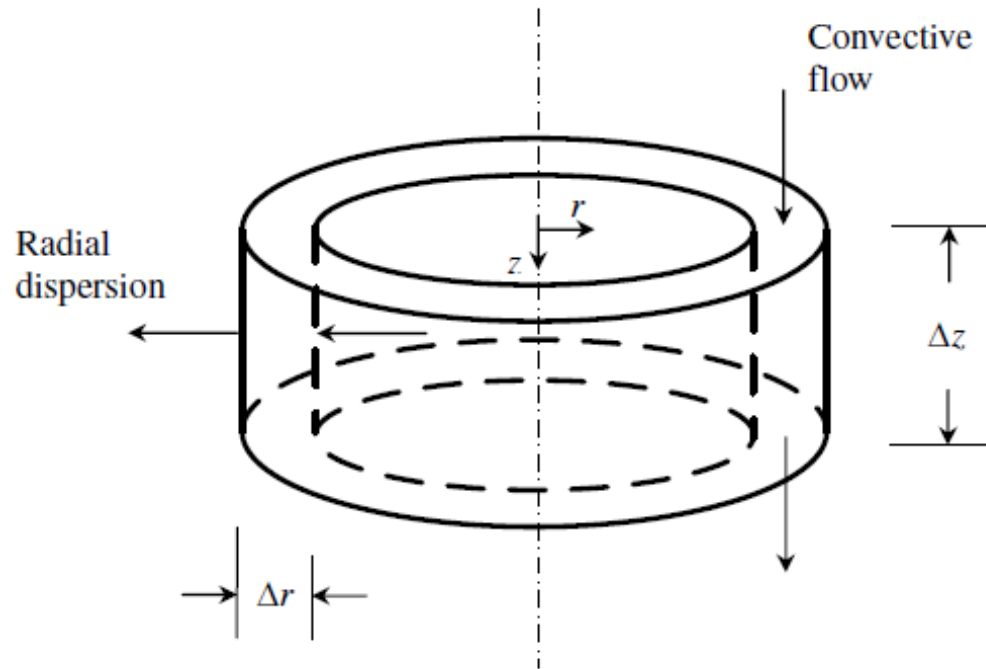


CHE 611

Advanced Chemical Reaction Engineering



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Types of adsorption

- + Physical adsorption (Physisorption)
- + Chemical adsorption (Chemisorption)

Comparison of physical and chemical adsorptions

Physical adsorption	Chemical adsorption
Binding forces are weak where binding occurs through van der Waals' forces.	Binding forces are strong where binding occurs through chemical bonding and electron transfer takes place.
Reversible with the adsorbed species unchanged when desorbed.	Mostly irreversible with the adsorbed species may be different when desorbed.
Occurs through multilayer coverage.	Occurs through monolayer coverage (only active sites are covered).
Applied in the determination of surface area, pore volume, and pore size of materials.	Applied in the determination of catalytic surface area.
Low heat of adsorption is involved such as that of liquefaction.	Heat of adsorption is many times greater and comparable to that of heat of reaction.
Usually occurs at low temperatures.	Usually requires high temperatures.
Rate of adsorption is fast.	Rate of adsorption may be fast.
Non-specific to the surface (adsorbent).	Any value between low and fast.
Low activation energies are involved.	Specific to the surface (adsorbent).
	Usually high activation energies are involved.

Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics

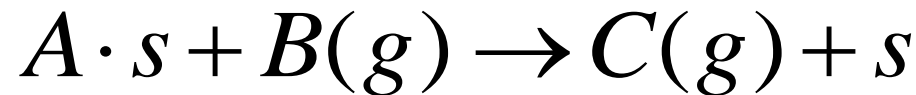
- # The Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach accounts for the surface concentrations of the species taking part in the reaction.
- # Relating surface species to the observed species partial pressures in the gas phase provides equations that can be fitted to the kinetic data.
- # Based on the Langmuir adsorption isotherm, the approach was first developed by Hinshelwood and therefore sometimes termed as Langmuir-Hinshelwood kinetics. Hougen and Watson [1943] developed a similar approach and popularize the Langmuir-Hinshelwood kinetics.

Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics

- ✚ The LHHW approach assumes that all active sites are energetically uniform and, upon adsorption, adsorbed species do not interact with species already adsorbed.
- ✚ Active sites have similar kinetic and thermodynamic characteristics and the entropy and enthalpy of adsorption are constant and not functions of the adsorbed amount.
- ✚ The species adsorption restricts itself to only monolayer coverage and the rate of adsorption is proportional to the concentration of the active sites not occupied (empty) and the partial pressure of the component in the gas phase.

