

國立中山大學99學年度碩士班招生考試試題

科目：物理化學【材光系碩士班甲組】

1. By definition, a van der Waals gas obeys the equation of state: $P = \frac{RT}{V-b} - \frac{a}{V^2}$ where P is the pressure, T the absolute temperature, V is the molar volume, and R is the gas constant (20%, 5% each)

(a) What are the physical meanings of parameters a and b , respectively?

(b) Explain why the critical point of the van der Waals gas corresponds to the simultaneous satisfaction of

$$\frac{dP}{dV} = \frac{d^2P}{dV^2} = 0 \quad \text{and show that the critical constants are related to the van der Waals parameters}$$

$$\text{according to } V_c = 3b, P_c = \frac{a}{27b^2}, \text{ and } T_c = \frac{8a}{27Rb}$$

(c) Show that the van der Waals equation of state is writing in the virial form

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots$$

$$\text{and the second virial coefficient is given by } B = b - \frac{a}{RT}$$

(d) Describe the Boyle temperature (T_B) and express T_B is term of van der Waals parameters a and b .

2. Naphthalene, $C_{10}H_8$, melts at 80.2°C . If the vapor pressure of the liquid is 1.3 kPa at 85.8°C and 5.3 kPa at 119.3°C , use the Clausius-Clapeyron equation to calculate (a) the enthalpy of vaporization, (b) the normal boiling point, and (c) the entropy of vaporization at the boiling temperature. (15%, 5% each)

3. 1 g of poly(ethylene oxide) (PEO, water soluble polymer) is dissolved in 100 g of water at room temperature in a sealed glass vial and observed to be perfectly clear solution. The vial is then taken to the laboratory sink and placed under a stream hot water. The polymer solvent mixture now becomes turbid and looks like milk. Next the vial is placed under a stream of water from the cold water tap and the polymer mixture reverts to a perfectly clear solution. How would you explain this phenomenon?

(10%)

4. Certain polymerizations involve reactions between $-\text{COOH}$ groups on one molecule and $-\text{NH}_2$ group on another. Suppose that the concentration of such functional groups is c and that the rate obeys the equation $-dc/dt = kc^2$. Obtain an equation relating the time t to the fraction f , of functional groups remaining and to the initial concentration c_0 of functional group. (10%)

5. If we already provide the gas speed that obeys the following equations

$$(1) v^2 = v_x^2 + v_y^2 + v_z^2$$

$$(2) F(v) = f(v_x)f(v_y)f(v_z)$$

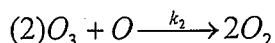
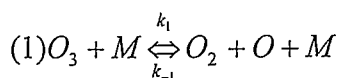
$$(3) \int_0^{\infty} F(v) dv = \int_{-\infty}^{\infty} f(v_x) dv_x = \int_{-\infty}^{\infty} f(v_y) dv_y = \int_{-\infty}^{\infty} f(v_z) dv_z$$

- (a) Show that the probability of gas speed is: $F(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{-mv^2}{2kT}\right) 4\pi v^2$ (15%)

- (b) Since there is a distribution of molecular speed, there are different measures of the average speed. Derive equations for the mean speed $\langle v \rangle$, the root-mean-square speed $\langle v^2 \rangle^{1/2}$, and the most probable speed v_p . (10%)

- (c) For carbon dioxide ($M = 44$ g/mol) at 1 bar and 298 K, calculate the most probable speed, mean speed, root mean square speed (Hint: $R = 8.314$ J)? (10%)

6. Derive the rate law for the decomposition of ozone in the reaction $2\text{O}_3 \rightarrow 3\text{O}_2$ on the basis of the mechanism: (10%)



國立中山大學99學年度碩士班招生考試試題

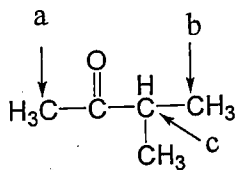
科目：有機化學【材光系碩士班甲組】

1. 選擇題 (單選, total 30%, each 2%)

(Questions 1)-4)) Match the following groups of the bond-type to the region of infrared spectrum to which they absorb? a) $4000-2500\text{ cm}^{-1}$, b) $2500-2000\text{ cm}^{-1}$, c) $2000-1500\text{ cm}^{-1}$, d) below 1500 cm^{-1} .

