# Catalysis

## The General procedure for determination reaction mechanism

This lecture is related to determination the rate limiting step in catalysis if it is adsorption, surface reaction or desorption step. This can be done by measuring the initial rate of reaction as a function of concentration (or pressure) graphically.

To do that, let us assume the following as reaction rate controlling steps and see what is the response of varying the concertation (or pressure) on the rate of reaction.

## 1. Case 1. Surface reaction controlling

$$-r_{surface} = k_f \frac{C_A C_B - \frac{C_C}{K_{eq}}}{(1 + K_A C_A + K_B C_B + K_C C_C)^2}$$

Assume initially there is no concertation of C, i.e $C_{Co} = 0$

Assume initially the concentration of A is equal to that of B, i.e $C_{Ao} = C_{Bo}$

$$C_{Ao} + C_{Bo} = f(total\ pressure)$$

$$C_{Ao} = \frac{1}{2}\text{Po} \qquad C_{Bo} = \frac{1}{2}\text{Po}$$

Substitute in the reaction rate expression, to obtain an expression as a function of pressure

$$-r_{surface} = k_f \frac{C_A C_B - \frac{C_C}{K_{eq}}}{(1 + K_A C_A + K_B C_B + K_C C_C)^2}$$

$$-r_{surface} = K_1 \frac{\left(\frac{P_0}{2}\right)\left(\frac{P_0}{2}\right) - 0}{\left(1 + K_A\left(\frac{P_0}{2}\right) + K_B\left(\frac{P_0}{2}\right) + 0\right)^2}$$

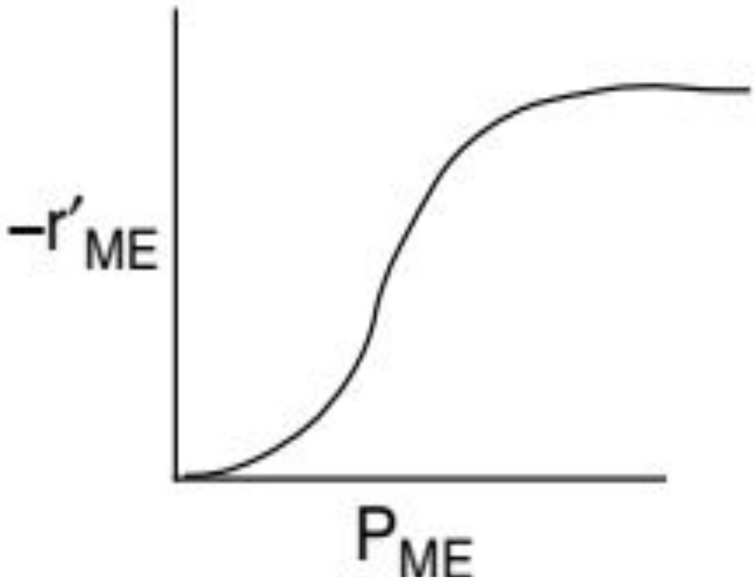
$$-r_{surface} = K_1 \frac{\left(\frac{P_0}{2}\right)\left(\frac{P_0}{2}\right) - 0}{\left(1 + K_A\left(\frac{P_0}{2}\right) + K_B\left(\frac{P_0}{2}\right) + 0\right)^2} = K_1 \frac{\left(\frac{P_0}{2}\right)^2}{\left(1 + (K_A + K_B)\left(\frac{P_0}{2}\right)\right)^2} = \frac{K_2 P_o^2}{(1 + K_3 P_0)^2}$$

- At low pressure, Po the denominator in the expression above becomes $1 > K_3 P_0$ and $K_3 P_0$ can be neglected when comparing to 1.

$$\Rightarrow \quad -r_{surface} = K_2 P_o^2$$

- At high pressure, Po the denominator in the expression above becomes $1 < K_3 P_0$ and the number 1 can be neglected when comparing to $K_3 P_0$ .

$$\Rightarrow \quad -r_{surface} = \frac{K_2 P_o^2}{(K_3 P_0)^2} = \text{constant}$$



## 2. Case 2. Surface reaction controlling where B in gas phase

$$-r_{surface} = k_{Sf} K_A C_T \frac{C_A C_B - \frac{C_C}{K_{eq}}}{(1 + K_A C_A + K_C C_C)}$$

