Rate equations for fluid-solid reactions (kinetic models)
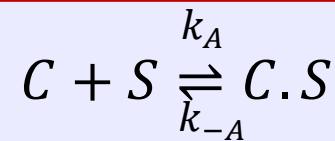
Developing the rate law for a catalytic reaction

The catalytic reaction to be studied is **decomposition of cumene** to form **benzene and propylene**
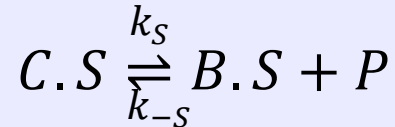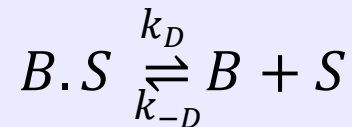
$$C_6H_5CH(CH_3)_2 \rightarrow C_3H_6(g) + C_6H_6$$

C = cumene   P = propylene   B = benzene

Steps in the Langmuir-Hinshelwood mechanism

$$C + S \underset{k_{-A}}{\overset{k_A}{\rightleftharpoons}} C.S \qquad \textit{Adsorption of cumene}$$

$$C.S \underset{k_{-S}}{\overset{k_S}{\rightleftharpoons}} B.S + P \qquad \textit{Surface reaction}$$

$$B.S \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} B + S \qquad \textit{Desorption of benzene}$$

Rate laws are written considering each step to be reversible and elementary

Adsorption $(C + S \rightleftharpoons C.S)$

$$r_A = k_A p_C C_v - k_{-A} C_{C.S}$$

$$\boxed{r_A = k_A \left[p_C C_v - \frac{C_{C.S}}{K_C} \right]}$$

where $\quad K_C = \dfrac{k_A}{k_{-A}}$

Unit of r_A is mol/gcat.s, $C_{C.S}$ and C_v is mol/gcat, K_C is 1/Pa, p_C in Pa,

k_A and k_{-A} are (1/Pa.s) and (1/s), respectively

Surface Reaction $(C.S \rightleftharpoons B.S + P)$

$$r_S = k_S C_{C.S} - k_{-S} p_P C_{B.S}$$

$$\boxed{r_S = k_S \left[C_{C.S} - \frac{p_P C_{B.S}}{K_S} \right]}$$

where $\quad K_S = \dfrac{k_S}{k_{-S}}$

Unit of r_S is mol/gcat.s, $C_{C.S}$ and $C_{B.S}$ is mol/gcat, p_P in Pa, k_S is 1/s, K_S is Pa

Desorption $(B.S \rightleftharpoons B + S)$

$$r_D = k_D C_{B.S} - k_{-D} p_B C_v$$

$$\boxed{r_D = k_D \left[C_{B.S} - \frac{p_B C_v}{K_{DB}} \right]}$$

$$\boxed{r_D = k_D [C_{B.S} - K_B p_B C_v]}$$

where $\quad K_{DB} = \dfrac{k_D}{k_{-D}}$

Unit of r_S is mol/gcat.s, $C_{B.S}$ and C_v is mol/gcat, p_B in Pa, k_D and k_{-D} are 1/s and (1/Pa.s) respectively, K_{DB} is Pa

Since desorption of B is the reverse of adsorption of B $\left[K_{DB} = \dfrac{1}{K_B} \right]$

We now assume several cases where each step to be rate limiting and establish the rate law for those cases

At steady state, $r_A = r_S = r_D = -r_C$

(a) Adsorption is rate limiting

Here, the adsorption step is considered to be the slowest step while the others (reaction and desorption) are fast and reaches equilibrium. Thus, adsorption step controls the rate of the reaction

$$r_A = k_A \left[p_C C_v - \frac{C_{C.S}}{K_C} \right]$$

As neither $C_{C.S}$ nor C_v can be measured, they are replaced by measurable quantities in the rate law. The other non-rate limiting steps are used for this purpose

For such adsorption limited reactions, k_A is small and k_S and k_D (for the surface reaction and desorption steps) is large

