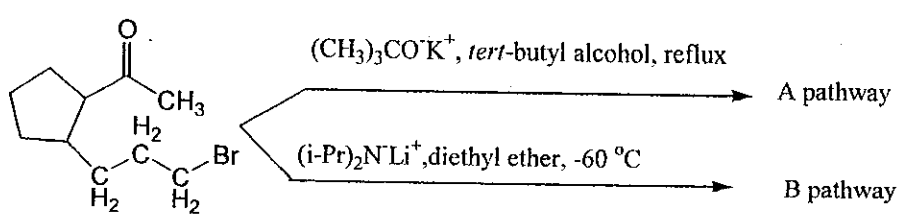
1) Aromatic substitution reaction provides lots of routes to prepare new organic compounds, however, a successful reaction relies on the reactivity of the starting compound and the reaction site, which determine the intermediates involved and the resulting products, a situation especially hold for mono-substituted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

i) Nitration of monosubstituted benzenes (X-Ph, Ph stands for phenyl ring) can be performed by reacting them with HNO_3/H_2SO_4. Schematically draw the possible two intermediates involved during nitration. (6 %)

ii) The nitration reactivity is strongly dependent on the subsitituent X. Which of the two substituents (X = OCH_3 and $-CH_3$) will have better reactivity towards nitration? (4 %) Why? (6%)

iii) Naphthalene undergoes similar nitration reaction by HNO_3/H_2SO_4, also. Suggesting that mono-nitration occurs, show the chemical structure of the main nitration product from naphthalene. (4 %) Give reason why substitution takes place exclusively on this particular position. (6 %) You are supposed to know the chemical structure of naphthalene; however, chemical formula of naphthalene $C_{10}H_8$ was given here for kind consideration)

2) Alkylation of carbonyl compounds proceeds through extraction of the proton on carbon α- to the carbonyl group and the enolates generated undergo the subsequent addition to alkylbromide, however, the products obtained are normally different dependent on the possible controlling factors, as generally recognized in view of either thermodynamic or kinetic aspect. It is to said, the intermediate enolates may be different if they are generated by thermodynamic or kinetic pathways. Consider the following reactions:



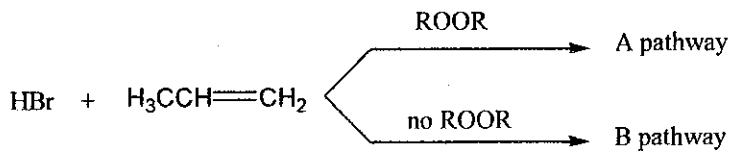
i) What are the main enolate involved in the respective A and B pathway? Draw the chemical structures including the involved counter-anion surrounding the central ion. (10 %)

ii) Specify the enolates involved in A and B pathways as thermodynamic or kinetic enolate. (4 %) And why? (6 %)

iii) Provide the chemical structures of the products from both A and B pathways. (10 %)

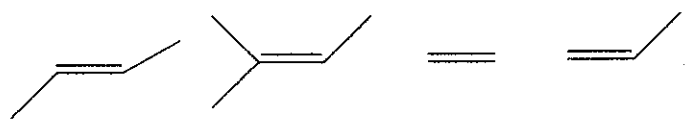
3) Addition to alkene generally proceeds by two pathways, either designated as Markovnikov or anti-Markovvikov's routes. Normally speaking, the main pathway is determined by the reagents used, which governed the reaction mechanism and also, the reaction intermediate. In the following reactions, two different products can be generated by pathways A and B:

i) Give the products from pathways A and B. (p.s. ROOR is organic peroxide) (10 %)



ii) Give the mechanisms involved in pathways A and B. (10 %)

iii) Suggesting that the addition of HBr was performed in the presence of ROOR, list the order of relative reactivity for the additions to four alkenes shown below: (4 %)



iv) Give explanations for the order you give in iii). (10 %)

4) A substance A with the empirical formula C_4H_8O has the following spectrum, what is its structure? ^{1}H NMR, δ:1.1 doublet (6 H), 2.4 multiplet (1 H), 9.6 finely split doublet (1 H). (10 %)