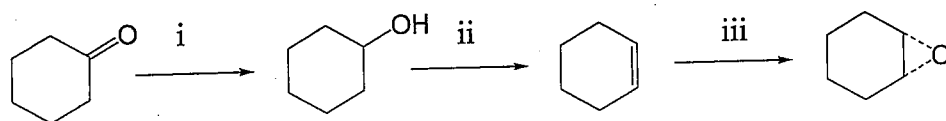
- 1) () C-C, C-O, C-N single bonds vibrate at _____.
- 2) () C=O, C=N and C=C bond absorptions at _____.
- 3) () N-H, C-H and O-H bond stretching and bending motions at _____.
- 4) () Triple bond stretching vibrations at _____.

(Questions 5)-7)). Refer to the structure of 3-methyl-2-butanone below to answer the following questions:



- 5) () What is the splitting pattern for the hydrogens in 3-methyl-2-butanone labeled a? a) septet, b) quartet, c) doublet, d) singlet.
- 6) () What is the splitting pattern for the hydrogens in 3-methyl-2-butanone labeled b? a) septet, b) quartet, c) doublet, d) singlet.
- 7) () What is the splitting pattern for the hydrogen in 3-methyl-2-butanone labeled c? a) septet, b) quartet, c) doublet, d) singlet.

(Question 8)-10)) There are three reagents i ~ iii required to perform the reaction scheme below

a) $m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$, b) H_2/Pd , c) warm $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$, d) PCC, CH_2Cl_2 , e) LiAlH_4 in ether, then H_3O^+ , f) NaOH , heat.

- 8) () Chose the right reagents i from the above reagent lists from a) to f).
- 9) () Chose the right reagents ii from the above reagent lists from a) to f).
- 10) () Chose the right reagents iii from the above reagent lists from a) to f).

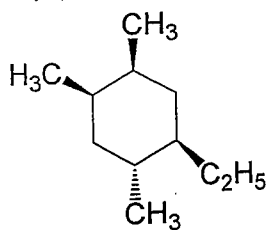
11) () The acid-catalyzed reaction of propanal with methanol goes from the hemiacetal to the acetal. This can mechanistically be thought of as: a) an addition reaction followed by a substitution reaction. b) a substitution reaction followed by an addition reaction. c) an elimination reaction followed by a substitution reaction. d) an addition reaction followed by an elimination reaction.

12) () Diel Alder reaction can be carried out between a diene and dienophile under what condition? a) basic condition. b) Lewis acid catalyst and heat. c) photochemical. d) thermal (heat). e) both thermal and photochemical.

13) () Which terms are related to the reaction of carbonium (or carbocation) with nucleophile? a) SN_2 . b) SN_1 . c) inversion product. d) racemic products. e) retention product.

To be continued --

14) () Consider the structure shown



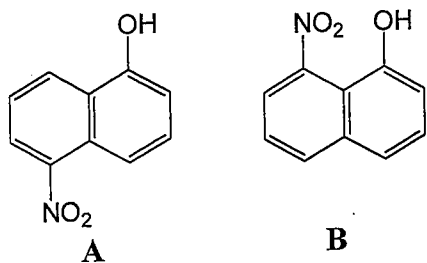
In the more stable chair conformation of this compound, how many of the groups will occupy equatorial position? a) 0. b) 1. c) 2. d) 3. e) 4.

15) () If 1-propyne is added to a solution of ethyl magnesium bromide, what gas will be evolved? a) HBr. b) H₂. c) Br₂. d) C₂H₆. e) C₂H₅Br.

