

Rate Limiting Step

The heterogeneous catalytic reaction goes through different steps and rates of the three major steps occurring in series (adsorption, surface reaction, desorption) are equal at steady state.

Among these three steps, one step is rate limiting or rate determining step.

If this step goes faster, the overall rate of the process will be faster or rate will be more, and vice-versa.

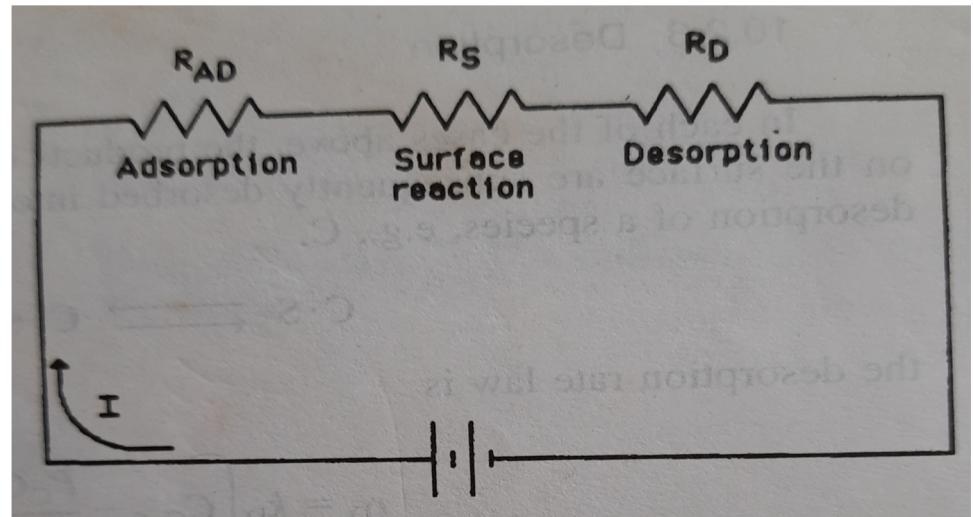
We consider the heterogeneous process is analogous to an electrical circuit.

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- EMF E as the driving force which is the concentration difference of the reactant from bulk phase to the catalyst surface
- Current I as rate of the reaction ($-r_A$, mol/s. g of catalyst)
- Total resistance R_t as the resistance associated with each step in series

$$I = \frac{E}{R_t} = \frac{E}{R_{AD} + R_S + R_D}$$

Among the three resistances, the value of one resistance is highest.



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The largest resistance in the circuit controls the amount of current passing through it.

Similarly, the step with largest resistance controls rate of the reaction in the heterogeneous catalytic process.

If we can somehow lower the largest resistance of the step, the rate of the reaction will increase.

Hence, the step with largest resistance is the rate limiting step.

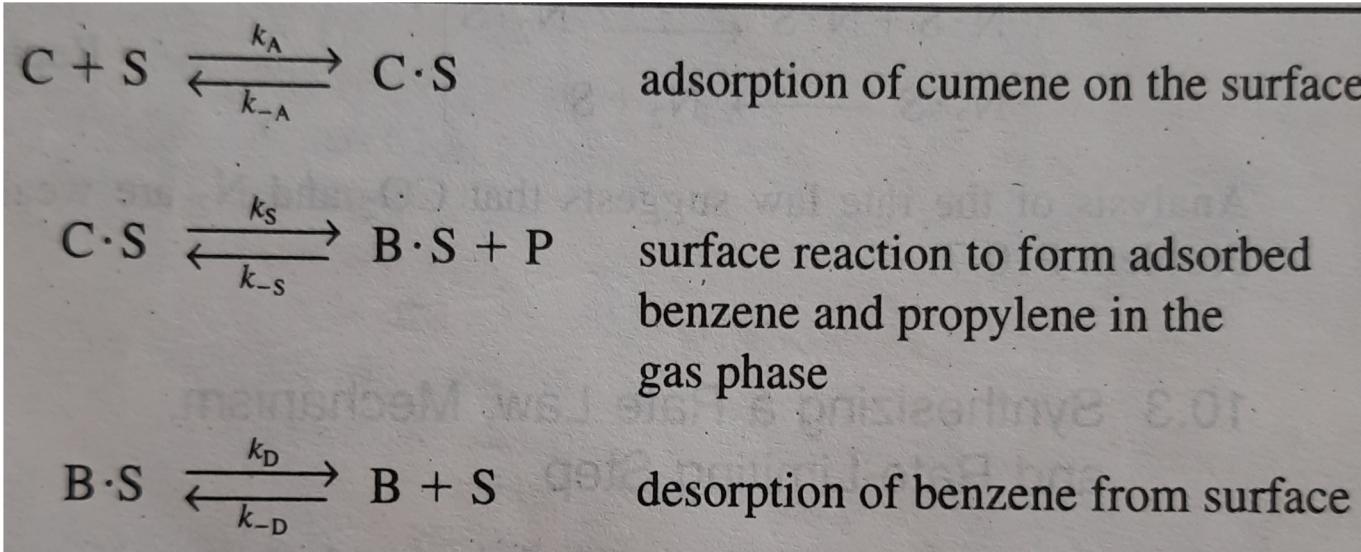
Synthesising a Rate Law: Rate Limiting Step

