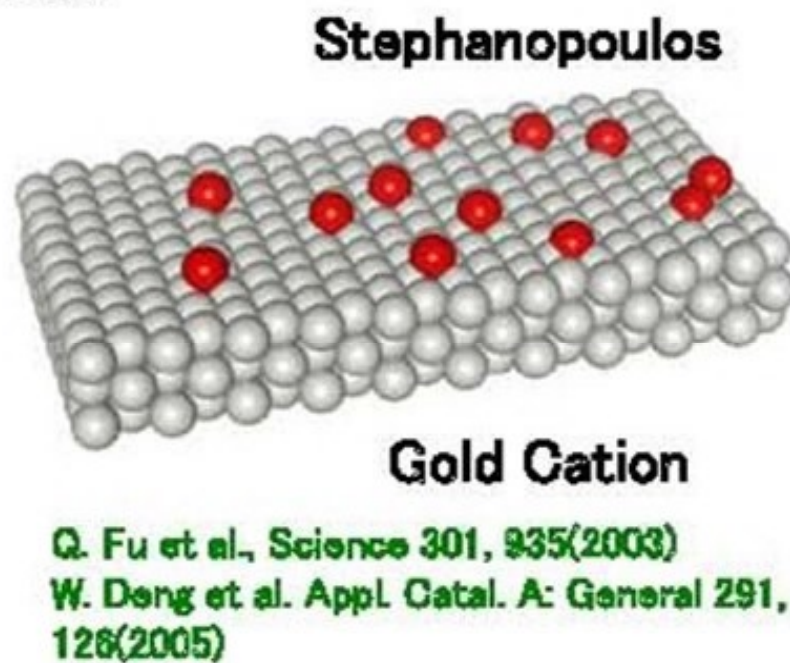
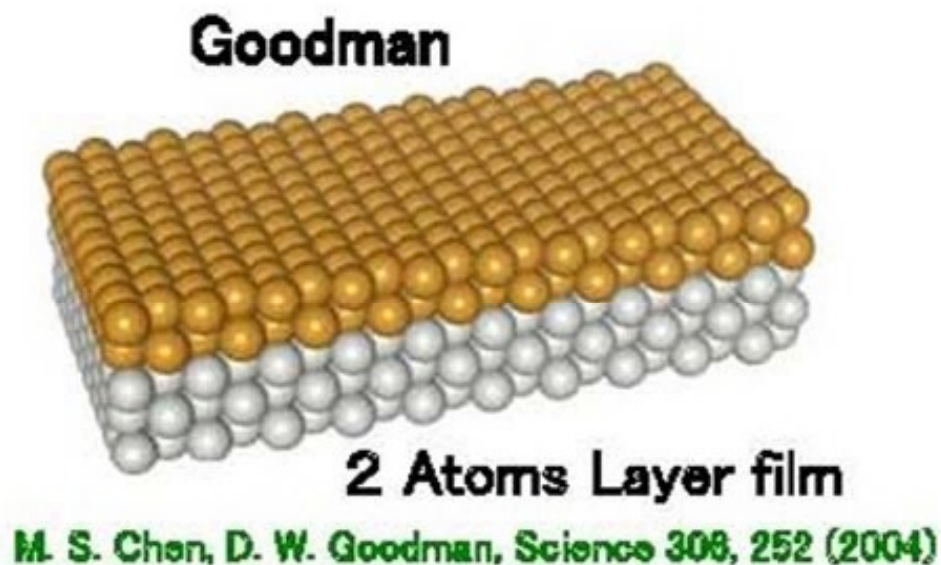


# 化学反应动力学-2

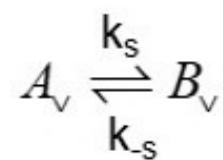
# 金催化剂吸附位和活性位



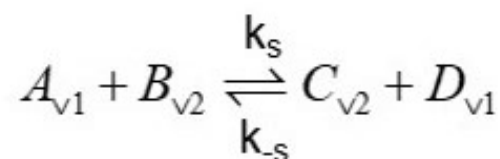
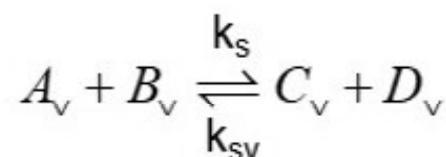
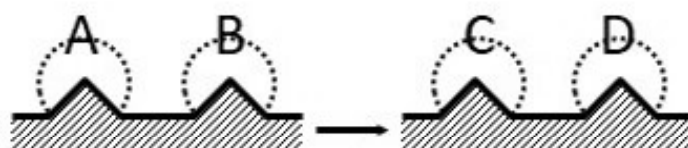
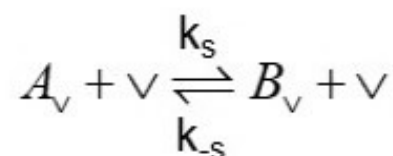
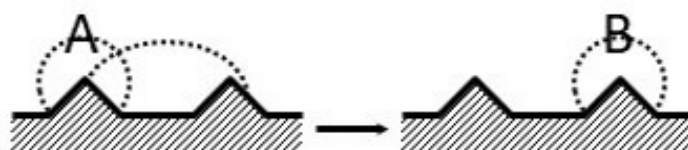
# 表面催化反应

## Langmuir-Hinshwood (L-H) 机理

单活性位

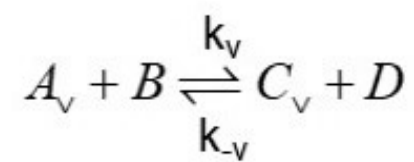
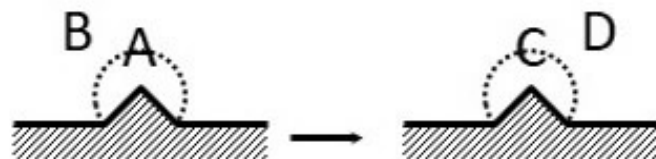


