

Prof. Kamal M.S. Khalil

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## Kinetics and activities of heterogeneous catalysis

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## 3 Heterogeneous Catalysis

- A catalyst acts by providing an alternative reaction path with a lower activation energy (See Table .3).
- It does not disturb the final equilibrium composition of the system, only the rate at which that equilibrium is approached.
- In this section we consider heterogeneous catalysis, in which (as mentioned in the introduction) the catalyst and the reagents are in different phases.
- For simplicity, we consider only gas/ solid systems.

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### 3.1 Heterogeneous Catalysis

- Table 3: Activation energies of catalyzed reactions

Reaction	Catalyst	$E_a / (\text{kJ mol}^{-1})$
$2 \text{ HI} \rightarrow \text{H}_2 + \text{I}_2$	None	184
	Au	105
	Pt	59
$2 \text{ NH}_3 \rightarrow \text{N}_2 + 3 \text{ H}_2$	None	350
	W	162

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### 3 Heterogeneous Catalysis

- Many catalysts depend on **co-adsorption**, the adsorption of two or more species.
- One consequence of the presence of a second species may be the modification of the electronic structure at the surface of a metal. For instance, partial coverage of *d*-metal surfaces by alkali metals has a pronounced effect on the electron distribution and reduces the work function of the metal.
- Such modifiers can act as **promoters** (to enhance the action of catalysts) or as **poisons** (to inhibit catalytic action).

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### 3.1 Mechanisms of heterogeneous catalysis

- Heterogeneous catalysis normally depends on at least one reactant being adsorbed (usually chemisorbed) and modified to a form in which it readily undergoes reaction.
- This modification often takes the form of a fragmentation of the reactant molecules.
- In practice, the active phase is dispersed as very small particles of linear dimension less than 2 nm on a porous oxide support.
- **Shape-selective catalysts**, such as the zeolites, which have a pore size that can distinguish shapes and sizes at a molecular scale, have high internal specific surface areas, in the range of 100–500 m<sup>2</sup>/g.

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### 3.1 Mechanisms of heterogeneous catalysis

- Consider the decomposition of phosphine (PH<sub>3</sub>) on tungsten.
- The reaction is first-order at low pressures and zeroth-order at high pressures. .
- To account for these observations, we write down a plausible rate law in terms of an adsorption isotherm and explore its form in the limits of high and low pressure.
- If the rate is supposed to be proportional to the surface coverage and we suppose that  $\theta$  is given by the Langmuir isotherm, we would write

$$vA = K\theta = \frac{kK_p}{1 + K_p} \quad \text{Eq(21)}$$

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### 3.1 Mechanisms of heterogeneous catalysis

$$vA = K\theta = \frac{kK_p}{1 + K_p} \quad \text{Eq(21)}$$

Where,  $p$  is the pressure of phosphine. When the pressure is so low that  $K_p \ll 1$ , we can neglect  $K_p$  in the denominator and obtain the decomposition is first-order.

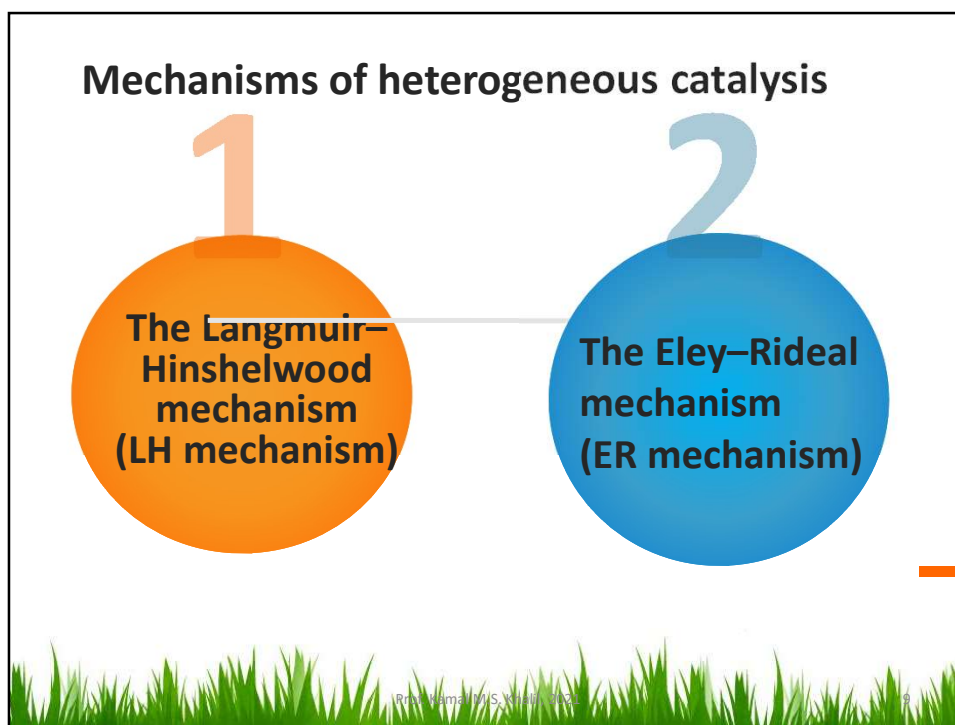
$$v = kK_p \quad \text{1<sup>st</sup> order a)}$$

When  $K_p \gg 1$ , we can neglect the 1 in the denominator, whereupon the  $K_p$  terms cancel and we are left with and the decomposition is zeroth-order.

$$v = K \quad \text{zero order b)}$$

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### 3.2 Langmuir–Hinshelwood mechanism (LH mechanism)

