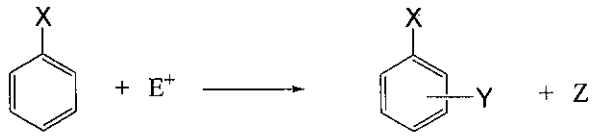
國立中山大學９６學年度碩士班招生考試試題

科目：有機化學【材料所碩士班甲組】

1) Most reactions of aromatic compounds are the electrophilic aromatic substitution, that is, an electron-poor reagent (an electrophile, E^+) reacts with an electron-rich aromatic ring (a nucleophile, Ph-X) and substitutes for one of the ring hydrogens: (total: 45%)

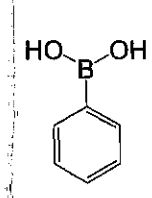


i) An alkyl group can be introduced by Friedel-Craft alkylation through a carbocationic electrophile (i.e. $E^+ = R^+$). Experimentally, most of the Friedel-Craft alkylation use aluminum chloride ($AlCl_3$) as catalyst to enhance the ionization of alkyl chloride (R-Cl) to become the desired carbocation R^+ species. From the characteristic of $AlCl_3$, comment on why $AlCl_3$ serves so effective to convert R-Cl into carbocation R^+? (10%)

ii) Substituent (X) affects the reactivity of the aromatic ring, that is, some substituents activate the aromatic ring for electrophilic reaction while some deactivate it. Rank the reactivity order of aromatic ring with X = F, CH_3, NO_2, C(=O)-H, OCH_3 and Br. (10%)

iii) Substituent X also affects the orientation of the reaction, for example, methoxy (X= O-CH_3) is an *ortho-para* but not a *meta* director. This orientation difference can be explained by the stability of the involved carbocationic intermediate. Using X = O-CH_3 as example, show the most stable two cationic intermediates after *ortho* and *para* attacks of R^+. (10%)

iv) Would you expect benzeneboronic acid to undergo nitration at the *ortho* and *para* or *meta* positions? (5%) Why? (10%)



benzeneboronic acid

2) Rate of chemical reaction is deeply affected by the involved mechanism and the best illustration for this remark is given by the nucleophilic attack of organic nucleophiles towards alkyl halides. (total: 20%)

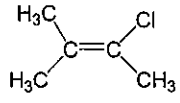
i) Suppose that there are two nucleophilic reactions involving two different aliphatic halides and nucleophiles as given below:

a) CH_3-Br + NaCN → CH_3-CN + NaBr

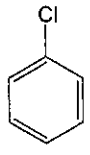
b) $(CH_3)_3C$-Br + CH_3-OH → $(CH_3)_3C$-OCH_3 + HBr

If concentrations of alkyl bromide (CH_3-Br or $(CH_3)_3C$-Br) and nucleophile (NaCN or CH_3-OH) are both doubled, what effect would you expect for the reaction rates of a) and b)? (4%) Why? (6%)

ii) Situation is different if the target molecules change from alkyl halides to vinylic (e.g. $(CH_3)_2C{=}C(CH_3)$-Br) and aryl (Ar-Br) chlorides, the nucleophilic attacks failed. Use the following examples as demonstrations, give your explanation: (10%)

a) 

+ NaCN → No reaction

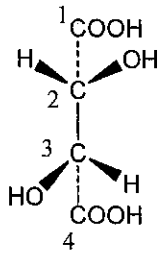
b) 

+ NaCN → No reaction

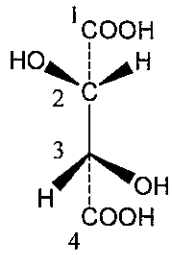
國立中山大學９６學年度碩士班招生考試試題

科目：有機化學【材料所碩士班甲組】

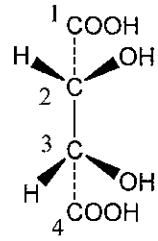
3) Stereochemistry concerns with three-dimensional structures of organic molecules, especially those containing stereo- (chiral) centers. One stereocenter gives rise to two stereoisomers and two stereocenters gives rise to a maximum of four stereoisomers (two pairs of enantiomers), simple example can be given by tartaric acid shown below: (total: 20%)



