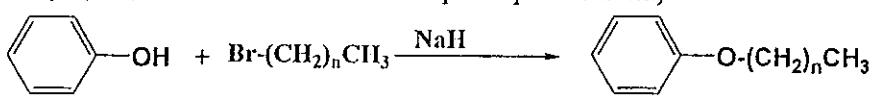
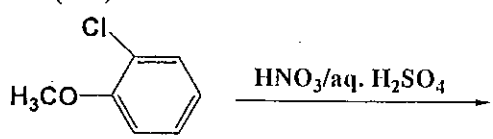
1) a) Give the chemical structures for methylene chloride, diethyl ether, methanol and dimethyl sulfoxide. (8 %)

b) All the four chemicals listed above are common solvents used in organic synthesis. Which of them is a dipolar aprotic solvent? (4 %)

c) The following reaction can be greatly enhanced by the dipolar aprotic solvent. Why? (8 %, illustrate it with the above dipolar aprotic solvent)



2) a) Draw all the possible intermediates for the following aromatic nucleophilic substitution. (8 %)



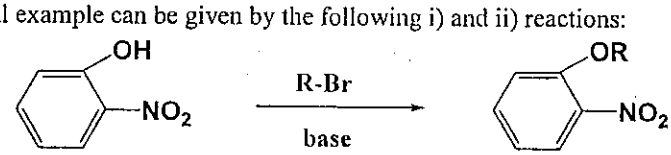
b) Which of the above intermediates is the most stable one? (4 %) Why? (8 %)

3) a) Cyclopentanone and cyclobutanone are all strained molecules. Which of them is more stable (less strained)? (2 %) Why? (8 %)

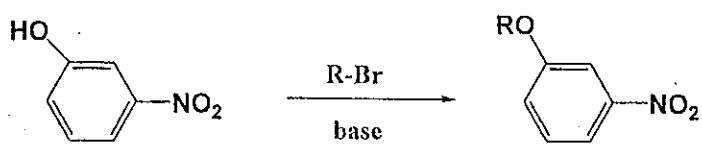
b) Infrared spectroscopy provides the characteristic carbonyl stretching modes in the vicinity of 1700 cm^{-1}. Anyway, the absorption peak was intimately related to the neighborhood environment of the carbonyl group situated. Which of the two moleculess listed above will have its carbonyl stretching located at higher wavenumber (cm^{-1})? (4 %) Why? (10 %)

4) Isomeric compounds may have different responses toward the same reactant. A typical example can be given by the following i) and ii) reactions:

i)



ii)



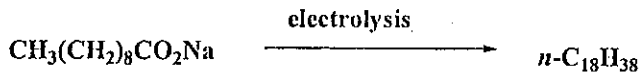
$R = -(CH_2)_nCH_3$

a) Which of the above reactions can not proceed well? (2 %)

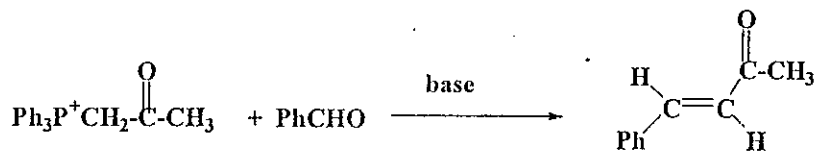
b) Give a plausible reason for this reactivity difference between i) and ii) reactions. (10 %)

5) Give the mechanistic steps for the following reactions. (24 %, 6 % for each)

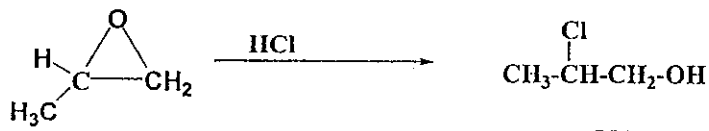
a)



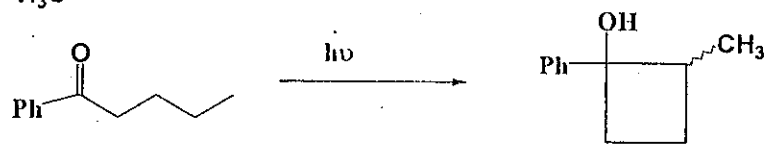
b)



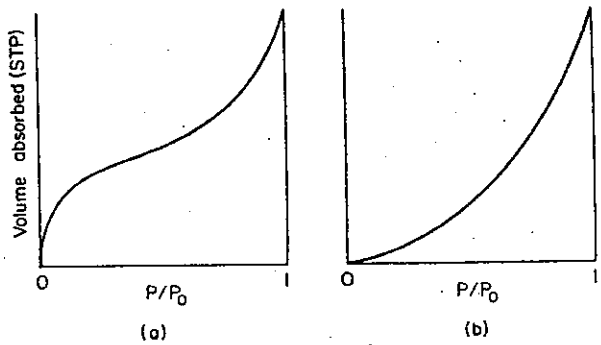
c)



d)



1. Explain qualitatively the reason for the difference in shape of the two following adsorption curves: (10%)



(a) N_2 on Fe at –195°C.
(b) Br_2 on SiO_2 at 79°C.
P_0 = vapor pressure of adsorbate.

