國立雲林科技大學 系所：化材系

101 學年度碩士班暨碩士在職專班招生考試試題 科目：單元操作與輸送現象

1. A liquid flows through a capillary with an inside radius $R=10^{-3}$ m and a length L=0.4 m. The viscosity of the liquid is 1.5×10^{-3} Pa·s. The velocity distribution inside the capillary is

$$v = 0.3\left[1-\left(\frac{r}{R}\right)^2\right] \text{ m/s,} \quad \text{where } r \text{ is the radial coordinate.}$$

(a) What is the volumetric flow rate? (10%)

(b) What is the pressure drop Δp across the capillary during flow? (10%)

Hint: the flux of r-momentum in the flow direction $\tau = \frac{\Delta p}{2L} r$

2. An oil with heat capacity $c_p = 2.5\,\text{kJ/kg}\cdot\text{K}$ is flowing through a double-pipe heat exchanger at a rate of 7500 kg/h and is to be cooled from 373 K to 343 K. Cooling water ($c_p = 4.187\,\text{kJ/kg}\cdot\text{K}$) entering at 298 K and flowing **counterflow** at a rate of 3500 kg/h is available.

(a) Calculate the outlet temperature of the cooling water (5%)

(b) Calculate the overall heat transfer coefficient in $\text{W/m}^2\cdot\text{K}$ if the heat-transfer area inside the heat exchanger is 6.5 m^2 (10%)

3. A Newtonian fluid is confined between two parallel infinite plates with a distance B apart. The lower plate is moving leftward at a constant velocity v_0 and the upper plate is moving rightward at a constant velocity $2v_0$. The pressure gradient in the flow is $\frac{P_0 - P_L}{L}$ Assuming that the flow is steady-state and laminar and gravity is negligible, find the velocity distribution (15%)

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4. 利用逆流式套管熱交換器(countercurrent double-pipe heat exchanger)，以 105 °C 凝結水蒸汽(condensing steam)將空氣自 30 °C 加熱至 80 °C。假設主要熱傳阻力控制在空氣熱對流部份。已知空氣熱對流的熱傳係數(h)經驗式為 $Nu = 0.023\,\mathrm{Re}^{0.8}\,\mathrm{Pr}^{0.4}$，式中 Nu 為納瑟數(Nusselt number)、Re 為雷諾數(Reynolds number)、Pr 為普蘭多數(Prandtl number)。若改用 120 °C 凝結水蒸汽加熱空氣同樣自 30 °C 加熱至 80 °C，試問所加熱空氣的流量為原所加熱空氣流量的多少倍？ (15 分)

5. 有一液珠懸浮於靜止不動氣體中，液珠成分為 A，氣體為 A 和 B。若 B 不溶於 A，而 A 自液珠表面蒸發，然後擴散至氣相中。因液珠很小可視為球狀，假設液體之蒸發速率緩慢，液珠的半徑 R 可視為不變。試推導出計算液珠蒸發速率的方程式。 (20 分)

6. 在298K及1atm下，一填料塔(packing tower)中利用有機胺溶液吸收二氧化碳。氣體進入時含 1.26 mol% 的二氧化碳，離去時含 0.04 mol%。假設在操作條件範圍，二氧化碳與有機胺溶液間平衡關係遵守亨利定律(Henry's law)，亦即 $y_{CO2}=1.575x_{CO2}$。氣體流速為 2.3 g-mol/s，液體流速為 4.8 g-mol/s。已知填料塔直徑為 40 cm，總體質傳係數(overall mass transfer coefficient) 與單位體積的表面積的乘積 K_ya 為 5.0×10^{-5} mol/(cm^3-s)，試計算填料塔高為多少 m? (15 分)

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1. 2.0 mol of ammonia gas with $C_{p,m} = 35.06 \text{J K}^{-1} \text{mol}^{-1}$ is initially at 298 K. It undergoes reversible adiabatic expansion from 1.00dm^3 to 4.00dm^3. Calculate the final temperature, the work done and the change of internal energy for the process. (16%)

