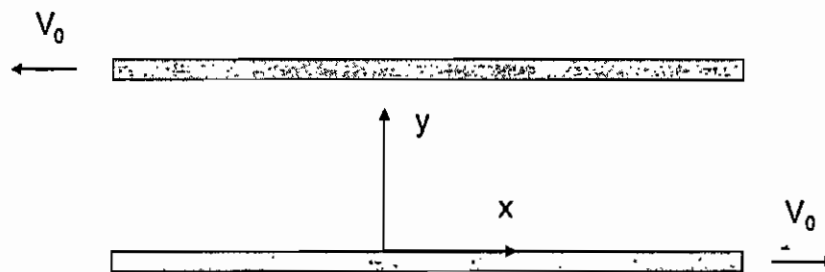


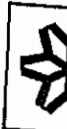


- What are the units of the following physical parameters in SI system? (12%)
 (a) viscosity, (b) thermal conductivity, (c) heat transfer coefficient,
 (d) kinematic viscosity
- Write out the following equation of motion for x-component in Cartesian coordinates (10%)

$$\frac{\partial}{\partial t} \rho \underline{v} = -[\nabla \cdot \rho \underline{v} \underline{v}] - \nabla p - [\nabla \cdot \underline{\tau}] + \rho \underline{g}$$

- A fluid with constant density and viscosity is bounded by two horizontal surfaces (the xz-plane at $y=0$ and $y=b$). Initially the fluid and the surfaces are at rest. Then at time $t=0$, the lower surface is set in motion in the positive x direction with velocity V_0 and the upper surface is set in the motion in negative x direction with velocity V_0 as shown in the figure. There is no pressure gradient or gravity force in the x direction, and the flow is presumed to be laminar. (a) Find the velocity distribution. (23%), (b) Can we use the method of combination of variables to solve the problem? (2%) Explain why? (3%)





4. A solid spherical particle, suspended motionless in a fluid, is heated dielectrically to promote a chemical reaction inside. The dielectric heating causes no thermal energy generation within the fluid but generates heat within the sphere at a rate \dot{q} per unit volume.
- (a) Develop an expression for the temperature profile inside the sphere. Express $T(r)$ relative to the surface temperature, T_R . (Ignore any heat effects from the chemical reaction.) (10%)
- (b) Eliminate T_R from the above expression so that the temperature inside the sphere is relative to T_∞ . (10%)
- (c) Show that $\frac{T_0 - T_R}{T_R - T_\infty} = \frac{1}{2} \frac{k_f}{k_s}$ (5%)
- Note: The heat transfer coefficient for a motionless sphere suspended in a fluid given by $\frac{hD}{k_f} = 2$, where D = sphere diameter.
- T_∞ = temperature of fluid far from the sphere
 T_R = surface temperature of sphere
 T_0 = temperature at the center of the sphere
 R = sphere radius
 k_s = thermal conductivity of sphere
 k_f = thermal conductivity of fluid
5. Ammonia must be stripped from wastewater before it can be treated for reuse. Experiments have measured the individual mass-transfer coefficients for ammonia transfer within a packed tower to be $k_G = 3.20 \times 10^{-9} \text{ kg mole/m}^2 \cdot \text{s}$ and $k_L = 1.73 \times 10^{-5} \text{ kg mole/m}^2 \cdot \text{s} \cdot (\text{kg mole/m}^3)$. The Henry's law constant for ammonia is given as $1.36 \times 10^3 \text{ Pa}/(\text{kg mole/m}^3)$. Please evaluate the overall gas-side mass-transfer coefficient. (10%)
6. An important step in the purification of uranium isotopes involves the conversion of uranium to uranium hexafluoride, UF_6 . In the present process, UF_6 is prepared by exposing uranium pellets, spherical in shape, to fluorine gas at 1000 K and 1 atm pressure. The molecular diffusion of fluorine gas to the pellet surface is thought to be the controlling step. If the reaction $\text{U(s)} + 3 \text{F}_2(\text{g}) \rightarrow \text{UF}_6(\text{g})$ occurs irreversibly and instantaneously on the pellet surface, and the diffusivity of fluorine gas through uranium hexafluoride gas is $0.273 \text{ cm}^2/\text{s}$ at 1000 K and 1 atm, determine the production rate of UF_6 when the pellet diameter is 0.4 cm (15%)



