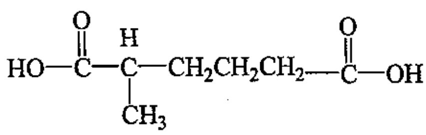
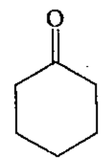
1) In an abandoned laboratory has been found a flammable liquid, A, in a bottle bearing only the label "compound **A**: C_7H_{12}". Government agents have offered you a considerable sum to determine the structure of this compound. After verifying the molecule formula by elemental analysis, you find that compound **A** reacts with a mol equiv of hydrogen and, after treating with acid $KMnO_4$, gives the dicarboxylic acid **C** (see below). Another bottle from the same laboratory is labeled "compound **B** (isomer of **A**)". Compound **B** also reacts with 1 mole equiv of hydrogen, but yields cyclohexanone after treatment with acid $KMnO_4$.



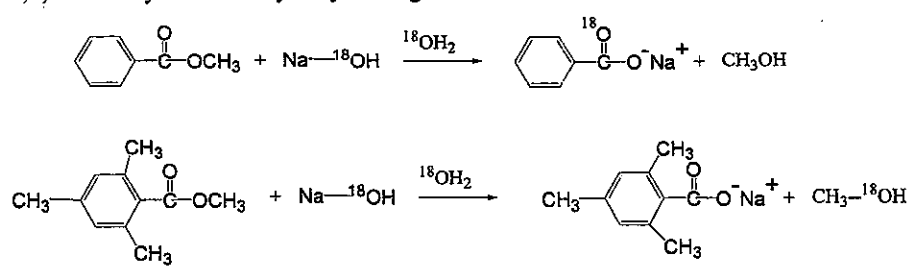
compound **C**



cyclohexanone

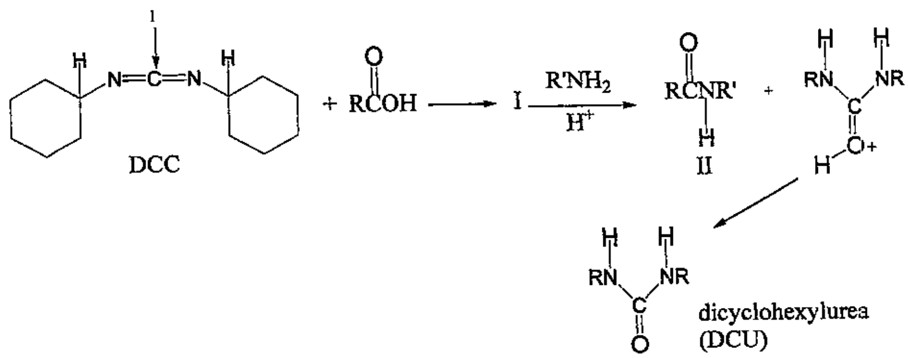
i) Suggest the structures for A and B. (8 points)
ii) What are the two possible products formed if compound A reacted with Br_2. (specify the stereochemistry) (6 points)
iii) Which one of the two products in ii) is more stable in considering the stereochemistry? (3 points) Why? (5 points)

(2) When methyl benzoate is treated with NaOH in water enriched with ^{18}O, the benzoic acid formed contains ^{18}O and the methanol does not. Under the same conditions methyl 2,4,6-trimethylbenzoate hydrolyzes to give unlabeled acid and ^{18}O–enriched methanol:



i) For each hydrolysis, write a mechanism that explains the experimental results. (10 points)
ii) Which ester will hydrolyze more slowly? (4 points) Why? (4 points)

(3) Dicyclohexylcarbodiimide (DCC) is a useful reagent for making amide from carboxylic acids and amine under mild condition. It reacts with aqueous acid first to give intermediate I, which under subsequent attack by amine, yields the desired amide (II) according to:



i) The above scheme shows that DCC is firstly attacked by the carboxylic acid (RC(=O)-OH) to obtain intermediate I. As we know, carboxylic acid is a weak nucleophile; to facilitate the reaction, the counterpart DCC should function strongly in accepting the electrons from the nucleophilic carboxylic acid. With this aspect, carbon 1 in DCC (see above) is suggested to play the role and should be easily attacked by the carboxylic acid due to its chemical nature. Explain why carbon 1 in this case is a good electron-acceptor. (5 points)

ii) Write down the chemical structure of intermediate I. (5 points)

iii) Write down the mechanism involved in the transformation from intermediates I to product II (amide). (8 points)

