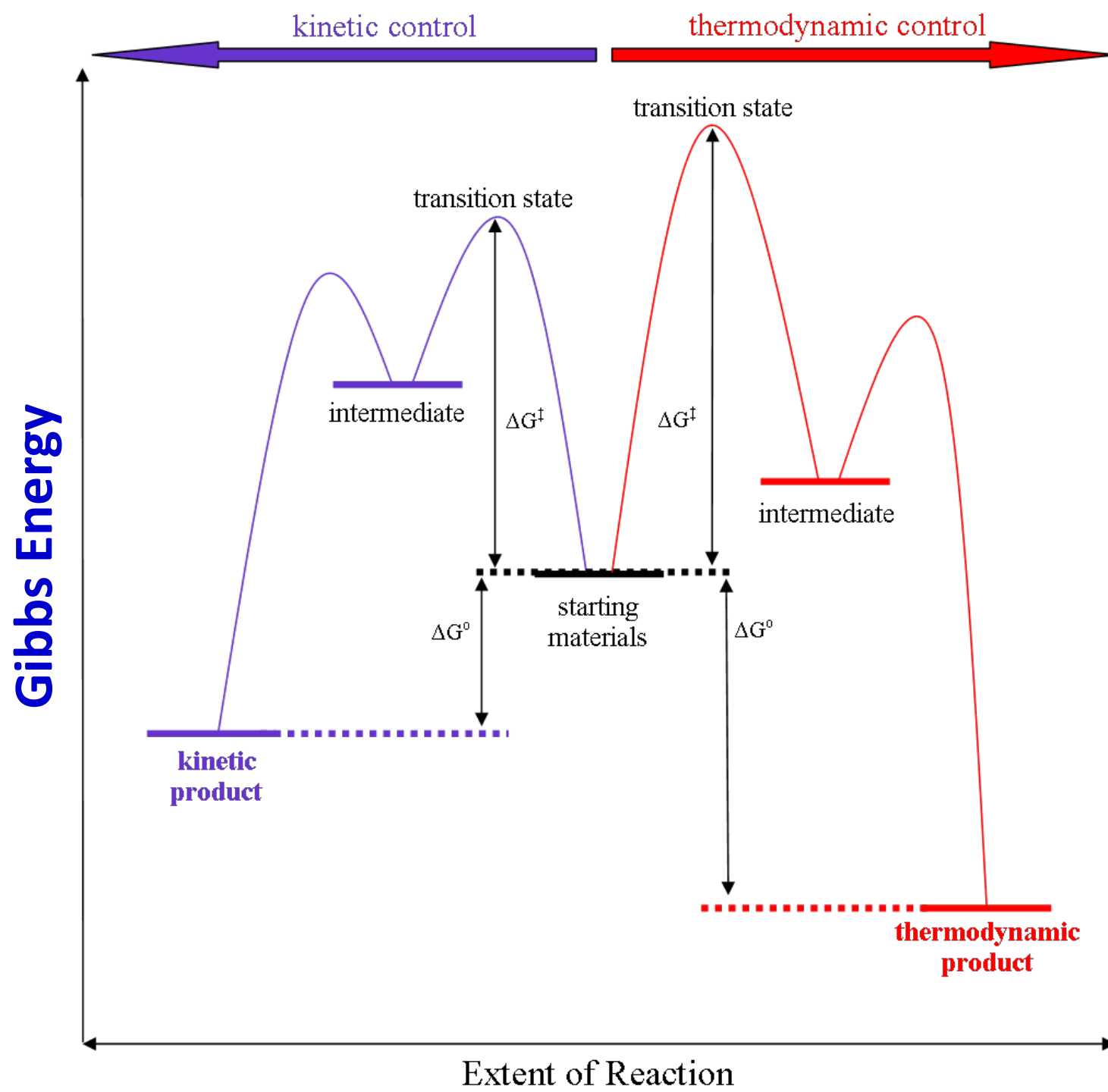


Requires High T and iron oxide (catalyst)