- In LH mechanism of surface-catalysed reactions, the reaction takes place by encounters between molecular fragments and atoms adsorbed on the surface.
- Therefore we expect the rate law to be second-order in the extent of surface coverage and given by:



- If A and B follow Langmuir isotherms, then:

### 3.2 Langmuir–Hinshelwood mechanism (LH mechanism)

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B}$$

$$\theta_B = \frac{K_B P_B}{1 + K_A P_A + K_B P_B}$$

$$v = \frac{k K_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B)^2}$$

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### 3.2 Langmuir–Hinshelwood mechanism (LH mechanism)

$$v = \frac{k K_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B)^2}$$

The parameters ***K*** in the isotherms and the rate constant ***k*** are all temperature dependent, so the overall temperature dependence of the rate may be strongly **non-Arrhenius** (in the sense that the reaction rate is unlikely to be proportional to  $e^{-E_a/RT}$ ). The Langmuir–Hinshelwood mechanism is dominant for the catalytic oxidation of CO to CO<sub>2</sub>.

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### 3.3 The Eley–Rideal mechanism (ER mechanism)

- In the **Eley–Rideal mechanism** (ER mechanism) of a surface-catalysed reaction, a gas-phase molecule collides with another molecule already adsorbed on the surface.
- The rate of formation of product is proportional to the partial pressure,  $p_B$ , of the non-adsorbed gas B and the extent of surface coverage,  $\theta_A$ , of the adsorbed gas A.



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### 3.3 The Eley–Rideal mechanism (ER mechanism)



If the adsorption of A follows a Langmuir isotherm, then the rate law would be

$$v = \frac{kKp_Ap_B}{1 + Kp_A}$$

Accordingly, when the partial pressure of A is high ( $Kp_A \gg 1$ ) there is almost complete surface coverage, and the rate is equal to  $k p_B$ . Now the rate determining step is the collision of B with the adsorbed fragments.

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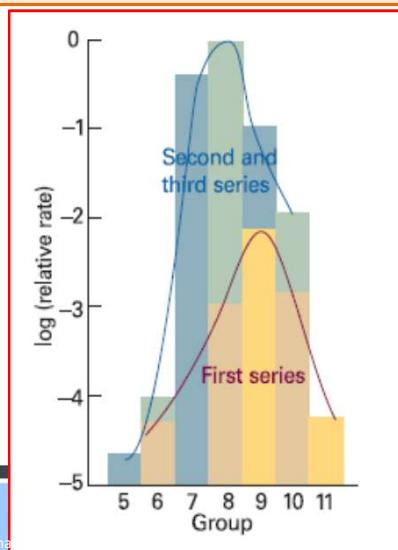
When the pressure of A is low ( $Kp_A \ll 1$ ), perhaps because of its reaction, the rate is equal to  $kKp_Ap_B$ ; now the extent of surface coverage is important in the determination of the rate.

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### 3.5 Relative activity of catalysts

The activity of a catalyst depends on the strength of chemisorption as indicated by the ‘volcano’ curve. To be active, the catalyst should be extensively covered by adsorbate, which is the case if chemisorption is strong.



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### 3.5 Relative activity of catalysts

- Many metals are suitable for adsorbing gases, and the general order of **adsorption strengths decreases** along the series **O<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, CO, H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>**.
- Elements from the *d* block**, such as iron, vanadium, and chromium, show a strong activity towards all these gases, but manganese and copper are unable to adsorb N<sub>2</sub> and CO<sub>2</sub>.
- Metals towards the left** of the periodic table (for example, magnesium and lithium) can adsorb (and, in fact, react with) only the most active gas (O<sub>2</sub>).

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### 3.5 Relative activity of catalysts

	O <sub>2</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	CO	H <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>
Ti, Cr, Mo, Fe	+	+	+	+	+	+	+
Ni, Co	+	+	+	+	+	+	-
Pd, Pt	+	+	+	+	+	-	-
Mn, Cu	+	+	+	+	±	-	-
Al, Au	+	+	+	+	-	-	-
Li, Na, K	+	+	-	-	-	-	-
Mg, Ag, Zn, Pb	+	-	-	-	-	-	-

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### 3.6 Catalysis in the chemical industry

#### General properties of catalysts

Catalyst	Function	Examples
Metals	Hydrogenation Dehydrogenation	Fe, Ni, Pt, Ag
Semiconducting oxides and sulfides	Oxidation Desulfurization	NiO, ZnO, MgO, Bi <sub>2</sub> O <sub>3</sub> /MoO <sub>3</sub> , MoS <sub>2</sub>
Insulating oxides	Dehydration	Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , MgO
Acids	Polymerization Isomerization Cracking Alkylation	H <sub>3</sub> PO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> , zeolites

### 3.6 Catalysis in the chemical industry

- Almost the whole of modern chemical industry depends on the development, selection, and application of catalysts (**Table. 5**).
- All we can hope to do in this section is to give a brief indication of some of the problems involved.
- Other than the ones we consider, these problems include the danger of the catalyst being poisoned by byproducts or impurities, and economic considerations relating to cost and lifetime.

### 3.6 Catalysis in the chemical industry

- **The hydrogenation of alkenes**
- **Formation of edible fats**
- **Partial and complete oxidation catalysts**
  - partial oxidation to propenal (acrolein,  $\text{CH}_2=\text{CHCHO}$ ) is the start of important industrial processes. Controlled oxidations of ethene to ethanol, ethanal (acetaldehyde). These oxidation reactions are catalyzed by *d*-metal oxides.
- **Hydrocarbons cracking catalysts**
  - The catalytically induced fragmentation of the long-chain hydrocarbons is called **cracking**, and is often brought about on silica– alumina catalysts.

**Self  
Study**

### Physical Chemistry of Heterogeneous Catalysis

**The End**