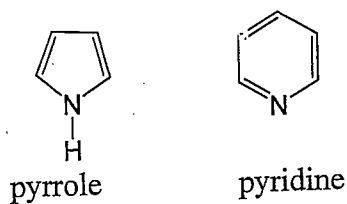
2. (Total: 30%) Relative acidity (or basicity) of organic compounds commonly relates to the stability of the chemical species involved in the relating conjugated base (or acid). Based on your knowledge on the structural stability of organic compounds, comment on the relative acidity (or basicity) of the following compounds.

a) For CF₃COOH and CCl₃COOH, which is stronger acid? (5%) Why? (5%)

b) Which of the following nitronaphthols (**A** or **B**) is the stronger acid (5%)? why? (7%)

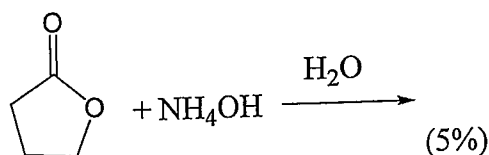


c) Pyrrole is a much weaker base than pyridine. Explain (8%)



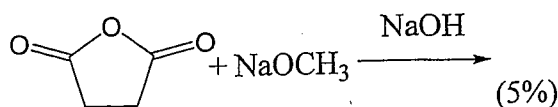
3. (Total: 23%) Ring-opening reaction of cyclic ester can be conducted with various reagents to result in different chemical products dependent on the reaction conditions. Predict the products for the reactions a)-c) shown below:

a)

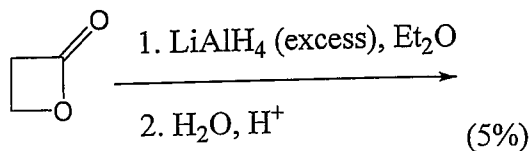


To be continued --

b)



c)



d) Write up the mechanistic steps involved in the reaction c) above: (8%)

4. (Total: 17%) Aromatic substitution reaction provides lots of routes to prepare new organic compounds, however, a successful reaction relies on the reactivity of the reagents used, the starting compound and the reaction site, which determine the intermediates involved and the resulting products, a situation especially hold for mono-substituted benzene derivative.

a) Nitration of monosubstituted benzenes (as X-Ph, X stands for the substituent) can be performed by reacting them with $\text{HNO}_3/\text{H}_2\text{SO}_4$. What is the real species (electrophile) responsible for the nitration reaction (in other word, the reaction species formed after reaction of HNO_3 and H_2SO_4)? (6%)

b) The nitration reactivity is strongly dependent on the substituent X. Which of the two substituents ($\text{X} = -\text{OCH}_3$ and $-\text{Cl}$) will have better reactivity towards nitration? (4%) Why? (7%)

-- Total 3 pages, end of examination --

1. Find general solution of $y'' - \frac{2x}{x^2+1}y' + \frac{2}{x^2+1}y = 12(x^2+1)$ (15%)

2. Find solution by using Laplace transform method
 $y'' + 4y' + 13y = 145 \cos 2t$, $y(0) = 10$, $y'(0) = 14$ (15%)

3. Solve the function (20%)

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} - u = 0$$

Boundary Condition: $u(x,0) = u(x,L) = u(0,y) = u(a,y) = u_b$

4. (a) Find the volume of the tetrahedron with vertices $(0,2,1)$, $(4,3,0)$, $(6,6,5)$, $(4,7,8)$ (10%)

(b) Find the directional derivative of f at P in the direction of a (10%)
 $f = 4x^2 + y^2 + 9z^2$, $P: (2,4,0)$, $a = [-2, -4, 3]$

5. Find the Fourier transform of $f(x)$. Show the details

$$f(x) = \begin{cases} x & \text{if } -1 < x < 1 \\ 0 & \text{otherwise} \end{cases} \quad (10\%)$$