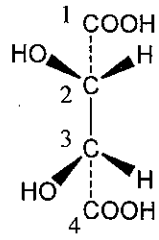
A



B



C



D

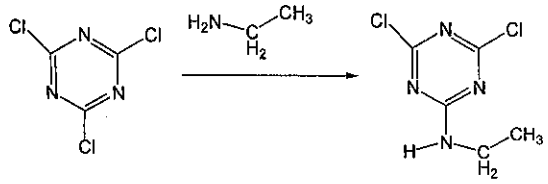
i) For each of the two pairs shown above, A and B (or C and D) are mirror image of the other. Assign the configurations (e.g. 2R,3S) for A, B, C and D. (10%)

ii) Which two structures are actually identical? (5%)

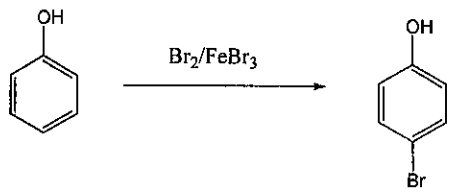
iii) Except the identical one given in ii), the rest two are enatiomeric pair. Do these two enatiomers have the same solubility toward organic solvent? (5%)

4) Propose reaction mechanism for the following reactions: (total: 15%)

i) (5%)



ii) (5%)



iii) (5%)

國立中山大學９６學年度碩士班招生考試試題

科目：物理化學【材料所碩士班甲組】

1. The equilibrium internuclear distances in HCl, HBr, and HI are 127, 141, and 161 pm, respectively. Their experimental values of the dipole moment are 3.60×10^{-30}, 2.67×10^{-30}, and 1.40×10^{-30} C m, respectively. Find the effective fractional charges on the H and X ions. How do you explain the difference? (8%)

2. In his 1924 doctoral thesis, de Broglie developed an equation for the wavelength of a particle by reasoning in analogy with photons. Calculate the de Broglie wavelengths of the following:
   (a) a 1 g bullet with velocity 300 m s^{-1} (3%)
   (b) a 10^{-10} g particle with velocity 10^{-10} m s^{-1} (3%)
   (c) an H_2 molecule with energy of $\frac{3}{2}kT$ at $T = 20$ K (4%)
   (d) an electron that has been accelerated through a potential difference of 100V (4%)

3. Prove that if Henry's law holds for the solute (component 2), Raoult's law holds for the solvent (component 1). (8%)

4. Nitrogen trioxide dissociates according to the reaction
   $$N_2O_3(g) = NO_2(g) + NO(g)$$
   When one more of $N_2O_3(g)$ is held at 25 °C and 1 bar total pressure until equilibrium is reached, the extent of reaction is 0.30. What is the value of the standard Gibbs energy for this reaction at 25 °C? (6%)

5. A molecule of mass m moves with velocity v. The probability density $F(v)$, for the Maxwell distribution of speeds, is
   $$F(v) = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right)$$
   As a result the probability density at a speed of 0 is zero. The probability density increases with the speed up to a maximum and then declines. Since there is a distribution of molecular speeds, there are different measures of the average speed. Derive equations for the most probable speed v_{mp}, the mean speed $\langle v \rangle$, and the root-mean-square speed $\langle v^2 \rangle^{1/2}$. (12%)
   Calculate the most probable speed v_{mp}, the mean speed $\langle v \rangle$, and the root-mean-square speed $\langle v^2 \rangle^{1/2}$ for hydrogen molecules at 0 °C. (6%)

Speed of light in vacuum $c = 2.988 \times 10^8$ m s^{-1}; Atomic mass of H is 1.00794;
Planck constant $h = 6.626 \times 10^{-34}$ J s; Avogadro constant $N_A = 6.022 \times 10^{23}$ mol^{-1};
Electron mass $m_e = 9.109 \times 10^{-31}$ kg; Elementary charge $e = 1.602 \times 10^{-19}$ C;
Boltzmann constant $k = 1.381 \times 10^{-23}$ J K^{-1}