Hence, the ratios of $\dfrac{r_S}{k_S}$ and $\dfrac{r_D}{k_D}$ are very small (~ 0) while $\dfrac{r_A}{k_A}$ is large

As $\frac{r_S}{k_S} \approx 0$, $\left[C_{C.S} - \frac{p_P C_{B.S}}{K_S}\right] \approx 0$

$$\therefore \boxed{C_{C.S} = \frac{p_P C_{B.S}}{K_S}}$$

and as $\frac{r_D}{k_D} \approx 0$, $[C_{B.S} - K_B p_B C_v] \approx 0$

$$\therefore \boxed{C_{B.S} = K_B p_B C_v}$$

Replacing the value of $C_{B.S}$ in the expression for $C_{C.S}$, we get $\boxed{C_{C.S} = \frac{K_B p_B p_P C_v}{K_S}}$

Now, $r_A = k_A \left[p_C C_v - \frac{C_{C.S}}{K_C}\right]$

Putting in the value of $C_{C.S}$ in this equation we have, $r_A = k_A \left[p_C C_v - \frac{K_B p_B p_P C_v}{K_C K_S}\right]$

or, $r_A = k_A C_v \left[p_C - \frac{K_B p_B p_P}{K_C K_S}\right]$

This can be simplified to, $\boxed{r_A = k_A C_v \left[p_C - \frac{p_B p_P}{K}\right]}$

where $K = \frac{K_C K_S}{K_B}$, $K = $ reaction equilibrium constant as determined from thermodynamics

$$RT\ln K = -\Delta G^o$$

For the reaction , $C \rightleftharpoons B + P,$ $\qquad K = \left(\dfrac{p_B p_P}{p_C} \right)_{eq}$

Since $\quad C_{B.S} = K_B p_B C_v \quad$ and $\quad C_{C.S} = K_C p_C C_v \quad$ at equilibrium, we can write

$$K = \frac{\left(\frac{C_{B.S}}{K_B C_v} \right)(p_P)}{\left(\frac{C_{C.S}}{K_C C_v} \right)} = \frac{(C_{B.S})(p_P)}{(C_{C.S})} \cdot \frac{K_C}{K_B} = \frac{K_S K_C}{K_B} \qquad \left[\text{As } \frac{r_S}{k_S} \approx 0, \quad K_S = \frac{C_{B.S} p_P}{C_{C.S}} \right]$$

$$\therefore \boxed{K = \frac{K_S K_C}{K_B}}$$

Carrying out a site balance gives us, $C_t = C_v + C_{B.S} + C_{C.S}$

or, $\qquad C_t = C_v + K_B p_B C_v + \dfrac{K_B p_B p_P C_v}{K_S}$

or, $\qquad C_t = C_v \left[1 + K_B p_B + \dfrac{K_B p_B p_P}{K_S} \right]$

or, $\qquad C_v = \dfrac{C_t}{1 + K_B p_B + \frac{K_B p_B p_P}{K_S}}$

Replacing the value of C_v in the rate of adsorption equation we get,

$$\boxed{r_A = \frac{k_A C_t \left[p_C - \dfrac{p_B p_P}{K} \right]}{1 + K_B p_B + \dfrac{K_B p_B p_P}{K_S}}}$$

Rate when adsorption is limiting is, $\quad r_A = \dfrac{k_A C_t \left[p_C - \dfrac{p_B p_P}{K} \right]}{1 + K_B p_B + \dfrac{K_B p_B p_P}{K_S}}$