6. Please find their eigenvalues and eigenvector (20%)

$$A = \begin{bmatrix} -2 & 2 & -3 \\ 2 & 1 & -6 \\ -1 & -2 & 0 \end{bmatrix}$$

請於答案卷上依序作答，清楚列出運算過程，並整理答案於每題目的最後部分

1. Please describe the meaning of (a) the state function, and (b) the partial molar quantities. (10%)
2. Water flows over a waterfall 100 meter in height. Consider 1 kg of water, and assume that no energy is exchanged between this 1 kg and its surroundings. (a) What is the potential energy of the water at the top of the falls with respect to the base of the falls? (5%) (b) What is the kinetic energy of the water just before it strikes the bottom? (5%) (c) After the 1 kg of water enters the river below the falls, what change has occurred in its state? (10%)
3. At a pressure of 1 atm the equilibrium melting temperature of zinc is 693 K, and, at this temperature, the latent heat of melting of zinc is 1740 cal/mole. Calculate the entropy produced when one mole of supercooled liquid zinc spontaneously freezes at 673 K constant temperature heat reservoir. Assume the constant pressure molar heat capacity of liquid zinc and solid zinc are the same. ($C_p = 7.5 \text{ cal/mole.K}$) (20%)
4. One mole of a monatomic ideal gas is subjected to the following sequence of steps:

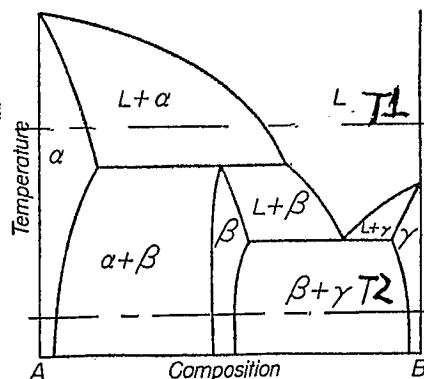
Step A. Starting at 300 K and 10 atm, the gas expands freely into a vacuum to triple its volume.

Step B. The gas is next heated reversibly to 400 K at constant volume.

Step C. The gas is reversibly expanded at constant temperature until its volume is again tripled.

Step D. The gas is finally reversibly cooled to 300 K at constant pressure.

Calculate the values of q and w and the changes in U , H and S . (25%) ($C_v = 1.5R$ per mole.K for ideal gas)
5. According to the following phase diagram, (a) write down the three phase reactions and name it. (5%) (b) Sketch the free energies of mixing (ΔG^M) for the liquid and phases as a function of composition at temperature T_1 and T_2 . (10%) (c) Sketch the activities of A and B as a function of composition at temperature T_1 and T_2 . (10%)



Reflection, Refraction, and Interference (60%, each question 12%)

1. Two harmonic light waves are incident into a piece of glass from the air. The two waves when propagating inside the glass have magnetic fields given by

$$\vec{H}_1 = \hat{x}H_0 e^{i\pi 10^6(z \cos \theta_1 - y \sin \theta_1 - 2 \times 10^8 t)}, \text{ and}$$

$$\vec{H}_2 = \hat{x}H_0 e^{i\pi 10^6(z \cos \theta_1 + y \sin \theta_1 - 2 \times 10^8 t)},$$

A screen is embedded inside the glass and is located on the plane $z = 0$. As shown in Fig. 1, the two waves interfere with each other and generate a periodic intensity distribution on the screen. The y - z axis is located in the figure plane and the x -axis is normal to the figure plane. The index of refraction of the air is 1 while that of the glass is n . Time is in seconds and x , y , and z are in meters.