Again, assume initially there is no concertation of C, i.e $C_{Co} = 0$ and $C_{Ao} = C_{Bo}$

$$-r_o = k_{Sf} K_A C_T \frac{\left(\frac{P_0}{2}\right)\left(\frac{P_0}{2}\right) - 0}{\left(1 + K_A\left(\frac{P_0}{2}\right) + K_C\left(\frac{P_0}{2}\right)\right)} = \frac{K_2 P_o^2}{1 + K_3 P_0}$$

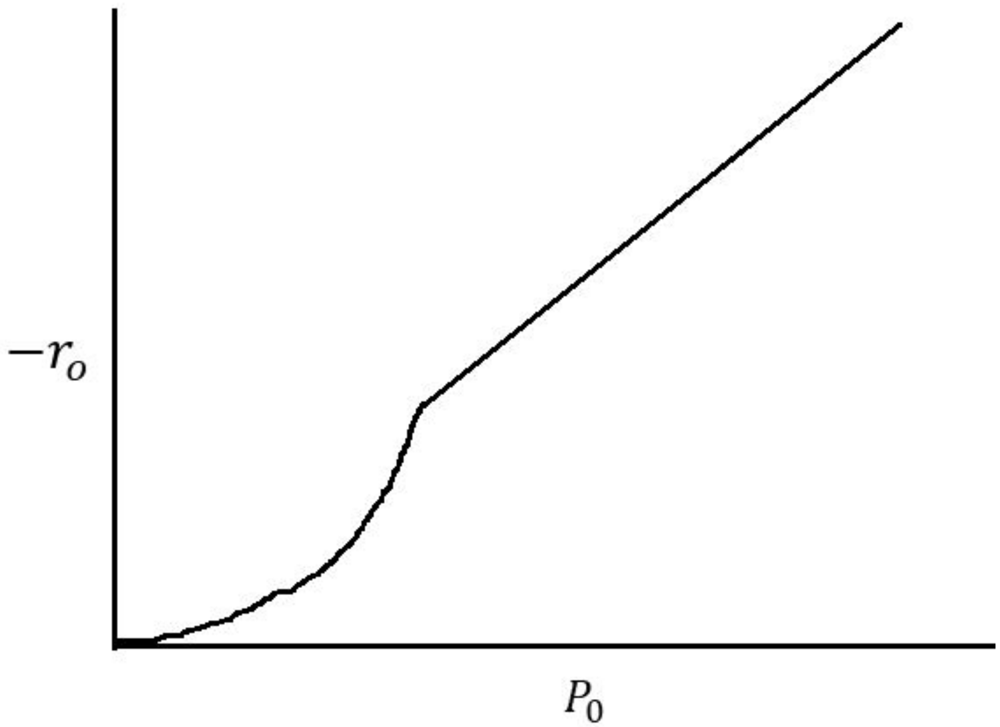
- At low pressure, Po the denominator in the expression above becomes $1 > K_3 P_0$ and $K_3 P_0$ can be neglected when comparing to 1.

  ⇨ $-r_0 = K_2 P_o^2$

- At high pressure, Po the denominator in the expression above becomes $1 < K_3 P_0$ and the number 1 can be neglected when comparing to $K_3 P_0$ .

  ⇨ $-r_0 = K_4 P_0$

When plotting the initial rate of reaction with initial pressure we get the shape



## 3. Case 3. Adsorption controlling

$$-r_0 = k_{Af} C_T \frac{\left(C_A - \frac{K_C}{K_A K_S K_B} \frac{C_C}{C_B}\right)}{\left(\frac{K_C C_C}{K_S K_B C_B} + K_B C_B + K_C C_C + 1\right)}$$

Assume initially there is no concertation of C, i.e $C_{Co} = 0$ and $C_{Ao} = C_{Bo}$

$$-r_0 = k_{Af} C_T \frac{\left(\frac{P_0}{2} - 0\right)}{\left(0 + K_B \frac{P_0}{2} + 0 + 1\right)} = \frac{k_1 P_0}{(1 + k_2 P_0)}$$