(There are altogether four questions, write up your answers in the right sequence)

國立中山大學九十三學年度碩士班招生考試試題

科目：物理化學 【材料科學研究所碩士班 甲組】

1. Explain the followining terms.
   (1) Azeotrope. [5%]
   (2) Eutectic point. [5%]
   (3) Born-Oppenheimer approximation. [5%]
   (4) Frank-Condon principle. [5%]
   (5) Stokes shift. [5%]

2. In vibrational spectroscopy, molecular interpretations are often made in terms of 'normal modes'.
   (1) What is the physical meaning/significance of 'normal modes'? [5%]
   (2) Show that there are generally 3N-6 normal modes of vibration for a molecule composed of N atoms but only 3N-5 normal modes in the special case of linear molecules. [5%]
   (3) Absorption bands are often referred to as IR-active or Raman-active. What factors determine the IR- or Raman-activity of a given normal mode? [5%]

3. In the ideal case, the ultraviolet-visible absorption spectrum and the fluorescence spectrum may appear as mirror images. Provide your explanation to this observation. [10%]

4. (1) Using an energy diagram, explain the differences between fluorescence and phosphorescence. [5%]
   (2) What are the typical time scales involved in these two processes? [5%]
   (3) Provide your explanation for the fact that the time scale of the phosphorescence is typically much longer than that of the fluorescence process? [5%]

5. (1) In the ideal limit of Langmuir adsorption of gas molecules at pressure P onto an ideal surface for which adsorption does not proceed beyond monolayer coverage and that occupation of any given surface site does not affect gas adsorption onto its neighboring sites, show that the fractional surface coverage (i.e., the 'adsorption isotherm') follows the form of $\theta = K_1P/(1+K_1P)$ where K_1 is a characteristic equilibrium constant. [5%]
   (2) For the case of 'dissociative adsorption' where an adsorbed diatomic molecule quickly dissociates into two adsorbed atoms (which represents a form of catalytic surface characteristics), show that the adsorption isotherm follows the form of $\theta = (K_2P)^{1/2}/[1+(K_2P)^{1/2}]$ where K_2 is a characteristic equilibrium constant.. [5%]

6. (1) Are there similarities between the ideal gas and the ideal solution in terms of the equations of state? Explain. [5%]
   (2) Extending the analogy into the slightly non-ideal cases, the virial expansion of osmotic pressure is typically given as $\pi/cRT = \pi_o + A_2c + \ldots$ where c is the solute concentration in g/L. What is the physical meaning of the second virial coefficient A_2 in this expression? [5%]
   (3) Which molecular characteristics would the value of π_o corresponds to? [5%]

7. (1) In crystalline metals, values of the elastic modulus determined from tensile and compression experiments, respectively, are exactly the same. Provide your explanation in terms of the shape of the inter-atomic potential function. [5%]
   (2) The isobaric thermal expansion coefficient of crystalline metals are typically positive, i.e., they expands as the temperature is increased. Provide your explanation in terms of the shape of the inter-atomic potential function. [5%]

國立中山大學九十三學年度碩士班招生考試試題

科目：工程數學甲(材料所)〈乙組〉

20% for each problem

1. Solve the following initial value problems.

   (a) $y' + 4y = 20,\ y(0) = 2$

2. Solve the given initial value problem by Laplace transforms.

   $y_1' = -y_2 + 1 - u(t-1), y_2' = y_1 + 1 - u(t-1)$, $y_1(0) = 0, y_2(0) = 0$. (u is the step function).

3. Find a basis of eigenvectors and diagonalize the following matrix.

$$\begin{bmatrix} 8 & -1 \\ 5 & 2 \end{bmatrix}$$

4. Given a curve *C*: **r**(t), find (a) a tangent vector **r**'(t) and the corresponding unit tangent vector **u**(t), (b) **r**' and **u** at the given point P.

