

Lectures for Graduates at DICP-2007

催化反应动力学-II

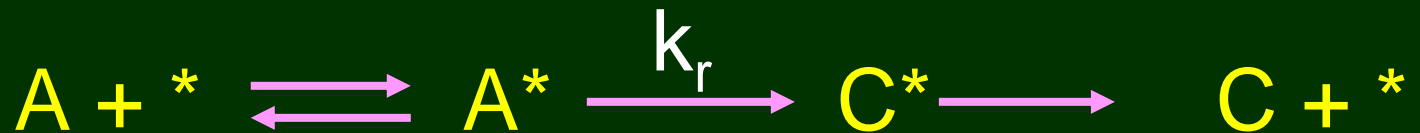
Principal of Catalytic Kinetics

徐柏庆

bqxu@mail.tsinghua.edu.cn

8. Rate equation of surface catalysis: 考虑逆反应时的 rate equation

1). 单一反应物: $A \longrightarrow C$



基元步骤	速控步	动力学项	推动力项	吸附项	n
$A + * \rightleftharpoons A^*$	I	k_1	$P_A - P_C / K$	$1 + (1 + 1/K_2) P_B / K_3$	1
$A^* \rightleftharpoons C^*$	II	$k_2 K_1$	$P_A - P_C / K$	$1 + K_1 P_A + P_B / K_3$	1
$C^* \rightleftharpoons C + *$	III	$k_3 K_1 K_2$	$P_A - P_C / K$	$1 + (1 + K_2) K_1 P_A$	1

$$\text{Rate} = \frac{(\text{Kinetic factor}) \cdot (\text{Driving force})}{(\text{Adsorption term})^n}$$

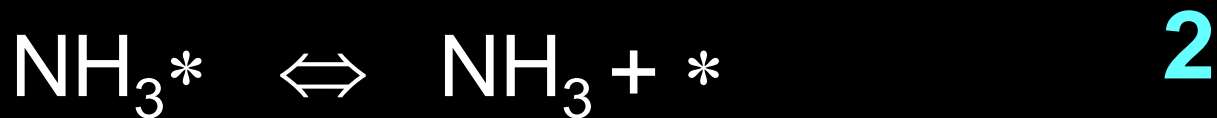
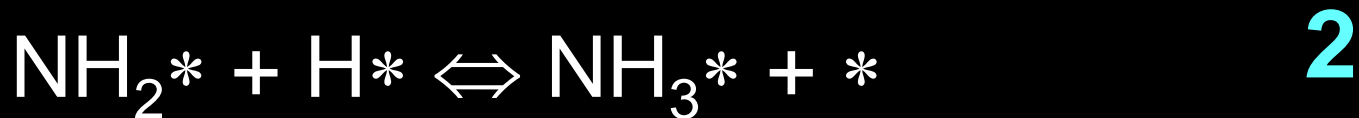
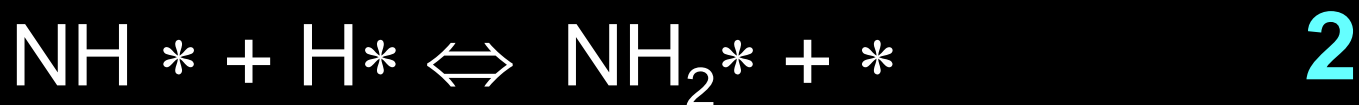
Kinetic factor — 总是包含决速步骤速率常数，活性位的浓度和吸附平衡常数。

Driving force — 代表总反应到达热力学平衡的化学结合力。它跟反应物浓度与它平衡浓度间的差。不含跟催化剂相关参数，反映催化剂不影响化学平衡。

Adsorption term — 代表由于吸附造成的总反应速率的减小，包含每一项能反映活性位在不同表面吸附物种和表面空位中的分布。

***** 如果涉及解离吸附，应包含分压的平方根项； n 为决速步骤所涉及的活性位的数目， $n = 0, 1, 2$.**

2). Kinetics of Ammonia Synthesis



Fe 催化剂上, N_2 吸附是合成 rxn 的 rds,
 N_2 脱附为分解 rxn 的 rds.

1). 对于 N_2 吸附而言, 假定吸附热随 θ 变化呈线性下降 (Temkin 关系):

$$\begin{aligned} r_a &= k_a p_{N_2} \exp(-E_a/RT) \\ &= k_a p_{N_2} \exp[-(E_{a_0} + \alpha\theta_{N_2})/RT] \\ &= k_{a_0} p_{N_2} \exp(-\alpha\theta_{N_2}/RT) \end{aligned}$$

因吸附步为 rds, 不能建立平衡。假设此时与真实的 θ_{N_2} 相平衡的氮气的分压为 $P_{N_2}^*$, 按 Temkin 方程:

$$\theta_{N_2} = \frac{1}{f} \ln(a_0 P_{N_2}^*)$$

由合成氨总反应的平衡关系:

$$\theta_{N_2} = \frac{1}{f} \ln(a_0 P_{NH_3}^2 / K P_{H_2}^3)$$

$$P_{N_2}^* = \frac{P_{NH_3}^2}{K P_{H_2}^3}$$

$$r_a = k_{a_0} p_{N_2} \exp \left[-\frac{\alpha}{RT} \frac{1}{f} \ln(a_0 p_{NH_3}^2 / K p_{H_2}^3) \right]$$

$$r_a = k_{a_0} p_{N_2} \left(\frac{K p_{H_2}^3}{a_0 p_{NH_3}^2} \right)^{\frac{\alpha}{\alpha + \beta}} = k_+ p_{N_2} \left(\frac{p_{H_2}^3}{p_{NH_3}^2} \right)^{\alpha'}$$

$$f = \frac{\alpha + \beta}{RT}$$

其中:

$$k_+ = k_{a_0} \left(\frac{K}{a_0} \right)^{\alpha'}$$

$$\alpha' = \frac{\alpha}{\alpha + \beta}$$

2). 对氨分解过程的 **rds** 作类似处理, 有:

$$r_d = k_{d0} \left(\frac{a_0 p_{\text{NH}_3}^2}{K p_{\text{H}_2}^3} \right)^{\frac{\alpha}{\alpha+\beta}} = k_- \left(\frac{p_{\text{NH}_3}^2}{p_{\text{H}_2}^3} \right)^{1-\alpha'}$$

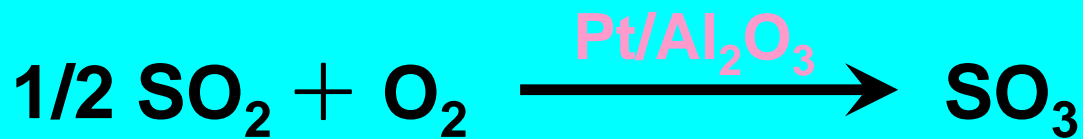
$$k_- = k_{d0} \left(\frac{a_0}{K} \right)^{1-\alpha'}$$

于是, 得到合成氨反应的净速率为:

当 $\alpha' = 0.5$ 时,
由该方程与实验结果相吻合!!

$$r = k_+ P_{\text{N}_2} \left(\frac{P_{\text{H}_2}^3}{P_{\text{NH}_3}^2} \right)^{\alpha'} - k_- \left(\frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3} \right)^{1-\alpha'}$$

3. 依据可能的反应机理建立催化反应动力学方程例举

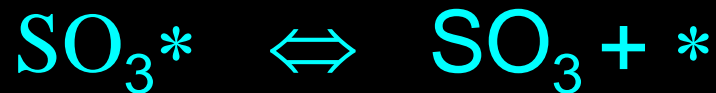
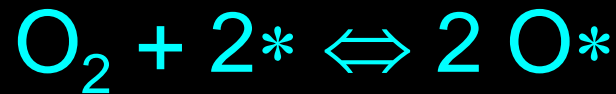


表、二氧化硫在 $\text{Pt/Al}_2\text{O}_3$ 上氧化的动力学测试结果

速率 (mol/h·g)	P_{SO_3} /kPa	P_{SO_2} /kPa	P_{O_2} /kPa
0.02	4.33	2.58	18.8
0.04	3.35	3.57	19.2
0.06	2.76	4.14	19.6
0.08	2.39	4.49	19.8
0.10	2.17	4.70	19.9
0.12	2.04	4.82	20.0



设想反应按照 Eley-Rideal 机理进行:



