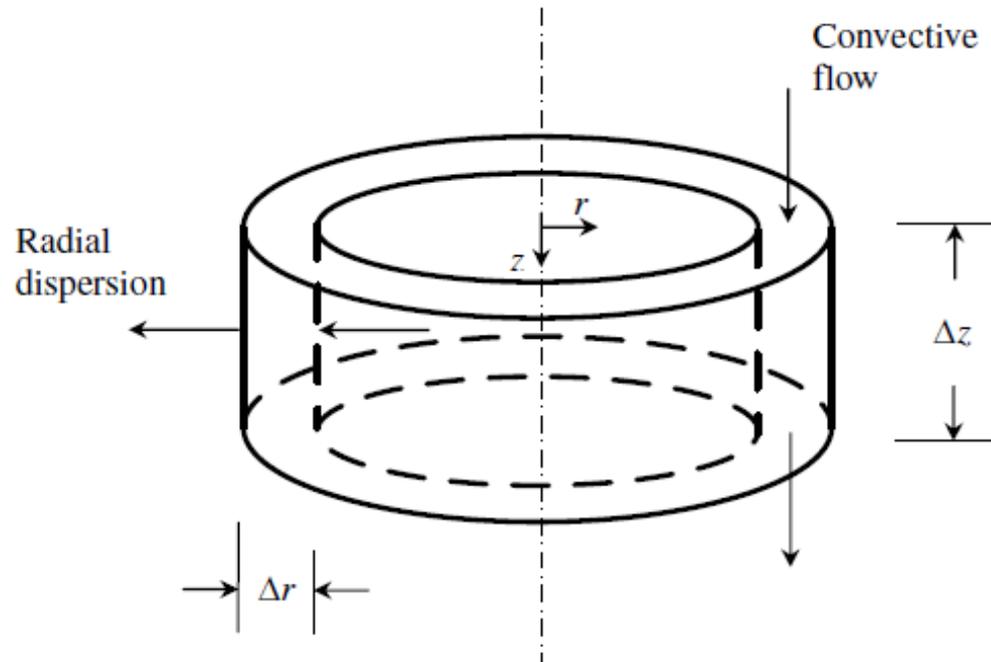


CHE 611

Advanced Chemical Reaction Engineering



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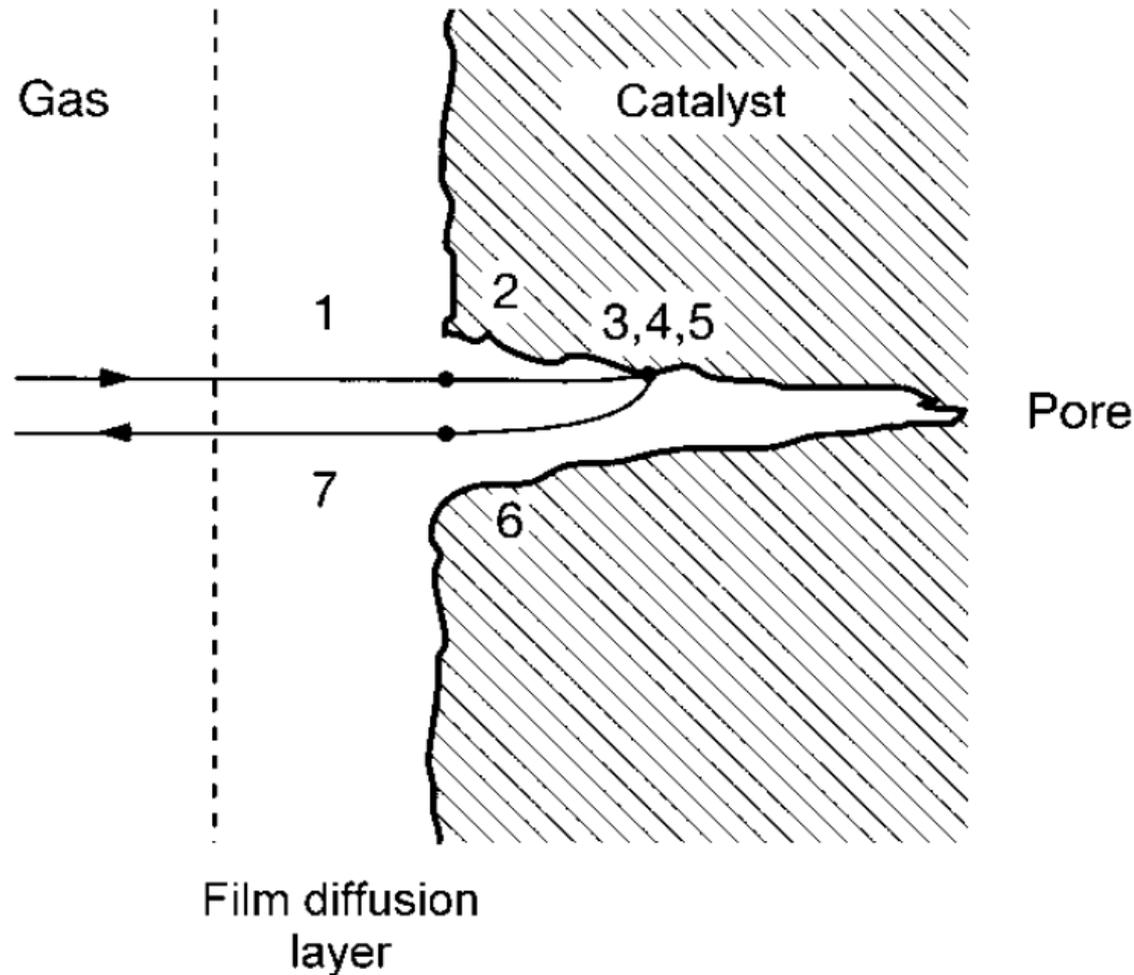
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Advanced Chemical Reaction Engineering