本試題共四題，共計 100 分，請依題號作答於答案卷上，違者不予計分。

1. (35 %)

Explain and state the physical meaning in detail for the following terminology:

- 何謂 “ionic coordinate number” ? 它以何種參數作為指標? 另外，它受那些因子影響? (10 %)
- 在 Substitutional solid solution 中，何謂 “Hume-Rothery rule” ? 有何意義? (12 %)
- 在相平衡中，何謂 “Gibbs Phase rule” ? 有何意義? 舉例說明。(13 %)

2. (15 %)

Molecular weight of Polyethylene $(C_2H_4)_n$ is 28000 a.m.u. The length of C-C bond is 0.154 nm and the bond angle is 109.5° . Find out

- Degree of polymerization? (5 %)
- Root mean square length of polymer? (5 %)
- Extended length of polymer? (5 %)



3. (25%)

The rate at which many processes occur is affected significantly by a change in temperature. The quantity of energy which is necessary to initiate a process is activation energy for the process. For the crystallization of cold worked aluminum, rates of linear growth of aluminum crystals are given below.

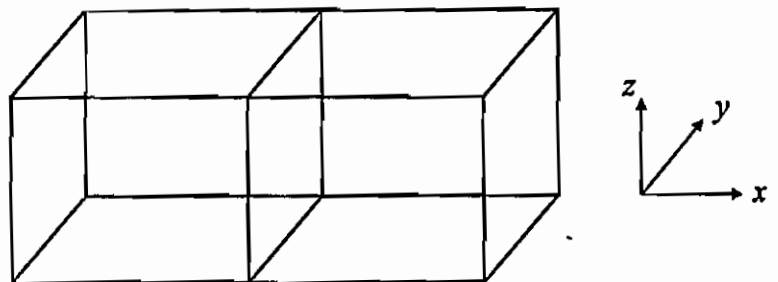
Temperature ($^{\circ}\text{C}$)	200	250	300	400
Rate (mm/s)	5.62×10^{-10}	1.38×10^{-7}	1.35×10^{-5}	1.82

- (a) Show graphically if these data are consistent with the Arrhenius law? (10%)
(b) Calculate the activation energy for the process (kJ/mol)? (15%)

4. (25%)

A crystal contains myriads of atoms arranged in a regular, repetitive pattern known as a space lattice (as shown in the figure below). It is necessary to refer to specific directions within a crystal lattice. The Miller indices ($h k l$), where these are the reciprocals of the intercepts of the plane with the principal axes, in terms of the lengths of the axes, are used as the notation.

You are assigned to sketch and mark the positions of the following planes in the lattice, (a) (100), (b) (111), (c) (231), (d) (122). Please list your calculations.

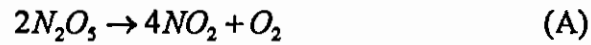




1. A gas cylinder of 2m^3 volume containing nitrogen initially at a pressure of 4 MPa and a temperature 200 K is connected to another cylinder of 2m^3 volume that is evacuated. A valve between the two cylinders is opened until the pressure equalize. Find the final temperature and pressure in each cylinder if there is no heat flow into or out of the cylinders or between gas and cylinder. (You may assume gas is ideal and $C_p=30\text{ J/mole} \cdot \text{K}$) (25%)
2. Determine whether the following process violates the laws of thermodynamics. An ideal gas of $C_p=30\text{ J/mole} \cdot \text{K}$ at 1MPa and 300 K enter a device which is thermally and mechanically insulated from the surroundings. One-half of the gas leaves the device at 400K and 0.1MPa, and the other half leaves at 200K and 0.1MPa. (25%)
3. The vapour pressure of pure liquid A at 293 K is 68.8 kPa and that of pure liquid B is 82.1 kPa. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.612. Calculate the total pressure (kPa) of the vapour and the composition of the liquid mixture. (25%)
4. In the ideal gas-phase reaction $A + 2B \rightleftharpoons 3C + 2D$, it was found that when 2.00 moles A, 1.00 mole B, and 3.00 moles D were mixed and allowed to come to equilibrium at 25°C, the resulting mixture contained 0.79 mole C at a total pressure of 1.00 bar. Calculate (a) the mole fractions of each species at equilibrium, (b) K_x , (c) K , and (d) $\Delta_r G^\circ$ (J/mole). (25%)