总包反应平衡常数: $K = \lambda_{\text{O}_2}^{1/2} K_2 (1 / \lambda_{\text{SO}_3})$

表面反应是 **rds**, 其速率即为总反应速率:

$$r = r_2 = k_+ P_{\text{SO}_2} \theta_{\text{O}} - k_- \theta_{\text{SO}_3}$$

O₂分子的解离吸附用 Langmuir 模型处理:

$$\theta_{\text{O}_2} = \frac{\lambda_{\text{O}_2}^{1/2} P_{\text{O}_2}^{1/2}}{1 + \lambda_{\text{O}_2}^{1/2} P_{\text{O}_2}^{1/2} + \lambda_{\text{SO}_3} P_{\text{SO}_3}}$$

$$\theta_{\text{SO}_3} = \frac{\lambda_{\text{SO}_3} P_{\text{SO}_3}}{1 + \lambda_{\text{O}_2}^{1/2} P_{\text{O}_2}^{1/2} + \lambda_{\text{SO}_3} P_{\text{SO}_3}}$$

$$r = r_2 = k_+ P_{\text{SO}_2} \theta_{\text{O}_2} - k_- \theta_{\text{SO}_3}$$

$$K_2 = \frac{k_{2+}}{k_{2-}} = \frac{k_+}{k_-}$$

$$r = \frac{k_+ P_{\text{SO}_2} \lambda_{\text{O}_2}^{1/2} P_{\text{O}_2}^{1/2} - k_- \lambda_{\text{SO}_3} P_{\text{SO}_3}}{1 + \lambda_{\text{O}_2}^{1/2} P_{\text{O}_2}^{1/2} + \lambda_{\text{SO}_3} P_{\text{SO}_3}}$$

$$K = \lambda_{\text{O}_2}^{1/2} K_2 / \lambda_{\text{SO}_3}$$

$$r = \frac{k_+ \lambda_{\text{O}_2}^{1/2} (p_{\text{SO}_2} p_{\text{O}_2}^{1/2} - p_{\text{SO}_3} / K)}{1 + \lambda_{\text{O}_2}^{1/2} p_{\text{O}_2}^{1/2} + \lambda_{\text{SO}_3} p_{\text{SO}_3}}$$

在过量氧气存在下，
反应中 P_{O_2} 近似为常数，
上式可简化为：

$$r = \frac{P_{O_2}^{1/2} P_{SO_2} - \frac{1}{K} P_{SO_3}}{A + B P_{SO_3}}$$

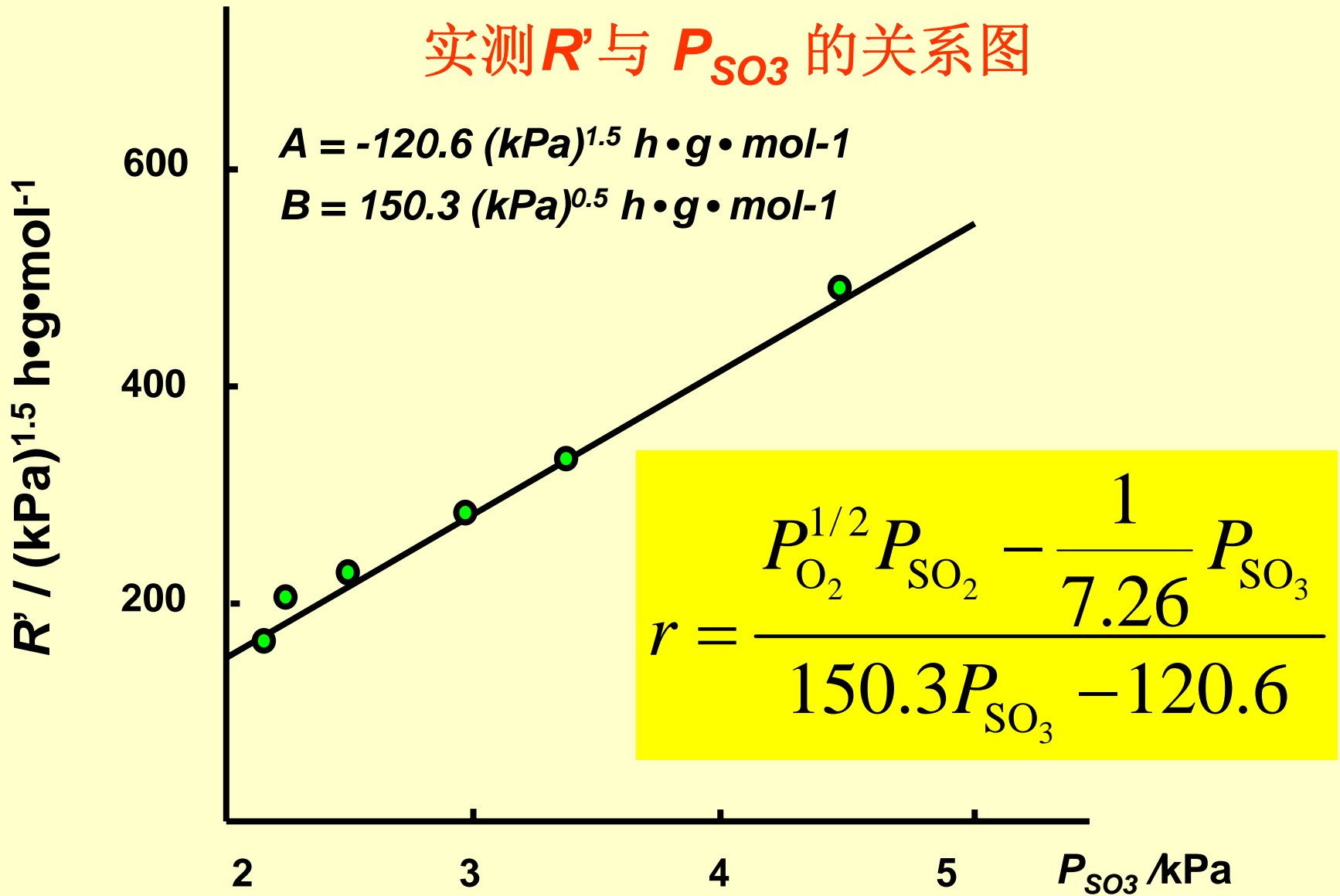
A、B为常数

$$A + B P_{SO_3} = \frac{P_{O_2}^{1/2} P_{SO_2} - \frac{1}{K} P_{SO_3}}{r} = R'$$

$$R' = \frac{p_{O_2}^{1/2} p_{SO_2} - p_{SO_3} / K}{r} = A + B p_{SO_3}$$

****** 利用实测的 r , P_{O_2} , P_{SO_2} 和 P_{SO_3} 求出 R' ，再对 P_{SO_3} 作图，
即可判断它与实验数据符合的程度。

实测 R' 与 P_{SO_3} 的关系图



Rxn space velocity

(反应空速):

(VH) SV & WHSV

**Rxn contact time or
rxn space time**

(反应的接触时间):

$$\tau = ST = V_{cat} / F_A$$

Rxn space time yield

(时空产率 / 时空收率)

9. Determination of Rxn Order

1). Determination of overall rxn order

反应类型: $a A \rightarrow P$



写出微分方程式:

$$r = -dc_A / dt = akc_A^n$$

拟定实验方案: ① 测定一组 $c \sim t$ 数据

② 测定多组 $c \sim t$ 数据

(1) Integral methods

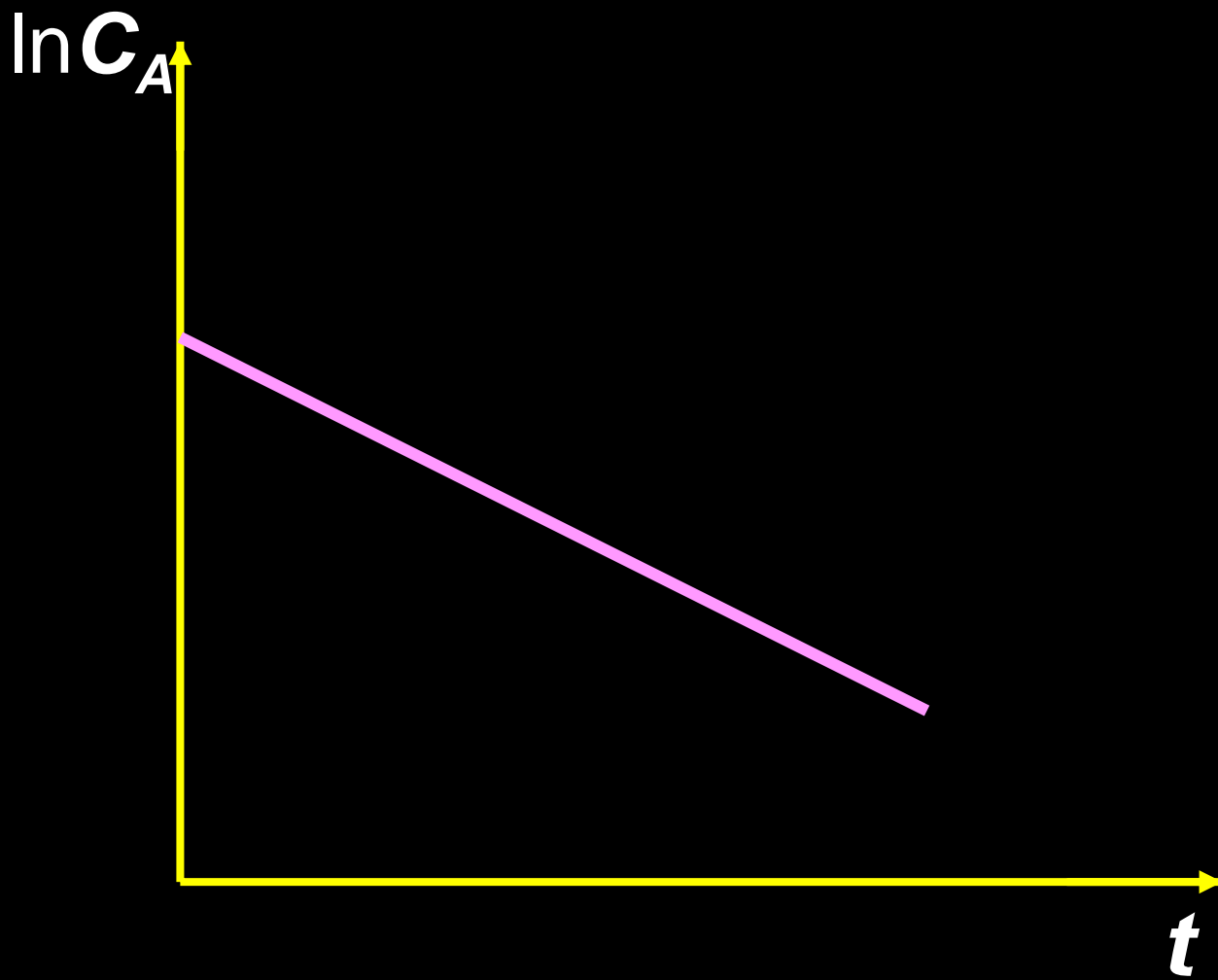
依据速率方程式积分形式的特点来确定反应级数

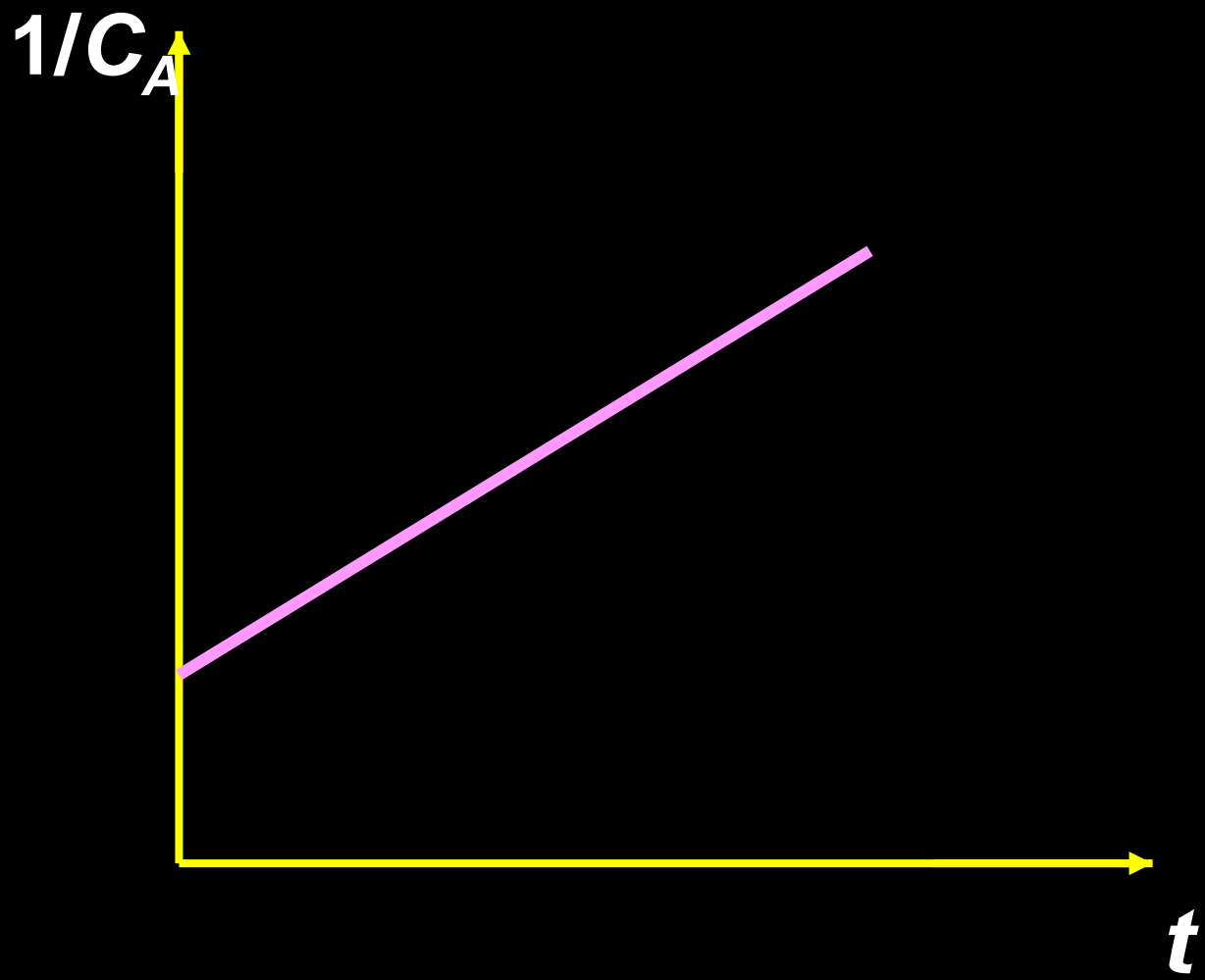
① Trial method (尝试法):

将不同时刻的速率和浓度数据带入不同级数的速率方程式求 k 值,若为一常数,则级数可确定.

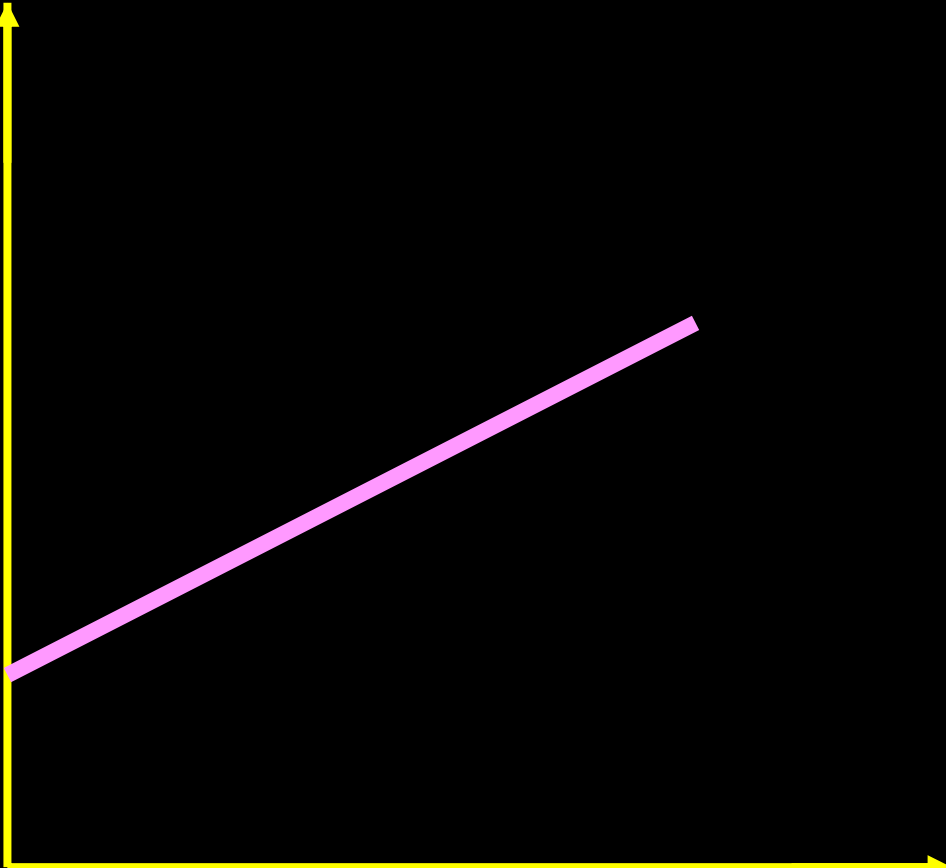
② Graphic method (图解法):

利用不同级数反应的线性关系





$1/C_A^2$



t

(2) Differential method

$$r = kc_A^n$$

$$\ln r = \ln k + n \ln c_A$$

图解法： $\ln r \sim \ln c_A$ 作图， 直线斜率：**n**

$$\text{解析法： } \ln \frac{r_1}{r_2} = n \ln \frac{c_{A,1}}{c_{A,2}}$$

2). Determination of partial order

$$r = kc_A^\alpha c_B^\beta \dots$$

(1). 改变反应物比例的初（始）速度方法

设计一组实验，每次改变一种物质的初始浓度，保持其它物质起始浓度不变，测定反应初始速率随该反应物起始浓度的变化关系，确定该反应物的分级数。

$$\frac{r_0'}{r_0''} = \left(\frac{c_{A,0}'}{c_{A,0}''} \right)^\alpha$$

$$\alpha = \frac{\ln\left(\frac{r_0'}{r_0''}\right)}{\ln\left(\frac{c_{A,0}'}{c_{A,0}''}\right)}$$

Why do we use initial rxn rates?