2. The normal boiling point of naphthalene ($C_{10}H_8$) is 491K. If the vapour pressure of the liquid is 1.3 kPa at 359 K and 5.3 kPa at 392 K. (a) use the Trouton's rule to estimate the enthalpy of vaporization; (b) use the Clausius-Clapeyron equation to calculate the enthalpy of vaporization and the entropy of vaporization at the normal boiling point. (18%)

3. The mass percentage composition of dry air at 298 K is approximately: N_2 = 75.5%; O_2 = 23.2%; Ar = 1.3%. Calculate the Gibbs energy, entropy, and enthalpy of mixing when it is prepared from the pure and perfect gases. (16%)

4. The equilibrium constant of a reaction is found to fit the expression $\ln K = A + B/T + C/T^2$ between 400 K and 600 K with A = –1.76, B = –1368 K, and $C = 1.1 \times 10^5 \text{ K}^2$. Calculate the standard reaction enthalpy and standard reaction entropy at 500 K. (20%)

5. Calculate the change in K_x for the reaction $2\ NH_3(g) <=> 3\ H_2(g) + N_2(g)$ when the total pressure is increased from 1.0 bar to 3.0 bar at constant temperature. (15%)

6. Deduce an expression for the time it takes for the concentration of a substance (A) to fall to one-third its initial value ($[A]_0$) in an nth-order reaction with a rate constant (k). (15%)

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1. (20%)

YunTech Industry (YTI) has a novel idea to conserve wasted thermal energy in plants. They want to use a set of "state-of the-art" Carnoco heat engines. YTI claims it can generate enormous quantities of electric power by converting waste heat that would be released in cooling tower. In one particular application for Douliou (斗六) city, they claim that 1 MW of electric power can be produced from a 100 kg/s of hot process water available at 150℃ and 2 bar. Water is also available from the Zhuoshuixi(濁水) river basin which has a seasonal average temperature of 24℃. Describe what you think of the proposed process, and what is the maximum power output? You can assume that the following properties apply to water from the Zhuoshuixi river and from the plant (C_p=4000J/kg, density 1000= kg/m^3).

2. (15%)

First, please explain the physical meaning of excess Gibbs energy. The excess Gibbs energy for binary systems consisting of liquids with similar chemical nature may be represented a reasonable approximation by the following equation:

$$G^E/RT = Bx_1x_2,$$

where B is a function of temperature only. Under such binary systems, it is often observed that the ratio of the vapor pressures of the pure components is nearly constant over a considerable temperature range. Let this ratio to be k. and assume the vapor phase to be an ideal gas. If an azeotrope exists, show B to be a function of k. In addition, determine the range of values of B at k = 1.2 as no azeotrope can exist.

3. (15%)

There is a piston/cylinder instrument. An operator used it to compressed one kilogram of water with a specific volume = 1003 cm^3/kg at 25℃ and 200 bar in a mechanically reversible, isothermal process to 2000 bar. Please determine total heat (Q), the internal energy change (ΔU), the enthalpy change (ΔH), the entropy and change (ΔS) of the system as well as the work (W) from the surrounding. A satisfactory assumption is that volume is constant at its arithmetic average value. Given that the volume expansivity = 2.5×10^{-4} $K^{-1}$and the isothermal compressibility = 4.5×10^{-5} bar^{-1}.

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4. (18%)

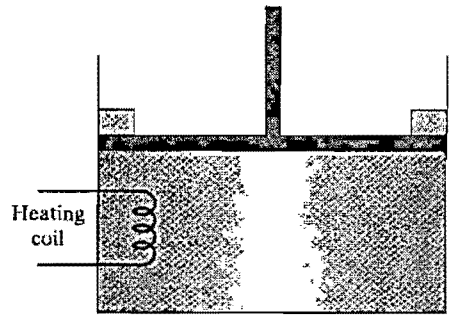
A rigid vessel of 0.06 m^3 volume contains an ideal gas (constant-volume heat capacity = (5/2)R, R is gas constant), at 500 K and 1 bar.