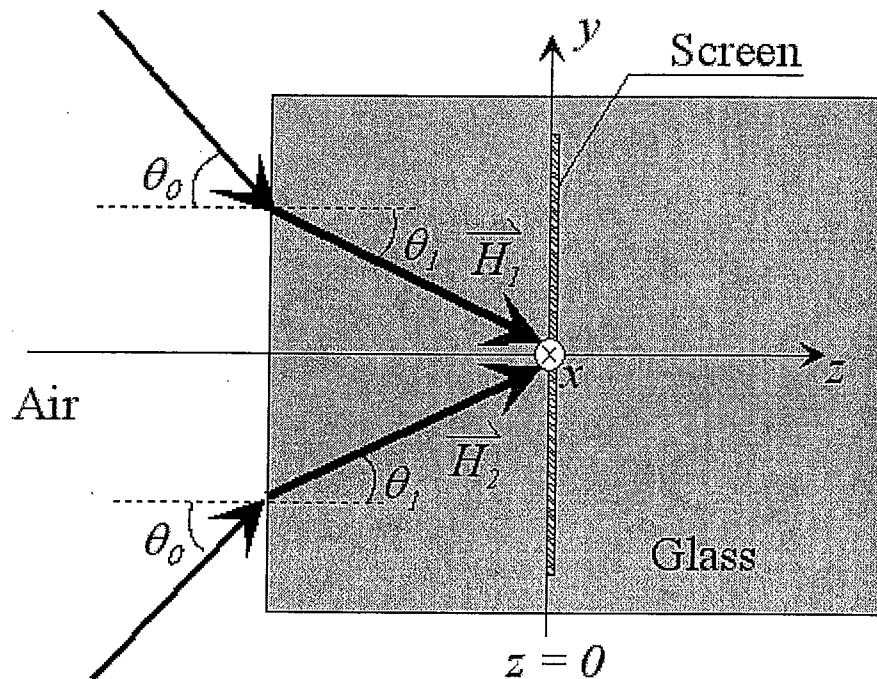


Fig. 1.

The amplitude reflection coefficient r , known as the Fresnel equation, is given by

$$r = \frac{n \cos \theta_0 - \cos \theta_1}{n \cos \theta_0 + \cos \theta_1}$$

For a specific incident angle θ_0 , there is no reflected beam and all of the two incident waves are transmitted from air to the glass. In such a situation, please find: (a) the frequency of the light waves, (b) the wavelength of the light waves in the glass, (c) the index of refraction of the glass, (d) the refraction angle θ_1 , (e) the period of the interference fringes on the screen (at the plane $z = 0$).

Potential distribution (40%)

2. A conductive duct and a cover are connected with electricity as shown in Fig. 2. The cover plate has a potential

$$\phi = V_0 \sin\left(\frac{4\pi x}{a}\right),$$

while the duct has $\phi = 0$. The duct and the cover are assumed to be infinite in extent in the z-axis. Please find the potential distribution $\phi(x, y)$ inside the cavity.

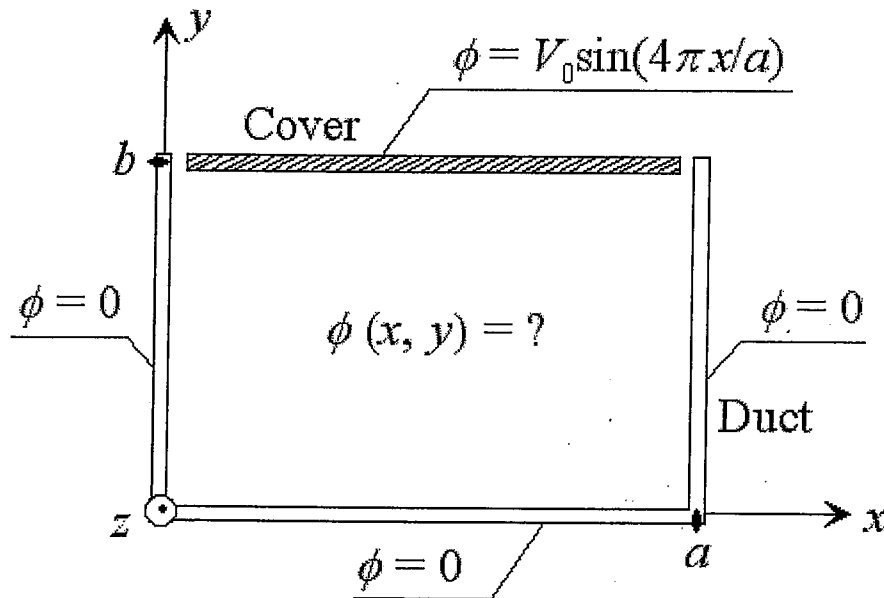


Fig. 2.