(2) Excess method

保持: $C_B, C_D, \dots \gg C_A$

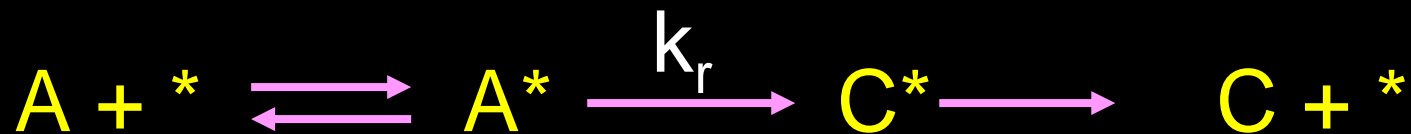
$$r = k' C_A^\alpha$$

用前面的各种方法求 α

Remarks:

- ① 反应条件不同, 级数可能不同
- ② 有时实验方法不同, 级数也可能不同
- ③ 并非所有的反应都有明确的级数

对于如下表面催化过程:



基元步骤	速控步	动力学项	推动力项	吸附项	n
$A + * \rightleftharpoons A^*$	I	k_1	$P_A - P_C/K$	$1 + (1 + 1/K_2) P_B/K_3$	1
$A^* \rightleftharpoons C^*$	II	$k_2 K_1$	$P_A - P_C/K$	$1 + K_1 P_A + P_B/K_3$	1
$C^* \rightleftharpoons C + *$	III	$k_3 K_1 K_2$	$P_A - P_C/K$	$1 + (1 + K_2) K_1 P_A$	1

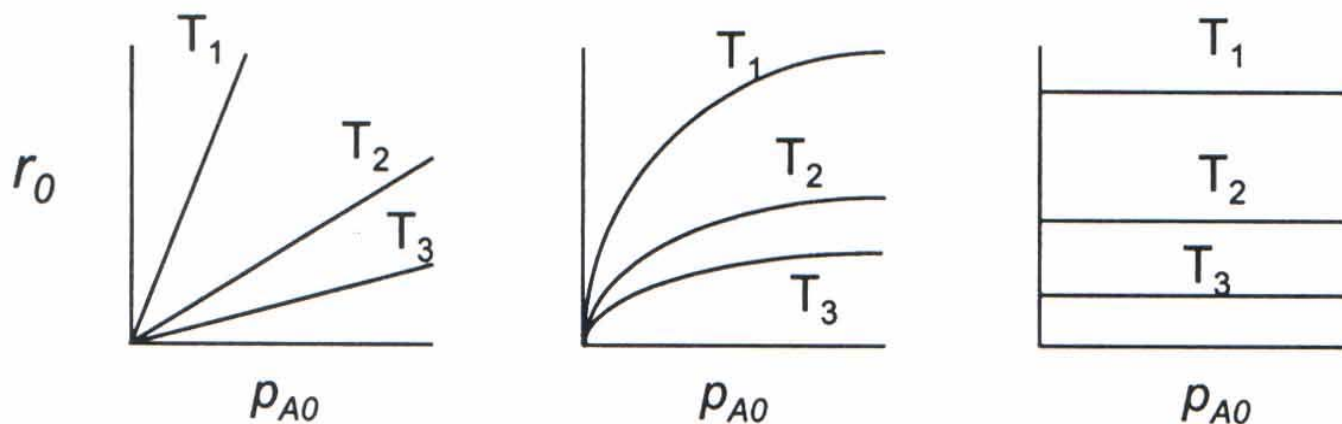
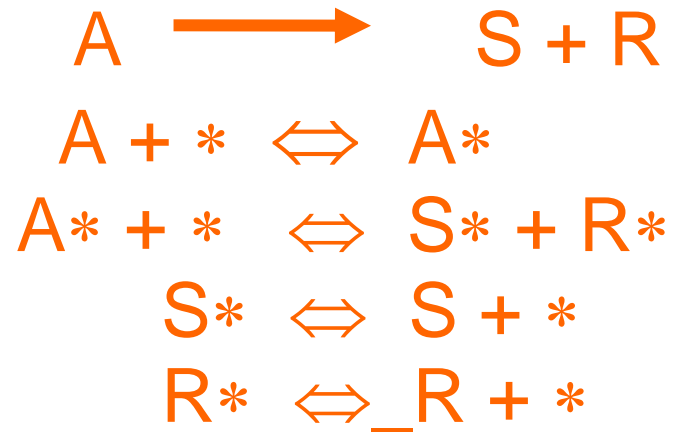


Fig. 3.4. Pressure dependency of the initial reaction rate for three different rate-determining steps and at increasing temperatures $T_1 > T_2 > T_3$.

应用反应的初速率分辨动力学模型 / **Discrimination of Kinetic Model by Using Initial Rates:**



Surface rxn control:

$$r_A = \frac{kK_A(P_A - P_R P_S / K)}{(1 + K_A P_A + K_R P_R + K_S P_S)^2} \dots \dots \dots (1)$$

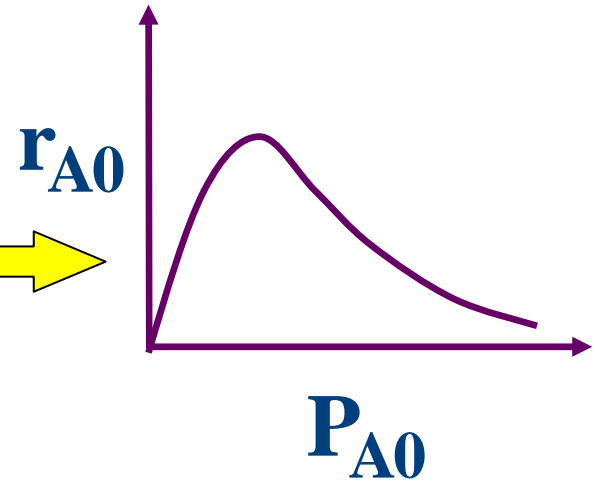
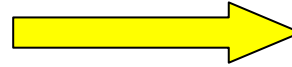
Adsorption control:

$$r_A = \frac{k(P_A - P_R P_S / K)}{1 + K_A P_A + K_R P_R + K_S P_S} \dots \dots \dots (2)$$

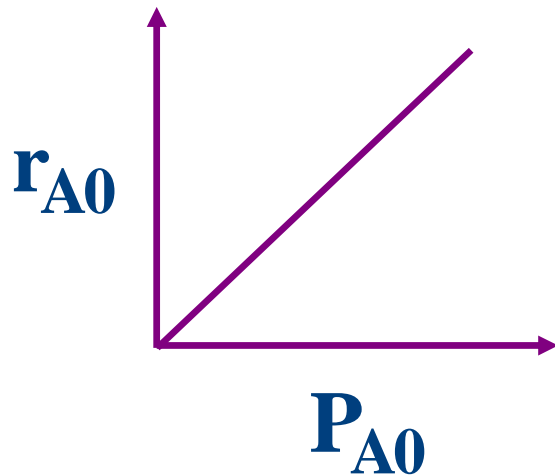
Desorption (R) control:

$$r_A = \frac{kK_R(P_A - P_R P_S / K)}{P_S + K_A P_A P_S + K_R P_A + K_S P_S^2} \dots \dots \dots (3)$$

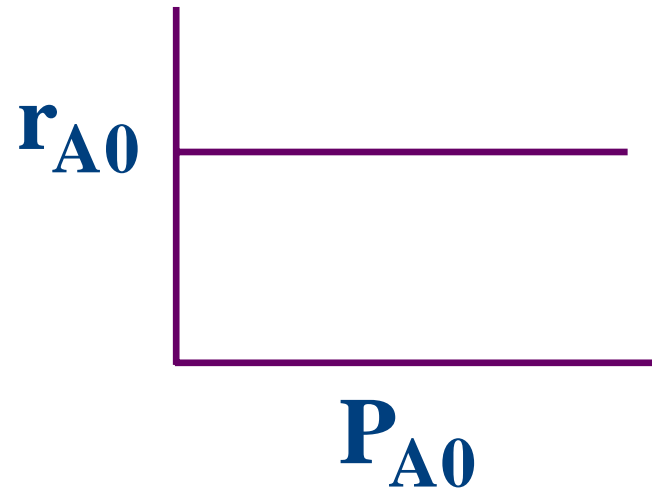
$$r_{A0} = \frac{kK_A P_{A0}}{(1 + K_A P_{A0})^2} \dots (1')$$



$$r_{A0} = k P_{A0} \quad (2')$$



$$r_{A0} = k \quad (3')$$



10. Experimental Determination of Kinetic Parameters of Flow Rxn

Consumption of a reactant A:

$$F_{A,out} - F_{A,in} = -r_{A,W} W = -X_A F_{A,in} = -X_A F_{A0}$$

平均速率: $r_A = r_{A,W} = -X_A F_{A0} / W = -\frac{X_A}{W / F_{A0}}$

对于一个催化剂薄层
(微分反应器):

$$r_A = -\frac{dX_A}{d(W / F_{A0})} = -\frac{\Delta X_A}{W / F_{A0}}$$

1). Differential reactor:

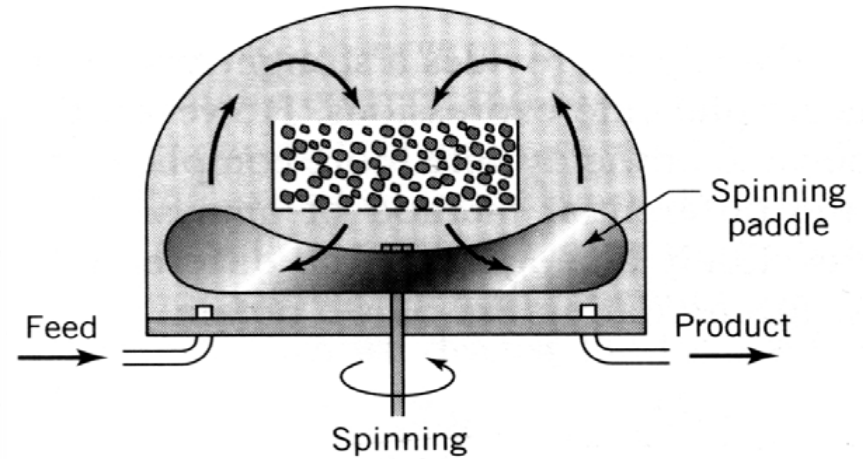
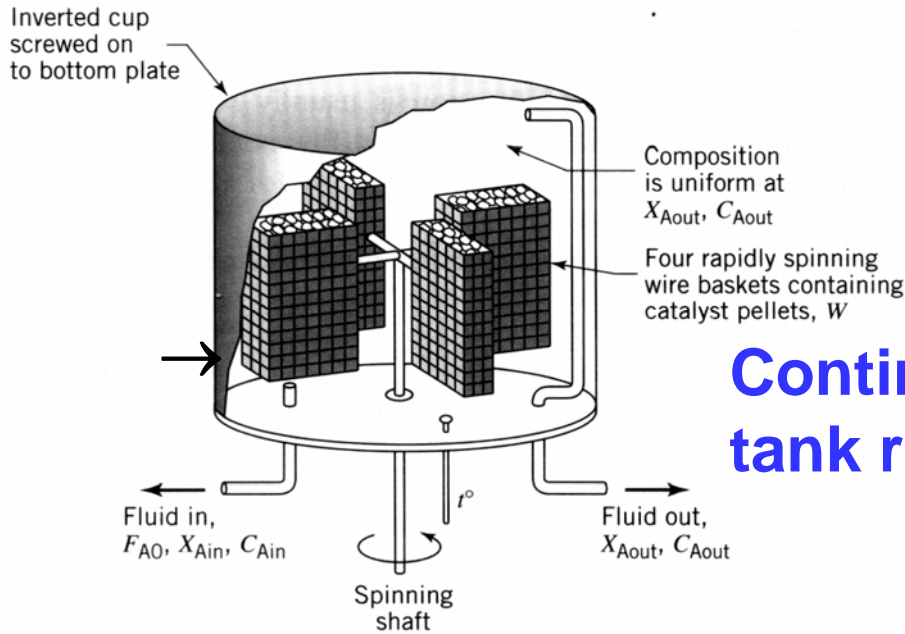
$$r_A = \frac{\Delta X_A}{W / F_{A0}} \quad \Delta X_A \text{ is very small}$$

2). Integral reactor:

$$r_A = - \frac{dX_A}{d(W / F_{A0})} = - \frac{\Delta X_A}{W / F_{A0}}$$

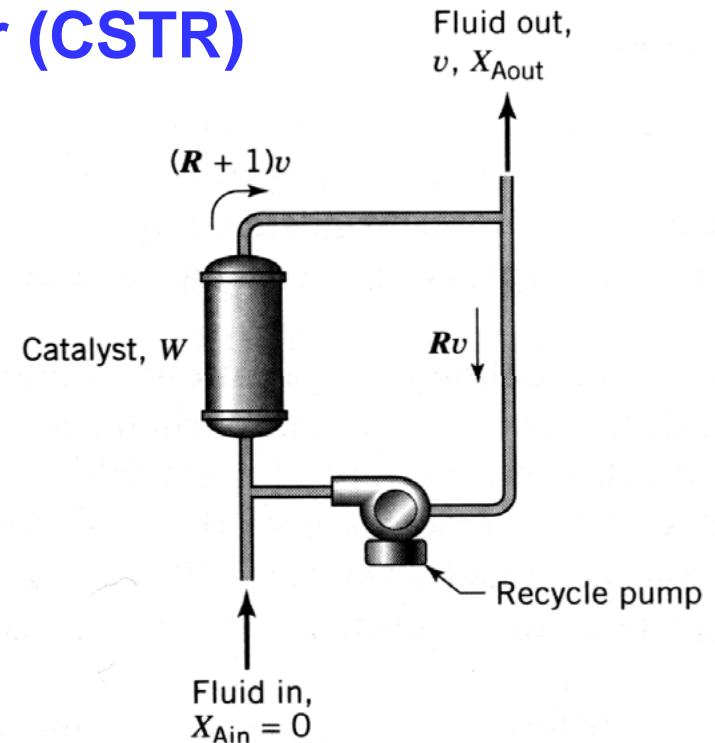
r_A : average rate

3). Gradientless Reactor



Continuous-flow stirred-tank reactor (CSTR)

- Carberry reactor (CSTR)
- Berty reactor (CSTR)
- External recycle reactor



几种典型的催化反应器

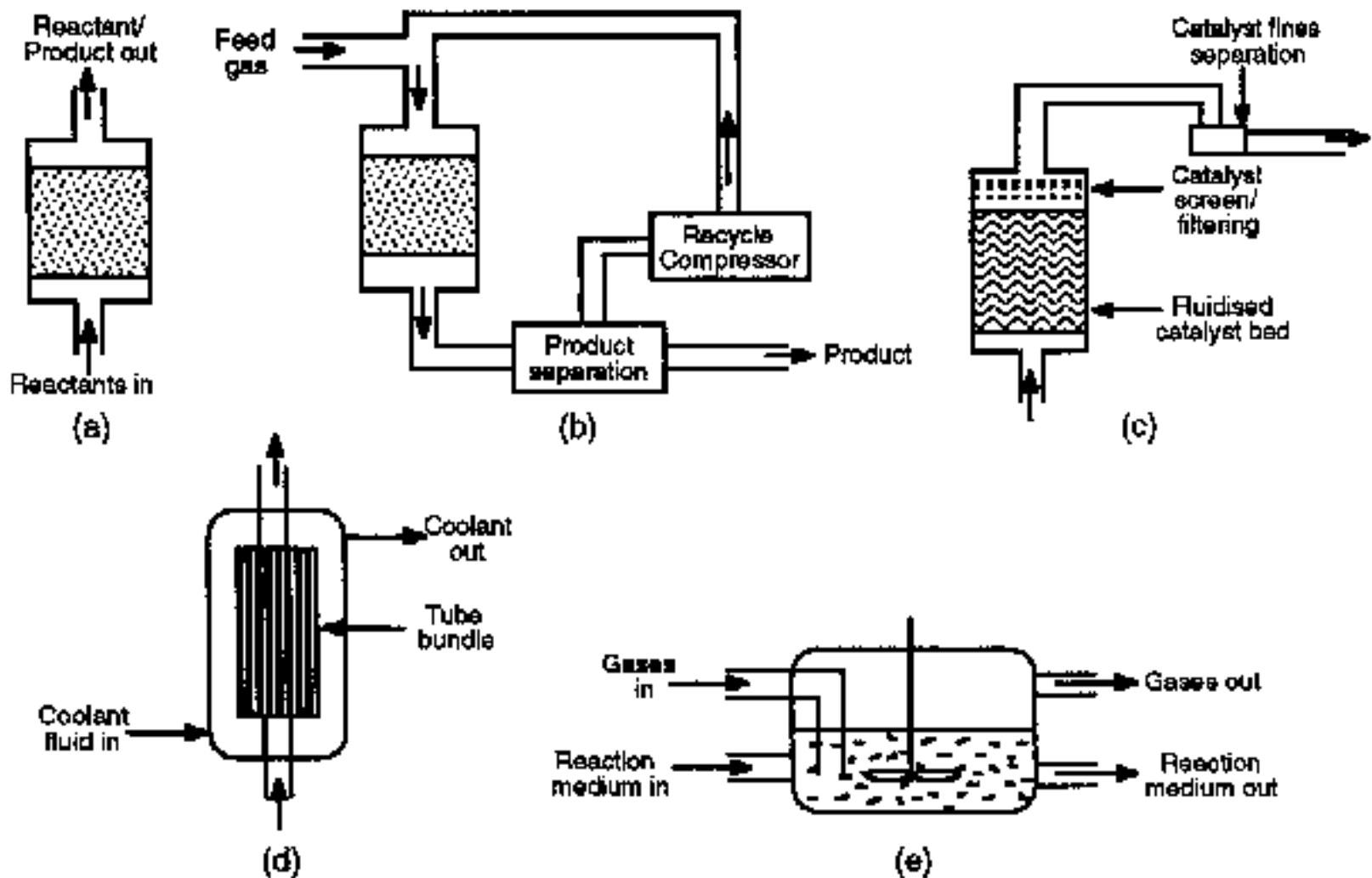


Fig. 6.2 Simplified schematic diagrams of various types of reactor (a) single pass (b) recycle (c) fluidised bed (d) multitubular (e) batch.

