國立雲林科技大學 102 學年度 系所：化材系
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. Fluid flows through a vertical circular tube in a length, L, with the following conditions:

(i) Steady state and laminar flow;

(ii) Fluid flow downward under pressure and gravity force, ($\mathcal{P}_0$-$\mathcal{P}_L$): ($\mathcal{P}$ = p-ρgz)

(iii) Boundary conditions, B.C. 1 at r= 0, $\tau_{rz}$= finite; B.C. 2 at r =R, $v_z$= 0;

iv) For Newtonian fluid, $\tau_{rz}$ = -μ ($dv_z/dr$) and for non-Newtonian polymer fluid,

$\tau_{rz}$= -m [$(dv_z/dr)^{n-1}$] ($dvz/dr$).

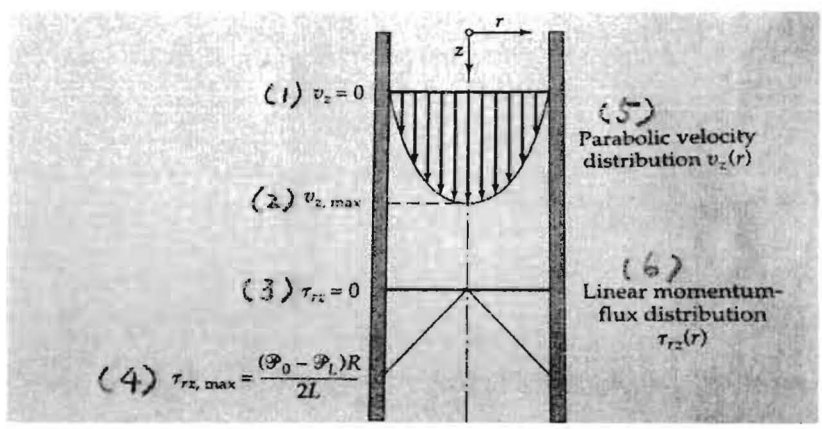
The momentum-flux and velocity distributions are shown in the figure.1:

**Questions**: (40%)

(A) Using momentum shell balance for calculating the fluid flow in the tube, you have the results: (1), (2)....and (6) shown on the figure.1. Which numbers can be applied to both Newtonian and non-Newtonian fluids and why? (15 %)

(B) Derive $v_z$ for a non-Newtonian fluid (18%), and calculate ($v_z/v_{max}$) ≈? (7%)

Fig. 1



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2. A heated sphere of radius $R$ is suspended in a large motionless fluid of temperature $T_0$. Suppose that the temperature of the sphere can be kept at a constant value $T_w$ and the free convection can be neglected. Determine the position far from the center of the sphere at which the fluid temperature is the average value of $T_w$ and $T_0$. Note that directly writing answer is not allowed. (16%)

3. A double-tube heat exchanger is employed to cool 0.45 kg/s of benzene from 370 K to 320 K by means of 0.55 kg/s cooling medium entering at 280 K. If the outside diameter of the inner tube is 3 cm, and the overall heat transfer coefficient based on the outside area is constant at 740 $W/m^2 \cdot K$, calculate the required length of the exchanger based on (a) the co-current flow arrangement (7%), and (b) the counter-current flow arrangement (7%). (c) Based on your estimation, which flow arrangement, (a) or (b), would you recommend for practical operation, and explain why? (5%) The specific heats of benzene and medium are 0.45 and 1 $Btu/lb_m \cdot °R$, respectively. For your conversion of units: 1Btu=1.055 $kW \cdot s$, $1 lb_m = 0.454 kg$, and $1 K = 1.8 °R$.