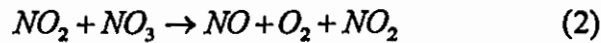


1. The decomposition of N_2O_5 to NO_2 and O_2 is a first-order reaction:



$$r_{O_2} = k_{obs} c_{N_2O_5}$$

A proposed mechanism is as follows:



- (a) Derive the rate law for this mechanism so as to show consistency with the observed form, and to explain k_{obs} in terms of the rate constants for the individual steps. (15%)
- (b) Relate $E_{A,obs}$ to the activation energies of the individual steps, if (i) step (2) is fast, and (ii) step (2) is the rate-determining step. (10%)

2. A gas phase reaction $A \rightarrow B + C$ is to be conducted in an isothermal batch reactor (initial volume 10 liter) at $25^\circ C$ at constant pressure. The reaction is second-order with respect to A, with $k_A = 0.046 \text{ L mol}^{-1} \text{ min}^{-1}$. Determine the time required for 75% conversion of 2 mol A. (25%)



3. Based on the general steady-state mole balance equation on species A, derive the following design equations:

(a). Plug flow reactor (PFR):

$$V = F_{A0} \int_0^{X_{Af}} \frac{dX_A}{(-r_A)} \quad \text{or} \quad \tau = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{(-r_A)} \quad (5\%)$$

(b). Mixed flow reactor (CSTR):

$$V = F_{A0} \frac{X_{Af}}{(-r_A)_f} \quad \text{or} \quad \tau = C_{A0} \frac{X_{Af}}{(-r_A)_f} \quad (5\%)$$

where V is the required reactor volume for conversion of species A changing from inlet $X_{A0}=0$ to outlet X_{Af} , $-r_A$ is the rate of disappearance of species A, F_{A0} and C_{A0} are the entering molar flow rate and entering concentration of species A, respectively, and τ is the space-time defined

as $\tau = C_{A0} V / F_{A0}$.

4. Consider a first-order liquid phase reaction ($-r_A = kC_A$) occurred in a system of N equal-size mixed flow reactors of volume V_i connected in series ($V = NV_i$). If density changes are assumed to be negligible, derive:

(a). $\tau_i = \frac{1}{k} \left[\left(\frac{C_{A0}}{C_{Af}} \right)^{1/N} - 1 \right]$ and $\tau_N = N\tau_i$. (5%)

(b). In the limit, for $N \rightarrow \infty$, this equation reduces to the plug flow

equation: $\tau_p = \frac{1}{k} \ln \frac{C_{A0}}{C_{Af}}$. (5%)

where C_{Af} is the exit concentration of species A calculated by

$$C_{Af} = C_{A0}(1 - X_{Af}).$$

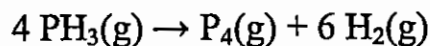


5. An aqueous reaction, $A + B \rightarrow \text{products}$, with the first-order rate equation: $-r_A = 0.158 C_A$, mol/(cm³.min) is considered. The feed rate to be treated is 582 cm³/min (F_{A0}) of solution, with the concentration of species A of 1.4×10^{-4} mol/cm³ (C_{A0}). Assuming volume does not change with reaction, calculate the conversion of species A of each of the following arrangements:

- (a). 3 mixed flow reactors in series (each $V_i=1.8$ liters). (3%)
- (b). 100 mixed flow reactors in series (each $V_i=0.054$ liters). (3%)
- (c). One plug flow reactor ($V=5.4$ liters). (3%)
- (d). One mixed flow reactor ($V_1=2.7$ liters) followed by one plug flow reactor ($V_2=2.7$ liters). (6%)

Hint: Using the equations derived from Problem 4 and 1 liters=1000 cm³.