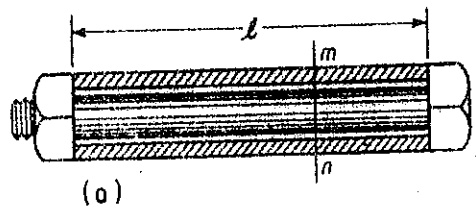
   $\mathbf{r}(t) = t\,\mathbf{i} + t^3\,\mathbf{j}$, P: (1, 1, 0)

5. Find the sum of $1 - \frac{1}{3} + \frac{1}{5} - \frac{1}{7} + - \cdots$, using the Fourier series of $f(x) = \begin{cases} 0 & \text{if } 0 < x < \pi \\ 1 & \text{if } \pi < x < 2\pi \end{cases}$ (f(x) is a periodic function with period 2π).

國立中山大學九十三學年度碩士班招生考試試題

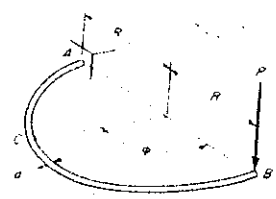
科目：材料力學 【材料科學研究所碩士班 乙組】

1. A cold-rolled steel bolt of length l = 12 in. passes through a bard-drawn copper tube of the same length, as shown below, and the nut at the left end is turned up just snug at room temperature T = 70°F. Subsequently the nut is tightened up n = ½ turn and the entire assembly is raised to a temperature T = 140°F. What stresses will exist in the bolt and the tube under these conditions? The cross-sectional area of the steel bolt is As = ½ sq in., its modulus of elasticity Es = $30x10^3$ ksi, the coefficient of thermal expansion is αs = 6.5x10⁻6 in/in/F and the thread pitch p = 1/8 in. For the copper tube, Ac = ¾ sq in., Ec = $16x10^3$ ksi and αc = 9.3x10⁻6 in/in/F.



(a)

2. A shaft of diameter d, bent in the form of a semicircle AB of radius R, is built-in at A and loaded at B by a force P acting perpendicular to the plane of the ring as shown in Fig. below. Thus any cross-section C of the ring is subjected to both bending and torsion. Assuming that d is small compared with R so that the theory of bending of straight bars may be used, find the value of angle for which the principal stress s will be maximum.



3. You are given a plate that is pulled in x and y directions. If the σx, σy and εx, εy are measured. Please determined the Young's modulus and Possion's ratio.

4. The above Plate is under pure shear τ. Please prove the change of volume of the plate is zero, and show the relationship between Young's modulus and shear modulus.

5. A simply supported beam is struck at its mid-point C by a ball of weight W freely falling from a height above the beam. Neglecting the weight of the beam and assuming that is behaves elastically, find the total deflection d that will be produced at point C.

20% for each problem

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3. Find a basis of eigenvectors and diagonalize the following matrix.

$$\begin{bmatrix} 8 & -1 \\ 5 & 2 \end{bmatrix}$$

4. Given a curve C: $\mathbf{r}(t)$, find (a) a tangent vector $\mathbf{r}'(t)$ and the corresponding unit tangent vector $\mathbf{u}(t)$, (b) $\mathbf{r}'$ and $\mathbf{u}$ at the given point P.

   $\mathbf{r}(t) = t\,\mathbf{i} + t^3\,\mathbf{j}$, P: (1, 1, 0)

5. Find the sum of $1 - \frac{1}{3} + \frac{1}{5} - \frac{1}{7} + - \cdots$, using the Fourier series of $f(x) = \begin{cases} 0 & \text{if } 0 < x < \pi \\ 1 & \text{if } \pi < x < 2\pi \end{cases}$ (f(x) is a periodic function with period 2π).

1. For a reaction with a free energy change of ΔG and the variation of ΔG with temperature and pressure have been measured. Explain how to obtain (a) the entropy change ΔS, (b) the volume change ΔV, and (c) the enthalpy change ΔH of the reaction. (15%)

2. List the following reactions in the order of <u>increasing</u> entropy of reaction ($\Delta S°$). Explain all your choices.