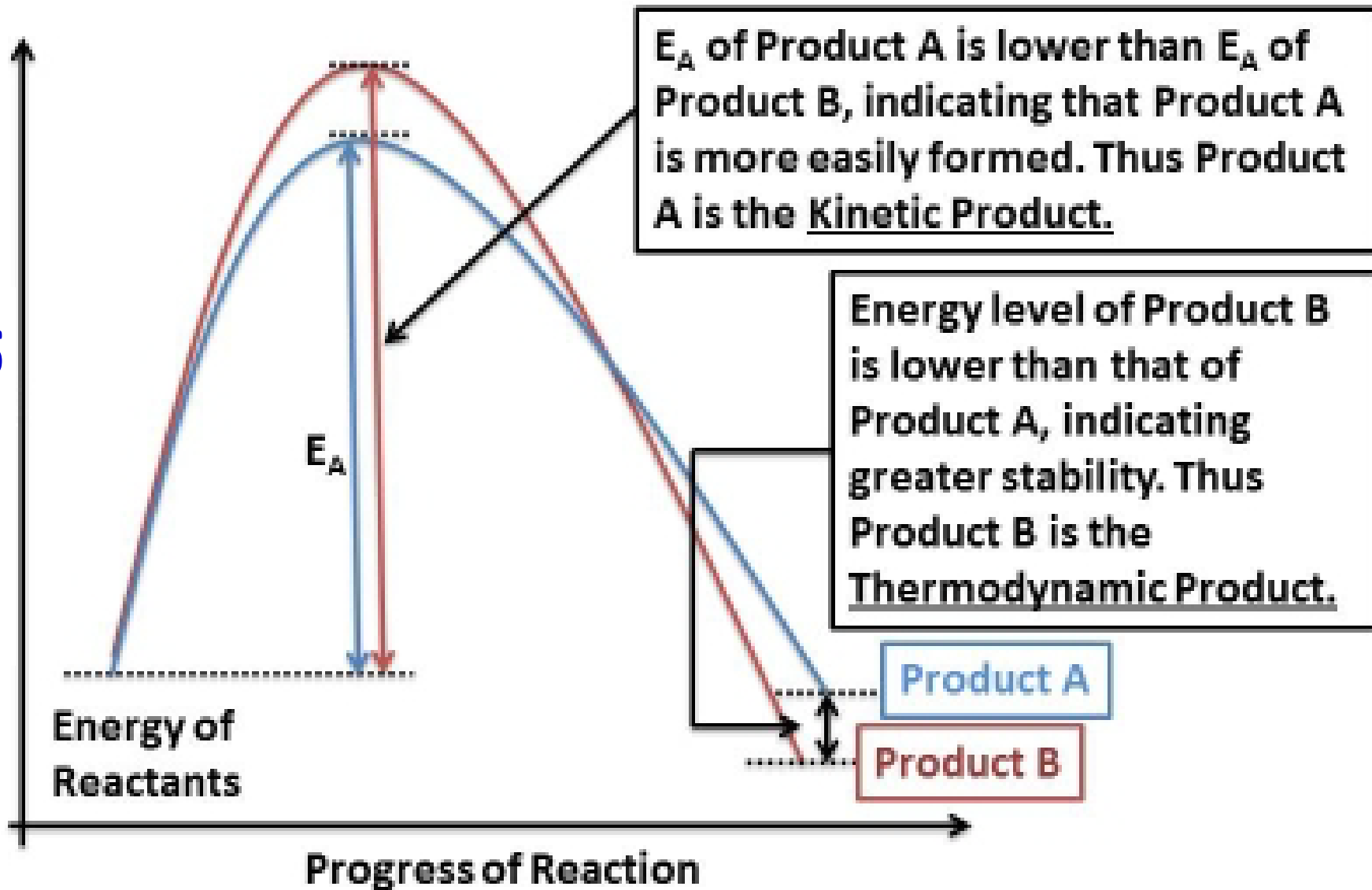
- ✓ Your skin wants to dissolve in soap when it is washed

# Thermodynamics/Kinetics Controlled Rxs

- ❑ Some reactions involve **competing pathways** that lead to different products (**A & B**) for same reaction and reaction conditions (**T, P, solvent**) influence selectivity.
- ❑ If A forms faster than B (i.e.,  $E_a(\text{A}) < E_a(\text{B})$ ), yet product B is more stable, **A** becomes the kinetic product and is favored under kinetic control and **B** is the thermodynamic product and is favored under thermodynamic control.
- ❑ Prevalence of **thermodynamic** or **kinetic control** determines the final composition of the product when these competing reaction pathways lead to different products.



Gibbs Energy





# Reaction kinetics

- ❑ **deals with** quantitative studies of reactions' rates, factors affecting these rates, and reactions' mechanism.
- ❑ **targets** the description of the behavior of reacting systems in terms of **macroscopically** observable quantities such as temperature, pressure, composition, and **Reynolds number** which predicts the flow pattern (**laminar, turbulent**) in different fluid flow situations.
- ❑ **focuses** on variations in chemical compositions with
  - ✓ **time** in a **batch** reactor (a closed system for which time is the only independent variable) or
  - ✓ **position** in a **continuous flow** reactor (open systems).

# Kinetics investigation

## Components of any kinetic investigation

- 1) Product and intermediate detection,
- 2) Concentration determination of all existing species present.
- 3) Deciding a method of following the rate,
- 4) Kinetic analysis
- 5) Mechanism determination.

