國立雲林科技大學 104 學年度 碩士班招生考試試題

系所：化材系

科目：化工動力學

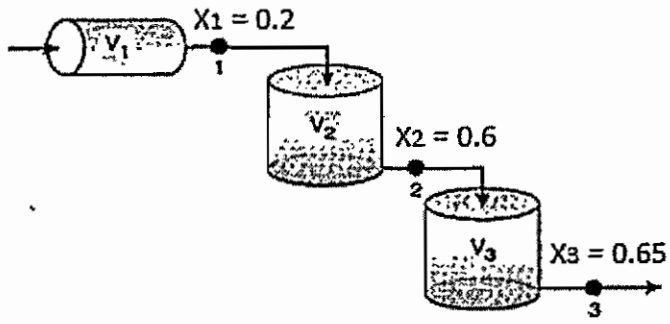
1. (20 分)

An irreversible reaction of A → B is carried out adiabatically in liquid phase, and the experimental data are listed below. The entering molar flow rate of reactant A is 50 kmol/h, and species B is absent in feed.

(a) What is the disadvantage of a plug-flow reactor ? (4 分)

(b) What is the advantage of a continuous stirred tank reactor ? (4 分)

(c) Calculate the volumes of the three reactors ? (12 分)



Conversion X	0	0.2	0.4	0.6	0.65
$-r_A$ (kmol/m^3-h)	39	53	59	38	25

2. (15 分)

The photochemical decay of aqueous bromine (Br_2) can be carried out under bright sunlight. For example, a small amount of liquid bromine is dissolved in water contained in a glass reactor, and then it was placed in direct sunlight. The following data are obtained at 25℃. Determine the rate law of the reaction by the integral method.

Time (min)	10	20	30	40	50	60
ppm Br_2	2.45	1.74	1.23	0.88	0.62	0.44

3. (15 分)

In silicon semiconductor industry, the chemical vapor deposition of silicon (Si) from silane (SiH_4) is known to proceed by the following irreversible two-step mechanism.

$$SiH_4 + S \xrightarrow{k1} SiH_2 \bullet S + H_2$$

$$SiH_2 \bullet S \xrightarrow{k2} Si + H_2 + S$$

The SiH_2 is irreversibly adsorbed on active sites (S) and then reacts as fast as it is formed, so that it can be assumed to behave as an active intermediate. Derive the rate law for silicon deposition expressed in terms of SiH_4 concentration and rate constants.

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4. (15 分)

The Fischer–Tropsch process involves a series of chemical reactions that produce a variety of hydrocarbons. The more useful reactions produce alkanes as follows:

$$(2n + 1)\ H_2 + n\ CO \rightarrow C_nH_{(2n+2)} + n\ H_2O$$

Generally, the process is operated in the temperature range of 150 ~ 300°C at high pressure condition with metal alkali catalyst and most of the alkanes produced tend to be straight-chain, suitable as diesel fuel. If the process is taken in a packing bed reactor with H_2/CO feed molar ratio = 3 and the side reactions are not considered:

i) Set up a stoichiometric table for the above reaction, if n = 10.

ii) Determine the final concentrations of each species as a function of conversion, if the above reaction is taken at 270°C and 27 atm constantly.

5. (15 分)

You are comparing different processes and reactor types for degradation of pollutant A in a waste effluent. The initial concentration of pollutant A in the effluent to be treated is 10 mM and the flow rate of the effluent is 1000 L/min. In presence of a dissolved enzyme, the degradation of pollutant follows Michaelis-Menten kinetics, with V_{max} = 50 mM/min and K_M = 5 mM. What reactor volume do you need to achieve 90% degradation of A in

i) CSTR?

ii) PFR?

6. (20 分)

The elementary isomerization

$$A \longrightarrow B$$

is carried out at 20 atm in a fluidized CSTR containing 100 kg of catalyst where 50% conversion is achieved. It is proposed to replace the CSTR with a packed bed reactor. What would be the conversion in the new PBR with following condition?

a) If no pressure drop?

b) If the entering pressure was 20 atm and the exit pressure was found to be 10 atm?