6. The homogeneous gas decomposition of phosphine:



proceeds at 649°C with the first order rate: $-r_{\text{PH}_3} = 10 C_{\text{PH}_3}$, mol/(m³.hr).

- (a). If the above first-order irreversible gas phase reaction ($-r_A=kC_A$) occurred in a plug flow reactor, derive the following equation:

$$k\tau = -(1 + \varepsilon_A) \ln(1 - X_{Af}) - \varepsilon_A X_{Af}$$

where ε_A is the fractional change in volume of the system between no conversion and complete conversion of reactant A. (7%)

Hint: The volume is related to the conversion by: $V = V_0(1 + \varepsilon_A X_A)$.

- (b). What size of plug flow reactor operating at 649°C and 460 kPa can produce 90% conversion of a feed consisting of 60 mol of pure phosphine per hour? (8%)

Hint: The gas constant $R=8.314$ Pa.m³/(mol.K).



1. (15%) Argue that a substance will move spontaneously from any phase of higher value of its chemical potential to any other phase of lower value of its chemical potential in a system with each phase at constant V and with both phases at the same constant T .
2. (15%) Explain why the thermodynamic entropy of the system changes in each of the following processes, and tell whether it increases or decreases. Do the same for the statistical entropy in each process. (a) A sample of a gas is heated at constant volume, (b) A sample of gas is expanded at constant temperature, (c) A sample of liquid water is heated, (d) A sample of liquid water is frozen, (e) A sample of liquid water is vaporated.
3. (20%) Find the final temperature if a stoichiometric mixture of methane and oxygen is ignited at 298.15 K and allowed to react adiabatically at a constant pressure. Assume that the reaction proceeds to completion and that the heat capacities of the products are constant and equal to their values at 2000 K. All thermodynamic quantities required for the calculation can be found in the appended table.



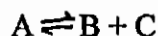
國立雲林科技大學
97 學年度碩士班入學招生考試試題

系所：化材系
科目：物理化學

Quantities						
$\frac{T}{K}$	$\frac{C_{P,m}^{\circ}}{J K^{-1} mol^{-1}}$	$\frac{S_m^{\circ}}{J K^{-1} mol^{-1}}$	$-\frac{(G_m^{\circ} - H_{m298}^{\circ})}{T}$ $J K^{-1} mol^{-1}$	$\frac{H_m^{\circ} - H_{m298}^{\circ}}{kJ mol^{-1}}$	$\frac{\Delta H_f^{\circ}}{kJ mol^{-1}}$	$\frac{\Delta G_f^{\circ}}{kJ mol^{-1}}$
CH ₄ (g)						
0	0	0		-10.024	-66.911	-66.911
298	35.639	186.251	186.251	0	-74.873	-50.768
500	46.342	207.014	190.614	8.200	-80.802	-32.741
1000	71.795	247.549	209.370	38.179	-89.849	19.492
2000	94.399	305.853	244.057	123.592	-92.709	130.802
H ₂ O(g)						
0	0	0		-9.904	-238.921	-238.921
298	33.590	188.834	188.834	0	-241.826	-228.582
500	35.226	206.534	192.685	6.925	-243.826	-219.051
1000	41.268	232.738	206.738	26.000	-247.857	-192.590
2000	51.180	264.769	228.374	72.790	-251.575	-135.528
CO ₂ (g)						
0	0	0		-9.364	-393.151	-393.151
298	37.129	213.795	213.795	0	-393.522	-394.389
500	44.627	234.901	281.290	8.054	-393.676	-394.939
1000	54.308	269.299	235.901	33.397	-394.623	-395.886
2000	60.350	309.293	263.574	91.439	-396.784	-396.333



4.(16%)A gas reaction



is endothermic and its equilibrium constant K_p is 1 atm at 25°C.