6. If reaction occurs with each collision, we can obtain the reaction rate in moles of collisions between molecules of type 1 and type 2 per unit volume per unit time by dividing by the Avogadro constant to obtain

$$\frac{-d[B_1]}{dt} = \frac{Z_{12}}{N_A} = \frac{\pi d_{12}^2 \langle v_{12} \rangle}{N_A} \rho_1 \rho_2$$

In discussing chemical kinetics, concentrations are used rather than number densities, and so we need to replace the number densities by using

$$\rho_i = \frac{N_i}{V} = \frac{n_i N_A}{V} = [B_i] N_A$$

Calculate the biomolecular rate constant at 298 K for the reaction of two different "average" small radicals with a reduced mass μ of 30×10^{-3} kg mol^{-1}/N_A = 4.98×10^{-26} kg and a collision diameter d_{12} of 500 pm. (6%)

7. In using buffers in the laboratory, it is convenient to use an acid dissociation constant $K(I)$ that is a function of the ionic strength as well as T and P. Prepare 1 liter of an acetate buffer of 0.1 ionic strength and pH 5.0 at 25 °C. How many moles of sodium acetate and acetic acid should you add if the apparent dissociation constant of acetic acid at this ionic strength is 2.69×10^{-5}? (6%)

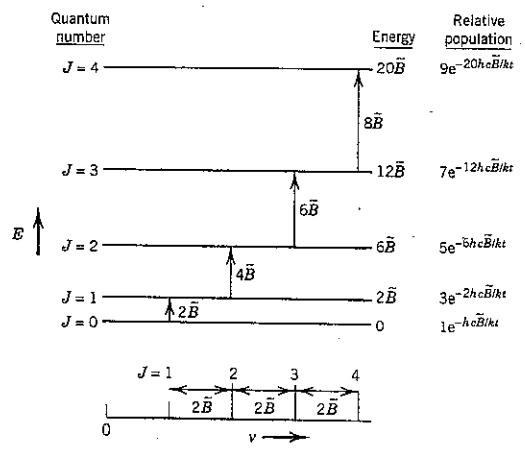
8. Calculate the ratios of populations at 25 °C of energy level separated by (a) 1 eV and (b) 10 eV. (c) Calculate the ratios at 1000 °C. (6%)

9. (a) Calculate the change in entropy of an ideal monatomic gas B in changing from P_1, T_1 to P_2, T_2. What does this indicate about the form of the expression for the molar entropy of the gas? (6%)
   (b) What is the change in molar entropy of helium in the following process?
   1 He(298 K, 1 bar) → 1 He(100 K, 10 bar) (4%)

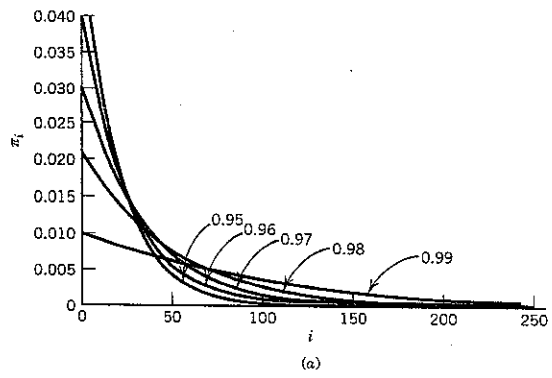
10. The percentage transmittance of an aqueous solution of disodium fumarate at 250 nm and 25 °C is 19.2% for a 5×10^{-4} mol L^{-1} solution in a 1 cm cell. (a) Calculate the absorbance A and the molar absorption coefficient ε. (b) What will be the percentage transmittance of a 1.75×10^{-5} mol L^{-1} solution in a 10 cm cell? (6%)