2. (a) Calculate the amount of work required to separate two hydrogen atoms, each of mass 1.7×10^{-24} g, from their equilibrium distance, 0.74 Å, to infinity, assuming that gravitational attraction between the two hydrogen atoms is the only force to be taken into account. The universal gravitational constant $G = 6.670 \times 10^{-8}$ dyne cm^2 g^{-2}. (5%)
(b) The experimental value for the H-H bond strength indicates that the actual amount of energy required to separate the two atoms in H_2 is 6.7×10^{-12} ergs. What is the significance of the discrepancy between this figure and the figure calculated in (a)? (5%)

3. (a) For each of the following gases, assumed ideal — (i) He; (ii) CF_4 (nonlinear); (iii) C_2F_2 (linear) — find the molar heat capacity at constant volume that is predicted by the application of classical mechanics to all motions of the nuclei. (5%)
(b) Would you expect the actual heat capacity of each gas at ordinary temperatures to be greater than, equal to, or less than that calculated in (a)? Explain. (5%)

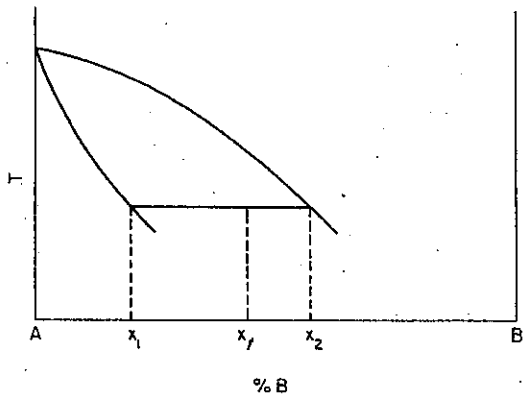
4. Explain why, even in a nonideal solution, the vapor pressure of the solvent is given by Raoult's law when the solution is sufficiently dilute. (10%)

5. At 300°K, the equilibrium constant K_p for the reaction
$N_2O_4(g) \Leftrightarrow 2NO_2(g)$
is 0.174. What would be the apparent molecular weight of an equilibrium mixture of N_2O_4 and NO_2 formed by the dissociation of pure N_2O_4 at a total pressure of 1 atm at this temperature? (10%)

6. At 298.2°C the standard enthalpy of formation of $Mg(NO_3)_2$ is –188,770 cal mol^{-1}, and the standard enthalpy of solution is –21,530 cal mol^{-1}; the standard enthalpy of formation of the NO_3^- ion is –49,320 cal (g ion)$^{-1}$. Calculate the standard enthalpy of formation of the Mg^{2+} ion at this temperature. (10%)

7. Calculate the final temperature for the adiabatic reversible expansion of 100 g of argon, initially at 25°C, from 10 liters to 50 liters. (10%)

8. For the system shown in the figure, prove that at equilibrium
$W_1/W_2 = (x_2-x_i)/(x_f-x_1)$



where W_1 = the weight of phase 1, W_2 = the weight of phase 2, x_1 = the weight percent of B in phase 1, x_2 = the weight percent of B in phase 2, and x_i = the weight percent of B in the total system. (10%)

9. According to Fox and Flory, the relationship between intrinsic viscosity and molecular weight for solutions of polyisobutylene at 20°C is given by the formula $[\eta] = 3.60 \times 10^{-4} M^{0.64}$. What is the molecular weight of a polyisobutylene fraction that gives a solution with intrinsic viscosity 1.80 deciliter g^{-1}? (10%)

10. Calculate ΔS for the isobaric heating of 1 mole of N_2 from 300°K to 1000°K. (10%)
$C_p = 6.4492 + 1.4125 \times 10^{-3}T - 0.807 \times 10^{-7}T^2$

Please note that (1) *a calculator can be used for this test,* and (2) *partial credits will be given only to incomplete answer relevant to the solution of the problem.*

1. (***Algebra***) In the formula below, there are ten alphabets (E, F, I, N, O, R, S, T, Y, X) representing ten numerical digits (0, 1, 2, 3, 4, 5, 6, 7, 8, 9). Please find the numerical value for each alphabet. (10 pts)

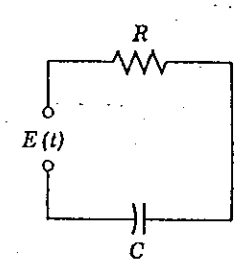
$$\begin{array}{r} \text{TEN} \\ \text{TEN} \\ +)\ \text{FORTY} \\ \hline \text{SIXTY} \end{array}$$