4. The membrane reactor is one of the best ways to simultaneously complete the reaction and separation processes within the membranes. Consider a disk-shaped membrane reactor consisting of two membranes separated by a porous catalyst gel, as shown in Figure 2. Suppose that the following reaction, $A \rightarrow B$, takes place between the membranes, and the conversation of $A$ to $B$ within the membranes is complete. The upper membrane ($z = 0$) is only permeable to $A$, while the lower ($z = \delta$) is penetrable to both $A$ and $B$.
   (a) If the reaction is first order in $A$ (i.e., $r_A = -\kappa a C_A$), derive the concentration profiles of $A$ and $B$ within the membranes and the flux of $B$ out of the membrane reactor. Suppose that the concentration of $A$ at $z = 0$ is kept at its original concentration $C_{A0}$. (18%)
   (b) Derive the expression for the effectiveness factor of the catalyst layer, $\eta_A$. (7%)

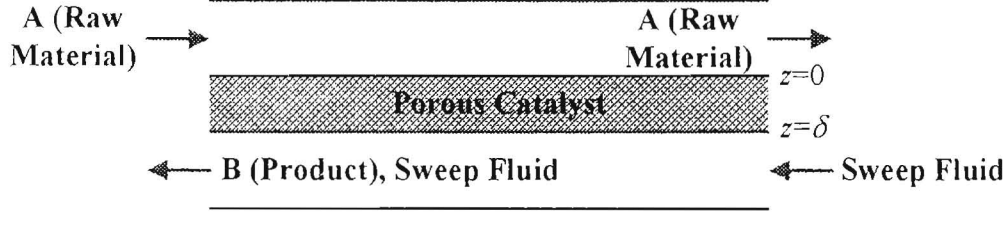


Figure 2.

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1. To consider liquid and vapor phase in equilibrium, the Clausius-Clapeyron equation is usually applied. Please show the expression of the Clausius-Clapeyron equation, and how to obtain it? (10%)

2. The standard reactions Gibbs energy for the hydrolysis of ATP in the reaction $ATP_{(aq)} \rightarrow ADP(aq)+P(aq)$, where P is inorganic phosphate, is 30 kJ per mole at 37℃. In a typical bacterial cell, the concentrations of ATP, ADP, and P are 8 mM, 2 mM, and 4 mM, respective. What is the reaction Gibbs energy under these conditions? (5%)

3. From a DSC instrument test, the phase change of a materials needs about 100W heat. Estimate the entropy change during phase transition in 1 min at 27℃. (5%)

4. The standard enthalpy of formation of gaseous water at 25℃ is -242 kJ per mole. Please its value at 100℃. It has been obtained that the molar constant-pressure heat capacities of $H_2O$, $H_2$, and $O_2$ are 34, 28, and 29 $JK^{-1}mol^{-1}$, respectively.(5%)

5. For a perfect gas of 10 moles to expand reversibly from volume 1V to 10V at constant 25℃, please calculate the work done by it. (5%)

6. What are Rault's Law and Henry's laws? The partial vapor pressures of each component in a mixture of acetone (A) and chloroform (C) were measured at 35℃ with the following data:

| $X_C$ | 0 | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |
|---|---|---|---|---|---|---|
| $P_C$ (torr.) | 0 | 35 | 82 | 142 | 219 | 293 |
| $P_A$(torr.) | 347 | 270 | 185 | 102 | 37 | 0 |

What condition do the mixtures conform to Rault's law and to Henry's law, respectively? Find the Henry's law constant. (10%)

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7. Acetic acid is esterified in the liquid phase with ethanol at 100℃ and atmospheric pressure to produce ethyl acetate and water according to the reaction
$CH_3COOH_{(l)} + C_2H_5OH \rightarrow CH_3COOC_2H_{5(l)} + H_2O_{(l)}$
If initial there is one mole each of acetic acid and ethanol, estimate the mole fraction of ethyl acetate in the reacting mixture at equilibrium (10%).
The standard Gibbs energies (ΔG) and the standard enthalpies (ΔH) of formation at 25℃ are listed in the following table:

| | acetic acid | ethanol | ethyl acetate | Water |
|---|---|---|---|---|
| ΔG( J/mole) | -389900 | -174780 | -318280 | -237130 |
| ΔH(J/mole) | -484500 | -277690 | -463250 | -285830 |