Eley-Rideal model

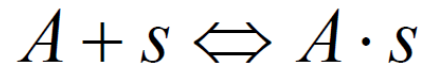
- ✚ A gas phase component reacts with an adsorbed species i.e. a component reacts from the gas phase with an adsorbed component



- ✚ Please find out the kinetic equation.

Langmuir adsorption isotherm

For the adsorption of a component A on a certain surface

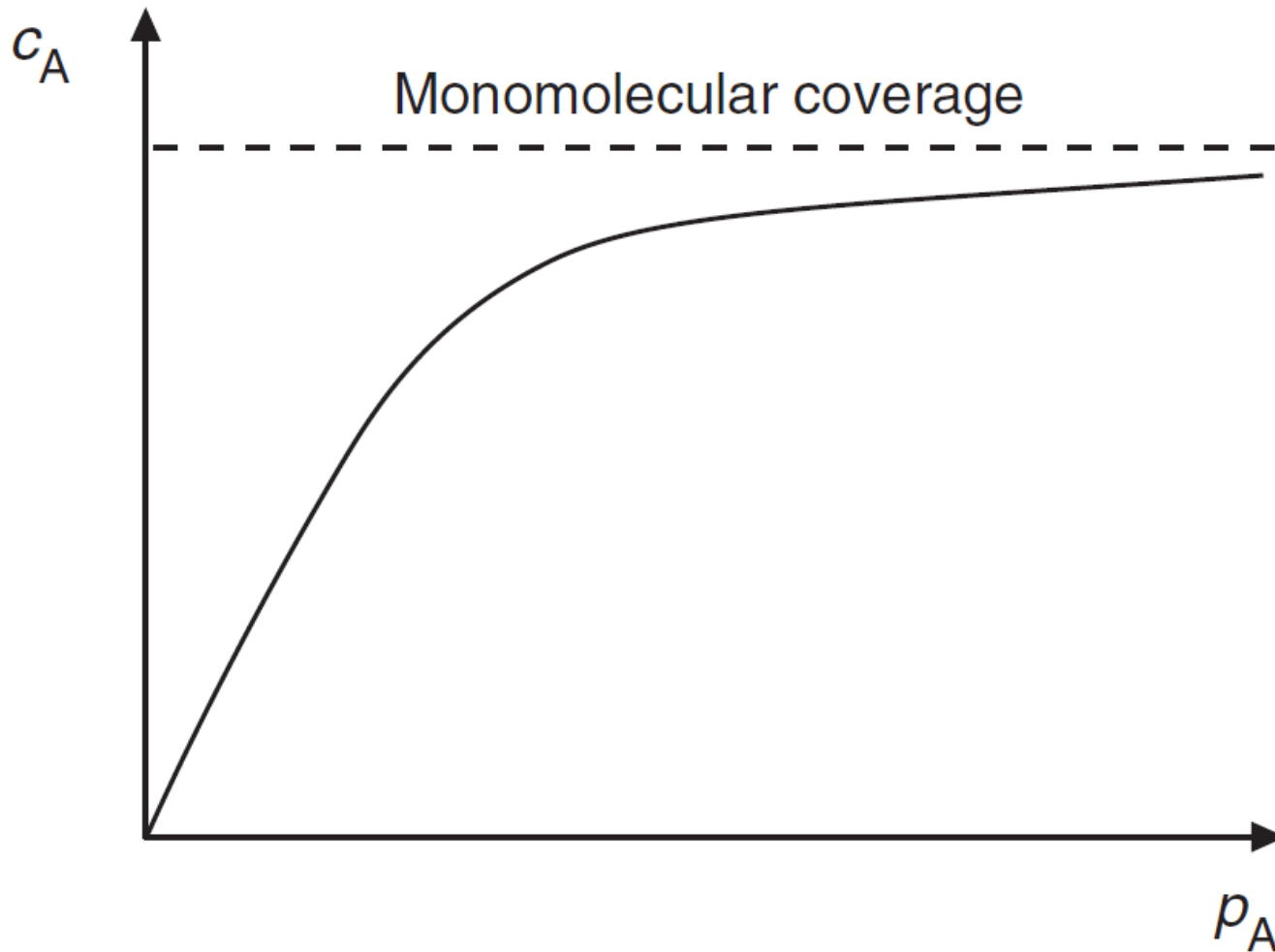


$$C_{A \cdot s} = \frac{C_T \cdot K_A \cdot p_A}{1 + K_A \cdot p_A}$$

$$\frac{C_{A \cdot s}}{C_T} = \frac{K_A \cdot p_A}{1 + K_A \cdot p_A}$$

$$\theta_A = \frac{K_A \cdot p_A}{1 + K_A \cdot p_A}$$

Langmuir adsorption isotherm



Dissociative and non-dissociative adsorption

Adsorption of a component may be **non-dissociative** or **dissociative**. The previous case is for non-dissociative adsorption. In non-dissociative case, the molecule is adsorbed as a whole and it may be called as molecular adsorption. In dissociative adsorption, the molecule such as of H_2 is dissociated into H-H form and adsorbed. Of course the dissociative case requires 2 sites for the adsorption.



Dissociative and non-dissociative adsorption

For dissociative adsorption:

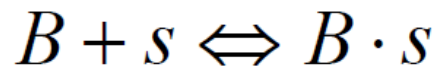
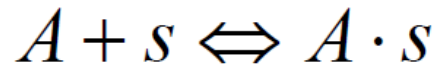
$$C_{A \cdot s} = \frac{C_T \cdot \sqrt{K_A \cdot p_A}}{1 + \sqrt{K_A \cdot p_A}}$$

$$\frac{C_{A \cdot s}}{C_T} = \frac{\sqrt{K_A \cdot p_A}}{1 + \sqrt{K_A \cdot p_A}}$$

$$\theta_A = \frac{\sqrt{K_A \cdot p_A}}{1 + \sqrt{K_A \cdot p_A}}$$

Dissociative and non-dissociative adsorption

If more than one component competes for the adsorption:



$$C_{A \cdot s} = \frac{C_T \cdot K_A \cdot p_A}{1 + K_A \cdot p_A + K_B \cdot p_B}, \quad \theta_A = \frac{K_A \cdot p_A}{1 + K_A \cdot p_A + K_B \cdot p_B}$$

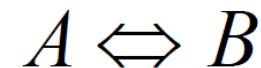
$$C_{B \cdot s} = \frac{C_T \cdot K_B \cdot p_B}{1 + K_A \cdot p_A + K_B \cdot p_B}, \quad \theta_B = \frac{C_T \cdot K_B \cdot p_B}{1 + K_A \cdot p_A + K_B \cdot p_B}$$

Development of a typical kinetic rate equation

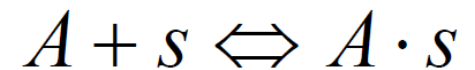
- ✚ Assume a reaction mechanism. The mechanism may include single-site or dual-site surface reactions and dissociated or non-dissociated adsorption steps.
- ✚ Assume the single rate determining step (rds).
- ✚ Assume all the other steps except the rate determining step are in equilibrium (pseudoequilibrium).
- ✚ Write down the adsorbed concentration variables in terms of measurable concentrations.
- ✚ Write down the total site balance, eliminate the variable C_s (concentration of empty sites), and simplify to get the required rate equation.

Development of kinetic rate equation based on LHHW kinetics single-site mechanism

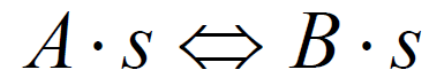
Overall:



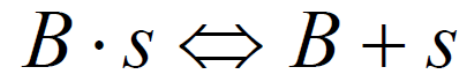
Adsorption of A :



Surface reaction of A to B :



Desorption of B :



Development of kinetic rate equation based on LHHW kinetics single-site mechanism

For surface reaction rate controlling, the final rate equation will be as follows:

$$(-r_A) = \frac{k \cdot K_A \cdot p_A \cdot \left(1 - \frac{p_B}{p_A \cdot K}\right)}{1 + K_A \cdot p_A + K_B \cdot p_B}$$

For the derivation, see class notes.