双活性位



# 表面催化反应

## Eley-Rideal (E-R) 机理



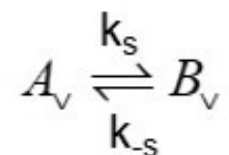


# (单步)基元反应动力学

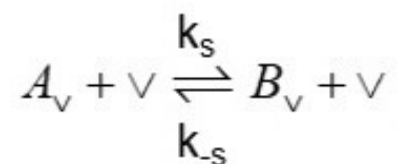
一、对每个表面基元步（包括吸/脱附和反应），把每个参与反应的吸附分子、气体分子、吸附位（可能不止一个，可能有不同），都当作一个反应分子

二、根据基元反应的计量关系直接写出速率方程：

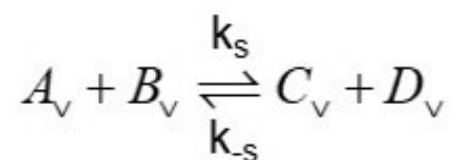
- (1) 表面浓度用覆盖度表示
- (2) 反应级数为基元反应的计量系数



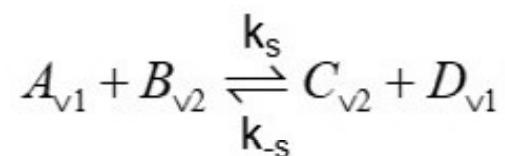
$$r_s = k_s \theta_A - k_{-s} \theta_R$$



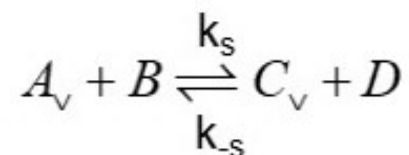
$$r_s = k_s \theta_A \theta_v - k_{-s} \theta_R \theta_v$$



$$r_s = k_s \theta_A \theta_B - k_{-s} \theta_C \theta_D$$



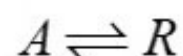
$$r_s = k_s \theta_{A1} \theta_{B2} - k_{-s} \theta_{C2} \theta_{D1}$$



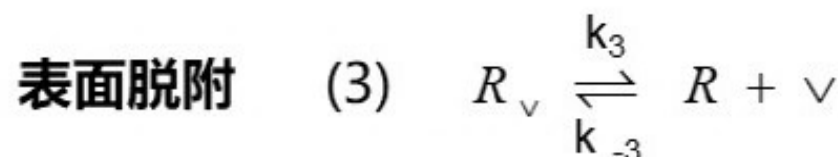
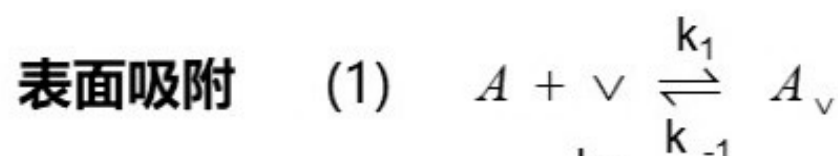
$$r_s = k_s \theta_A P_B - k_{-s} \theta_C P_D$$

# 表面催化反应动力学

## 单分子反应



表面反应机理（基元步，包括吸附和反应）：



第一步：写出  
各基元步的净  
生成速率方程

$$r_1 = k_1 P_A \theta_{\vee} - k_{-1} \theta_A$$

$$r_2 = k_2 \theta_A - k_{-2} \theta_R$$

$$r_3 = k_3 \theta_R - k_{-3} P_R \theta_{\vee}$$

- 如果我们考虑所有的基元步，就是微观动力学，其中有难以测量的表面覆盖度；
- 为了应用的便利，我们要用宏观动力学，其中只有易测量的气相组成（浓度或分压）；
- 为了建立宏观动力学，需要消除表面覆盖度 >>>>>>>

决速步假定  
拟定态假定

# 表面催化反应动力学

基元步

$$\begin{cases} r_1 = k_1 P_A \theta_v - k_{-1} \theta_A \\ r_2 = k_2 \theta_A - k_{-2} \theta_R \\ r_3 = k_3 \theta_R - k_{-3} P_R \theta_v \end{cases}$$



第二步：假定其中某一步为决速步，其他所有步都达到平衡



**决速步：**串联步骤中最慢的一步，决定整个反应的速率

$$r = r_2 = k_2 \theta_A - k_{-2} \theta_R$$

**其他步达到平衡**

$$r_1 = k_1 P_A \theta_v - k_{-1} \theta_A = 0$$

$$\theta_A = \frac{k_1}{k_{-1}} P_A \theta_v = K_A P_A \theta_v$$

$$r_3 = k_3 \theta_R - k_{-3} P_R \theta_v = 0$$

$$\theta_R = \frac{k_{-3}}{k_3} P_R \theta_v = K_R P_R \theta_v$$



# 表面催化反应动力学

$$\theta_A = \frac{k_1}{k_{-1}} P_A \theta_v = K_A P_A \theta_v$$

$$\theta_R = \frac{k_3}{k_{-3}} P_R \theta_v = K_R P_R \theta_v$$



第三步：利用吸附  
位数量平衡，消去  
表面覆盖度



$$\theta_A + \theta_R + \theta_v = 1 \quad K_A P_A \theta_v + K_R P_R \theta_v + \theta_v = 1 \quad \theta_v = \frac{1}{1 + K_A P_A + K_R P_R}$$