(4) Assign structures to each of the following sets, given the formula, NMR or IR spectroscopic data were given.

i) $C_5H_{10}O_2$

IR (cm^{-1}), 1725; ^{1}H NMR (δ): 1.2 doublet (6H), 2.5 septet (1H), 3.7 singlet (3H)

(4 points)

ii) $C_4H_6Cl_4$

^{1}H NMR (δ): 3.9 doublet (2H), 5.6 triplet (4H)

(4 points)

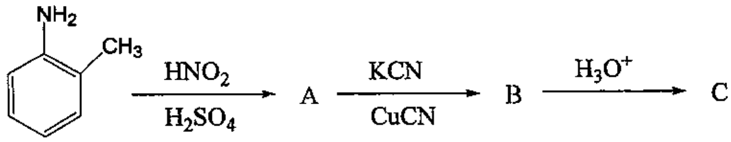
iii) $C_3H_5ClO_2$

IR (cm^{-1}), 1720, 3300-2500; ^{1}H NMR (δ): 1.7 doublet (3H), 4.5 quartet (1H), 12.7 singlet (1H)

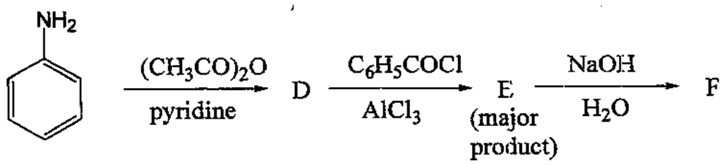
(4 points)

(5) Write down the chemical structures of products A to J (Each for 3 points, totally 30 points)

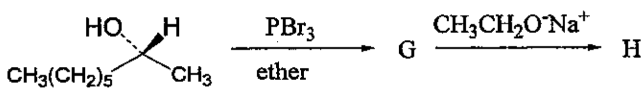
i)



ii)

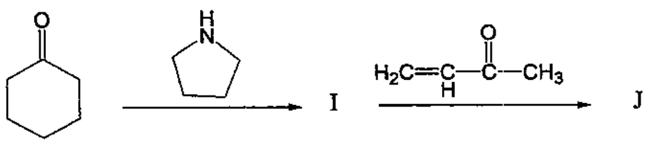


iii)



(Specify the stereochemistry of the chiral center above)

iv)



國立中山大學95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. Explain the following terms.
   (1) Azeotrope. [3%]
   (2) Eutectic mixture. [3%]
   (3) Congruent and incongruent melting. [4%]
   (4) Einstein-de Broglie postulate. [3%]
   (5) Born-Oppenheimer approximation. [3%]
   (6) Pauli exclusion principle. [3%]
   (7) Spin-orbit coupling. [3%]
   (8) Spin-spin correlation. [3%]
   (9) Russel-Saunders coupling. [3%]
   (10) jj-Coupling. [3%]
   (11) Frank-Condon principle. [4%]
   (12) Stokes and anti-Stokes shifts. [4%]