Homework Problem

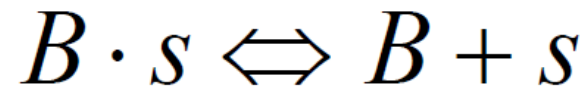
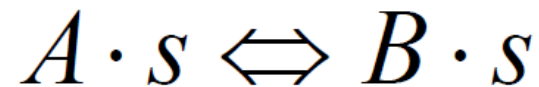
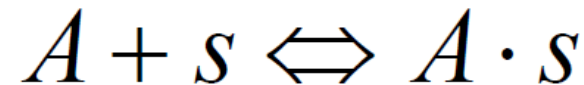
Workout for the other possible rate equations based on the mechanism given earlier, i.e. develop rate equation when

- ✚ First step (adsorption of A) is the rate controlling step
- ✚ Third step (desorption of B) is the rate controlling step

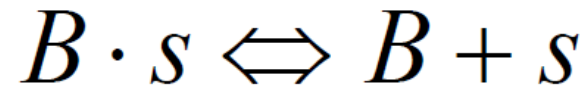
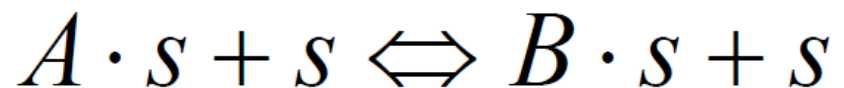
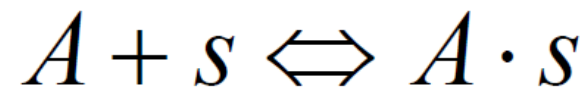
Development of kinetic rate equation based on LHHW kinetics single-site mechanism

The surface reaction may be single-site or dual-site, i.e., a single site or two sites may be involved:

Single-site



Dual-site



General kinetic equation

$$(-r) = \frac{\textit{kinetic term} \times \textit{potential term}}{\textit{adsorption term}}$$

General kinetic equation

- ✚ For intrinsic kinetics, the *kinetic term* contains the reaction velocity constant and may or may not contain adsorption constants.
- ✚ The *potential term* is the simple driving potential and for an essentially irreversible reaction should be equal to unity.
- ✚ The *adsorption term* contains the adsorption coefficients and partial pressures of species and provides a means of quantifying the competition among the species to occupy the active centres. This is useful in the sense that it helps in interpreting the effect of partial pressures of reaction species and even inert and poisons on the rate of reaction.

General kinetic equation for LHHW kinetics [1]

Reaction	<i>Driving-Force Groups</i>			
	$A \rightleftharpoons R$	$A \rightleftharpoons R + S$	$A + B \rightleftharpoons R$	$A + B \rightleftharpoons R + S$
Adsorption of <i>A</i> controlling	$p_A - \frac{p_R}{K}$	$p_A - \frac{p_R p_S}{K}$	$p_A - \frac{p_R}{K p_B}$	$p_A - \frac{p_R p_S}{K p_B}$
Adsorption of <i>B</i> controlling	0	0	$p_B - \frac{p_R}{K p_A}$	$p_B - \frac{p_R p_S}{K p_A}$
Desorption of <i>R</i> controlling	$p_A - \frac{p_R}{K}$	$\frac{p_A}{p_S} - \frac{p_R}{K}$	$p_A p_B - \frac{p_R}{K}$	$\frac{p_A p_B}{p_S} - \frac{p_R}{K}$
Surface reaction controlling	$p_A - \frac{p_R}{K}$	$p_A - \frac{p_R p_S}{K}$	$p_A p_B - \frac{p_R}{K}$	$p_A p_B - \frac{p_R p_S}{K}$
Impact of <i>A</i> controlling (<i>A</i> not adsorbed)	0	0	$p_A p_B - \frac{p_R}{K}$	$p_A p_B - \frac{p_R p_S}{K}$
Homogeneous reaction controlling	$p_A - \frac{p_R}{K}$	$p_A - \frac{p_R p_S}{K}$	$p_A p_B - \frac{p_R}{K}$	$p_A p_B - \frac{p_R p_S}{K}$

General kinetic equation for LHHW kinetics [1]

Replacements in the General Adsorption Groups
 $(1 + K_A p_A + K_B p_B + K_R p_R + K_S p_S + K_I p_I)^n$