- What is ΔG° at 25°C (standard state: 1 atm)?
- Is ΔS° , with the same standard state, positive or negative?
- For the standard state of 1 M, what are K_c and ΔG° ?
- Will K_p at 40°C be greater than or less than 1 atm?
- Will ΔG° at 40°C (standard state: 1 atm) be positive or negative?

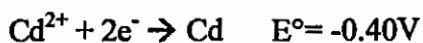
5. (12%)Benzene and toluene form nearly ideal solutions. If, at 300K,

$P^*(\text{toluene})=3.572\text{kPa}$ and $P^*(\text{benzene})=9.657\text{kPa}$, compute the vapor pressure of a solution containing 0.60 mol fraction of toluene. What is the mole fraction of toluene in the vapor over this liquid?

6. (12%)a. Write both electrode reactions and the over-all reaction for the cell

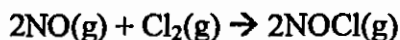


b. Calculate the E and E° for this cell at 298.15 K from the following information:



The solubility product for $\text{TlCl} = 1.6 \times 10^{-3} \text{ mol}^2\text{dm}^{-6}$ at 298.15K.

7.(10%)The reaction



is second order in NO and first order in Cl_2 . In a volume of 2 dm^3 , 5 mol of nitric oxide and 2 mol of Cl_2 were brought together, and the initial rate was $2.4 \times 10^{-3} \text{ mol dm}^{-3}\text{s}^{-1}$. What will be the rate when one-half of the chlorine has reacted?



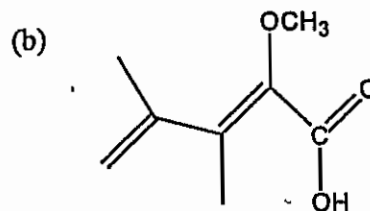
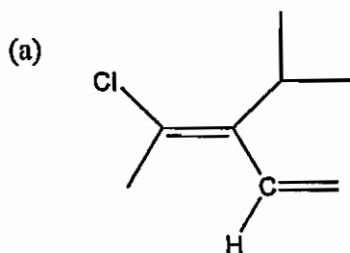
1. (10%)

解釋下列名詞

- (1) Transition state
- (2) Endergonic reaction
- (3) Radical Reaction
- (4) Enantiomers
- (5) Chirality center
- (6) Levorotatory
- (7) Dextrorotatory
- (8) Define R and S configuration
- (9) Diastereomer
- (10) Prochirality

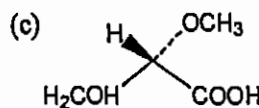
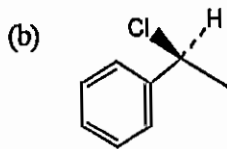
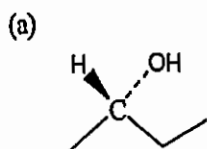
2. (5%)

Assign stereochemistry (E or Z) to each of the following alkenes :



3. (5%)

Assign R or S configurations to the chirality centers in the following molecules:



4. (15%)

Consider 2-methylbutane (isopentane) . Sighting along the C2-C3 bond :

- (1) Draw a Newman projection of the most stable conformation.
- (2) Draw a Newman projection of the least stable conformation.
- (3) Since a CH₃-CH₃ eclipsing interaction costs 11 kJ/mol (2.5 kcal/mol) and a CH₃-CH₃ gauche interaction costs 3.8 kJ/mol(0.9 kcal/mol), make a quantitative plot of energy versus rotation about the C2-C3 bond.



5. (15%)

The following compound, with the formula $C_4H_8O_2$, is an ester. Give its structure and assign the chemical shift values.



6. (15%)

- What is the ring substitution in aromatic amine? (5%)
- What is the sulfonation of aromatic amine? (5%)
- What is the nucleophilic addition? (5%)

7 (20%)

Please describe five methods to prepare alcohols.

8 (15%)

Please describe reaction of epoxides.

- acid-catalyzed cleavage (5%)
- base-catalyzed cleavage (5%)
- reaction with Grignard reagents (5%)