TEMPERATURE DEPENDENCE OF RATE LAW

Specific reaction rate constant k follows Arrhenius temperature dependence and increases exponentially with temperature.

Adsorption of all species on the surface is exothermic, hence, higher the temperature smaller is the adsorption equilibrium constant.

Therefore, the denominator of the catalytic rate law approaches 1.

For surface reaction controlled irreversible reaction, $A \rightarrow B$,

The rate law is $-r_A = \dfrac{kP_A}{1+ K_A P_A + K_B P_B}$

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At high temperature i.e, lower surface coverage, $1 >> (K_A P_A + K_B P_B)$

$$\therefore -r_A = k P_A$$

For a reversible reaction, the rate equation at high temperature becomes,

$$-r_A = k\left(P_A - \frac{P_B}{K_P}\right)$$

We can never really prove a mechanism by comparing the derived rate law with the experimental data. Independent spectroscopic or tracer experiments are needed to prove the mechanism.

To reduce the catalyst weight, the temperature of the reacting mixture should be increased , provided that side reactions do not prevail at high temperature.

EVALUATION OF RATE LAW PARAMETERS

Assuming a reaction, $A.S + T\,(g) \rightarrow B.S$

Rate law for surface reaction, $-r_A = \dfrac{kP_A P_T}{1 + K_A P_A + K_B P_B}$

The rate law parameters, k, K_A and K_B are to be determined by analyzing the experimental data in the best possible way. This is called *Parameter Estimation*.

Linearising the rate law, $\dfrac{P_A P_T}{-r_A} = \dfrac{1}{k} + \dfrac{K_A P_A}{k} + \dfrac{K_B P_B}{k}$

One can use linearized least square analysis or non-linear regression analysis. The equation can be solved by using three sets of experimental data to determine three unknowns.

CATALYST DEACTIVATION

Reasons for catalyst deactivation

✓Sintering or ageing: It is the loss of catalytic activity due to loss of active surface area, resulting from prolonged exposure to high gas phase temperature. The active surface area may be lost either by crystal agglomeration and growth of metals deposited on the support or by narrowing or closure of pores inside the catalyst pellet. A change in surface structure may also result.

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✓Fouling or coking: This mechanism of decay is common to reactions involving hydrocarbons. It results from a carbonaceous material (Coke) deposited on the surface of a catalyst.

✓Poisoning: This deactivation occurs when poisoning molecules are irreversibly chemisorbed to active sites, thereby reducing the number of sites for main reaction.

DIFFUSIONAL RESISTANCE TO MASS TRANSFER ON HETEROGENEOUS REACTION

Here the mass transfer effect on the overall reaction rate will be discussed. The reaction rate will include both chemical reaction and resistance to mass transfer.

Two types of diffusional resistances are focused:

➢External resistance: During diffusion of reactants/products between the bulk and external surface of the catalyst

➢Internal resistance: During diffusion of reactants/products from the external pellet surface to the interior of the pore.

FUNDAMENTALS OF DIFFUSION:

Diffusion: Movement of a species from high concentration to low concentration relative to bulk movement.

The molar flux of a species A due to a concentration gradient against a fixed coordinate is defined as,
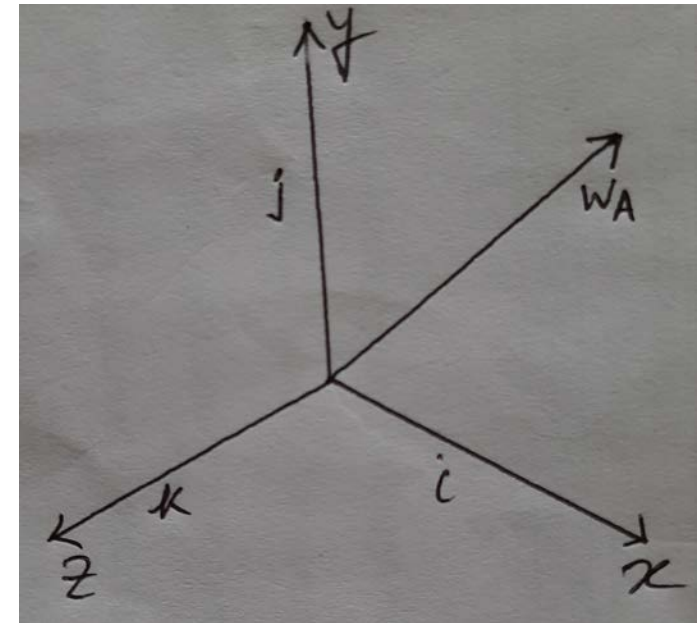
$$W_A = iW_{A_x} + jW_{A_y} + kW_{A_z}$$

W_A in moles/area.time

Now, $W_A = J_A + B_A$

Where, J_A = diffusional flux relative to the bulk

Flow,

B_A = bulk flow or bulk motion

Now, if, U_A = total molar velocity of A

U' = average molar velocity of A due to bulk motion,

Then, $U_A - U'$ = velocity due to diffusion

$\therefore U_A = U' + (U_A - U')$,   or, $C_A U_A = C_A U' + C_A(U_A - U')$

$$W_A = C_A\left(\frac{U_A C_A + U_B C_B}{C}\right) + J_A,$$

where, $\left(\dfrac{U_A C_A + U_B C_B}{C}\right)$ = molar average velocity due to bulk motion

$W_A = C_A U_A$ = (moles/cc)(cm/s) = moles/cm^2.s

Now, $W_A = \dfrac{C_A}{C}(U_A C_A + U_B C_B) + J_A = y_A(W_A + W_B) + J_A$ ----(1)

Fick's 1st law of diffusion:

Diffusional flux is represented as

$$J_A = -D_{AB}C\nabla y_A,$$

where C = concentration in moles/dm³

$\qquad D_{AB}$ = diffusivity of A in B (dm³/s)

$$\nabla y_A = i\frac{\delta y_A}{\delta x} + j\frac{\delta y_A}{\delta y} + k\frac{\delta y_A}{\delta z}$$

Putting J_A in eq. (1),

$$W_A = y_A(W_A + W_B) + J_A$$
$$= y_A(W_A + W_B) + (-D_{AB}C\nabla y_A)$$
$$= C_A U' + (-D_{AB}C\nabla y_A)$$

Equimolar Counter Diffusion (EMCD): If one mole of A goes to a given direction, one mole of B goes to the opposite direction.

So, $W_A = -W_B$

$$\therefore W_A = J_A + y_A(W_A + W_B) = J_A = -D_{AB}C\nabla y_A$$

Dilute Concentration: Here, bulk motion is considered to be small, so $y_A(W_A + W_B)$ term can be neglected.

$$\therefore W_A = J_A$$

This equation can be applied to porous catalyst system, where the pore radii is very small.

Diffusion under this condition is called *Knudsen diffusion.*

This diffusion occurs when mean free path of the reactant gas molecules is greater than the diameter of the pore. Here the reacting molecules collide more often with the pore wall than with each other and molecules of different species do not affect each other.

The flux of A for Knudsen diffusion, when bulk flow is neglected,

$$\therefore W_A = J_A = -D_K C \nabla y_A, \quad \text{where } D_K \text{ is called Knudsen diffusivity.}$$

Diffusion through a stagnant gas: When A is a solute gas in the mixture of A and B and B is stagnant, then $W_B = 0$.

$$\therefore W_A = J_A + y_A(W_A + W_B) = J_A + y_A W_A$$