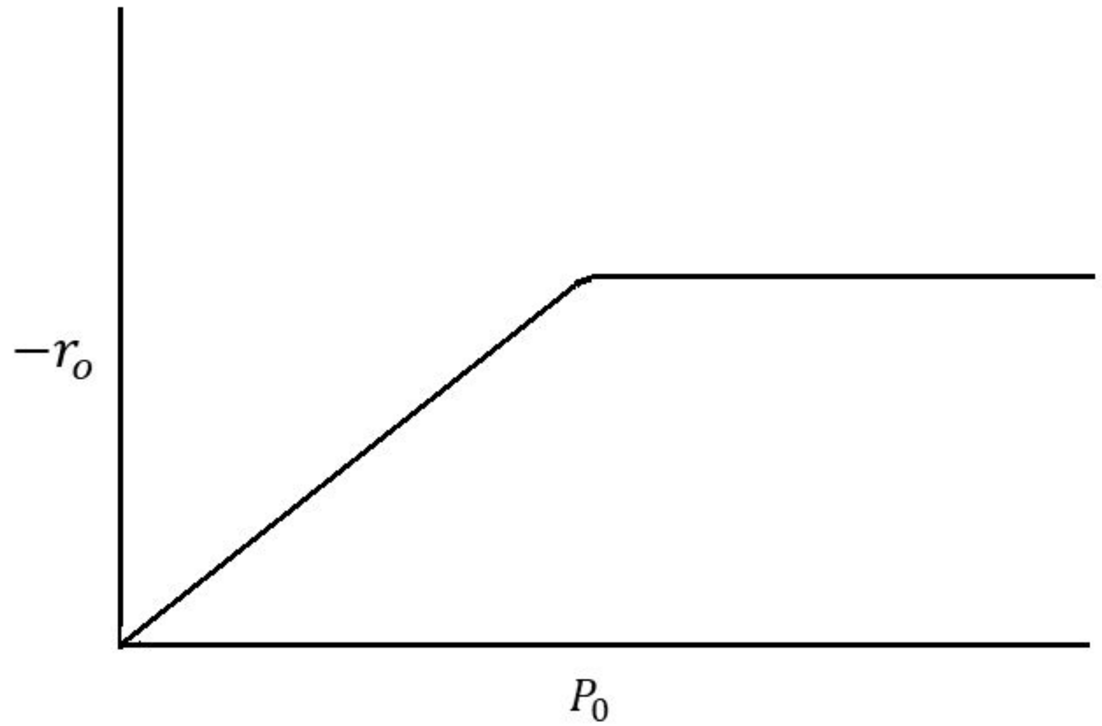
- At low pressure, Po the denominator in the expression above becomes $1 > K_2 P_0$ and $K_2 P_0$ can be neglected when comparing to 1.

  ⇨ $-r_0 = k_1 P_0$

- At high pressure, Po the denominator in the expression above becomes $1 < K_2 P_0$ and the number 1 can be neglected when comparing to $K_2 P_0$.

  ⇨ $-r_0 = constant$

When plotting the initial rate of reaction with initial pressure we get the shape



## 4. Case 4. Desorption controlling

$$-r_{Des.C} = k_{cf}\ C_T \frac{\left(K_S\ K_A K_B\ C_A\ C_B\ -\ \frac{C_C}{K_C}\right)}{(\ K_A C_A + K_B C_B + K_S\ K_A K_B\ C_A\ C_B\ +\ 1)}$$

Assume initially there is no concertation of C, i.e $C_{Co} = 0$ and $C_{Ao} = C_{Bo}$

$$-r_{Des.C} = k_{cf}\ C_T \frac{\left(K_S\ K_A\ K_B \frac{P_0}{2}\frac{P_0}{2} - 0\right)}{\left(K_A \frac{P_0}{2} + K_B \frac{P_0}{2} + K_S\ K_A\ K_B \frac{P_0}{2}\frac{P_0}{2} +\ 1\right)}$$

$$-r_o = \frac{K_1 P_o^2}{(\ 1 + K_2 P_0 + K_3 P_o^2\ )}$$

$$-r_o = \frac{K_1 P_o^2}{(\ 1 + K_2 P_0 + K_3 P_o^2\ )}$$

- At low pressure, Po  the denominator in the expression above becomes $1 > K_2 P_0 + K_3 P_o^2$

$$\Rightarrow \quad -r_0 = K_1 P_o^2$$

- At intermediate pressure, Po  the denominator in the expression above becomes $1 < K_2 P_0 + K_3 P_o^2$

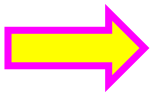
$$\Rightarrow \quad -r_0 = \frac{K_1 P_o^2}{(\ K_2 P_0 + K_3 P_o^2\ )} = \frac{K_1 P_0}{(\ K_2 + K_3 P_0\ )}$$

$$-r_o = \frac{K_1 P_o^2}{(\,1 + K_2 P_0 + K_3 P_o^2\,)}$$

- At high pressure, Po the denominator in the expression above becomes

$$1 + K_2 P_0 < K_3 P_o^2$$

and the rate becomes constant.



$$-r_0 = constant$$