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_R P_R} \quad \theta_R = \frac{K_R P_R}{1 + K_A P_A + K_R P_R}$$



# 表面催化反应动力学

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_R P_R} \quad \theta_R = \frac{K_R P_R}{1 + K_A P_A + K_R P_R}$$

$$r = k_2 \theta_A - k_{-2} \theta_R = \frac{k_2 K_A P_A - k_{-2} K_R P_R}{1 + K_A P_A + K_R P_R}$$

# 极端情况

$$r = k_2\theta_A - k_{-2}\theta_R = \frac{k_2K_AP_A - k_{-2}K_RP_R}{1 + K_AP_A + K_RP_R}$$

不可逆

$$r = \frac{k_2K_AP_A}{1 + K_AP_A + K_RP_R}$$

## ■ (A) R 弱吸附

$$r = \frac{k_2K_AP_A}{1 + K_AP_A}$$

(i) 高  $P_A$ ,  $K_AP_A \gg 1$

$$r = k_2$$

零级

(ii) 低  $P_A$ ,  $K_AP_A \ll 1$

$$r = k_2K_AP_A = k_2'P_A$$

一级

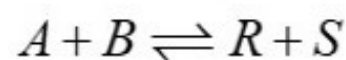
## ■ (B) R 强吸附 $K_RP_R \gg 1 + K_AP_A$

$$r = \frac{k_2K_AP_A}{K_RP_R} = k_2'' \frac{P_A}{P_R}$$

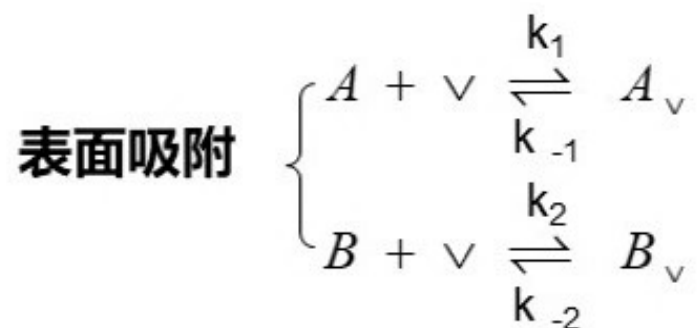
产物负一级

# 表面催化反应动力学

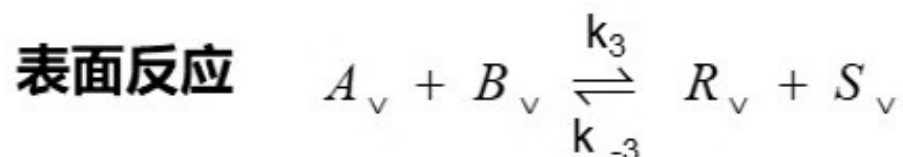
## 双分子反应



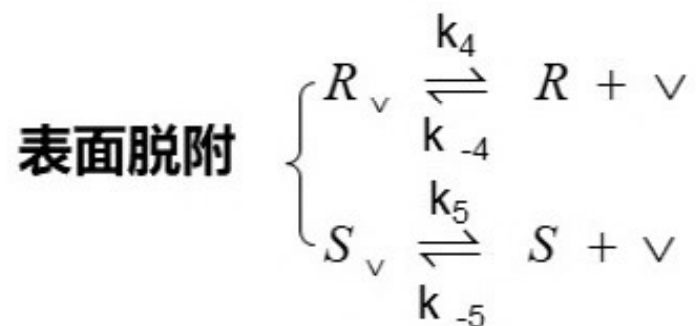
表面吸附



表面反应



表面脱附



第一步：写出  
各基元步的净  
生成速率方程

$$r_1 = k_1 P_A \theta_{\vee} - k_{-1} \theta_A$$

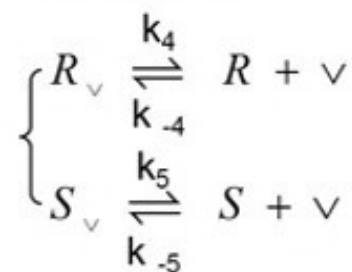
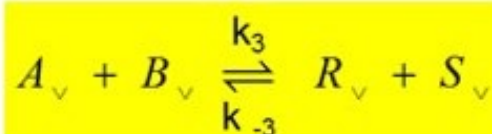
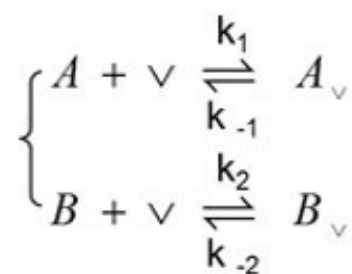
$$r_2 = k_2 P_B \theta_{\vee} - k_{-2} \theta_B$$

$$r_3 = k_3 \theta_A \theta_B - k_{-3} \theta_R \theta_S$$

$$r_4 = k_4 \theta_R - k_{-4} P_R \theta_{\vee}$$

$$r_5 = k_5 \theta_S - k_{-5} P_S \theta_{\vee}$$

# 表面催化反应动力学



第二步：假定其中某一步为决速步，其他所有步都达到平衡

第三步：利用吸附位数量平衡，消去表面覆盖度

$$\theta_A + \theta_B + \theta_R + \theta_S + \theta_{\vee} = 1$$

$$\theta_{\vee} = \frac{1}{(1 + K_A P_A + K_B P_B + K_R P_R + K_S P_S)}$$

$$r = r_3 = k_3 \theta_A \theta_B - k_{-3} \theta_R \theta_S$$

$$k_1 P_A \theta_{\vee} - k_{-1} \theta_A = 0 \longrightarrow \theta_A = K_A P_A \theta_{\vee}$$