2. By definition, a van der Waals gas obeys the equation of state $p = RT(V-b)^{-1} - aV^{-2}$ where p is the pressure, T the absolute temperature, V the molar volume, and R the gas constant.
   (1) What are the physical meanings of parameters a and b, respectively? Why is the 2[nd] term on the right-hand side involves V^{-2} instead of, say V^{-1} or V^{-3}? [4%]
   (2) Explain why one may say that the critical point of the van der Waals gas corresponds to the simultaneous satisfaction of $dp/dV = d^2p/dV^2 = 0$. [3%]
   (3) On the basis of (2), show that the critical constants are related to the van der Waals parameters according to $V_c = 3b$, $p_c = a/27b^2$, and $T_c = 8a/27Rb$. [6%]
   (4) From (3), one finds that critical compressibility $Z_c = 3/8$, in reasonable agreement with experimentally observed correlation for quite a number of real gases that $Z_c \approx 0.3$. It is therefore interesting to compare the van der Waals equation with the virial expression that compressibility $Z \equiv PV/RT = 1 + BV^{-1} + CV^{-2} + \cdots$, a frequently adopted empirical form for presentation of experimental data. Expand the van der Waals equation in powers of V^{-1} and then express particularly the second virial coefficient B in terms of van der Waals parameters a and b. [3%]
   (5) On the basis of (4), explain why one may say that, for a real gas at its Boyle temperature T_B, the relationship $dZ/d(V^{-1}) = 0$ holds. In addition, show that T_B corresponds to the temperature at which $B = 0$. [4%]
   (6) Based on (4) and (5), express T_B in terms of van der Waals parameters a and b. [3%]

3. Consider the Debye-Hückel model for dilute electrolyte solutions.
   (1) What is the physical origin of the "shielding" (or sometimes referred to as "screening") effects? [3%]
   (2) In this model, modification to the intermolecular potential function is made through the introduction of an exponential shielding (or screening) factor involving the characteristic *Debye length* λ_D. What is the physical meaning of λ_D then? [3%]
   (3) In the derivation of Debye-Hückel limiting law, the ionic strength $I = 2^{-1}\sum_i c_i z_i^2$ arises quite naturally. In this expression, in addition to effects of ion concentrations c_i, the ionic charges z_i are particularly emphasized via the quadratic form of z_i^2. What is the physical origin of this quadratic dependence? [3%]

4. Write down the electronic configurations and give the corresponding term symbols for each of the following species in their *lowest-energy* states.
   (1) *Na* (atomic number = 11). [3%]
   (2) *Cl* (atomic number = 17). [3%]
   (3) *Sc* (atomic number = 21). [3%]

5. Consider a modified version of the 1D particle-in-a-box problem: a slight change to the square-well potential is made in such a way that there now exists a "trap" of width a and depth $-\varepsilon$ at the center of the well of infinite depth (cf. Figure 1).
   (1) On the basis of the perturbation theory, derive expression for the 1st-order correction to the *ground state* and the *first excited state* energies. Note that, in the absence of the trap, the "unperturbed" wavefunctions are of the form $\psi_n(x) = (2/L)^{1/2}\sin(n\pi x/L)$ with corresponding energies $E_n = n^2h^2/8mL^2$ for $0 \le x \le L$ and n = 1, 2, 3, etc. [6%]
   (2) Show that the ground-state energy is always negative (i.e., the ground-state wavefunction is more or less confined in the shallow trap), no matter how shallow the trap is. [3%]

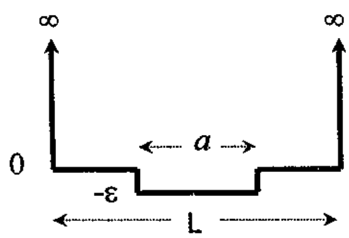


Figure 1. 1D box with a shallow trap.

6. Following the sequence of steps given below, derive an expression for the density of states *N(E)*, defined as the number of allowed states per unit energy per unit volume, for an electron of mass m_e in a 3D cubic box of edge length L.
   (1) Consider the electron as a standing de Broglie wave with $\lambda = h/p$, show that $n_x = 2p_xL/h$ along the x-direction. [2%]
   (2) Hence, for a 3D cube of side L, $L^3dp \equiv L^3dp_xdp_ydp_z = 8h^3$. This means that the gap between neighboring states *in momentum space* is $8h^3L^{-3}$. As the "volume element" in momentum space is $4\pi \cdot p^2dp$, show that the number of states between p and $p+dp$ is $N(p)\cdot dp = \pi \cdot p^2L^3h^{-3}dp$ if the two possible spins for an electron are considered. [2%]
   (3) Now, for a unit volume in real space (i.e., $L=1$) and $E = p^2/2m_e$, show that $N(E)\cdot dE = 2^{1/2}\pi \cdot h^{-3} \cdot m_e^{3/2}E^{1/2}\cdot dE$. [3%]
   (4) This expression for $N(E)$ is often adopted as a simple description for the density of states in the conduction band of semiconductors. Are there important dissimilarities that should be kept in mind in drawing such an analogy? In your opinion, is it legitimate to adopt the same equation for the density of states in the valence band? Explain. [4%]