The initial rate $(t \rightarrow 0)$, r_A^0 can be written as, $-r_{C0} = r_A^0 = k_A C_t p_{C0} = k p_{C0}$

$$\boxed{-r_{C0} = r_A^0 = k p_{C0}}$$

If adsorption of cumene is rate limiting, then the initial rate will be linear with the partial pressure of cumene as shown below
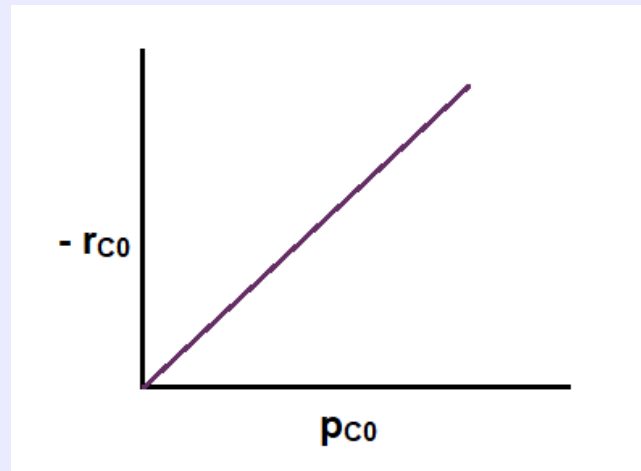
If this is the mechanism the reaction is following, then the experimental data should be consistent with the above equation

(b) Surface reaction is rate limiting

In this case, the surface reaction is the slowest step while the others (adsorption and desorption) are fast and reaches equilibrium

$$r_S = k_S \left[C_{C.S} - \frac{p_P C_{B.S}}{K_S} \right]$$

As adsorption and desorption steps are fast, $\frac{r_A}{k_A} \approx 0$ and $\frac{r_D}{k_D} \approx 0$

$\therefore$ $\quad C_{C.S} = K_C p_C C_v$ $\quad$ and $\quad C_{B.S} = K_B p_B C_v$

Substituting these values in the rate expression we have, $\quad r_S = k_S \left[K_C p_C C_v - \frac{K_B p_B p_P C_v}{K_S} \right]$

or, $\quad r_S = k_S K_C C_v \left[p_C - \frac{K_B p_B p_P}{K_C K_S} \right]$

or, $\quad r_S = k_S K_C C_v \left[p_C - \frac{p_B p_P}{K} \right]$ $\qquad \left(\text{as } K = \frac{K_S K_C}{K_B} \right)$

Carrying out a site balance gives us, $C_t = C_v + C_{B.S} + C_{C.S}$

or, $C_t = C_v + K_B p_B C_v + K_C p_C C_v$

or, $C_t = C_v[1 + K_B p_B + K_C p_C]$

or, $\boxed{C_v = \dfrac{C_t}{1 + K_B p_B + K_C p_C}}$

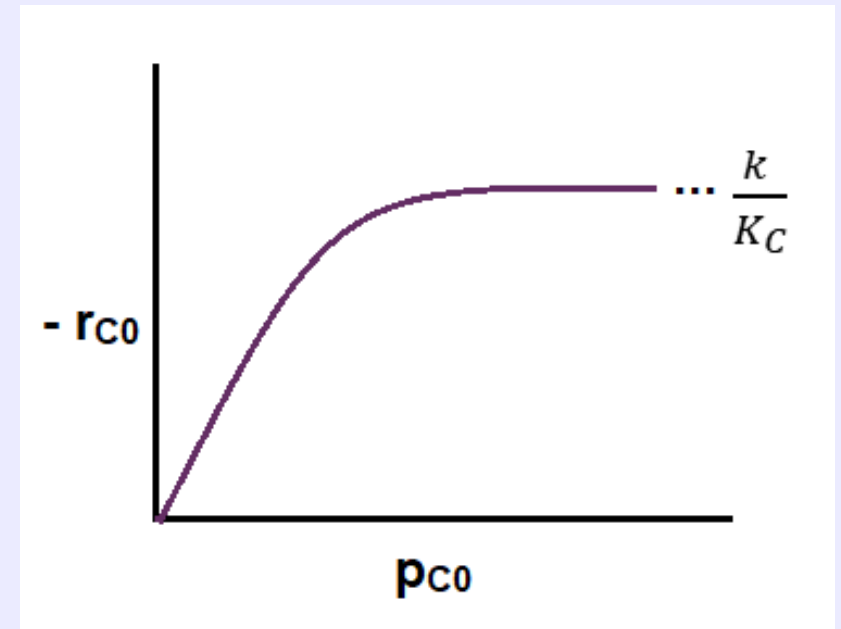Replacing the value of C_v in the rate of surface reaction equation we get,

$$\boxed{r_S = \frac{k_S K_C C_t \left[p_C - \dfrac{p_B p_P}{K}\right]}{1 + K_B p_B + K_C p_C}}$$