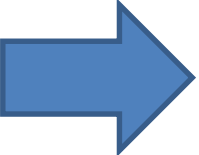
Concept of


*Stoichiometry*

# Stoichiometric Coefficient & Number

Consider this balanced Eq.  $aA + bB + \dots \rightarrow rR + sS + \dots$

**A, B, R and S** are the chemical species, and **a, b, r and s** are their corresponding **stoichiometric coefficients**, which are the positive numbers before the chemical formula that balance the reaction.

Rearrange   $-aA - bB - \dots + rR + sS + \dots = 0$

Or   $v_1A_1 + v_2A_2 + \dots + v_{i-1}A_{i-1} + v_iA_i = 0$

Or 
$$\sum_{i=1}^i v_i A_i = 0$$

$v_i$  (**Nu, New**): **stoichiometric numbers** which equal numerically stoichiometric coefficients but have a negative sign for reactants and positive sign for products.

# Example

Determine the stoichiometric coefficients and numbers for the following reaction for synthesis of ammonia:



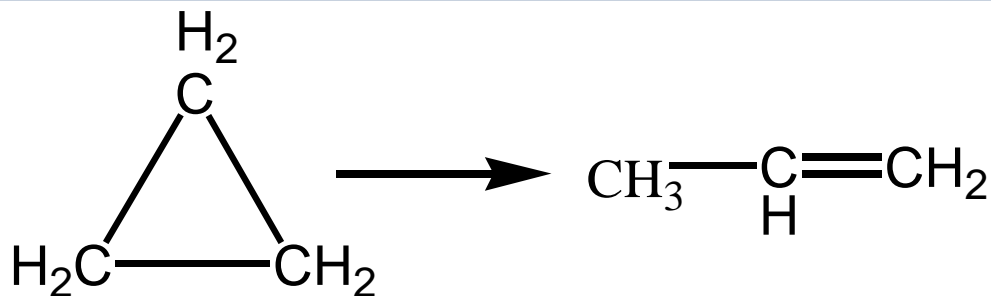
	Stoichiometric coefficients	Stoichiometric numbers, $\nu_i$
<b>a</b>	<b>1</b>	<b>-1</b>
<b>b</b>	<b>3</b>	<b>-3</b>
<b>r</b>	<b>2</b>	<b>2</b>

# Molecularity

- is the **number of molecules** coming together to react in an elementary step.
- **number of molecules** involved at the actual moment of a chemical transformation
  - Elementary reactions are simple reactions described by **molecularity**.

**Uni-molecular:**

**Mono-molecular:**



**Bi-molecular:**



**Tri-molecular:**

**Ter-molecular:**

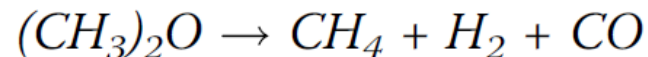
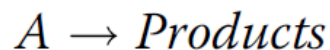
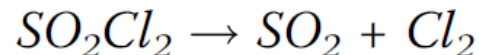
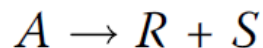
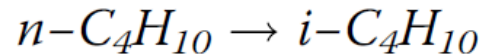
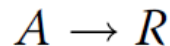


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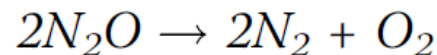
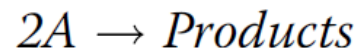
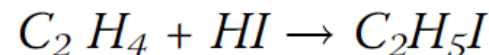
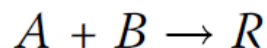
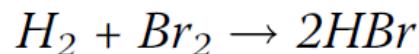
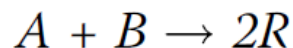
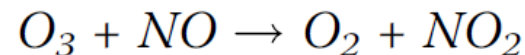
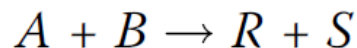
**Molecularity****Examples**

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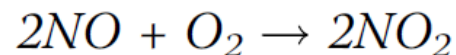
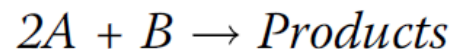
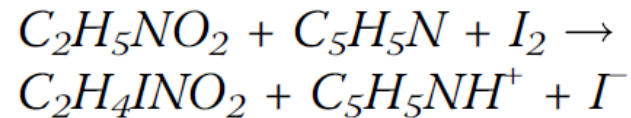
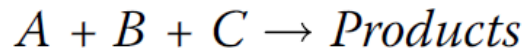
1



2



3



- **Tri-molecular reactions** are rare since they need the simultaneous collision of three molecules to produce one or several products.