11. The followed figure shows the rotational levels for a rigid diatomic molecule and the absorption spectrum that results from $\Delta J = 1$. The energies and relative populations of the two levels are indicated on the right. How to derive their levels of energies and relative populations in terms of the rotational constant? (6%)

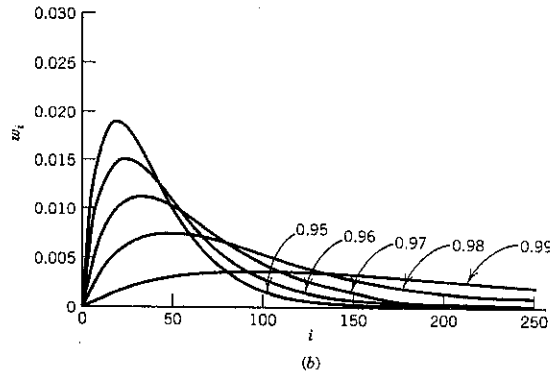
    (where the rotational constant is written as $\tilde{B} = h/8\pi^2 Ic$, c is the speed of light)



12. The followed figure plots (a) mole fraction distribution of condensation polymer for extents of reaction p of 0.95, 0.96, 0.97, 0.98, and 0.99. (b) weight fraction distribution of condensation polymer for extents of reaction p of 0.95, 0.96, 0.97, 0.98, and 0.99. Describe or discuss this figure in detail. (6%)



(a)



(b)

國立中山大學９６學年度碩士班招生考試試題

科目：工程數學【材料所碩士班乙、丙組】

Prob. #1. The following matrix is Hermitian ? Skew-Hermitian ? Unitary ? Find their eigenvalues and eigenvector (20%)

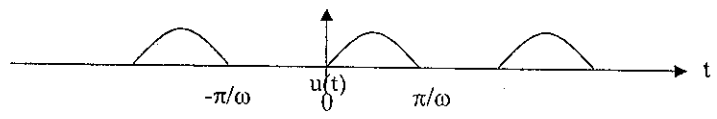
$$\begin{bmatrix} 0 & 1+i & 0 \\ 1-i & 0 & 1+i \\ 0 & 1-i & 0 \end{bmatrix}$$

Prob. #2. Find the Fourier transform of f(x). Show the details

(a) $$f(x)=\begin{cases} e^{kx} & \text{if } x<0,\ (k>0) \\ 0 & \text{if } x>0 \end{cases}$$ (10%)

(b) $$f(x)=\begin{cases} e^{2ix} & \text{if } -1<x<1 \\ 0 & \text{otherwise} \end{cases}$$ (10%)

Prob. #3. A sinusoidal voltage $E\cdot\sin\omega t$, where t is time, is passed through a half-wave rectifier that clips the negative portion of the wave, like the figure. Find the Fourier series of the resulting periodic function (20%)



$$u(t)=\begin{cases} 0 & \text{if } -L<t<0 \\ E\cdot\sin\omega t & \text{if } 0<t<L \end{cases} \qquad p=2L=\frac{2\pi}{\omega},\ L=\frac{\pi}{\omega}$$

Prob. #4. Solve the ordinary differential equation with Logarithmic term (20%)

$$(x^2-x)\cdot y''-x\cdot y'+y=0$$

Prob. #5. A damping mass-spring system was acted upon by a sinusoidal force for some time interval. The sinusoidal force r(t) is as below:

$$r(t)=10\cdot\sin(2t),\ \text{if } 0<t<\pi$$
$$r(t)=0,\ \text{if } t>\pi$$

The system is governed by a second order differential equation $y''+2y'+2y=r(t)$ with the initial condition of $y(0)=1$, $y'(0)=-5$. Please solve this initial value problem and make a plot of y(t). (20%)

國立中山大學９６學年度碩士班招生考試試題

科目：材料力學【材料所碩士班乙組】

1. (30%) Describe the physical meaning of the following terminology.
   (a) Elastic and plastic deformation
   (b) Brittle, ductile and crystalline materials
   (c) Solid solution strengthening and precipitation hardening

2. (20%) For a plane stress state $\sigma_z = \tau_{xz} = \tau_{yz} = 0$, if the strains ε_x and ε_y have been determined experimentally, determine the expressions for σ_x, σ_y, and ε_z in terms of E, ν, ε_x, and ε_y.