$$k_2 P_B \theta_{\vee} - k_{-2} \theta_B = 0 \longrightarrow \theta_B = K_B P_B \theta_{\vee}$$

$$k_4 \theta_R - k_{-4} P_R \theta_{\vee} = 0 \longrightarrow \theta_R = K_R P_R \theta_{\vee}$$

$$k_5 \theta_S - k_{-5} P_S \theta_{\vee} = 0 \longrightarrow \theta_S = K_S P_S \theta_{\vee}$$

$$r = \frac{k_3 K_A K_B P_A P_B - k_{-3} K_R K_S P_R P_S}{(1 + K_A P_A + K_B P_B + K_R P_R + K_S P_S)^2}$$



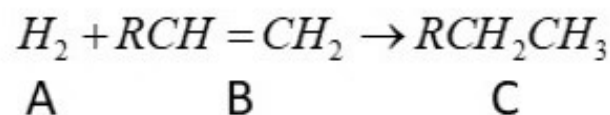
# 极端情况

$$r = \frac{k_3 K_A K_B P_A P_B - k_{-3} K_R K_S P_R P_S}{(1 + K_A P_A + K_B P_B + K_R P_R + K_S P_S)^2} \xrightarrow{\text{不可逆}} r = \frac{k_3 K_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B + K_R P_R + K_S P_S)^2}$$

## (1) R和S弱吸附

$$r = \frac{k_3 K_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B)^2}$$

$$= \frac{k P_A P_B}{(1 + K_A P_A + K_B P_B)^2}$$

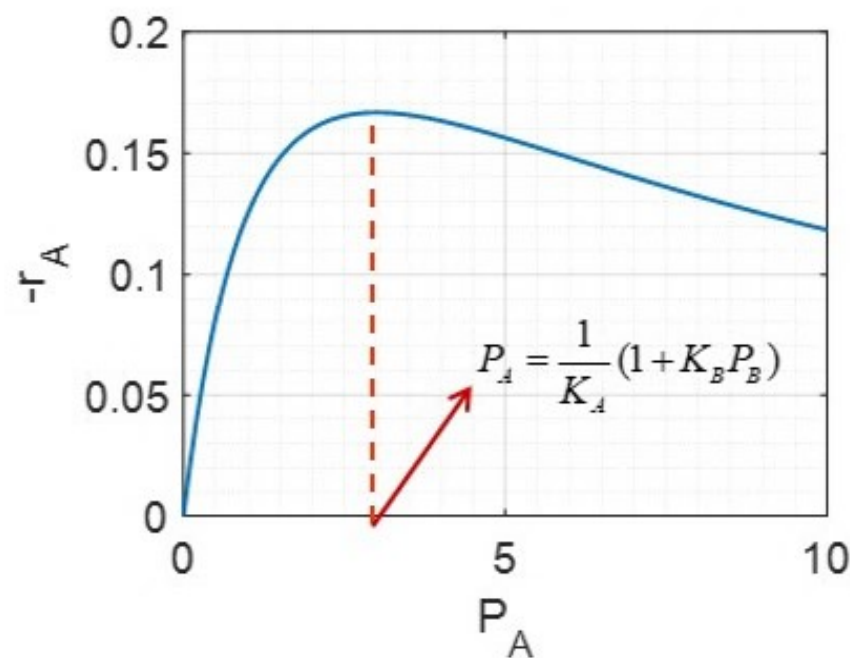


$P_B$  如果恒定, 最大反应速率出现在

$$P_A = \frac{1}{K_A} (1 + K_B P_B)$$

如果A和B强吸附  $r = \frac{k P_A P_B}{(K_A P_A + K_B P_B)^2} \quad \theta_v \approx 0$

最大反应速率出现在  $P_A = \frac{1}{K_A} K_B P_B \quad \theta_A = \theta_B$



$$\theta_A = \theta_v + \theta_B$$

## (2) A和B弱吸附 (如在高温条件下)

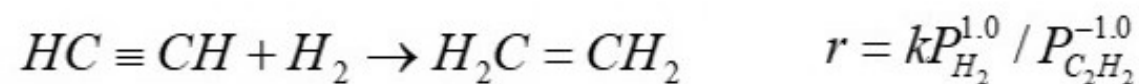
$$1 \gg K_A P_A + K_B P_B$$

$$r = k_3 K_A K_B P_A P_B = k_3' P_A P_B \quad \text{二级反应}$$

## (3) A弱吸附, B强吸附 (如乙炔加氢)

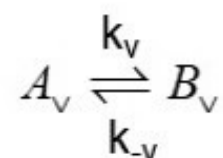
$$r = \frac{k_3 K_A K_B P_A P_B}{(K_B P_B)^2} = k_3'' \frac{P_A}{P_B} \quad \text{B 类似毒物}$$