- ✓ The rate limiting step, mechanism of the reaction and the rate law consistent with the experimental observation can be obtained by taking the example of a reaction which is not diffusion controlled.
- Click to add text
- ✓ To find out the rate limiting step, each step (adsorption, surface reaction and desorption) can be assumed as rate limiting one by one and analysed them.
- ✓ In doing this, Cumene disproportionation reaction is taken as model reaction

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Cumene disproportionation reaction catalyzed by Pt as solid catalyst

Steps of this heterogeneous reaction:



Each step is considered as elementary step.

Concentration of gas phase is replaced by its partial pressure.

Rate Law for adsorption limited reaction

Assuming adsorption is rate limiting

To determine this, the rate law following adsorption as rate limiting should be consistent with the experimental data.

Writing the rate expressions of all the steps,

$$\text{Adsorption: } r_{AD} = k_A P_C C_v - k_{-A} C_{C.S} = k_A \left(P_C C_v - \frac{C_{C.S}}{K_{AD}} \right)$$

$$\text{Surface reaction: } r_s = k_s C_{C.S} - k_{-s} C_{B.S} P_p = k_s \left(C_{C.S} - \frac{C_{B.S} P_p}{K_s} \right)$$

$$\text{Desorption: } r_D = k_D C_{B.S} - k_{-D} P_B C_v = k_D \left(C_{B.S} - \frac{P_B C_v}{K_{D_B}} \right)$$

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At steady state, $-r_C = r_{AD} = r_D = r_s$,

In adsorption-limited reaction, $k_A \ll k_s, k_D$

Therefore, $\frac{r_{AD}}{k_A} \gg \frac{r_s}{k_s}, \frac{r_D}{k_D}$, $\frac{r_s}{k_s} \approx 0, \frac{r_D}{k_D} \approx 0$ compared to $\frac{r_{AD}}{k_A}$

Hence, surface reaction can be written as:

$$r_s = k_s(C_{C.S} - \frac{C_{B.S}P_P}{K_S}), \quad \frac{r_s}{k_s} = (C_{C.S} - \frac{C_{B.S}P_P}{K_S}) = 0, \quad \therefore C_{C.S} = \frac{C_{B.S}P_P}{K_S}$$

Similarly for desorption,

$$r_D = k_D(C_{B.S} - \frac{P_B C_v}{K_{D_B}}), \quad \frac{r_D}{k_D} = (C_{B.S} - \frac{P_B C_v}{K_{D_B}}) = 0, \quad \therefore C_{B.S} = \frac{P_B C_v}{K_{D_B}}$$

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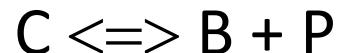
Hence, putting the expression of $C_{B.S}$, we get,

$$C_{C.S} = \frac{C_{B.S} P_P}{K_S} = \frac{P_B C_v P_P}{K_{D_B} K_S}$$

Hence, putting this expression of $C_{C.S}$ into the adsorption rate expression,

$$r_{AD} = k_A (P_C C_v - \frac{C_{C.S}}{K_{AD}}) = k_A (P_C C_v - \frac{P_B C_v}{K_{D_B}} \frac{P_P}{K_{AD} K_S}) = k_A (P_C - \frac{P_B}{K_{D_B}} \frac{P_P}{K_{AD} K_S}) C_v$$