Reaction	$A \rightleftharpoons R$	$A \rightleftharpoons R + S$	$A + B \rightleftharpoons R$	$A + B \rightleftharpoons R + S$
When adsorption of A is rate controlling, replace $K_A p_A$ by	$\frac{K_A p_R}{K}$	$\frac{K_A p_R p_S}{K}$	$\frac{K_A p_R}{K p_B}$	$\frac{K_A p_R p_S}{K p_B}$
When adsorption of B is rate controlling, replace $K_B p_B$ by	0	0	$\frac{K_B p_R}{K p_A}$	$\frac{K_B p_R p_S}{K p_A}$
When desorption of R is rate controlling, replace $K_R p_R$ by	$K K_R p_A$	$K K_R \frac{p_A}{p_S}$	$K K_R p_A p_B$	$K K_R \frac{p_A p_B}{p_S}$
When adsorption of A is rate controlling with dissociation of A , replace $K_A p_A$ by	$\sqrt{\frac{K_A p_R}{K}}$	$\sqrt{\frac{K_A p_R p_S}{K}}$	$\sqrt{\frac{K_A p_R}{K p_B}}$	$\sqrt{\frac{K_A p_R p_S}{K p_B}}$
When equilibrium adsorption of A takes place with dissociation of A , replace $K_A p_A$ by (and similarly for other components adsorbed with dissociation)	$\sqrt{K_A p_A}$	$\sqrt{K_A p_A}$	$\sqrt{K_A p_A}$	$\sqrt{K_A p_A}$
When A is not adsorbed, replace $K_A p_A$ by (and similarly for other components that are not adsorbed)	0	0	0	0

General kinetic equation for LHHW kinetics [1]

Kinetic Groups

Adsorption of A controlling	k_A
Adsorption of B controlling	k_B
Desorption of R controlling	$k_R K$
Adsorption of A controlling with dissociation	k_A
Impact of A controlling	$k_A K_B$
Homogeneous reaction controlling	k

Surface Reaction Controlling

	$A \rightleftharpoons R$	$A \rightleftharpoons R + S$	$A + B \rightleftharpoons R$	$A + B \rightleftharpoons R + S$
Without dissociation	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A K_B$	$k_{sr} K_A K_B$
With dissociation of A	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A K_B$	$k_{sr} K_A K_B$
B not adsorbed	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A$
B not adsorbed, A dissociated	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A$

General kinetic equation for LHHW kinetics [1]

Exponents of Adsorption Groups

Adsorption of A controlling without dissociation	$n = 1$
Desorption of R controlling	$n = 1$
Adsorption of A controlling with dissociation	$n = 2$
Impact of A without dissociation $A + B \rightleftharpoons R$	$n = 1$
Impact of A without dissociation $A + B \rightleftharpoons R + S$	$n = 2$
Homogeneous reaction	$n = 0$

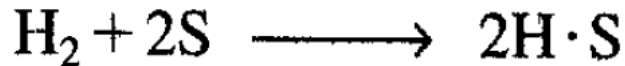
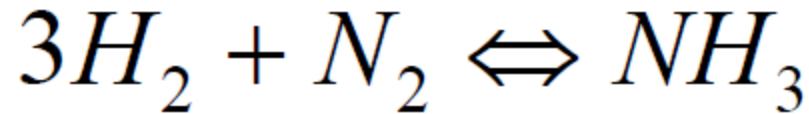
Surface Reaction Controlling

	$A \rightleftharpoons R$	$A \rightleftharpoons R + S$	$A + B \rightleftharpoons R$	$A + B \rightleftharpoons R + S$
No dissociation of A	1	2	2	2
Dissociation of A	2	2	3	3
Dissociation of A (B not adsorbed)	2	2	2	2
No dissociation of A (B not adsorbed)	1	2	1	2

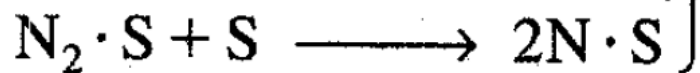
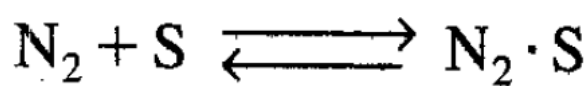
General kinetic equation

For the mechanisms just described, workout the rate expressions taking each step as rate controlling step (rds) using the tables given on previous slides.

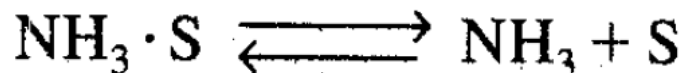
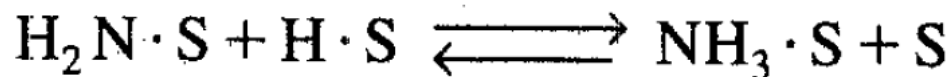
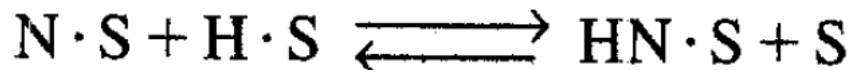
Example mechanism [2]



Rapid



Rate-limiting



Rapid

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