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科目：化工熱力學

1. The practical equation of state proposed by J.D. van der Waals is shown as follows:

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

(a)Please explain physical meanings of (a/V^2) and b values. (5%)
(b)Please derive "a" and "b" values as functions of *Tc* (critical temperature), *Pc* (critical pressure). (20%)

2. (a) Please draw the *P-V* diagram of Carnot heat-engine cycle and make a description about heat absorbed, isothermal and adiabatic procedures, wherein ideal gas serves as working fluid. (5%)
(b) Please derive the efficiency of Carnot cycle as functions of temperatures and pressures shown in the *P-V* diagram. (10%)
(c) Please prove that the ratio of (heat discard)/(heat absorb) is only a function of operating temperature. (10%)

3. For the binary system 1 and 2, the following equations provide a reasonable correlation for the activity coefficients: $\ln\gamma_1=Ax_2^2$; $\ln\gamma_2=Ax_2^2$; where A=2.771-0.00523T; In addition, the following Antoine equations provide vapor pressures:

$\ln P_1^{sat}=16.6-\frac{3643.3}{T-33.4}$; $\ln P_2^{sat}=14.25-\frac{2665.5}{T-53.4}$; where T is in kelvins and the vapor pressures are in kPa. Assume the validity of modified Rault's law with γ_i, an activity coefficient, calculate: (25%)

(*a*) P and $\{y_i\}$, for T = 318.15 K and x_1 = 0.25.

(*b*) P and $\{x_i\}$, for T = 318.15 K and y_1 = 0.60.

(*c*) T and $\{y_i\}$, for P = 101.33 kPa and x_1 = 0.85.

(*d*) T and $\{x_i\}$, for P = 101.33 kPa and y_1 = 0.40.

(*e*) The azeotropic pressure, and the azeotropic composition, for T = 318.15 K.

4. The enthalpy of a binary liquid system of species 1 and 2 at fixed T and P represented by the equation : $H = 200x_1+300x_2+x_1x_2(20x_1+10x_2)$, where H is in J/mol. (a)Determine expressions for partial enthalpies as functions of x_1, (b) numerical values for the pure-species H_1 and H_2, and (c) numerical values for the partial enthalpies at the infinite dilution.(15%)

5. (a) Please write the Maxwell's equations, and (b) show how to obtain the following equation. (10%)

$$dS=C_p\frac{dT}{T}-\left(\frac{\partial V}{\partial T}\right)_p dP$$

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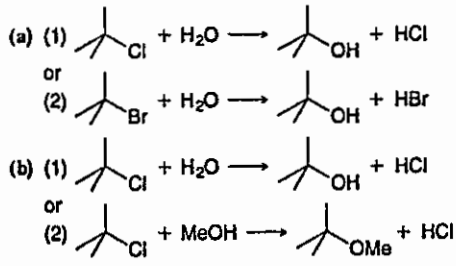
系所：化材系

科目：有機化學

1. Define the following nouns. (15%)
   (a) Shielded effect of NMR
   (b) HOMO and LUMO
   (c) Benzylic hydrogens
   (d) Cannizzaro reaction
   (e) Keto-enol tautomerism

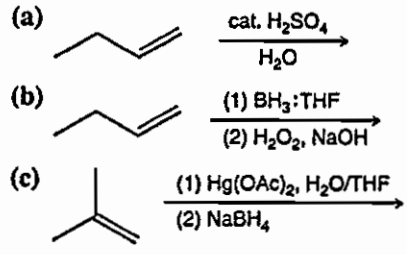
2. Which S_N1 reaction of each pair would you expect to take place more rapidly? Explain your answer. (10%)



3. Which of the following are chiral and, therefore, capable of existing as enantiomers? (15%)

(a) 2-butanol
(b) 1,1-dibromopropane
(c) 2-chloro-2-methylpropane

4. Predict the major products of the following reactions (15%)



5. Starting with benzene, outline a synthesis of each of the following: (10%)
   (a) tert-Butylbenzene
   (b) m-Dinitrobenzene

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6. (a) Which of the following groups are electron-withdrawing groups?
(b) Which of the following groups are electron-donating groups? (10 %)
–CN, –CHO, $–NH_2$, –OH, $–SO_3H$, –COOH, $–C_2H_5$, –NHCOCH$_3$, $–N(CH_3)_3^+$, and $–C_6H_5$.

7. Compound A, C_3H_8O, has infrared absorptions at 3600 ~ 3200 cm^{-1} (br) and give ^1H NMR spectra: δ 1.1 (d, 6H), 3.8 (m, 1H), 4.4 (s, 1H). Propose a structure for A. (6%)

8. (a) Depict the major differences between S_N1 and S_N2 nucleophilic substitutions (5 %). (b) Depict the major differences between E1 and E2 nucleophilic eliminations (3 %).

9. Depict the limitations of Friedel-Crafts alkylations. (5 %)

10. (a) Please arrange the order for the ease of abstraction of hydrogen atoms on halogenations of primary alkanes, secondary alkanes, tertiary alkanes and methane. (3 %). (b) Give the reason for question (a) (3 %).