3. (25%) At a point of interest in an engineering component, the stresses with respect to a convenient coordinate system are: $\sigma_x = 100, \sigma_y = -60, \sigma_z = 40, \tau_{xy} = 80, \tau_{yz} = \tau_{zx} = 0$ MPa.
   Determine the principal normal and shear stresses.

4. (25%) Consider a thin-walled tube with closed ends and internal pressure p. The wall thickness is t, the radius to mid-thickness is r, and the ductile material has a yield strength σ_0.
   (a) Derive the stress state in the tube. (b) If the maximum shear stress yield criterion is applied, derive an equation for the required thickness corresponding to the specified value of r against yielding.

國立中山大學９６學年度碩士班招生考試試題

科目：熱力學【材料所碩士班丙組】

請於答案卷上依序作答，並清楚標明題號

1. The greenhouse effect is experienced on a larger scale on earth. The surface of the earth, which warms up during the day as a result of the absorption of solar energy, cools down at night by radiating part of its energy into deep space as infrared radiation. Carbon dioxide, water vapor and nitrogen oxides act like a blanket and keep the earth warm at night by blocking the heat radiated from the earth.
   A geothermal power plant is generating electricity using geothermal water extracted at 180 °C, and re-injected back to the ground at 85 °C. It is proposed to utilize the re-injected brine for heating the residential in the area, and calculations show that the geothermal heating system can save $2*10^9$ million joules (MJ) of natural gas a year.
   (a) Give one example of the greenhouse effect in our living environment. (5%)
   (b) Determine the amount of nitrogen oxides and carbon dioxide emissions the geothermal system will save a year. Take the average nitrogen oxides and carbon dioxide emission of gas furnace to be 0.045 g/MJ and 60.7 g/MJ, respectively. (10%)
   (c) Also, a typical car on the road generates about 9 kg of nitrogen oxides and 6000 kg of carbon dioxide per year. The effect of geothermal heating system is equivalent to taking how many of cars off the road? (10%)

2. Thermodynamics deals with equilibrium states. The word equilibrium implies a state of balance. There are many types of equilibrium, and a system is not in thermodynamic equilibrium unless the conditions of all the relevant types of equilibrium are satisfied. Please describe four important types of equilibrium related with the materials filed. (20%)

3. Consider an isolated system (no heat, matter or work may be exchanged with the surroundings) considering of three internal compartments A, B and C, of equal volumes. The compartments are separated by partitions; each partition has a valve, which may be opened remotely. Initially the central volume B is filled with a gas at 298 K and the outer two are evacuated. Consider the following two processes:
   (a) The valve to the A side is opened, the gas expands freely into the compartment A, and the system comes to equilibrium. Then the valve to the C side is opened, and the system again comes to equilibrium.
   (b) Both valves are opened simultaneously, the gas expands freely into both compartments, and the system comes to its equilibrium.
   Explain which of these processes produces more entropy? (15%)
4. If 2 kg of liquid water at 90 °C is mixed adiabatically and at constant pressure with 3 kg of liquid water at 10 °C, what are the changes of total internal energy and total entropy resulting from this process? Heat capacity of water will be assumed constant at 4.184 J/g.K. (20%)
5. 1000 cc amount of water is broken into droplets having a diameter of one micrometer (1 υm) at 20 °C.
   (a) What is the total area of the droplets?
   (b) Calculate the minimum work required to produce the droplets. Water has a surface tension of 72.75 erg/cm^2 at 20 °C. Assume that the droplets are at rest (i.e., have zero velocity). **(total 20%)**

國立中山大學９６學年度碩士班招生考試試題

科目：光電概論【材料所碩士班丁組】

Light Waves in a Medium (28%)

1. A harmonic light wave traveling in a piece of material has an electric field given by

$$\vec{E} = (\hat{y} + \hat{z})E_o e^{i\pi 10^{15}(\frac{x}{0.65c} + t)},$$

where $c = 3 \times 10^8$ m/sec. Time is in seconds and x in meters. Please find: (a) the direction of motion, (b) the direction of polarization, (c) its vibrating amplitude, (d) the frequency of the light, (e) its phase velocity in the medium, (f) its wavelength in space, and (g) the index of refraction of the material.