乙炔加氢



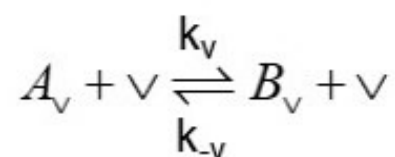
# 表面反应为决速步和不可逆

## 单活性位

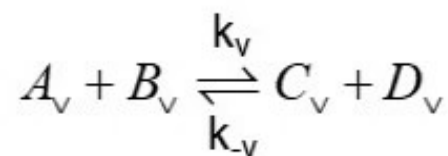


$$r = \frac{kP_A}{1 + K_A P_A + K_R P_R}$$

## 双活性位

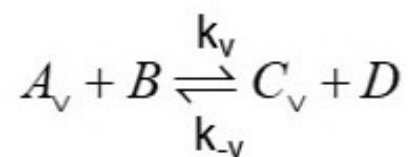


$$r = \frac{kP_A}{(1 + K_A P_A + K_B P_B)^2}$$



$$r = \frac{kP_A P_B}{(1 + K_A P_A + K_B P_B + K_C P_C)^2}$$

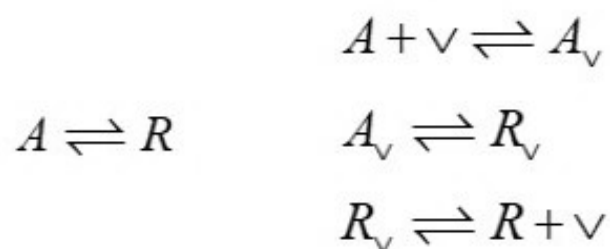
## Eley-Rideal



$$r = \frac{kP_A P_B}{1 + K_A P_A + K_C P_C}$$

# 表面催化反应动力学

## 利用拟定态假定



$$r = \frac{k_2 K_A P_A - k_{-2} K_R P_R}{1 + K_A P_A + K_R P_R}$$

Pseudo-steady-state hypothesis:

$$\begin{array}{l}
 \theta_A \\
 \theta_R
 \end{array}
 \quad \text{在反应中保持不变}$$



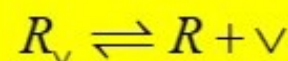
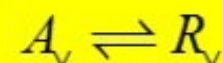
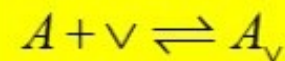
# 拟定态假定

拟定态

$$r_{Av}^* = k_A \theta_v P_A - k_{-A} \theta_A - k_S \theta_A + k_{-S} \theta_R = 0$$

拟定态

$$r_{Rv}^* = k_S \theta_A - k_{-S} \theta_R - k_R \theta_R + k_{-R} P_R \theta_v = 0$$



$$k_A \theta_v P_A - (k_{-A} + k_S) \theta_A + k_{-S} \theta_R = 0 \quad k_S \theta_A - (k_{-S} + k_R) \theta_R + k_{-R} P_R \theta_v = 0$$

吸附位  
数量平衡

$$\theta_A + \theta_R + \theta_v = 1 \quad \theta_v = 1 - (\theta_A + \theta_R)$$

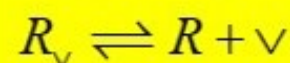
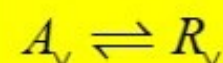
$$\begin{cases} k_A [1 - (\theta_A + \theta_R)] P_A - (k_{-A} + k_S) \theta_A + k_{-S} \theta_R = 0 \\ k_S \theta_A - (k_{-S} + k_R) \theta_R + k_{-R} P_R [1 - (\theta_A + \theta_R)] = 0 \end{cases}$$

$$\Rightarrow \begin{cases} k_A P_A - (k_A P_A + k_{-A} + k_S) \theta_A + (k_{-S} - k_A P_A) \theta_R = 0 \\ k_{-R} P_R + (k_S - k_{-R} P_R) \theta_A - (k_{-S} + k_R + k_{-R} P_R) \theta_R = 0 \end{cases}$$

# 拟定态假定

$$k_A P_A - (k_A P_A + k_{-A} + k_S) \theta_A + (k_{-S} - k_A P_A) \theta_R = 0$$

$$k_{-R} P_R + (k_S - k_{-R} P_R) \theta_A - (k_{-S} + k_R + k_{-R} P_R) \theta_R = 0$$



$$\theta_A = \frac{P_A k_A k_R + P_A k_A k_S + P_R k_R k_S}{k_R k_S + k_R k_A + k_A k_S + P_A k_A k_R + P_A k_A k_S + P_A k_A k_S + P_R k_S k_R + P_R k_A k_R + P_R k_R k_S}$$

$$\theta_R = \frac{P_A k_A k_S + P_R k_S k_R + P_R k_A k_R}{k_R k_S + k_R k_A + k_A k_S + P_A k_A k_R + P_A k_A k_S + P_A k_A k_S + P_R k_S k_R + P_R k_A k_R + P_R k_R k_S}$$

$$\theta_v = \frac{k_R k_S + k_R k_A + k_A k_S}{k_R k_S + k_R k_A + k_A k_S + P_A k_A k_R + P_A k_A k_S + P_A k_A k_S + P_R k_S k_R + P_R k_A k_R + P_R k_R k_S}$$

$$-r_A = k_A P_A \theta_v - k_{-A} \theta_A$$

$$= \frac{P_A k_A k_R k_S - P_R k_A k_R k_S}{k_R k_S + k_R k_A + k_A k_S + P_A k_A k_R + P_A k_A k_S + P_A k_A k_S + P_R k_S k_R + P_R k_A k_R + P_R k_R k_S}$$

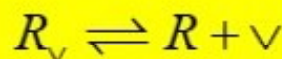
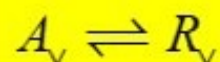
# 拟定态和决速步假定对比

$$-r_A = \frac{k_A k_R k_S P_A - k_{-A} k_{-R} k_{-S} P_R}{k_R k_S + k_R k_{-A} + k_{-A} k_{-S} + (k_A k_R + k_A k_S + k_{-A} k_{-S}) P_A + (k_S k_{-R} + k_{-A} k_{-R} + k_{-R} k_{-S}) P_R}$$