(a) If heat in the amount of 15000 J is transferred to the gas, determine its entropy change. (8%)

(b) If the vessel is fitted with a stirrer that is rotated by a shaft work so that work in the amount of 15000 J is done on the gas, what is the entropy change of the gas if the process is adiabatic? What is the total entropy change of the process? Justify the irreversible feature of the process? (10%)

5. (15%)

The frictionless piston-and-cylinder system shown is subjected to 1.013 bar external pressure. The piston mass is 200 kg and has an area of 0.15 m^2, and the initial volume of the entrapped ideal gas is 0.12 m^3. The piston and cylinder do not conduct heat, but heat can be added to the gas by a heating coil. The gas has a constant-volume heat capacity of 30.1 J/mol-K and an initial temperature of 298 K, and 10.5 kJ of energy are to be supplied to the gas through the heating coil. If stops placed at the initial equilibrium position of the piston prevent it from rising, what will be the final temperature and pressure of the gas?



6. (17%)

A chemical engineer is asked to estimate the solubility of gaseous nitrogen in liquid carbon tetrachloride at 25 °C and a partial pressure of nitrogen of 1 bar. Assume that the liquid nitrogen fugacity at 25 °C is 1000 bar.

(a) Calculate the mole fraction of nitrogen present in the liquid CCl_4 at equilibrium if the two species form an ideal solution. (7%)

(b) From the regular solution theory, it is estimated that

$$\ln \gamma_{N2} = 0.526(1 - X_{N2})^2$$ where γ: activity coefficient; X: mole fraction in liquid.

What is the equilibrium mole fraction of nitrogen in CCl_4 under these circumstances? (10%)

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本科目總分為 100 分

1. (10 分)(a) It has been well known that equilibrium constants (K) will be decreased with an increase of temperature for an exothermic reaction. Please explain the above concept by *van't Hoff* equation:

$$\frac{d(\ell nK)}{dT} = \frac{\Delta H^o}{RT^2}$$

where ΔH^o is the standard state enthalpy change for the reaction.

(10 分)(b) For an elementary reversible reaction whose rates are rapid enough to achieve a dynamic equilibrium, please derive the Arrhenius equation form "$k = Ae^{-E/RT}$" using the *van't Hoff* equation.

2. (10 分)(a) For a first-order irreversible elementary reaction, please derive the concentration of reactant $C_A(t)$ as a function of C_{Ao} (initial concentration), k (rate constant) and t.

(20 分)(b) For a first-order reversible elementary reaction, please derive the concentration of reactant $C_A(t)$ as a function of C_{Ao} (initial concentration), k_1 (forward rate constant), K (equilibrium constant), C_{Ae} (equilibrium concentration) and t.

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[ln (2) = 0.693, ln (3) = 1.099, and ln (5) = 1.609]

3. (20分) Consider a feed of gaseous pure A (100 mol/liter) to a steady-state 2 liters mixed flow reactor, and the isothermal reaction is

$$2A \longrightarrow R, \quad -r_A = 0.05\, C_A^2 \text{ mol/liter-min}$$

Find what feed rate (liter/h) will give an outlet concentration C_A = 50 mol/liter?

4. (15分) The rate for a gaseous reaction $A \longrightarrow B + C$ at any point in a cylindrical plug-flow reactor of constant diameter is $-r_A = k_A C_A$ (where k_A = 0.254 s^{-1} at 1000 K). The reactor operates isothermally and at constant pressure. Assume: (1) The feed is pure A at 1 kg/s, 1000 K and 2 bar. (2) The flowing system behaves as an ideal-gas mixture. (3) The fractional conversion of A (f_A) = 0.20 at the outlet. Calculate the residence time, t.