8. A liquid-phase irreversible reaction A → 2B was carried out in an isothermal beaker. The reaction is third order with respect to A and the rate constant is $10^{-4}$ $L^2$ $mol^{-2}$ $s^{-1}$. Calculate the time required for the concentration of A to change from 0.06 to 0.02 mol/L. (15%)

9. (a)What is Kohlrausch's law? (5%)
(b) At 25℃, the limiting molar conductivities of KCl, $KNO_3$, and $LiNO_3$ are 14.99, 14.5, and 11.01 mS $m^2$ $mol^{-1}$, respectively. Estimate the limiting molar conductivity of LiCl at this temperature. (10%)

10. The radius of a given capillary is 0.3 mm. A liquid with the density of 0.8 $g/cm^3$ rises in the capillary to a height of 6.25 cm. Assuming that the contact angle for the liquid on the wall of the capillary is close to zero, what is the surface tension of the liquid? (10%)

11. For BCC iron with a lattice constant of 0.2866 nm,
(a) Calculate the inter-planar spacing for the (220) set of planes. (5%)
(b) What is the diffraction angle ($2\theta$) for the (220) planes when the X-ray wavelength is 0.154 nm? Assume that the order of reflection is 1 (5%)

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1. Please explain the following items: ( 20% )
   (a) Isentropic process ( 4% )
   (b) Reversible and irreversible process ( 4% )
   (c) Clapeyron equation ( 4% )
   (d) Phase rule ( 4% )
   (e) First law of thermodynamics ( open system ) ( 4% )
2. The following expressions have been reported for the activity coefficients of species 1 and 2 in a binary liquid mixture at given $T$ and $P$:

   $$\ln r_1 = x_2^2(0.5 + 2x_1)$$
   $$\ln r_2 = x_1^2(1.5 - 2x_2)$$

   (a) Show that the expressions satisfy the Gibbs/Duhem equation. ( 10% )
   (b) Determine the implied expression for $G^E$ / RT. ( 10% )
3. A heat pump is used to heat a house in the winter and to cool it in the summer. During the winter, the outside air serves as a low-temperature heat source; during the summer, it acts as a high temperature heat sink. The heat-transfer rate through the walls and roof of the house is 0.75 kJ/s for each °C difference between the inside and outside of the house, summer and winter. The heat pump motor is rated at 1.5 kW. Determine the minimum outside temperature for which the house can be maintained at 20 °C during the winter and the maximum outside temperature for which the house can be maintained at 25 °C during the summer. ( 20% )
4. A piston/cylinder device operating in a cycle with steam as the working fluid executes the following steps:
   (1) Steam at 525 kPa and 175 °C is heated at constant volume to a pressure of 750 kPa.
   (2) The steam then expands, reversibly and adiabatically, to the initial temperature of 175 °C.
   (3) Finally, the steam is compressed in a mechanically reversible, isothermal process to the initial state.
   (a) Please calculate Q, W, and ΔU for each of the process. ( 10% )
   (b) What is the thermal efficiency of the cycle? ( 10% )
5. Determine whether the following process violates the laws of thermodymics. An ideal gas of constant heat capacity ($C_P$ = 30kJ/(kmol.K))at 10 MPa and 300K enters a device which is thermally and mechanically insulated from the surroundings. One-half of the gas leaves the device at 360K and 1MPa, while the other half leaves at 240K and 1MPa. ( 20% )

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本科目總分爲 100 分

1. (20 分) The reactant is converted to product by the transformation of a catalyst. That is, R → P . In the reactor, a part of the catalysts will be adsorbed by the reactants. Additionally, the following behaviors are observed.
   (a) The rate of product formed is proportional to the concentration of catalyst introduced into the mixture [$S_o$].
   (b) At low reactant concentration, the rate of product formed is proportional to the concentration of reactant [R].
   (c) At high reactant concentration, the rate of product formed levels off and becomes independent of reactant concentration.
   Propose a mechanism to account for these behaviors.