If $k_S K_C C_t = k$, the initial rate, r_S^0 can be written as,

$$\boxed{-r_{C0} = r_S^0 = \frac{k\, p_{C0}}{1 + K_C p_{C0}}}$$

At low p_{C0}, $1 \gg K_C p_{C0}$ and $-r_{C0} = r_S^0 = k\, p_{C0}$

At high p_{C0}, $1 \ll K_C p_{C0}$ and $-r_{C0} = r_S^0 = \dfrac{k}{K_C}$

(c) Desorption of benzene is rate limiting (controlling)

In this case, the desorption step is the slowest step while the others (adsorption and reaction) are fast and reaches equilibrium

$$r_D = k_D[C_{B.S} - K_B p_B C_v]$$

As adsorption and reaction steps are fast, $\dfrac{r_A}{k_A} \approx 0$ and $\dfrac{r_S}{k_S} \approx 0$

$\therefore$ $\qquad C_{C.S} = K_C p_C C_v$ $\qquad$ and $\qquad C_{B.S} = \dfrac{K_S C_{C.S}}{p_P} = \dfrac{K_S K_C p_C C_v}{p_P}$

Substituting these values in the rate expression we have, $\qquad r_D = k_D \left[\dfrac{K_S K_C p_C C_v}{p_P} - K_B p_B C_v \right]$

or, $\qquad r_D = k_D K_C K_S C_v \left[\dfrac{p_C}{p_P} - \dfrac{K_B p_B}{K_C K_S} \right]$

or, $\qquad r_D = k_D K_C K_S C_v \left[\dfrac{p_C}{p_P} - \dfrac{p_B}{K} \right]$ $\qquad\qquad \left(\text{as } K = \dfrac{K_S K_C}{K_B} \right)$

Carrying out a site balance gives us, $\quad C_t = C_v + C_{B.S} + C_{C.S}$

or, $\qquad C_t = C_v + \dfrac{K_S K_C p_C C_v}{p_P} + K_C p_C C_v$

or, $\qquad C_t = C_v \left[1 + \dfrac{K_S K_C p_C}{p_P} + K_C p_C \right]$

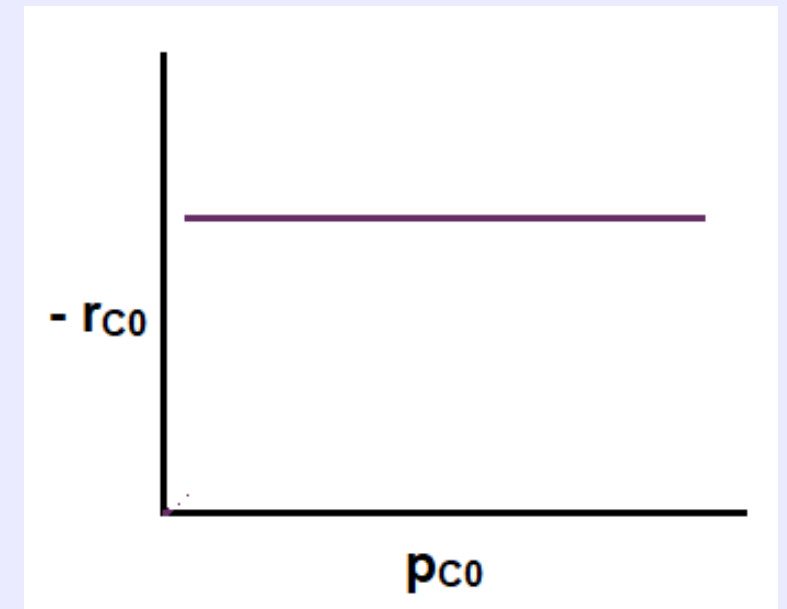or, $\qquad \boxed{C_v = \dfrac{C_t}{1 + \dfrac{K_S K_C p_C}{p_P} + K_C p_C}}$