國立雲林科技大學 104 學年度 碩士班招生考試試題

系所：化材系

科目：物理化學

1. The following consecutive reactions are elementary:

$$\mathrm{A} \xrightarrow{k_a} \mathrm{I} \xrightarrow{k_b} \mathrm{P}$$

If the initial concentration of A is $[A]_0$ and no I as well as P are present initially. Show that the expression for the concentration of P as a function of the time when $A \rightarrow I$ is the rate-determining step is the same as that solved by the steady-state approximation. (28%)

2. Show that $\pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$ where π_T is internal pressure. (12%)

3. For a reversible process with constant pressure and no additional work, show that $\Delta H = q_p$. (10%)

4. A gas obeys the van der Walls equation with $a = 0.76\,\mathrm{Pa\,m^6\,mol^{-2}}$. Its volume is $4.00\times10^{-4}\ \mathrm{m^3\ mol^{-1}}$ at 290 K and 4.4 Mpa. (a) Calculate the van der Walls constant b. (b) What is the compression factor for this gas at 290 K and 4.4 Mpa? (12%)

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科目：物理化學

5. The vapour pressure of a substance at 293 K is 60 kPa and its enthalpy of vaporization is $32.8\ \text{kJ mol}^{-1}$. Estimate the temperature at which its vapour pressure is 66.0 kPa. (12%)

6. Calculate the Gibbs energy, entropy and enthalpy of mixing when 1.00 mol hexane is mixed with 1.00 mol heptanes at 298 K; treat the solution as ideal. (12%)

7. The gas phase decomposition of acetic acid at 1189 K proceeds by way of two parallel reactions:

   (1) $CH_3COOH \rightarrow CH_4 + CO_2$ $\qquad k_1 = 3.74\,s^{-1}$

   (2) $CH_3COOH \rightarrow CH_2CO + H_2O$ $\qquad k_2 = 4.65\,s^{-1}$

   What is the maximum percentage yield of ketene (CH_2CO) obtainable at 1189K? (14%)

國立雲林科技大學 104 學年度 碩士班招生考試試題

系所：化材系

科目：單元操作與輸送現象

1. (20%) A Newtonian fluid (density ρ and viscosity μ) **flows down** along a vertical and flat wall (length L and width W). The mass flow rate is ω and a liquid film forms on the surface of the wall. Assuming that the thickness of the liquid film is uniform, the flow is laminar, and the edge effects are negligible,
   (a) What is the average velocity?
   (b) What is the thickness of the liquid film?

2. (15%) Heat is being generated by an electric current in a cylindrical metal wire of radius R. The volumetric rate of heat generation $\dot{q}$ is non-uniform and depends on the radial distance from the central line r, which can be expressed as $\dot{q} = a + br$. At steady state, the temperature of the surface of the wire is T_0 Assuming that the thermal conductivity of the wire k is constant, determine the center-line temperature and the heat flux on the surface of the wire.

3. (15%) Water ($\rho = 1\,\text{g/cm}^3$, $\mu = 1\,\text{cP}$) with an average velocity of 5 m/s flows through a rough circular pipe ($k/D = 0.001$) with an inside diameter D of 0.01m and a length L of 0.1 m.
   (a) According to Figure 1, find the pressure drop between the ends of the pipe?
   (b) As the flow rate becomes faster, what happens to the corresponding friction factor and friction force?