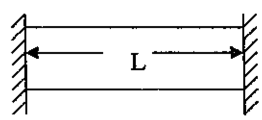
1. (20%) Describe the physical meaning of the following terminology. You may use any words or phrases to explain or elucidate as many aspects as possible for each item. Furthermore, schematic diagrams, plots, curves or any symbols can also be employed to assist your interpretation. However, irrelevant topics or materials should not be presented as they may cause unnecessary confusion and waste precious time of the reader.
(a) Baushinger effect
(b) Principal stresses
(c) Von-Mises stress
(d) Stress tensor

(每小題5分)

2. (20%) By definition, a plane stress state is a stress state with $\sigma_z = \tau_{xz} = \tau_{yz} = 0$, where σ_z and τ_{xz}, τ_{yz} are normal and shear stress components on thee face perpendicular to the Z axis. In isotropic linear elasticity, if the normal strains ε_x and ε_y along the x and y axes have been determined experimentally, determine the expressions for normal stresses along the x and y axes σ_x, σ_y, and normal strain ε_z along the Z axis in terms of Young's modulus E, Poisson's ratio ν, and normal strains ε_x, and ε_y. Note in isotropic linear elasticity, stress-strain obeys Hook's law and mechanical properties of the studied body are independent of orientation.

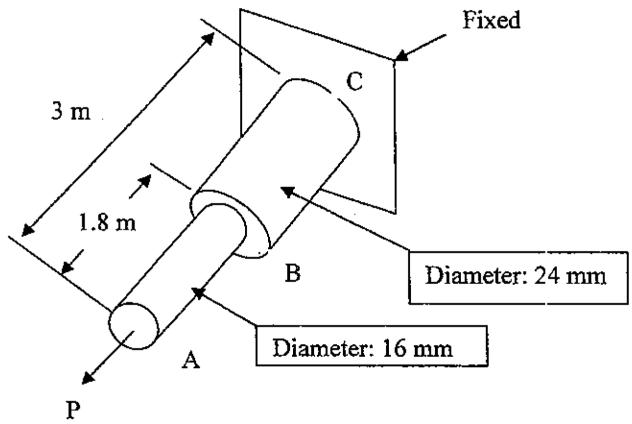
3. (20%) A steel rod of length L and uniform cross section of area A is attached to rigid supports at the two ends as shown in the following figure and is unstressed at a temperature of 15°C. The steel is assumed to be elastoplastic with Young's modulus E = 200 GPa and yielding stress σ_Y = 250 MPa. Knowing that the thermal expansion coefficient of the steel α=11.7 x 10^{-6}/°C, determine (a) the stress in the rod after the temperature has been raised to 180°C, (b) the residual stress after the temperature has returned to 15°C.

(每小題10分)



4. (20%) A two-section aluminum rod ABC is attached to a rigid support at the C end as shown in the following figure. Using Young's modulus E=75 GPa for the aluminum rod, (i) if the force exerted at the A end P = 60 kN, determine (a) the total strain energy of the aluminum rod ABC, (b) the corresponding strain-energy density in portions AB and BC of the rod in terms of energy per unit volume. (ii) If yielding stress for the aluminum rod σ_Y = 400 MPa, determine the maximum load P that can be applied without causing any permanent deformation in ABC.

(每小題10分；其中(A)小題中二小題各5分)



(20%)

5. A strain state at any point of a sample can be described by a 9-component strain tensor. However, the numerical value of each component changes as the coordinate system changes from one to another (for example from XYZ to X'Y'Z'). For a fixed point in a sample, some strain components may be zeros in one coordinate system and some other components may be zeros in another coordinate system. Given the following strain state for a point under a specific coordinate system xyz,

$$\varepsilon_{ij} = \begin{pmatrix} .002 & .003 & .001 \\ .003 & -.002 & .005 \\ .001 & .005 & -.004 \end{pmatrix}$$

What are the maximum and minimum normal strains in the yz plane at the point?