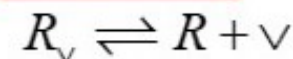
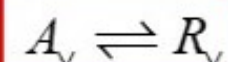
$$k_1 = \frac{k_A k_R k_S}{k_R k_S + k_R k_{-A} + k_{-A} k_{-S}}, k_{-1} = \frac{k_{-A} k_{-R} k_{-S}}{k_R k_S + k_R k_{-A} + k_{-A} k_{-S}}$$

$$K_A = \frac{k_A k_R + k_A k_S + k_{-A} k_{-S}}{k_R k_S + k_R k_{-A} + k_{-A} k_{-S}}, K_R = \frac{k_S k_{-R} + k_{-A} k_{-R} + k_{-R} k_{-S}}{k_R k_S + k_R k_{-A} + k_{-A} k_{-S}}$$

$$-r_A = \frac{k_1 P_A - k_{-1} P_R}{1 + K_A P_A + K_R P_R}$$

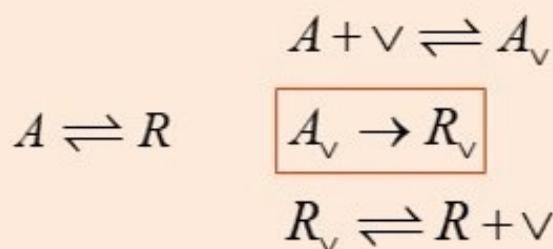


$$-r_A = \frac{k_2 K_A P_A - k_{-2} K_R P_R}{1 + K_A P_A + K_R P_R}$$



# 表面催化反应动力学

决速步假定



$$-r_A = \frac{kP_A}{1 + K_A P_A + K_R P_R}$$



拟定态假定

如果  $k_{-s}$  很小  
 $k_{-1} \approx 0$

$$-r_A = \frac{k_1 P_A - k_{-1} P_R}{1 + K_A P_A + K_R P_R}$$



$$r = \frac{kP_A}{1 + K_A P_A + K_R P_R}$$

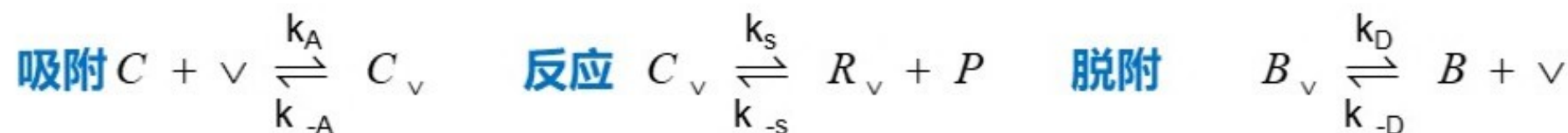
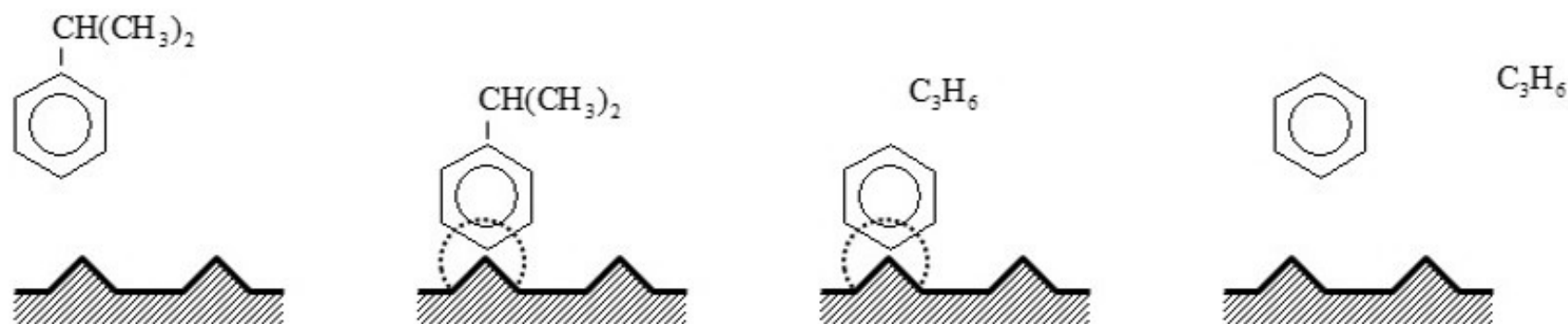
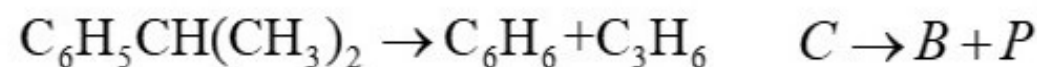
$$k_{-1} = \frac{k_{-R} k_{-S}}{\frac{k_R k_S}{k_{-A}} + (k_R + k_{-S})}$$

$k_s, k_{-s}$ : 表面反应速率常数

**SSHP适用于多步为动力学相关步的情况!**



# 表面反应机理辨识



吸附为速控步

$$r_1 = \frac{k_A(P_C - P_P P_B / K_P)}{1 + K_B P_P P_B / K_S + K_B P_B} \quad K_P = \frac{K_S K_C}{K_B} = K_P$$