**Development of rate
equation for a gas-solid
catalytic reaction**

Steps involved in a heterogeneous catalytic gas-solid reaction



Steps involved in a heterogeneous catalytic gas-solid reaction

1. Diffusion of reactant/s through external gas film to the catalyst surface.
2. Diffusion through pores of the catalysts.
3. Adsorption of the reactants on the surface of the catalyst (within the pores).
4. Surface chemical reaction on the catalytic surface.
5. Desorption of the reaction products from the catalyst surface.
6. Diffusion of the reaction products through the pores back to the external surface.
7. Diffusion of the products into the gas phase.

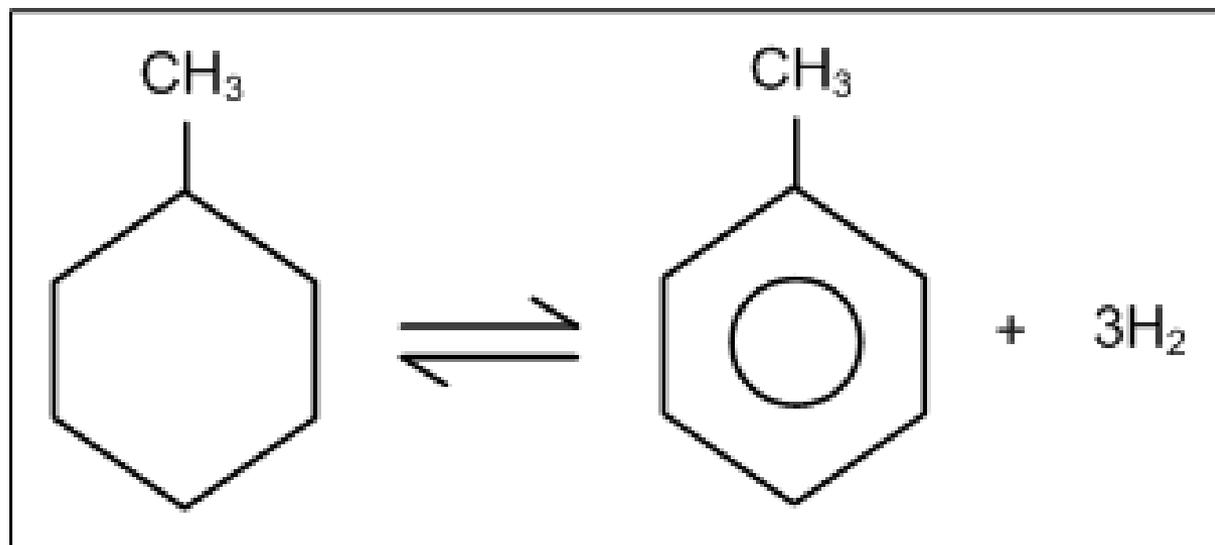
Intrinsic and global rates of reaction

When mass transfer resistances are also considered in the development of a rate equation, the rate of the corresponding chemical reaction is known as **global rate**.