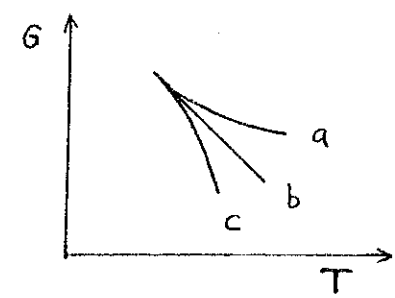
   (a) $C_{(s)} + MgO_{(s)} = Mg_{(g)} + CO_{(g)}$
   (b) $C_{(s)} + O_{2(g)} = CO_{2(g)}$
   (c) $Zr_{(s)} + O_{2(g)} = ZrO_{2(s)}$
   (d) $C_{(s)} + CO_{2(g)} = 2\ CO_{(g)}$ (15%)

3. The isothermal compressibility is defined as $\beta_T = -(1/V)(\partial V/\partial P)_T$ and the adiabatic compressibility is defined as $\beta_S = -(1/V)(\partial V/\partial P)_S$. Which one of the two is larger? Explain. (10%)

4. The melting point of silver is 1234 K and the heat of fusion is 11.2 kJ/mole. For the case of freezing of super-cooled liquid silver at 1073 K,
   (a) how much heat is released?
   (b) What is the entropy change of the system?
   (c) What is the entropy change of the universe? (25%)
   Data: $Ag_{(s)}$: $C_p = 21.2 + 8.55 \times 10^{-3} T + 1.50 \times 10^{5} T^{-2}$ (J/K mole)
   $Ag_{(l)}$: $C_p = 30.5$ (J/K mole)

5. (a) Prove that if $(\partial U/\partial V)_T = 0$, then $(\partial U/\partial P)_T = 0$, where U is the internal energy.
   (b) Prove that if $(\partial U/\partial V)_T = 0$, then $P/T = f(V)$. That is, P/T is a function of V only.
   (c) How can the function f(V) be determined? Give an example. (25%)

6. The temperature dependence of Gibbs free energy of an element in solid state is shown schematically in the figure by three curves (a, b, and c). Determine which can be correct and which cannot be. Explain your result. (Hint: take the first and second derivitives of the curves) (10%)



國立中山大學九十三學年度碩士班招生考試試題

科目： 應用數學 （材料所 丁組）

Please note that (1) *partial credits will be given **only** to incomplete answer relevant to the solution of the problem*, and (2) *the test has four problems.*

1. ***(Heat Flow)*** (15%)
   In a temperature field, heat flows in a direction of maximum decrease of temperature T:

$$T(x,y) = 1 - \frac{x^3}{3a} - \frac{y^2}{2b}.$$

   Please find (a) the direction of the flow at P: (-a, $e^{1/b}$), and
   (b) the path of the heat flow started from point P.

2. ***(Differential and Integral Equations)*** (45%)
   Please solve for $y(t)$, or y_1 and y_2 from

   (a) $\frac{d^2y}{dt^2} - 2\frac{dy}{dt} + 2y = 2e^t \cos t$,

   (b) $y(t) = t + \int_0^t y(\tau)\sin(t-\tau)\, d\tau$, and

   (c) $\begin{cases} \frac{dy_1}{dt} = y_1(t) + 2y_2(t) \\ \frac{dy_2}{dt} = -2y_1(t) + 6y_2(t) \end{cases}$

   (Hint: The Fourier transform, Laplace transform, or diagonization of a matrix might be necessary for solving these equations)

3. ***(Fourier Transform)*** (25%)
   $F(w)$ is the Fourier transform of $f(x)$. Please derive
   (a) the Fourier transform of $e^{iax}f(x)$, and
   (b) the Fourier transform of $f(x/a)$, where a > 0.

