

Catalysis – continue
(Adsorption resistance
controlling)

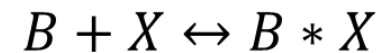
For the catalytic reaction



We will have four main intermediate steps; adsorption of A and B by the surface of the catalyst, surface reaction of both adsorbed A and B, and desorption of the produced C from the surface of the catalyst.

This class we will consider the adsorption of A is the controlling step:

Adsorption (controlling)



Surface Reaction



Desorption



The rate of reaction for controlling step (Adsorption of A) is

$$-r_{Ads.A} = k_{Af} \left(C_A C_v - \frac{C_{A*X}}{K_A} \right)$$

But the surface concentration for B and C were developed previously as

$$C_{B*X} = K_B C_B C_v$$

$$C_{C*X} = K_C C_C C_v$$

But from the surface reaction step we have:

$$K_S = \frac{C_{C*X} C_v}{C_{A*X} C_{B*X}} \quad \longrightarrow \quad C_{A*X} = \frac{C_{C*X} C_v}{K_S C_{B*X}} = \frac{K_C C_C C_v C_v}{K_S K_B C_B C_v} = \frac{K_C C_C C_v}{K_S K_B C_B}$$

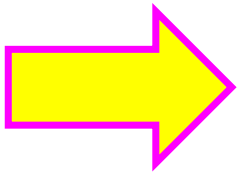
The site balance is

$$C_T = C_{A^*X} + C_{B^*X} + C_{C^*X} + C_v$$

or

$$C_T = \frac{K_C C_C C_v}{K_S K_B C_B} + K_B C_B C_v + K_C C_C C_v + C_v$$

$$C_T = C_v \left(\frac{K_C C_C}{K_S K_B C_B} + K_B C_B + K_C C_C + 1 \right)$$



$$C_v = \frac{C_T}{\left(\frac{K_C C_C}{K_S K_B C_B} + K_B C_B + K_C C_C + 1 \right)}$$

$$-r_{Ads.A} = k_{Af} \left(C_A C_v - \frac{C_{A^*X}}{K_A} \right) = k_{Af} \left(C_A C_v - \frac{\frac{K_C C_C C_v}{K_S K_B C_B}}{K_A} \right) = k_{Af} C_v \left(C_A - \frac{K_C}{K_A K_S K_B} \frac{C_C}{C_B} \right)$$

$$-r_{Ads.A} = k_{Af} C_v \left(C_A - \frac{K_C}{K_A K_S K_B} \frac{C_C}{C_B} \right) \qquad C_v = \frac{C_T}{\left(\frac{K_C C_C}{K_S K_B C_B} + K_B C_B + K_C C_C + 1 \right)}$$

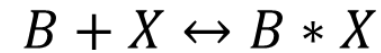
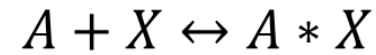
$$-r_{Ads.A} = k_{Af} \frac{C_T}{\left(\frac{K_C C_C}{K_S K_B C_B} + K_B C_B + K_C C_C + 1 \right)} \left(C_A - \frac{K_C}{K_A K_S K_B} \frac{C_C}{C_B} \right)$$

or

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

Catalysis – continue
(Desorption resistance
controlling)

Adsorption



Surface Reaction



Desorption (controlling)



The rate of reaction for controlling step (Desorption of C) is

$$-r_{Des.C} = k_{cf} \left(C_{C*X} - \frac{C_C C_v}{K_C} \right)$$

But the surface concentration for A and B were developed previously as

$$C_{B*X} = K_B C_B C_v$$

$$C_{A*X} = K_A C_A C_v$$

And the surface equilibrium reaction

$$K_S = \frac{C_{C^*X} C_v}{C_{A^*X} C_{B^*X}} \quad \text{Re-arrange to get}$$

$$C_{C^*X} = \frac{K_S C_{A^*X} C_{B^*X}}{C_v}$$

$$C_{C^*X} = \frac{K_S K_A C_A C_v K_B C_B C_v}{C_v}$$

$$C_{B^*X} = K_B C_B C_v$$

$$C_{A^*X} = K_A C_A C_v$$

$$\text{or} \quad C_{C^*X} = K_S K_A K_B C_A C_B C_v$$

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

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

The site balance is

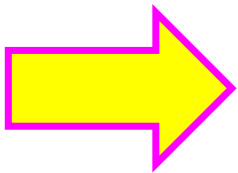
$$C_T = C_{A*X} + C_{B*X} + C_{C*X} + C_v$$

$$C_{C*X} = K_S K_A K_B C_A C_B C_v$$

or

$$C_T = K_A C_A C_v + K_B C_B C_v + K_S K_A K_B C_A C_B C_v + C_v$$

$$C_T = C_v (K_A C_A + K_B C_B + K_S K_A K_B C_A C_B + 1)$$

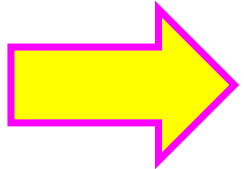


$$C_v = \frac{C_T}{(K_A C_A + K_B C_B + K_S K_A K_B C_A C_B + 1)}$$

Substitute the vacant site in the rate equation

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

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



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

Conclusion

- If the denominator in the rate expression is raised to a power of 2 and contains the expressions $K_A C_A$, $K_B C_B$, and $K_C C_C$, then the controlling step is surface reaction of type I
- If the denominator contains only $K_A C_A$ and $K_C C_C$, then the controlling step is surface reaction of type II where B is reacted in gas phase with adsorbed A
- If the denominator contains a fraction of concentration of a species with respect to other species such as $\frac{C_C}{C_B}$, then adsorption of the remaining species is controlling, here the remaining species is A
- If the denominator contains multiplication of concentration of more than one species such as $C_A C_B$, then a desorption step of the remaining species is controlling. Here the desorption step of the missing species C is the controlling.