90.2

博士班資格考試---化工動力學 2002/5/15

1. CVD of TiO_2 thin films, TiO_2 薄膜可經由化學氣相沉積方法合成，沉積的反應基元步驟包括下面步驟，其中 I 代表活潑的反應中間物，P_1 P_2 是反應產物，假設氣相反應已達到平衡，請推導沉積反應速率式。

   TTIP(g) + TTIP(g) = I + P_1 k_1 (forward rate constant), k_{-1}(backward)

   I + S = I•S k_2 (forward) k_{-2} (backward) S (surface site)

   I•S → TiO_2 + P_2 + S k_3

   假設 TTIP 壓力很低，請討論沉積速率與[TTIP]間的關係；

   假設 TTIP 壓力足夠高且氣相反應(第一個反應式)達平衡，請討論沉積速率與[TTIP]間的關係。 (20%)

2. Semibatch 反應器進行 A+B→C+D 之恆溫液相反應，反應物 B 飼入反應器與反應物 A 反應，反應速率式在反應初期，對 A 是零階對 B 是一階反應，因此反應速率式 $-r_B=kC_B$，已知反應時間 $t=0$，體積 $V=V_0$，飼入反應器之流率 v_0，反應物 B 飼入濃度 C_{B0} ，已知 $V=V_0+v_0t$ ，

   (a) 證明 $\frac{dC_B}{dt}=r_B+\frac{v_0(C_{B0}-C_B)}{V}$ (10%)

   (b) 代入反應速率式，利用適當之初始條件，解濃度隨時間之變化。 (20%)

3. The reaction A⟶ B is carried out catalytically in an isothermal reactor. The external mass transfer coefficient $k_m a_m$ is estimated to be 50 cm^3/g-cat s. The intrinsic reaction rate constant k is 40 cm^3/g-cat s. The effectiveness factor is 0.8. If the bulk concentration of A is $1x10^{-5}$ mol/cm^3, determine

   (a) the reaction rate $-r_A'$ (10%)

   (b) the global effectiveness factor (5%)

4. The following data were obtained by Sinfelt and co-workers [*J. Phys. Chem.*, 64, 1559 (1960)] for the dehydrogenation of methylcyclohexane (M) to toluene (T) at 315°C :

P_M(bar.)	P_{H2} (bar)	$-r_M'$ (kmol/kg-cat h)
0.36	1.1	0.012
0.36	3.0	0.012
0.07	1.4	0.0085
0.24	1.4	0.0114
0.72	1.4	0.0126

In addition, they found that the product toluene had essentially no effect on the rate. Based on the data,

(a) Propose a Langmuir-Hinshelwood rate model for the reaction. (5%)

(b) Suggest a reaction mechanism and indicates which of the steps- adsorption, surface reaction, or desorption might be the rate controlling step. (5%)

(c) Estimate the kinetic parameters of the rate model proposed in (a) (5%)

5. The following rates were observed for a first-order irreversible reaction, carried out on spherical catalysts of different diameters:

run	d_p (cm)	$-r_{A,obs}$ (mol/g-cat h)
1	0.3	0.162
2	0.6	0.09

Determine

(a) the Thiele moduli of the reactions (You need only list the required equations and assume a computer program is available to solve the equations and to obtain ϕ_1=5.5, ϕ_2=11) (10%)

(b) the true rate of reaction. (5%)

(c) the effectiveness factor with d_p= 0.1 cm. (5%)

Additional information:

For spherical catalyst, the Thiele modulus and effectiveness factor are

$$\phi=\frac{d_p}{2}\sqrt{\frac{k_v}{D_e}} \qquad \eta=\frac{3}{\phi^2}(\phi\coth\phi-1)$$