Reflection, Refraction, and Brewster's Law (9%)

2. Sunlight reflects off the smooth surface of a piece of glass. The index of refraction of the air is 1 while that of the glass is n. At what angle of reflection is the light completely polarized?

Interference (18%)

3. Two narrow parallel slits separated by a distance of $1mm$ are illuminated by a laser. The wavelength of the laser is $0.6\mu m$. The plane of slit is located at a distance of $800mm$ from the observation screen.
   (a) What is the spacing between the zero and tenth-order fringes.
   (b) In the case of (a), suppose the entire apparatus (laser, slits, screen, and space in between) is immersed in water (index of refraction $n = 1.33$). Then what is the spacing between the zero and tenth-order fringes?

Electric Fields (45%)

4. Find the electric field at a distance r from a very long line of charge with linear charge density (charge per unit length) λ.
5. A spherical charge distribution is given by

$$\rho = \rho_0(1 - r^2/a^2), \quad (r \le a)$$
$$\rho = 0 \qquad\qquad\quad (r > a)$$

   (a) Calculate the total charge Q.
   (b) Find the electric field intensity E and the potential V outside the charge distribution.
   (c) Find E and V inside.
   (d) Where are the maximum values of E and V?

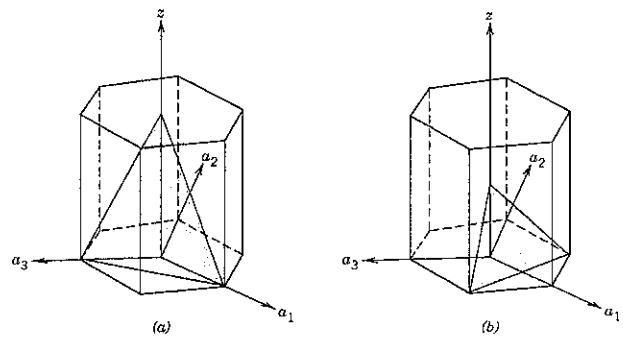
國立中山大學９６學年度碩士班招生考試試題

科目：材料科學【材料所碩士班丁組】

(1) Explain the difference between ionic bonding, covalent bonding and metallic bounding in solid crystals. 6 points

(2) Explain why the properties of polycrystalline materials are most often isotropic. For rolled sheet metals, however, the properties are most often anisotropic, give the reason for this. 8 points

(3) Determine the indices for the planes shown below. 6 points



(4) Use your own words, not equations, to describe Fick's first and second laws. 10 points

(5) Explain the difference between true and engineering stress. 5 points

(6) Describe the physical meaning of critical resolved yield stress. 8 points

(7) Explain the following terms: (a) slip system, (b) recovery, (c) solid solution strengthening, and (d) creep. 12 points

(8) Discuss how the cooling rate affects the microstructure of a eutectoid structure. 8 points

(9) Give a schematic drawing of a peritectic reaction. 5 points

(10) Explain the physical meaning of the activation energy of a diffusion process in crystalline solids. 8 points

(11) It is well known that second phase particles have dragging force on a migrating boundary. Explain this effect by using thermodynamics concept. 8 points

(12) There are six factors affecting the relative intensity of the diffraction lines on an X-ray powder pattern. One factor among these six factors is the multiplicity factor. Explain what is the multiplicity factor. 8 points

(13) Explain the mechanism for the formation of a cellular structure during solidification. 8 points