2. For many reactions, the rate can be expressed as: $r = k \cdot f$(composition)
   (a) (5 分)Please make a description and an equation for Arrhenius' law.
   (b) (5 分)Please make a description to find the activation energy.

3. The autocatalytic reaction is occurred in the reator, wherein one of the products acts as a catalyst. That is, R + P → P + P. The rate equation of reactant consumed can be expressed as: $-r = kC_RC_P$. The initial concentrations of reactant and product are $C_{Ro}$ and $C_{Po}$ respectively.
   (a) (10 分)Please find the maximum reaction rate as a function of $C_{Ro}+C_{Po}$, $k$.
   (b) (10 分)Please find the conversion of reactant ($X_R$) as a function of $C_{Po}/C_{Ro}$, $C_{Ro}+C_{Po}$, $k$, $t$.

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本試題之第二頁，請依題號作答；須將演算過程及答案寫在答案卷上方予計分。
[ln (2) = 0.693, ln (3) = 1.099, and ln (5) = 1.609]

4. (15分) The reactant vapor A decomposes at 649 °C as follows: $4A \longrightarrow B_{(g)} + 6C$ and $-r_A = (10\ hr^{-1})\ C_A$. What size of plug flow reactor operating at 649 °C and 11.4 atm is needed for 75% conversion of 10 mol/hr of A in a feed of 2/3 A and 1/3 inert? (R = gas constant = 0.082 atm-dm$^3$ mol-K)

5. (15分) A liquid reaction A → B was carried out in a batch reactor and the following data were recorded:

| $C_A$, mol/dm$^3$ | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 1.0 | 1.3 | 2.0 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $-r_A$ (mol/dm$^3$-min) | 0.1 | 0.3 | 0.5 | 0.6 | 0.5 | 0.25 | 0.10 | 0.06 | 0.05 | 0.045 | 0.042 |

The entering molar flow rate of A was 1000 mol/hr at $C_{A0}$ = 1.2 mol/dm$^3$. What size of the well-mixed flow reactor is needed to achieve 75% conversion?

6. (20分) Through graphical representation method, find the minimum size of two well-mixed flow reactors in series to achieve a specified conversion of feed which reacts with arbitrary but known kinetics.

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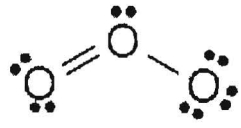
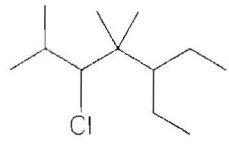
1. (5%) What are the formal charges on each oxygen atoms in ozone? Write your answer in the below blank blocks. All lone pairs are shown.



Formal charge from left to right: ☐☐☐

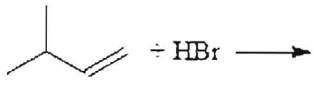
2. (5%) What is the correct IUPAC (systematic) name for this molecular?

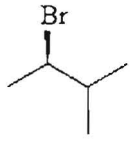


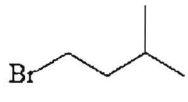

3. (5%) Rank the order of **decreasing reactivity** of the following alkyl chlorides when reacted in formic acid. (A) 1-chlorohaxane, (B)2-chlorohaxane, (C) 2-chloro-2-methylpentane

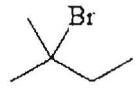
4. (10%) What **is/are** the major **product(s)** of the following reactions?