國立中山大學95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、丁組】

1. We know that in a body heat will flow in the direction of decreasing temperature. Physical experiments show that the rate of flow is proportional to the gradient of the temperature. This means that the velocity $\vec{v}$ of heat flow in a body is of the form $\vec{v} = -K \cdot \nabla T$, where $T(x, y, z, t)$ is temperature, t is time, and K is called the thermal conductivity of the body; in ordinary physical circumstance K is a constant. Using this information, one can further set up the mathematical model of the heat flow, the so-called heat equation, $\frac{\partial T}{\partial t} = c^2 \cdot \nabla^2 T$, where c^2 is called the thermal diffusivity of the material.
Let us consider the temperature in a wire with the length L of constant cross section, which is oriented along the x-axis and is perfectly insulated laterally, so that heat flows in the x-direction only. If the initial temperature value is $T_o \sin(\pi x/L)$ and the ends are kept at zero, how long will it take for maximum temperature in the wire to drop to $T_o/2$? What is the velocity $\vec{v}$ of heat flow? ~~(20%)~~ (30%)

2. Please solve for $y(t)$, or y_1 and y_2 from
   (a) $\frac{d^2y}{dt^2} - 6\frac{dy}{dt} + 13y = 4e^{3t}$, $y(0) = 2$, $y'(0) = 4$, (15%)
   (b) $\frac{d^3y}{dt^2} - 3\frac{d^2y}{dt^2} + 3\frac{dy}{dt} - y = 0$, $y(0) = 2$, $y'(0) = 2$, $y''(0) = 10$, (15%)
   (c) $\begin{cases} \frac{dy_1}{dt} = y_1(t) + y_2(t) \\ \frac{dy_2}{dt} = 4y_1(t) + y_2(t) \end{cases}$, $y_1(0) = 4$, $y_2(0) = 4$. (15%)

3. The Fourier transform of $U(t)$ is represented as

$$\hat{U}(\nu) = \int_{-\infty}^{\infty} U(t) e^{-2\pi\nu t} dt.$$

The nature of the inverse Fourier transform,

$$U(t) = \int_{-\infty}^{\infty} \hat{U}(\nu) e^{2\pi\nu t} dt,$$

becomes clear if we think of it as a superposition of sinusoidal oscillations of all possible frequencies, called a spectral representation. This name is suggested by optics, where light is such a superposition of colors (frequencies). Now, an electromagnetic light wave propagated in space is known as

$$U(x,t)=\begin{cases} a_o\cos[2\pi\nu_o(t-x/c)], & 0<t<t_0 \quad at \quad x=0 \\ 0, & otherwise \end{cases},$$

where a_o is the amplitude, c is the speed, and ν_o is a known frequency of the light wave. What is its spectral representation at $x=0$? If this light wave is inspected by a spectrometer at $x=0$, what is its intensity distribution, $\left|\hat{U}(\nu)\right|^2$? (25%)

國立中山大學95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】

Please mark the answers and clearly write down the calculation procedures.

1. The most celebrated equation of state for nonideal gases is the van der Waals equation which for n mole of gas is given as,

   $(P + a*n^2/V^2)(V-n*b) = RT$

   Where P is the measured pressure of the gas and V is the measured volume of the gas.

   (a) Please describe the physical meaning of the correction factors a and b. (10%)

   (b) You are responsible for the purchase of oxygen gas which, before use, will be stored at a pressure of 200 atm at 27 °C in a cylindrical vessel of diameter 0.2 meters and height 2 meters. Would you prefer that the gas behaved ideally or as a van der Waals gas? Please explain your answer. (10%)

   The van der Waals constants for oxygen are a=1.36 $\text{liters}^2*\text{atm}*\text{mole}^{-2}$ and b=0.0318 liter/mole.