# Reaction extent, $\xi$ ( $X_i$ , ZZ-eye)

For a **closed system** where a **single** chemical reaction is occurring, the change in the number of moles ( $\Delta n$ ) of a chemical species is directly related to its stoichiometric number,  $\nu$

$$\Delta n \propto \nu$$

Or

$$\frac{\Delta n_2}{\Delta n_1} = \frac{\nu_2}{\nu_1}$$

Or

$$\frac{dn_2}{dn_1} = \frac{\nu_2}{\nu_1}$$

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \frac{dn_3}{\nu_3} = \dots = \frac{dn_i}{\nu_i} = d\xi$$

$$dn_i = \nu_i d\xi$$



$$\int_{n=n_{i0}}^{n=n_i} dn_i = \nu_i \int_{\xi=0}^{\xi} d\xi$$



$$\xi = \frac{n_i - n_{i0}}{\nu_i}$$

Valid for all species  $A_i$

**“Law of definite proportions”**





# Features of $\xi$



is a **time-dependent** **extensive** variable



is measured in **moles**



is useful to measure the **progress** of the reaction



is not tied to any particular species  $A_i$

## For two species i and j

$$\xi = \frac{n_i - n_{i0}}{\nu_i} = \frac{n_j - n_{j0}}{\nu_j} \quad \gg$$

$$n_j = n_{j0} + \nu_j \left( \frac{n_i - n_{i0}}{\nu_i} \right) \quad \gg \gg \gg$$

$$n_j = n_{j0} + \frac{\nu_j}{\nu_i} (n_i - n_{i0})$$

# $\xi_k$ for multiple “simultaneous” reactions



$\xi_k$  is the extent of the  $k^{\text{th}}$  reaction



$\nu_{ki}$  is the stoichiometric number of species  $i$  in reaction  $k$

The total change in the number of moles of species  $A_i$  as a consequence of  $r$  reactions is:

$$n_i - n_{i0} = \sum_{k=1}^{k=r} \nu_{ki} \xi_k$$

# Molar fractional conversion, $f$



is an **intensive (mass independent)** measure of the progress of a reaction.



is a variable that is simply related to  $\xi$ .



depends on the particular species chosen as a reference substance (**LIMITING REACTANT**)



For a **closed system** where a **single** chemical reaction is occurring,  $f$  of a reactant  $A_i$  is given by:

$$f = \frac{n_{i0} - n_i}{n_{i0}} = 1 - \frac{n_i}{n_{i0}}$$



$$n_i = n_{i,0}(1 - f)$$

For limiting reactant



$$n_{\text{lim}} = n_{\text{lim},0}(1 - f)$$

Also

$$n_{\text{lim}} = n_{\text{lim},0} + v_{\text{lim}}\xi$$

Irreversible Rxs

$$\xi = -\frac{fn_{\text{lim},0}}{v_{\text{lim}}}$$

$$\xi_e = -\frac{f_e n_{\text{lim},0}}{v_{\text{lim}}}$$

Reversible Rxs



The maximum extent of an irreversible reaction ( $\xi_{\text{max,irr}}$ ) can be obtained by setting  $f = 1$ .



For reversible Rxs, the maximum reaction extent,  $\xi_e$ , is limited by the position of chemical equilibrium.

**Always**

$$\xi_e < \xi_{\text{max,irr}}$$



In many cases,  $\xi_e$  is approximately equal to  $\xi_{\text{max,irr}}$ . The formation of products is favored and only an extremely small quantity of the limiting reagent remains in the system at equilibrium. These reactions are classified as “irreversible”.



When  $\xi_e$  differs substantially from  $\xi_{\text{max,irr}}$ , the reaction is classified “reversible”.

# Feed compositions in chemical reactions

## Stoichiometric feeds



ratio between the stoichiometric coefficients of the reactants is equal to the ratio between the amount of moles or the molar initial concentrations of reactants.

## Non-stoichiometric feeds



ratio between the stoichiometric coefficients of reactants is different from the ratio between the amount of moles or the molar initial concentrations of reactants.

## Equimolar feeds



same amount of reactants are used at the beginning of the reaction

# Limiting reactant



is the chemical species in a chemical reaction that is **consumed** before all of the other reactants.



is the chemical species that has the **lowest** value of maximum reaction extent ( $\xi_{i,\max}$ ).



For reactions between two or more components with **stoichiometric feed** composition, any of the reactants can be **limiting** since they are consumed at the same rate.

# Example

Determine the limiting reactant if, in the following reaction, 5 moles of ethylene bromide (A) and 2 moles of potassium iodide (B) are fed:



# Solution



$$n_{\text{A}_0} = 5 \text{ mol}$$

$$v_{\text{A}} = -1$$

$$\xi_{\text{A,max}} = -\frac{n_{\text{A},0}}{v_{\text{A}}} = \frac{-5}{-1} = 5$$

$$n_{\text{B}_0} = 2 \text{ mol}$$

$$v_{\text{B}} = -3$$

$$\xi_{\text{B,max}} = -\frac{n_{\text{B},0}}{v_{\text{B}}} = \frac{-2}{-3} = \frac{2}{3}$$

**limiting reactant is B**