4) Plug-flow Reactor (*PFR*)

-- 轴向无反混、径向浓度无梯度

PFR 对反应管和催化剂床层要求:

$d_t/d_p > 10$, d_t 为反应管内径,

d_p 催化剂颗粒的直径

$L_b/d_p > 50$, L_b 催化剂床层高度

PFR 很容易实现低转化率, 此时:

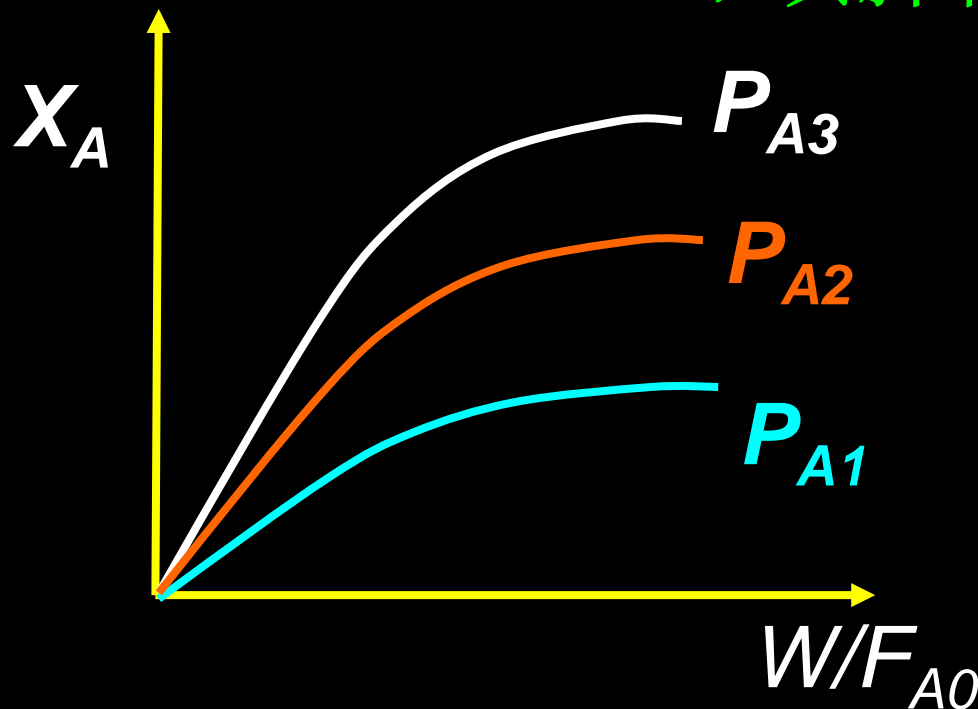
$$r_A = - \frac{X_A}{W / F_{A0}}$$

利用 *PFR* 测定催化反应的初速度:

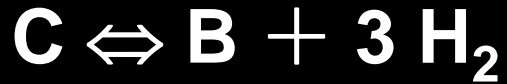
$$r_A = \frac{dX_A}{d(W/F_{A0})} = \frac{X_A}{W/F_{A0}}$$

$$X_A = r_A (W/F_{A0})$$

** 利用实测的 X_A , 对 W/F_{A0} (接触时间) 作图, 其斜率即为反应速率。

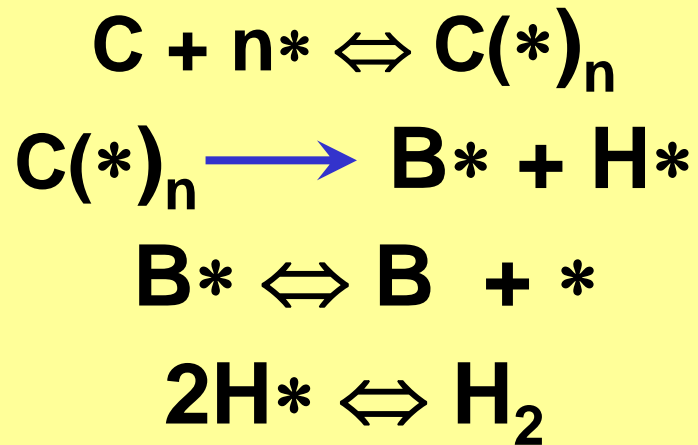


举例. Pt 催化剂上环己烷的脱氢反应:



(2). 拟定一个机理, 猜测一个决速基元步骤 (rds), 导出速率表达式:

(1). 固定 $P_H/P_C = m$, 在不同的 P_C 改变接触时间, 控制 C 的转化率小于 5%, 测定 C 的初速度 r_C , 此时 P_B 近似为零。



$$r_C = k_s K_c p_C / (1 + K_c p_C + K_B p_B + K_H p_H)^n$$

(3). 将速率表达式转变为初速率:

$$r_C = k_s K_c p_C / (1 + K_c p_C + K_B p_B + K_H p_H)^n$$

$$r_{C0} = k_s K_c p_C / (1 + K_c p_C + K_H p_H)^n$$

$$1 + K_c p_C + K_H p_H = (k_s K_c)^{1/n} \left(\frac{p_C}{r_{C0}} \right)^{1/n}$$

由 $P_H/P_C = m$ 有:

$$1 + (K_c + mK_H) p_C = (k_s K_c)^{1/n} \left(\frac{p_C}{r_{C0}} \right)^{1/n}$$

$$1 + (K_c + mK_H)p_c = (k_s K_c)^{1/n} \left(\frac{p_c}{r_{c0}} \right)^{1/n}$$

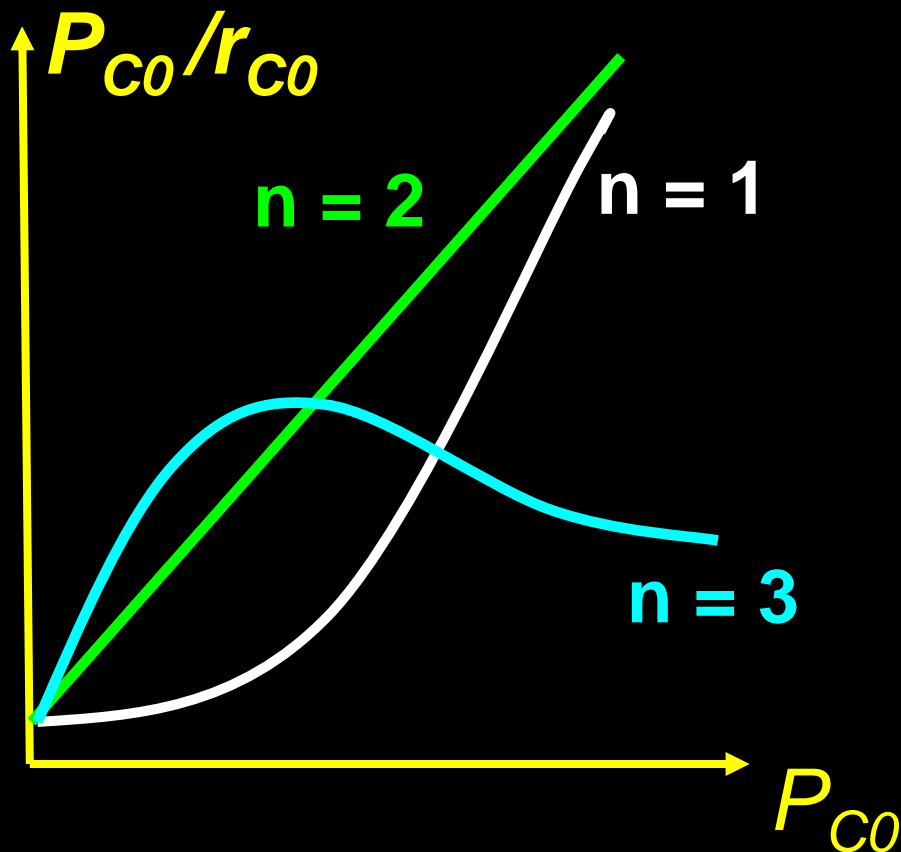
$$\left(\frac{p_c}{r_{c0}} \right)^{1/n} = (k_s K_c)^{-1/n} + (K_c + mK_H)p_c / (k_s K_c)^{1/n}$$

$$\left(\frac{p_c}{r_{c0}} \right)^{1/n} = A + Bp_c$$

$$A = (k_s K_c)^{-1/n}; \quad B = (K_c + mK_H)A$$

(4). 用 $(p_c/r_{c0})^{1/2}$ 对 p_c 作图:

$n = 2$



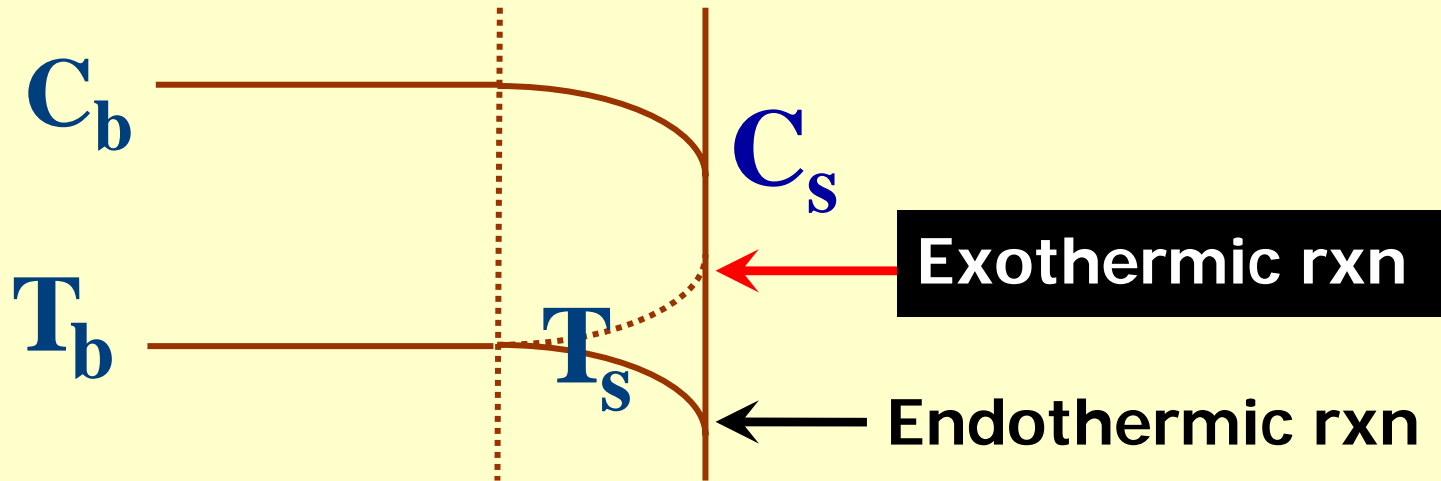
(5). 求出 k_s, K_H, K_C , 后两个由吸附数据得到。

(6). 求出表观活化能, 固定 p_c 改变 T , 测定活化能。

(7). $TOF = r_{c0}/N_s$ * $\lg r_{c0} = \lg(Ap_{c0}) - E_{\text{表}}/RT$

- **动力学参数的合理性:** k , K , T -effect, Arrhenius relationships, 同系物的相同类型的反应的动力学行为相似。
- **反应（器）工艺参数的最佳化:** 控制产率, 最佳反应温度、压力（分压）、反应物组成等。
- **反应的动力学耦合:** 利用不同反应动力学上的差异, 促进所期望的反应, 减少或阻止不需要的副反应。

11. Mass & Heat Transport Effects

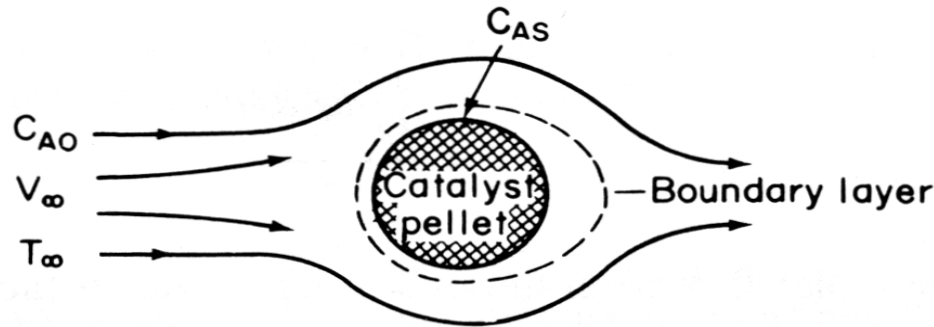


$C_b - C_s$: depend on mass transfer coefficient k_m , and rxn rate constant k . $k_m A_m (C_b - C_s) = r(C_s, T_s)$

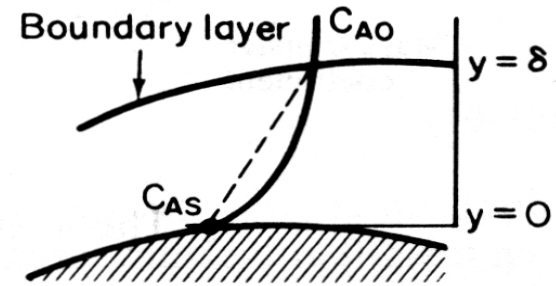
$T_b - T_s$ depend on heat transfer coefficient h , rxn rate constant k , surface concentration C_s , rxn heat $-\Delta H$.
 $h A_m (T_s - T_b) = (-\Delta H) r(C_s, T_s)$

$$\eta = \frac{\text{Actual rate}}{\text{Ideal reaction rate with } C_i = C_{is} \text{ everywhere}}$$

1). External mass transport effect



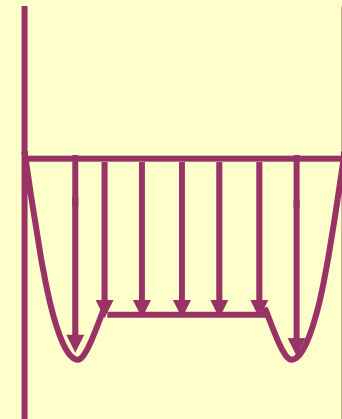
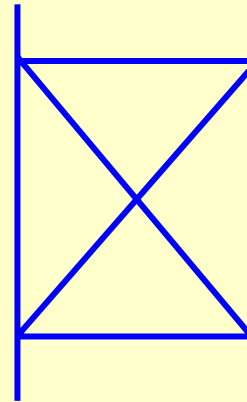
(a)



(b)

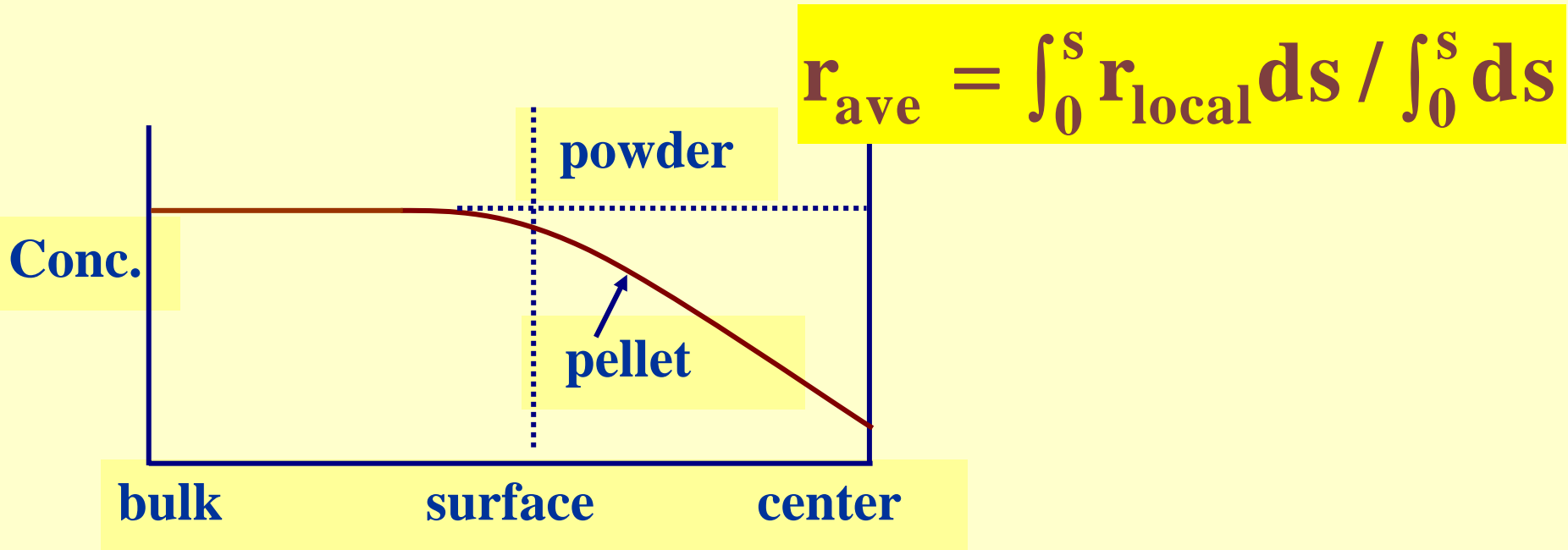
* local k_m and h depend on local flow

Fixed bed reactor:



* In this case, the k_m and h are the average value.