When the external and internal diffusions are removed or highly reduced, the rate of a gas-solid reaction is based only on the **intrinsic kinetics**. The intrinsic kinetics of a gas-solid reaction involves only the following three steps as outlined in the previous slide.

- ✚ Adsorption of the reactants on the surface of the catalyst (within the pores)
- ✚ Surface chemical reaction on the catalytic surface.
- ✚ Desorption of the reaction products from the catalyst surface.

The dehydrogenation of methylcyclohexane: Example reaction



Methylcyclohexane

Toluene

Hydrogen

Common kinetic models

- + The power law (PL) kinetics
- + The Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics
- + The Eley-Rideal (ER) kinetics

The power law kinetics

The power law is an empirical kinetic model and assumes homogenous gas-solid reaction.

See the following article in favor of the power law.

Weller, S. (1956). Analysis of kinetic data for heterogeneous reactions. *AIChE J.* 2, 59–62.

The power law kinetics

- ✚ For the reaction



- ✚ According to law of mass action, a rate equation can be written as:

$$(-r) = k \cdot C_A^a \cdot C_B^b \quad (3)$$

- ✚ The sum of a and b is called overall order of the reaction.

Eq. 3 (from the law of mass action) seldom represents the true rate of the reaction and in most of the cases, rate equation has to be found empirically.

The power law kinetics

- ✚ For the power law, the empirical rate equation may be of the type

$$(-r) = k \cdot C_A^{n_1} \cdot C_B^{n_2} \quad (4)$$

Where sum of n_1 and n_2 is called the overall order of the reaction and may be denoted as n .

- ✚ n_1 and n_2 are not necessarily be equal to a and b in Eq. 3. It happens rarely when reaction is elementary in nature.

The power law kinetics

For the dehydrogenation of methylcyclohexane to toluene (Eq. 1)



Where A , B , and C are methylcyclohexane, toluene, and molecular hydrogen, respectively.

Assuming irreversible reaction (for the forward reaction only), the power law rate equation may be written as

$$(-r_A) = k \cdot C_A^n \quad (6)$$

The power law kinetics

As the reaction is a gas-phase chemical reaction, Eq. 6 may also be written as

$$(-r_A) = k \cdot p_A^n \quad (7)$$

For Eq. 7, the parameter k and n are the regression parameters to be found (fitted) against the experimental data.

Rate constant k is described a function of temperature and usually represented by the Arrhenius equation, therefore Eq. 7 will be used with Arrhenius equation and additional parameters (Arrhenius parameters) are also to be fitted.

Temperature dependence of the rate of a chemical reaction

Arrhenius equation is frequently applied to approximate the temperature dependency of reaction rate and the rate constant or velocity constant, k , is related to temperature, T , by the following expression:

$$\frac{d \ln k}{dT} = \frac{E_a}{R \cdot T^2}$$

$$k = k_0 \cdot e^{-\frac{E_a}{RT}}$$

Where,

k_0 = pre-exponential factor and has units similar to that of k .

E_a = activation energy, $\text{J} \cdot \text{mol}^{-1}$.

Temperature dependence of the rate of a chemical reaction

- ✚ A plot of $\ln k$ vs $1/T$ will be straight line, the slope of which is E_a/R . The units of the slope are K. A large slope of Arrhenius plot means large value of E_a and vice versa.
- ✚ Reactions having large value of E_a are more temperature sensitive while with low value of E_a are less temperature dependent.
- ✚ Arrhenius equation may be written in terms of two rate constants and two temperatures. It is then equal to:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Temperature dependence of the rate of a chemical reaction

E_a and k_0 are called Arrhenius parameters. To estimate the effect of temperature on the rate of a chemical reaction, the values of Arrhenius parameters are to be known, otherwise **experimental data of rate vs temperature** can be used to calculate the parameters.

Laboratory experimental data

Let us go to the laboratory to generate some experimental reaction data.

- ✚ The kinetic analysis may be carried out empirically in a batch, semi-batch, CSTR, or a **PFR**.
- ✚ Both **differential** and **integral** methods may be used for the kinetic analysis.
- ✚ Both linear and **non-linear** regression may be applied.