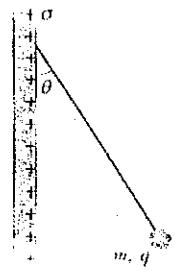
4. ***(Linear Algebra)*** (15%)
   A system of 3 linear equations

$$\begin{cases} x_1 + 5x_2 + 2x_3 = b_1 \\ 4x_1 + 2x_2 + 2x_3 = b_2 \\ 2x_1 + 4x_2 + 2x_3 = b_3 \end{cases}$$

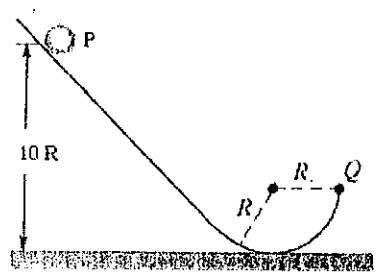
   can be expressed in the form $\mathbf{Ax} = \mathbf{b}$. Please find
   (a) the rank of $\mathbf{A}$, and
   (b) the relations between b_1, b_2, and b_3 if this system has solutions.

General Physics

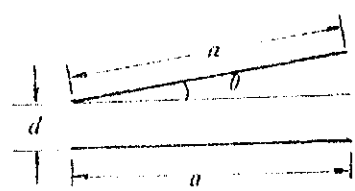
1. A small nonconducting ball of mass m carries a charge q hangs in the earth's gravitational field from a silk thread that makes an angle 0 with a large, uniformly charged nonconducting sheet (as shown in the figure, the sheet extends vertically into and out of the page). Calculate the uniform surface charge density σ of the sheet. (15 points)



2. A uniform hoop of radius R and mass m starts from rest and rolls down without slipping from the point P, as shown in the figure. The velocity direction of the center of mass is directly upward at the end of the loop Q. What is the maximum height this object can reach as calculated from the bottom of the loop? (*Hint:* The rotational inertia for such a hoop about its central axis is mR^2.) (15 points)



3. A thin insulating rod of length L carries a uniformly distributed charge Q. Find the field strength at a point along its axis at a distance a from one end. (12 points)
4. When the kinetic energy of a particle equals its own rest energy, what are the momentum and velocity of this particle? (15 points)
5. A very long solenoid of n turns per unit length and radius a carries a current i that is increasing at a constant rate di/dt. (a) Calculate the induced electric field at a point inside the solenoid at a distance r from the solenoid axis. (b) What is the magnitude of the poynting vector at this point? (16 points)
6. A uniform solid sphere of radius R produces a gravitational acceleration of a_g on its surface. At what two distances from the center of the sphere is the gravitational acceleration $a_g/3$? (*Hint:* Consider distances both inside and outside the sphere.) (12 points)
7. A capacitor has square plates, each of side a, making an angle 0 with each other (as shown in the figure). What is the capacitance C if $\theta << 1$. (15 points)



Modern Physics

1. Show that the relativistic form of Newton's second law is
   $F = m_0 \frac{dv}{dt}(1-\frac{v^2}{c^2})^{-\frac{3}{2}}$. (12 points)
2. Show that the group velocity and phase velocity can be related by
   $v_{group} = v_{phase} - \lambda \frac{dv_{phase}}{d\lambda}$, where λ is the wavelength. (12 points)
3. Show that when a gamma ray produces an electron-positron pair in the neighborhood of an electron at rest in accordance with the relation $\gamma + e^- \rightarrow e^- + e^- + e^+$, the threshold energy of the photon is $4m_0c^2$, where m_0 is the rest mass of electron. (15 points)
4. What are the allowed energy levels of a particle of mass m moving in a one-dimensional potential well $V(x) = \frac{1}{2}kx^2$ according to the Bohr-Sommerfeld quantization rule? (15 points)
5. For a particle moving in a one-dimensional potential $V(x)$, derive the Ehrenfest theorem $\frac{d<P_x>}{dx} = <-\frac{\partial V(x)}{\partial x}>$. What does it mean? What is its significance? (16 points)
6. A light beam is propagating through a block of glass with index of refraction n. If the glass is moving at constant velocity v in the same direction as the beam, what is the velocity of light in the block as measured by an observer in the laboratory? (15 points)
7. A particle of total energy $9\,V_0$ is incident from the $-x$ axis on a potential given by
   $V(x) = 8\,V_0,\ x < 0$
   $0\ ,\ 0 < x < a$
   $5\,V_0,\ x > a$
   Find the probability that the particle will be transmitted to the positive side of the x-axis, $x > a$. (15 points)