Replacing the value of C_v in the rate of desorption equation we get,

$r_D = \dfrac{k_D K_C K_S C_t \left[\dfrac{p_C}{p_P} - \dfrac{p_B}{K} \right]}{1 + \dfrac{K_S K_C p_C}{p_P} + K_C p_C}$ or $\boxed{r_D = \dfrac{k_D K_C K_S C_t \left[p_C - \dfrac{p_P p_B}{K} \right]}{p_P + K_S K_C p_C + K_C p_C p_P}}$

If $\quad k_D K_C K_S C_t = k$, the initial rate, r_D^0 can be written as,

$-r_{C0} = r_D^0 = \dfrac{k\, p_{C0}}{K_S K_C p_{C0}}$ or $\boxed{-r_{C0} = r_S^0 = k_D\, C_t}$

Actual experimental observations for cumene to benzene conversion

- The figure shows the actual experimental data for initial rate ($-r_{C0}$) as a function of initial partial pressure of cumene (p_{C0})

- The plot show that the reaction is neither limited by adsorption or desorption but by the surface reaction and the rate law is given by

$$r_S = \frac{k\left[p_C - \dfrac{p_B p_P}{K}\right]}{1 + K_B p_B + K_C p_C}$$
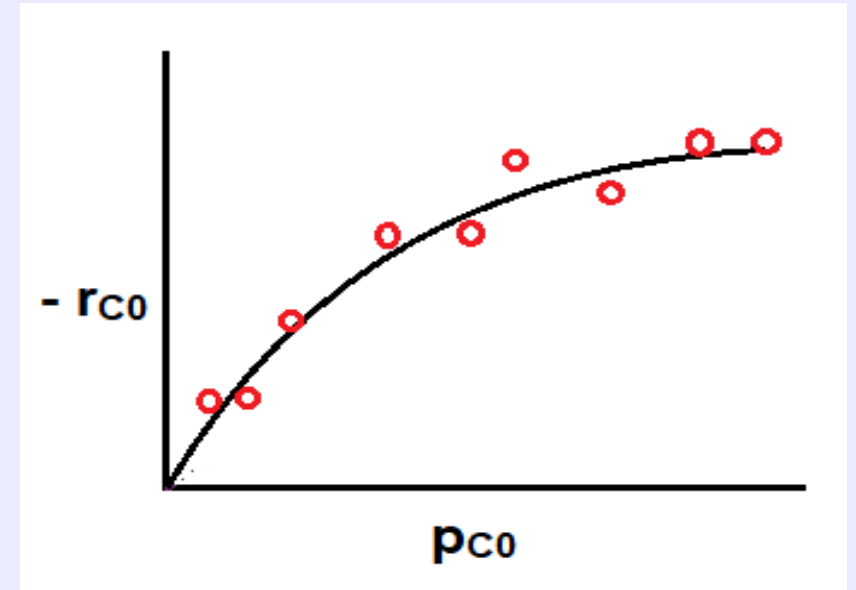
- In some cases, the **reactant is diluted by an inert (I)**. If the inert is an adsorbing one, then it does not participate in the reaction but only covers vacant sites

$$I + S \rightleftharpoons I.S$$
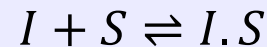
Site balance gives, $C_t = C_v + C_{B.S} + C_{C.S} + C_{I.S}$

Since adsorption of the inert is at equilibrium, $C_{I.S} = K_I p_I C_v$

And the rate law now becomes, $r_S = \dfrac{k\left[p_C - \dfrac{p_B p_P}{K}\right]}{1 + K_B p_B + K_C p_C + K_I p_I}$