Now, when there is no adsorption, we can look at the reaction as,



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If k_1 and k_2 are the forward and reverse rate constants respectively and K_p is the equilibrium constant, then the rate equation can be written as,

$$r_{s1} = k_1 \left(P_C - \frac{P_B P_P}{K_p} \right)$$

Now, comparing this equation with the adsorption rate equation,

$$r_{AD} = k_A \left(P_C - \frac{P_B}{K_{DB}} \frac{P_P}{K_{AD} K_s} \right) C_v, \quad \text{we can write,}$$

$$K_p = K_{DB} K_{AD} K_s$$

Therefore, the adsorption rate equation can be written as,

$$r_{AD} = k_A \left(P_C - \frac{P_B P_P}{K_p} \right) C_v$$

Now, we have to eliminate C_v using site balance equation,

$$C_t = C_v + C_{B.S} + C_{C.S}$$

$$= C_v + \frac{P_B C_v}{K_{D_B}} + \frac{P_B C_v}{K_{D_B}} \frac{P_P}{K_s}$$

$$= C_v \left(1 + K_B P_B + \frac{K_B P_P P_B}{K_s} \right)$$

$$C_v = \frac{C_t}{1 + K_B P_B + \frac{K_B P_P P_B}{K_s}}$$

Combining the equations we can write the rate of the reaction as,

$$-r_c = r_{AD} = k_A \left(P_C - \frac{P_B P_P}{K_p} \right) \left(\frac{C_t}{1 + K_B P_B + \frac{K_B P_P P_B}{K_s}} \right)$$

$$= \frac{k_A C_t}{1 + K_B P_B + \frac{K_B P_P P_B}{K_s}} \left(P_C - \frac{P_B P_P}{K_p} \right)$$

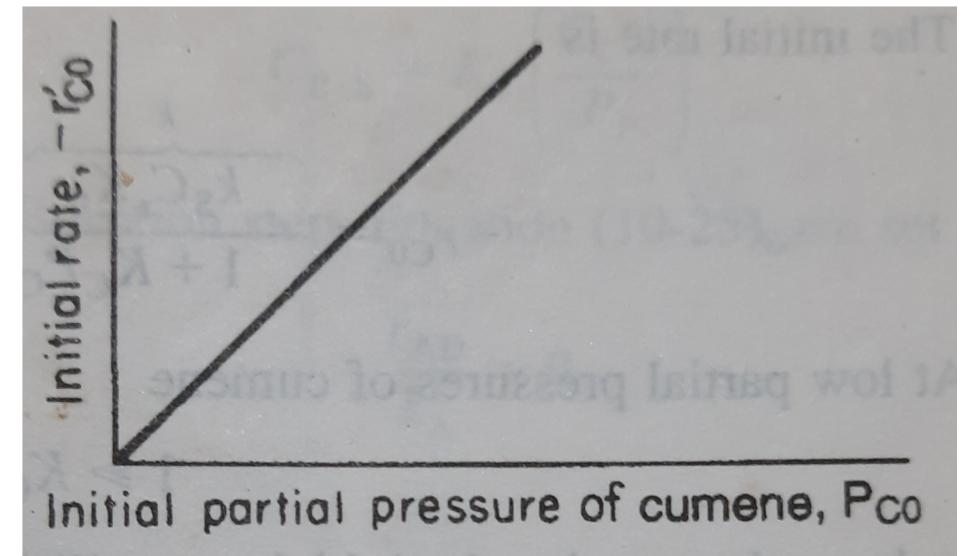
At the initial condition, initial rate ($-r_{C_0}$) can be determined.

$-r_{C_0} = C_t k_A P_{C_0} = k P_{C_0}$ ----(1), P_{C_0} is the initial pressure of C.

Initially there is no product, hence P_B and P_p are zero.

$C_t k_A = k$ constant.