2). Pore transport effect: Internal diffusion

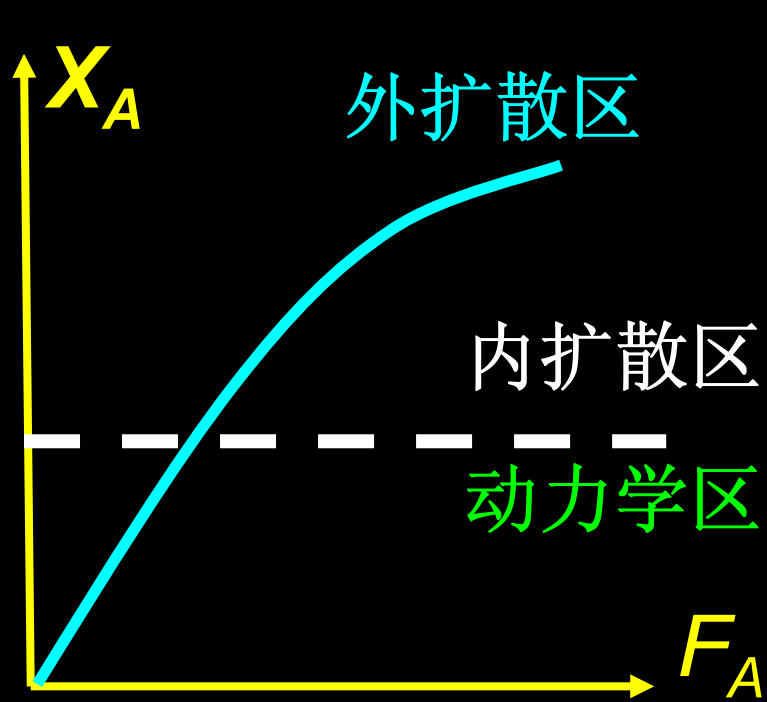


The idealized equation will be $r_{ave} = r_{surface} \times \eta$

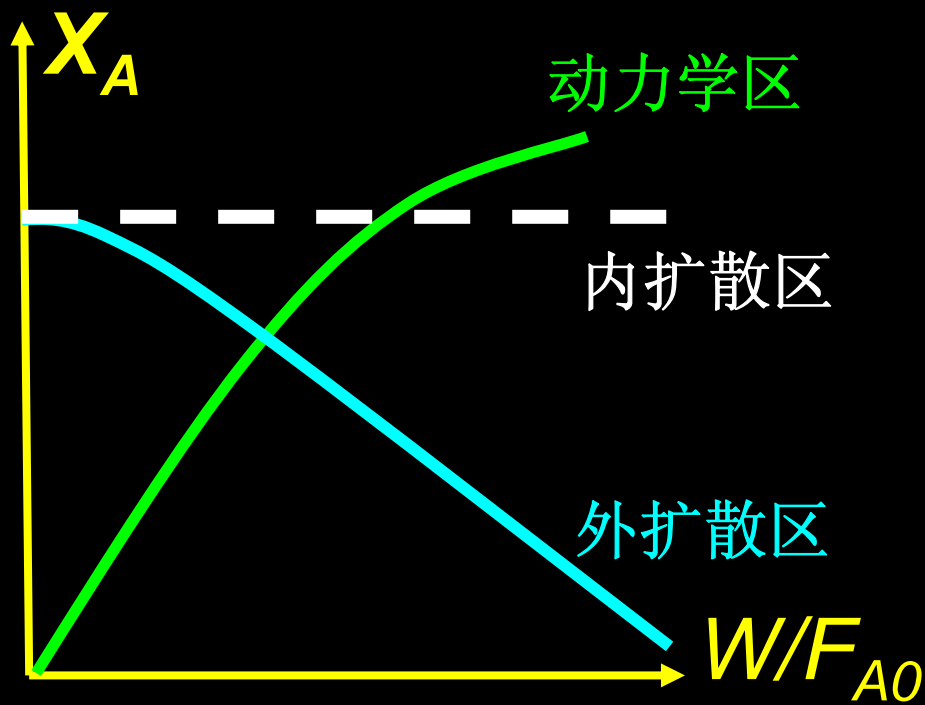
$$\eta = \frac{\text{Actual reaction rate for the pellet}}{\text{rate based on external surface concentration}}$$

Exothermic rxn: $\eta < 1$ or = or < 1 ; Endothermic rxns: $\eta < 1$

3). 判断扩散效应的实验方法



(1). 接触时间一定时改变线速度



(2). 线速度一定时改变接触时间

(4). 改变催化剂粒度试验

(3). 在宽温度范围验证 Arrhenius 关系

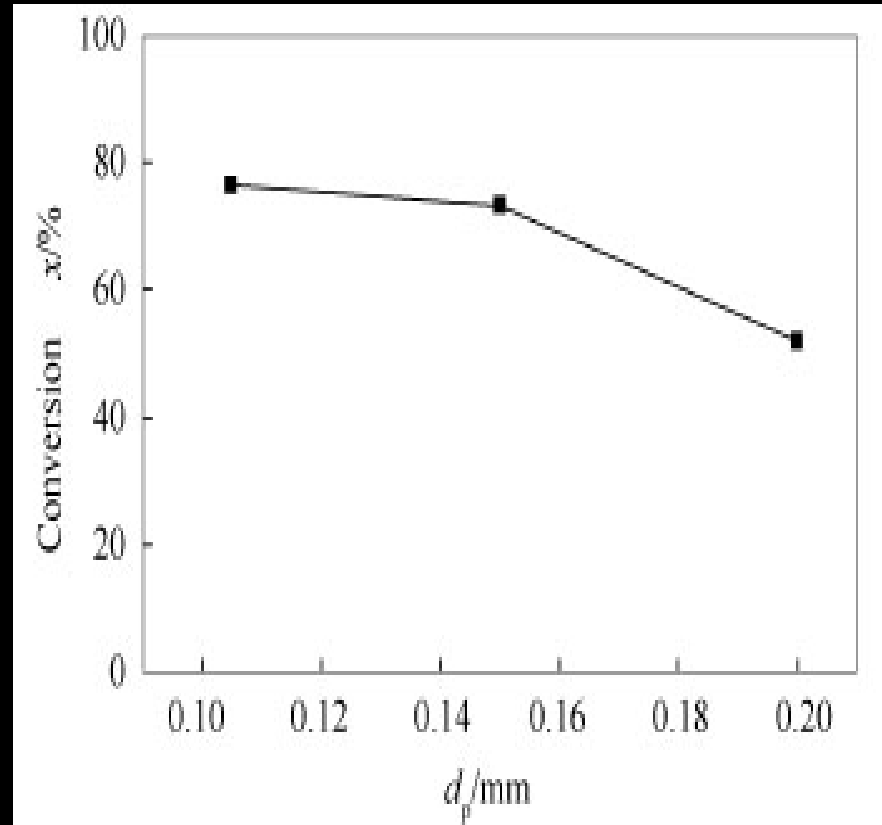
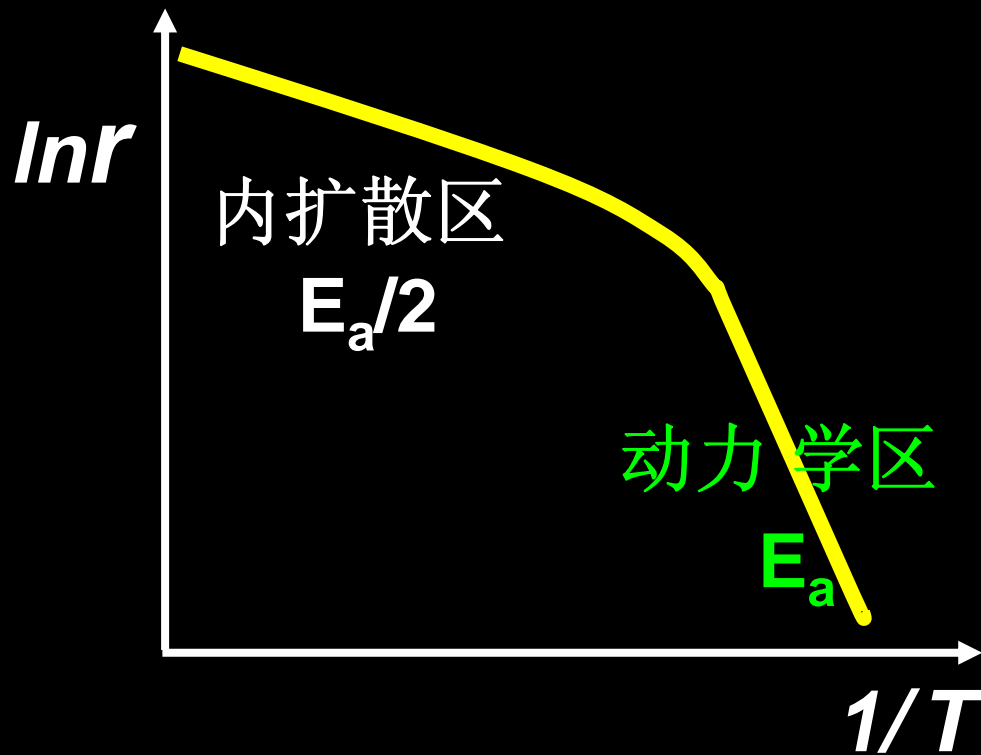


图 3 内扩散影响检验

Figure 3 Internal diffusion test of catalyst particles