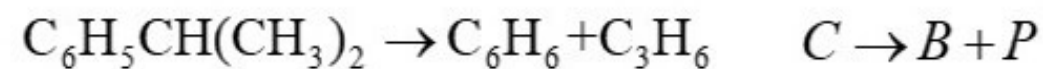
反应为速控步

$$r_2 = \frac{k_S K_C (P_C - P_P P_B / K_P)}{1 + K_B P_B + K_C P_C}$$

脱附为速控步

$$r_3 = \frac{k_D K_S K_C (P_C - P_P P_B / K_P)}{P_P + P_C K_C K_S + K_C P_P P_C}$$

# 表面反应机理辨识

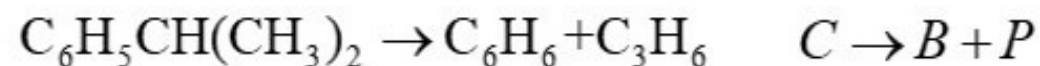


$$r_1 = \frac{k_A(P_C - P_P P_B / K_P)}{1 + K_B P_P P_B / K_S + K_B P_B}$$

$$r_2 = \frac{k_s K_C (P_C - P_P P_B / K_P)}{1 + K_B P_B + K_C P_C}$$

$$r_3 = \frac{k_D K_s K_C (P_C - P_P P_B / K_P)}{P_P + P_C K_C K_s + K_C P_P P_C}$$


# 表面反应机理辨识



$$r_1 = \frac{k_A(P_C - P_P P_B / K_P)}{1 + K_B P_P P_B / K_S + K_B P_B}$$

$$r_2 = \frac{k_s K_C (P_C - P_P P_B / K_P)}{1 + K_B P_B + K_C P_C}$$

$$r_3 = \frac{k_D K_s K_C (P_C - P_P P_B / K_P)}{P_P + P_C K_C K_s + K_C P_P P_C}$$

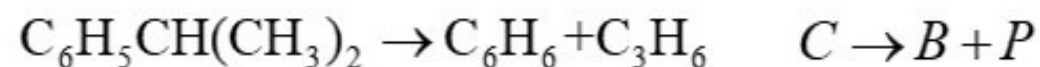
$$P_P = P_B \doteq 0$$


$$r_{10} = k_A P_{C0}$$

$$r_{20} = \frac{k P_{C0}}{1 + K_C P_{C0}}$$

$$r_{30} = k_D$$

# 表面反应机理辨识



$$r_1 = \frac{k_A(P_C - P_P P_B / K_P)}{1 + K_B P_P P_B / K_S + K_B P_B}$$

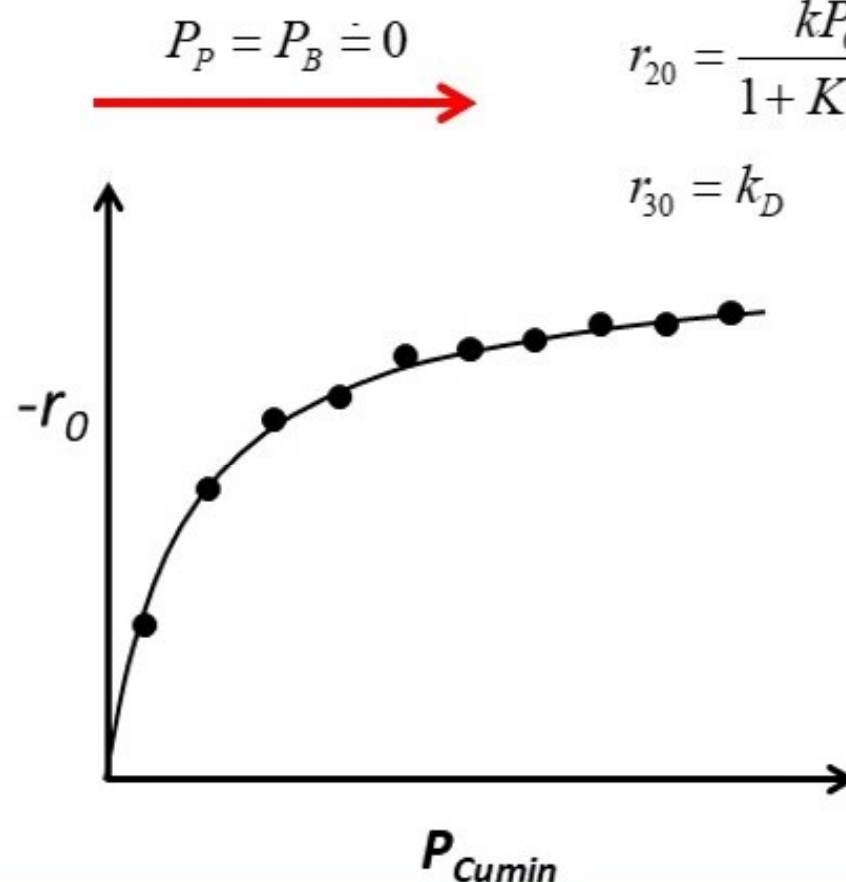
$$r_2 = \frac{k_s K_C (P_C - P_P P_B / K_P)}{1 + K_B P_B + K_C P_C}$$

$$r_3 = \frac{k_D K_s K_C (P_C - P_P P_B / K_P)}{P_P + P_C K_C K_s + K_C P_P P_C}$$

$$r_{10} = k_A P_{C0}$$

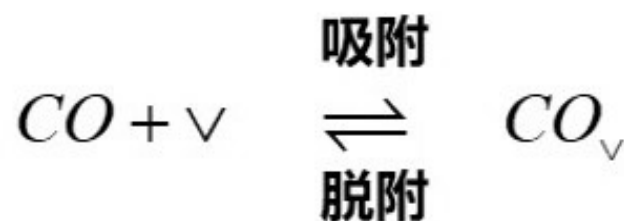
$$r_{20} = \frac{k P_{C0}}{1 + K_C P_{C0}}$$