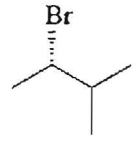
(i)



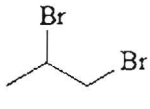

(A) 

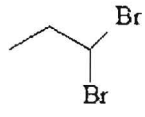

(B) 

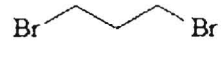

(C) 

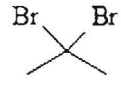

(D) 


(ii)


(A) 


(B) 


(C) 


(D) 

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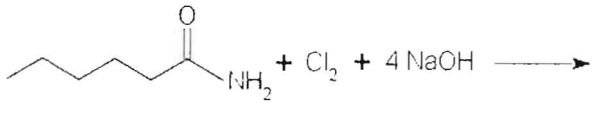
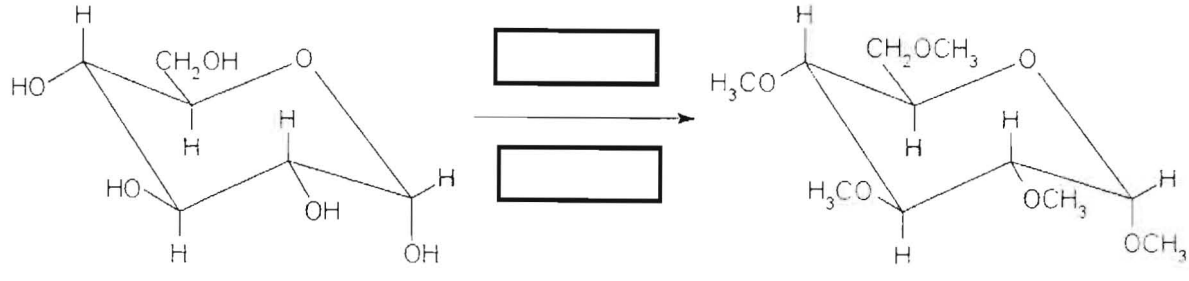
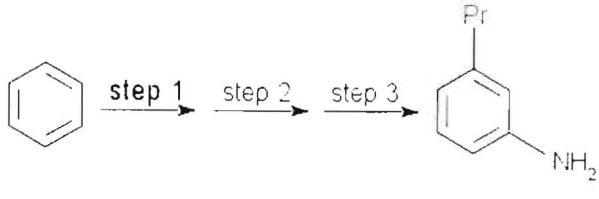
5. (8%) Please complete the following reaction, the Hofmann rearrangement of hexanamide.




6. (8%) Please give suitable **reagents** and/or **condition** to make the following reaction happen.




7. (9%) What is the best sequence to complete the following reaction?




| | Step 1 | Step 2 | Step 3 |
|---|---|---|---|
| **(A)** | $AlCl_3/EtCOCl$ | $HNO_3/H_2SO_4$ | $H_2/Pd$ |
| **(B)** | $PrMgBr/H_3O+$ | $H_2/Pd$ | $HNO_3/H_2SO_4$ |
| **(C)** | $AlCl_3/PrCl$ | $HNO_3/H_2SO_4$ | $H_2/Pd$ |
| **(D)** | $HNO_3/H_2SO_4$ | $PrMgBr/H_3O+$ | $H_2/Pd$ |
| **(E)** | $HNO_3/H_2SO_4$ | $AlCl_3/PrBr$ | $H_2/EtCOCl$ |

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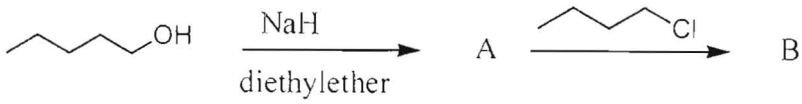
8. (9%) Draw all isomers of $C_3H_8O$ and classify each according to functional group.

9. (5%) What final product is likely to be obtained through the following series of reactions?




10. (9%) Which is the best method to prepare ethoxycyclopentane via the Williamson method?

11. (9%) Suggest a reasonable synthetic strategy for the synthesis of 3-ethyl-3-heptanol from pentanoic acid, $CH_3CH_2CH_2CH_2CO_2H$.

12. (12%) Outline the steps involved in the synthesis of 4-bromo-3-nitro-aniline from 4-bromobenzaldehyde.

13. (6%) Draw the structures corresponding to the following names: (a) 3-ethyl-4,4-dimethylhexanenitrile; (b) 2-hydroxy-4-(3-methylcyclopentyl)benzoic acid.