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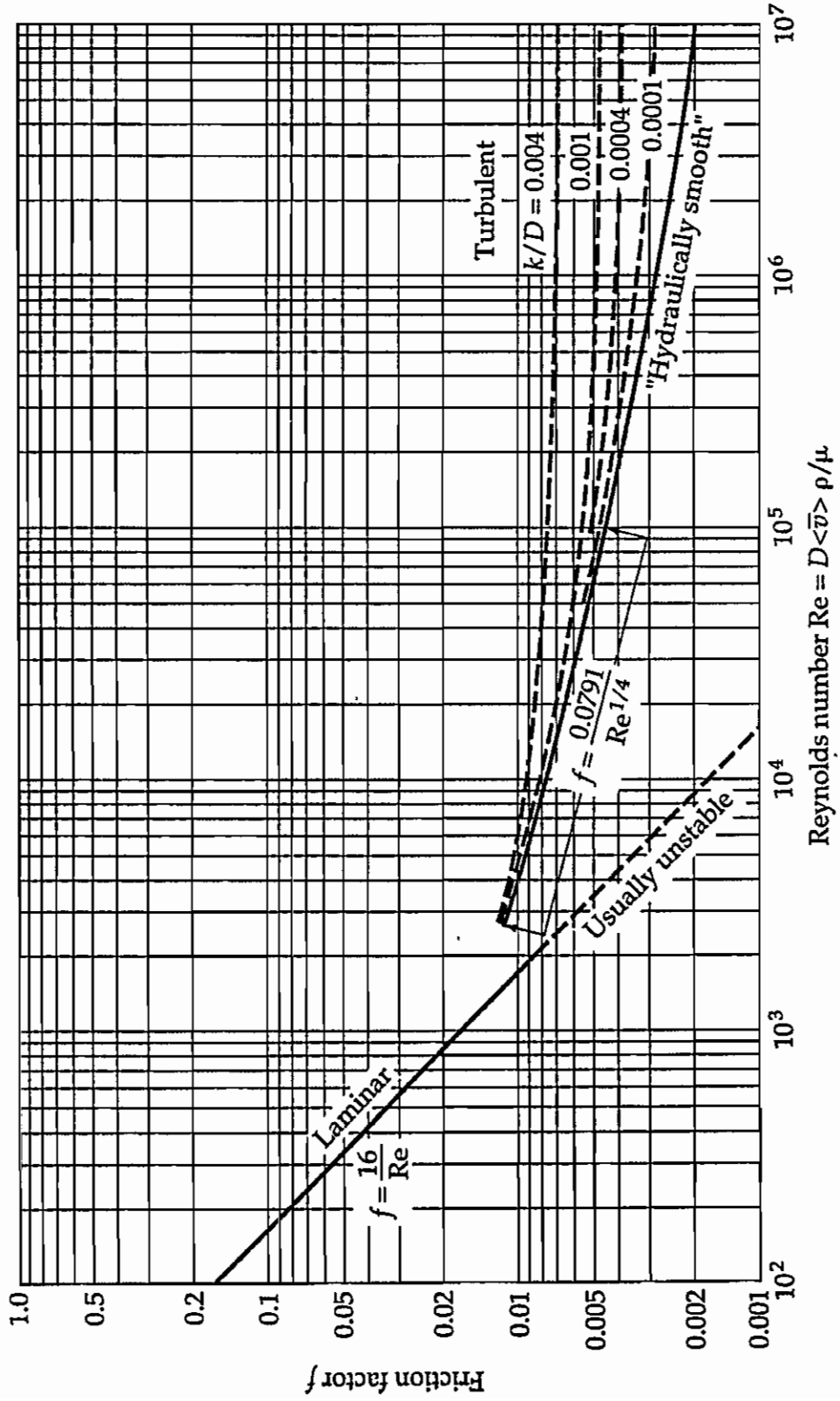

Figure 1

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4. (1) Explain the physical meaning of the Biot number (Bi)? (2%)
   (2) Describe the major difference for two cases where $Bi \ll 1$ and $Bi \gg 1$. (4%)
   (3) A solid sphere of radius 0.01 ft was placed in a cooling medium with a temperature 100 °F. It is known that the average temperature of the sphere, after a time (t), was quenched from 250 to 200 °F. Estimate the above required time (t). Assume that the averaged convective heat transfer coefficient of the air (h) adjacent to the sphere is 10 Btu/hr-ft^2-°F, and the thermal conductivity, heat capacity, and the density of the sphere are 200 Btu/hr-ft-°F, 0.1 Btu/lbm-°F and 500 lbm/ft^3, respectively (12%).

5. (1) What is the Fick's 1st law of diffusion in terms of N_A (the molar flux relative to a stationary coordinate) for a binary system with species A and B? (3%)
   (2) A cylindrical container, having a diameter of 2 cm and a height of 30 cm, is open to the atmosphere. If the container is half full of liquid toluene, what is the instantaneous rate of toluene loss to the surroundings by evaporation in kgmol/s? Assume that the whole system is kept at 18 °C and the gases in container are ideal. Under the conditions, the vapor pressure and diffusivity of toluene are 20 mmHg and 8.4×10^{-6} m^2/s, respectively. (The gas constant $R = 0.082$ atm-m^3/kgmol-K) (15%)

6. A flash distillation is used to separate a liquid mixture (feed) containing 55 mol% benzene (A) and 45 mol% toluene (B). Suppose that vapor and liquid of the mixture reach equilibrium during the entire process and the corresponding relative volatility of this benzene/toluene system $\alpha_{AB} = 2.5$. If the molar fraction of benzene (y_A) in the vapor phase leaving the flash distillation tower is 0.6, calculate (1) the molar fraction of benzene (x_A) in the liquid phase leaving the flash distillation tower (8%) and (2) how many percentage of feed is vaporized (6%).