$$r_{30} = k_D$$





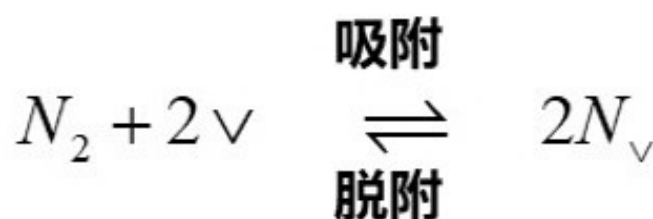
# 焦姆金吸附



朗格缪尔  
吸附

$$r_a = k_A P_{CO} C_v = k_{A0} e^{-E_a/RT} P_{CO} \theta_v$$

$$r_d = k_{-A0} e^{-E_d/RT} \theta_{CO_v}$$



焦姆金 (Temkin)  
吸附

$$E_a = E_a^0 + \alpha \theta_A$$

$$E_d = E_d^0 - \beta \theta_A$$

吸附速率

$$= k_{A0} e^{-(E_a + \alpha \theta_N)/RT} P_{N_2} f(\theta_N) = k'_A P_{N_2} e^{-g \theta_N}$$

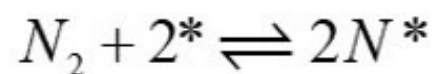
脱附速率

$$= k_{-A0} e^{-(E_d - \beta \theta_N)/RT} f'(\theta_N) = k'_{-A} e^{h \theta_N}$$

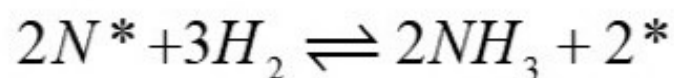
$$r_a = r_d \quad \theta_N = \frac{1}{g+h} \ln\left(\frac{k'_A}{k'_{-A}} P_{N_2}\right) = \frac{1}{f} \ln(K_A P_{N_2})$$

适用于吸附覆盖度不大不小的情况

# 基于焦姆金吸附的反应动力学



决速步



平衡步

平衡步  $\left(\frac{\theta_N}{\theta_v}\right)^2 = \frac{P_{NH_3}^2}{P_{H_2}^3 K_2}$   $\left(\frac{\theta_N}{\theta_v}\right)^2 \equiv K_1 P_{N_2}^*$

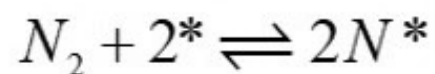
$P_{N_2}^*$  与表面覆盖度达平衡的 $N_2$ 分压。

$P_{N_2}^* \neq P_{N_2}$   $N_2$ 吸附为速控步骤。

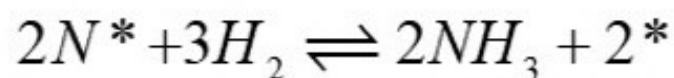
➔  $P_{N_2}^* = \frac{P_{NH_3}^2}{P_{H_2}^3 K_1 K_2}$

➔  $\theta_N = \frac{1}{f} \ln(K_A P_{N_2}^*) = \frac{1}{f} \ln\left(\frac{K_A}{K_1 K_2} \frac{P_{NH_3}^2}{P_{H_2}^3}\right)$

# 基于焦姆金吸附的反应动力学



决速步



平衡步

$$\theta_N = \frac{1}{f} \ln(K_A P_{N_2}^*) = \frac{1}{f} \ln\left(\frac{K_A}{K_1 K_2} \frac{P_{NH_3}^2}{P_{H_2}^3}\right)$$

决速步  $r_{NH_3} = k_A P_{N_2} e^{-g\theta_N} - k_{-A} e^{h\theta_N}$

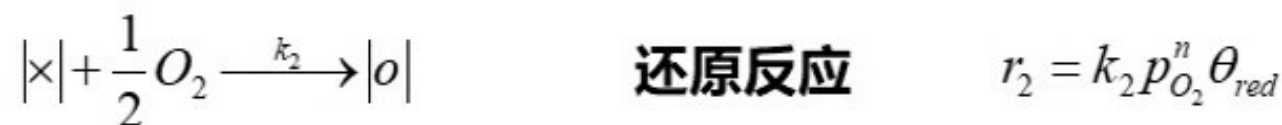
$$= k_A P_{N_2} \left(\frac{P_{H_2}^3}{P_{NH_3}^2}\right)^a - k_{-A} \left(\frac{P_{NH_3}^2}{P_{H_2}^3}\right)^b \quad \xrightarrow{a \doteq b \doteq 0.5}$$

$$= k_1 P_{N_2} \frac{P_{H_2}^{1.5}}{P_{NH_3}} - k_2 \frac{P_{NH_3}}{P_{H_2}^{1.5}}$$

# Mars-van Krevelen 动力学

金属氧化物催化反应物氧化的过程中，反应物首先与金属氧化物中的晶格氧反应，然后氧气再与金属氧化物反应，完成一次催化循环（Redox）。

催化剂表面的结晶氧和氧空穴覆盖度分别为  $\theta_{ox}$ ,  $\theta_{red}$        $\theta_{ox} + \theta_{red} = 1$



$$-r_A = r_1 = r_2 = \frac{1}{\frac{1}{k_1 p_A^m} + \frac{b}{k_2 p_{O_2}^n}} \quad \begin{cases} -r_A = \frac{k_2}{b} p_{O_2}^n & \text{氧化速率控制} \\ -r_A = k_1 p_A^m & \text{还原速率控制} \end{cases}$$

$|o|$  晶格氧       $|\times|$  氧空穴



# LH-MK 动力学

反应物首先在晶格氧上发生化学吸附：



然后发生氧化反应：



催化剂氧化反应：



$$-r_A = \frac{k_r K_A p_A}{[1 + K_A p_A + \frac{b K_A k_r}{k_2} (\frac{p_A}{p_{O_2}})]}$$