If cumene disproportionation reaction is adsorption controlled, then the experimental data should follow equation (1) and plotting them will form a straight line passing through origin.



Surface Reaction Limited Rate Law

As before, we can determine the rate expression for surface reaction when the process is limited by the surface chemical reaction.

$$-r_c = r_s = \frac{k_s C_t K_C (P_C - \frac{P_P P_B}{K_P})}{1 + P_B K_B + K_C P_C}$$

writing the initial rate expression where P_P and P_B are zero,

Substituting $k_s C_t K_C = K$,

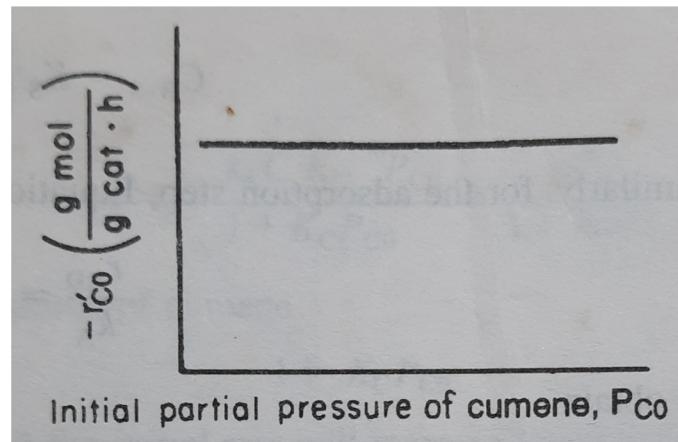
$$-r_{c_0} = \frac{k_s C_t K_C P_{C_0}}{1 + K_C P_{C_0}} = \frac{K P_{C_0}}{1 + K_C P_{C_0}}$$

At low partial pressure of cumene, $1 \gg K_C P_{C_0}$

$\therefore -r_{c_0} = K P_{C_0}$, so, at this condition, rate linearly varies with partial pressure.

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When desorption is the controlling step, plotting experimental data will give a straight line parallel to X axis, which means that the initial rate is independent of the partial pressure of cumene.

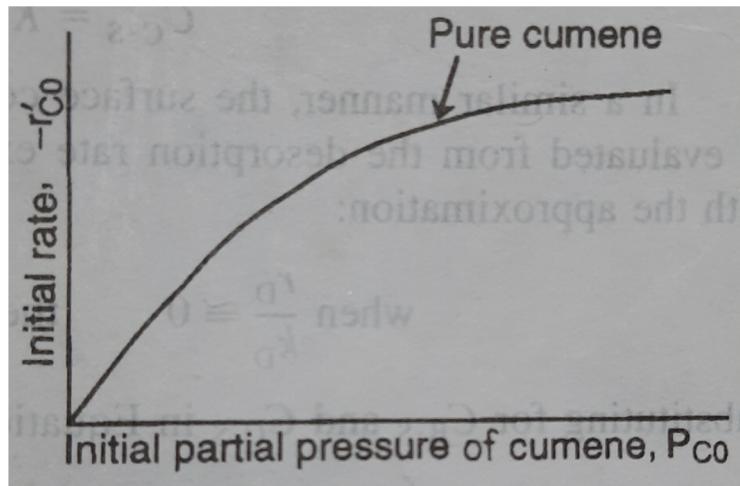


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At high partial pressure of cumene, $1 \ll K_C P_{C_0}$,

The rate equation is written as $-r_{C_0} = \frac{K}{K_C} = \text{constant}$

At this condition, rate is independent of partial pressure.



If the process is surface reaction controlled, then plotting the experimental data will generate the graph as shown here.

Desorption as Rate Limiting Step

When desorption is assumed as the rate limiting step, the rate equation will be

$$-r_C = r_D = \frac{k_D C_t K_S K_C (P_C - \frac{P_P P_B}{K_P})}{P_P + P_C K_C K_S + K_C P_P P_C}$$

To determine the dependence of the initial rate on partial pressure of cumene, setting $P_P = P_B = 0$, the rate law reduces to,

$$-r_{C_0} = k_D C_t = \text{constant}$$