科目：材料科學【材光系碩士班丙組】

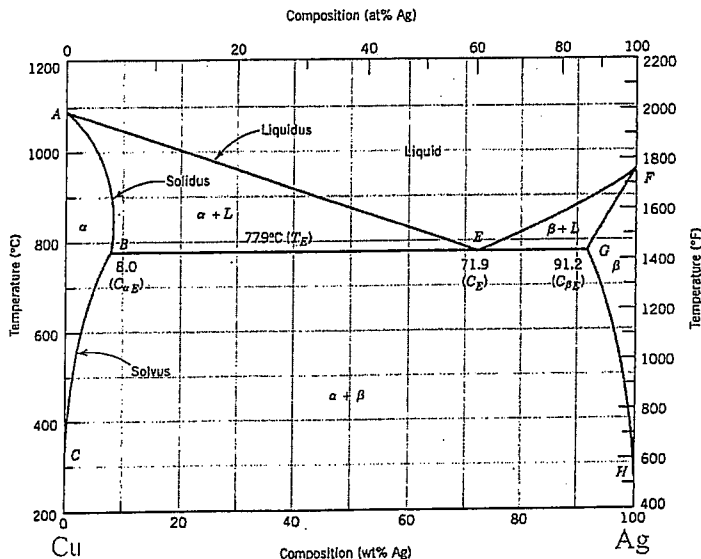
- (1) It is well known that ordinary glass is susceptible to thermal shock, therefore, tempered glass has been developed to overcome this problem. Describe the process to produce tempered glass, and explain why tempered glass can stand thermal shock. 10 points

- (2) The dislocation density of 12 inch (diameter) silicon wafers produced by company A is $6 \times 10^4 \text{ cm}^{-2}$. The thickness of the silicon wafers is 0.5 mm. The dislocation density of cold rolled aluminum sheet produced by company B is $3 \times 10^{10} \text{ cm}^{-2}$. The thickness of the aluminum sheet is the same as the silicon wafers. How many silicon wafers are needed to have the same total dislocation length as in a piece of 1 cm x 1 cm cold rolled aluminum sheet? 5 points

- (3) Give a schematic drawing of a tensile engineering stress-strain curve of a ductile metal. Indicate (a) 0.2% yield stress, (b) ultimate tensile stress, (c) proportional limit, and (d) fracture strain on the stress-strain curve. If specimen necking occurred during tensile test of this material, at which position necking started to form? 10 points

- (4) Explain the following terms: (a) Fick's second law, (b) Fracture toughness, (c) lever rule, (d) stoichiometry composition, (e) subgrain boundary, (f) metastable phase. 30 points

- (5) A Cu-5wt% Ag alloy is heated at 1173K for a long enough time so that a single solid phase developed. Will there be a single or multiple phases when this alloy is cooled down to room temperature? The Cu-Ag phase diagram is shown below. 5 points



- (6) The variation and scatter in fracture strength for specimens of a brittle ceramic material is often quite large. Give the reason for this. 5 points
- (7) A material which has an hcp structure with the c/a ratio equals to 2. Give schematic drawings of atom positions of $(10\bar{1}0)$ and $(11\bar{2}0)$ of this material. On your drawings, directions and atomic spacing need to be specified. The length of the c axis is 1 nm. 10 points
- (8) Recrystallized grain size is the grain size immediately at the end of a recrystallization process, it depends on the nucleation rate and the growth rate of the recrystallization process. Explain how the nucleation rate and the growth rate affect the recrystallized grain size? 10 points
- (9) It is well known that reduce grain size can increase the yield strength of a material, it is also well known that increase grain size can increase the creep strength of a material. Explain the difference! 10 points
- (10) Explain what is piezoelectric effect? 5 points