2. Given that the volume change on mixing of a solution obeys the relation

   $\Delta V_{mix} = 2.7X_1(X_2)^2$ (cc/mole)

   (a) Derive expressions for the partial molar volumes of each of the components as functions of composition. (10%)

   (b) Please describe the meaning of the partial molar volume or partial moral quantities. (10%)

3. Water flows over a waterfall 100 m in height. Consider 3 kg of the water, and assume that no energy is exchanged between this 3 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 3 kg of water enters the river below the falls, what change has occurred in its state? (10%)

4. Titanium metal is capable of dissolving up to 30 atomic percent oxygen. Consider a solid solution in the system Ti-O containing oxygen atom fraction, $X_O = 0.12$. The molar volume of this alloy is 10.64 cc/mole. The gram atomic weight of oxygen is 16.0; that of titanium is 47.90. Calculate:

   (a) The weight percent of O in the solution. (5%)

   (b) The molar concentration (gm-atoms/cc) of O in the solution. (5%)

   (c) The mass concentration (gms/cc) of O in the solution. (5%)

   (d) When the oxygen content larger than 30 atomic percent, what will be happen for this Ti-O alloy? (5%)

5. A central power plant, whether the energy source is nuclear or fossil fuel, is a heat engine operating between the temperatures of the reactor or furnace and the surroundings, usually represented by a river or other body of water. Consider a modern nuclear power plant generating 750,000 kj/sec for which the reactor temperature is 375 °C and a river is available with a water temperature of 23 °C.

   (a) What is the maximum possible thermal efficiency of the plant and what is the minimum amount of heat that must be discarded to the river? (10%)

   (b) If the actual thermal efficiency of the plant is 70% of the maximum, how much heat must be discarded into the river, and what will be the temperature rise of the river if it has a flow rate of 200 m^3/sec? (10%)

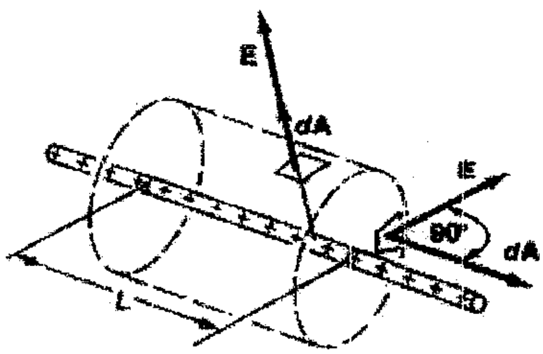
   [hint: the maximum thermal efficiency = 1- T_L/T_H in absolute temperature]

國立中山大學９５學年度碩士班招生考試試題

科目：電磁學【材料所碩士班丁組】

Problem #1: (25%)

Consider a long line of charge with a linear (positive) charge density λ (in C/m). Please see the figure. Find the electric field and the electric potential close to the line of the charge and far from either end. And make the graphs of both electric field and electric potential versus the distance. "Far from either end" implies there are no end effects to worry about that would destroy the cylindrical symmetry of the line of charges.



Problem #2: (25%)

An isolated conducting sphere of radius R has a charge q. Show that the total energy stored in the surrounding electric field equals the expression for the potential energy of a charged capacitor : $U = 0.5\cdot(q^2/C)$.

Problem #3: (25%)

(1) Please write down Maxwell equations

(2) Please prove that the potential function in a static and a time varying cases are

$$\vec{E} = -\vec{\nabla}V \quad \text{and} \quad \vec{E} = -\vec{\nabla}V - \frac{\partial \vec{A}}{\partial t} \quad \text{respectively.}$$

(3) What is the wave equation that can be derived from equation (1)

(4) What are the boundary conditions at the interface where divided two dielectrics (ε_1,μ_1) and (ε_2,μ_2).

Problem #4: (25%)

The **E**-field of a uniform plane wave propagating in a dielectric medium is given by

$$E(z,t) = \hat{i}3\cos\left(10^8 t - \frac{z}{\sqrt{3}}\right) - \hat{j}\sin\left(10^8 t - \frac{z}{\sqrt{3}}\right) \quad \text{(V/m)}$$

6% (1) Determine the frequency and wavelength of the wave

6% (2) What is the dielectric constant of the medium?

6% (3) Describe the polarization of the wave

7% (4) Find the corresponding **H**-field.