The rate law has specific reaction rate constant, k and adsorption constants K_C, K_B, K_I etc
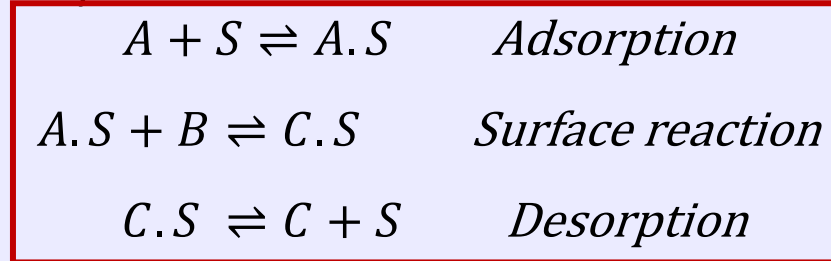
The reaction rate constant, k follow Arrhenius equation and increases exponentially with temperature

The adsorption process is exothermic and the adsorption constants, K_i decrease with temperature

Eley-Rideal mechanism

The reaction, $A + B(g) \rightleftharpoons C$ follows the Eley-Rideal mechanism

The steps for the reaction is given by:

$$A + S \rightleftharpoons A.S \qquad Adsorption$$

$$A.S + B \rightleftharpoons C.S \qquad Surface\ reaction$$

$$C.S \rightleftharpoons C + S \qquad Desorption$$

If the **surface reaction is considered to be the rate limiting (controlling) step**

$$r_s = k_s C_{A.S} p_B - k_{-s} C_{C.S}$$

and the reaction rate law is given by, $\quad r_s = k_s \left[C_{A.S} p_B - \dfrac{C_{C.S}}{K_S} \right]$

As adsorption and desorption steps are fast, $\dfrac{r_A}{k_A} \approx 0$ and $\dfrac{r_D}{k_D} \approx 0$ and they reach equilibrium

$\therefore \qquad C_{A.S} = K_A p_A C_v \qquad$ and $\qquad C_{C.S} = K_C p_C C_v$

Substituting these values in the rate expression we have, $\qquad r_S = k_S \left[K_A p_A C_v p_B - \dfrac{K_C p_C C_v}{K_S} \right]$

Now, $r_S = k_S \left[K_A p_A C_v p_B - \dfrac{K_C p_C C_v}{K_S} \right]$

or, $r_S = k_S K_A C_v \left[p_A p_B - \dfrac{K_C p_C}{K_A K_S} \right]$

Carrying out a site balance gives us, $C_t = C_v + C_{A.S} + C_{C.S}$

or, $C_t = C_v + K_A p_A C_v + K_C p_C C_v = C_v [1 + K_A p_A + K_C p_C]$

or, $\boxed{C_v = \dfrac{C_t}{1 + K_A p_A + K_C p_C}}$

Replacing the value of C_v in the rate of surface reaction equation we get, $r_S = \dfrac{k_S K_A C_t \left[p_A p_B - \dfrac{K_C p_C}{K_A K_S} \right]}{1 + K_A p_A + K_C p_C}$

or, $\boxed{r_S = \dfrac{k_S K_A C_t \left[p_A p_B - \dfrac{p_C}{K} \right]}{1 + K_A p_A + K_C p_C}}$ $\left(\text{as } K = \dfrac{K_S K_A}{K_C} \right)$

If $k_S K_A C_t = k$, the initial rate, r_S^0 can be written as,

$$\boxed{-r_{A0} = r_S^0 = \dfrac{k p_{A0} p_{B0}}{1 + K_A p_{A0}}}$$

At low p_{A0}, $1 \gg K_A p_{A0}$ and $-r_{A0} = r_S^0 = k p_{A0} p_{B0}$

At high p_{A0}, $1 \ll K_A p_{A0}$ and $-r_{A0} = r_S^0 = \dfrac{k p_{B0}}{K_A}$

at constant p_B

$\cdots \dfrac{k p_{B0}}{K_A}$

r_S^0

p_{A0}