2. (***Matrix***) A 3 x 3 matrix $\boldsymbol{B}$ is given below. Please find the inverse matrix $\boldsymbol{B}^{-1}$ which satisfies $\boldsymbol{B}\,\boldsymbol{B}^{-1} = \boldsymbol{B}^{-1}\boldsymbol{B} = \boldsymbol{I}$, here $\boldsymbol{I}$ is the unitary matrix as shown. (15 pts.)

$$B = \begin{bmatrix} 1 & 1 & 2 \\ 2 & 2 & 3 \\ 3 & 1 & 1 \end{bmatrix}, \quad \text{and} \quad I = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

3. (***Integral Equation***) A simple *RC* circuit obeys the following integral equation.

$$R\,I + \frac{1}{C}\int I\,dt = E(t)$$



If electromotive force $E(t) = E_0 \sin(\omega t)$, please solve the equation for current $I(t)$. (20 pt.)

4. (***Fourier Series***) Please derive the Riemann zeta function $\zeta(2)$ using Fourier expansion for $f(x) = x^2$ for the range of $-\pi \leqq x \leqq \pi$. (25 pts.)

$$\frac{\pi^2}{6} = \sum_{n=1}^{\infty} \frac{1}{n^2} = \varsigma(2)$$

5. (***Gamma Function***) Gamma function $\Gamma(z)$ can be defined as

$$\Gamma(z) = \lim_{n\to\infty} \frac{1\cdot 2\cdot 3\cdots n}{z(z+1)(z+2)\cdots(z+n)}\, n^z$$

(A) Please prove that $\Gamma(z+1) = z\,\Gamma(z)$ (5 pts.)

(B) Please also prove that $\Gamma(z)\,\Gamma(1-z) = \pi / \sin(\pi z)$ (25 pts.)

(1) A beam is simply supported and loaded as shown in Fig. 1. Determine (a) The reaction forces at A and B, (b) the shear force variation along the beam, (c) the moment variation along the beam, (d) Given the section moduli of S_1=8 in^3 and S_t =2 in^3 for top and bottom of the beam, respectively, calculate the maximum tensile and compressive stresses in the beam. (25%)

(2) Determine the deflection at A of the system shown in Fig. 2. (I and 2I are moments of inertia). (25%)

(3) As shown in Fig.3,σ_x=400 psi, σ_y=100 psi, σ_z = -100 psi, (a) calculate the maximum shear stresses for planes parallel to x, y and z axis, respectively. (b) Which one in (a) corresponds to a pure shear condition? (25%)

(4) A hollow shaft and a solid shaft have the same outside radius r. The inner radius of the hollow shaft is kr (0<k<1). Assuming that both shafts are subjected to the same torque, compare their weights and maximum shear stresses. To reduce the weight by 1/2 by replacing a solid shaft with a hollow shaft of the same outside diameter, how much the maximum shear stress will be increased under a fixed torque? (25%)

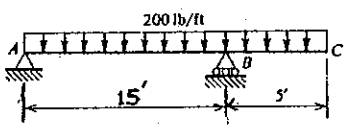


Fig. 1.

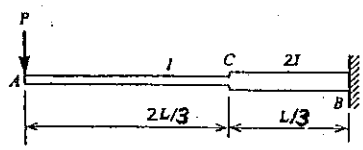


Fig. 2

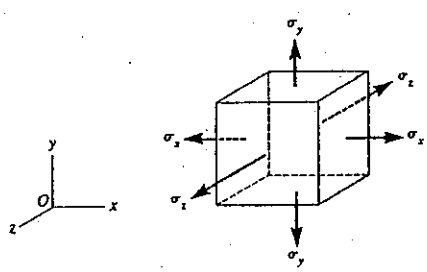


Fig. 3

請於答案卷上依序作答，並清楚標明題號

1. Distinguish among states of stable equilibrium, metastable equilibrium and unstable equilibrium according to the free energy curve and related state equations. (15%)
2. For an ideal gas, plot a reversible Carnot cycle on the P-V diagram under the adiabatic expansion and isothermal compression steps. Describe the changes of pressure (ΔP), temperature (ΔT) and volume (ΔV) through the above two steps. (25%)
3. A gold jewelry alloy contains 8 at%Ag, 10 at%Cu and 5 at%Pt and balance with gold. The alloy is in single homogeneous phase. Calculate the molar configuration entropy of this alloy. (10%)
4. Deduce from the second law of thermodynamics why the makers of turbines, rockets and other "heat engines" continually strive for higher operation temperatures. (20%)
5. An exothermic chemical reaction occurred spontaneously within a constant temperature and pressure system. Please describe the changes of enthalpy, entropy and free energy as positive, negative, zero, or undetermined. (15%)
6. The tire pressure measured during winter at 15 °C was 35 psi. The same tire was used during summer at 32 °C . If we assume that the volume of the tire did not change, and no air leaked out, what is the new tire pressure? (15%)