5. (15分) An aqueous reactant (A) is decomposed in the presence of a catalyst according to

$$-r_A = r_{max} C_A/(K_M + C_A) \quad \text{with} \quad K_M = 10 \text{ g/L} \quad \text{and} \quad r_{max} = 7 \text{ g/L-min}$$

If we operate two one-liter mixed flow reactors in series at steady state, what will be the concentration of the reactant leaving the second reactor? The flow rate is 0.5 L/min. The inlet reactant concentration is 50 g/L and the catalyst concentration in the two reactors is maintained at the same value all of the time.

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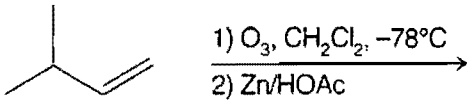
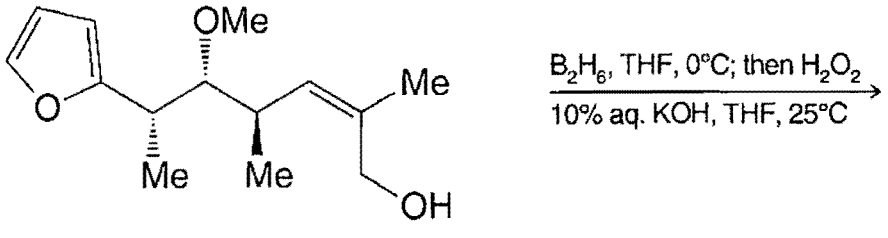
1. Arrange the following compounds in order of decreasing acidity: (8%)
Pentane, 1-Pentene, 1-Pentyne, 1-Pentanol

2. Write structures for the major organic products from the following reactions. Show stereoisomers where applicable. (10%)

(a)



(b)



3. Which reagent in each pair listed here would be the more reactive nucleophile in a polar aprotic solvent? (12%)

(a) CH_3NH^- or CH_3NH_2

(b) CH_3O^- or $CH_3CO_2^-$ (^-OAc)

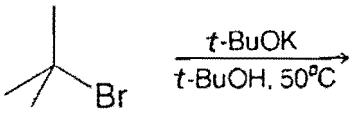
(c) $(C_6H_5)_3N$ or $(C_6H_5)_3P$

(d) CH_3SH or CH_3OH

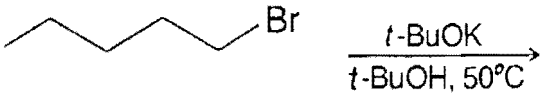
4. Write formulas for all of the isomers of each of the following. Designate pairs of enantiomers and achiral compounds where they exist. (10%)
   (a) 1-Bromo-2-chlorocyclohexane
   (b) 1-Bromo-4-chlorocyclohexane

5. Which product (or products) would you expect to obtain from each of the following reactions? In each part give the mechanism (S_N1, S_N2, E1 or E2) by which each product is formed and predict the relative amount of each product (i.e., would the product be the only product, the major product, a minor product, etc.?). (10%)

(a)



(b)



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6. 請列出下列常用原料的化學結構式(10%)

(a). N,N-dimethyl formamide (b).urea (c).styrene
(d).caprolactame (e). bis- phenol –A

7. 請列出下列反應式的產物: (12%)

(a). cyclohexene $+Cl_2+H_2O \rightarrow$ A
(b). ethylchloride +sodium ethoxide → B
(c). $(CH_3)CCH_2CH_2CH_2Br + NH_3$ (excess) → C
(d). 1-methylcyclohexene + CH_3COOOH → D

8. 請列出丙醛在鹼催化下,經由 Aldol condensation 而生成的 Aldol 產物的化學式(8%)

9. 丙酮是重要的化工原料,請列出化學式?以說明如何由丙烯與苯製造丙酮與酚過程中的中間產物及反應. (10%)

10.請說明爲何我們日常生活中所用的聚乙烯醇(PVA)膠水,不能由乙烯醇聚合製造?請以化學式說明其真實的原料單體爲何?並經由那些反應及中間體而製得. (10%)