



1. Based on the definitions for symbols of Table I, II and III and the dimensional analysis using Buckingham method, we can derive the following well known parameters: Re, Nu, St, Pr, Gr (heat convection), Sc and Sh number.
  - (a). Please write the definition of those numbers and physical meaning of those numbers. (21%)
  - (b). Using the form of correlating relations of  $Z = F(X, Y)$ , where X, Y and Z are those number, to express the possible relations of those relations that are well known in Transport phenomena and Unit operation of Chemical Engineering (state three or more relations): (6 %)
  
2. For Bingham plastic fluids: (Fig. 1)
 
$$\tau_{rx} = \tau_0 + \mu (-dV_x/dr),$$
 Where :  $\tau_0$  yield stress in  $N/m^2$ .  
Calculate velocity distribution of the fluids in a pipe in a laminar flow, and proof that  $V_x = [(P_0 - P_L)/4\mu L] R^2 [1 - (r_0/R)]^2$ , at  $r = r_0$ .  
 Where  $(P_0 - P_L)/L$  is pressure drop along the pipe with length L;  $\mu$  is the viscosity of the fluid. R is the radius of the pipe.  
 (Note: the plug flow region is from  $r = 0$  to  $r = r_0$ ;  
 the shear stress of the region  $\tau_{rx} < \tau_0$ .) (13 %)
  
3. Calculate the approximation equation for food freezing (Fig. 2).  
 The assumptions in the derivation are listed: All the food is at the freezing temperature but is unfrozen, initially. The thermal conductivity, k, of the frozen part is constant. All the material freezes at the freezing point, with a constant latent heat,  $\lambda$  (J/Kg). The heat transfer by conduction in the frozen layer occurs slowly enough that it is under pseudo-steady state conditions.  
 In Fig. 2 a slab of thickness, a (m), is cooled from both sides by convection. At a given time t (s), a thickness of x (m) of frozen layer has formed on the both sides. The temperature of the environment is constant at  $T_1$  (K) and the freezing temperature is constant at  $T_f$  (K). An unfrozen layer in the center at  $T_f$  is present. The heat-transfer coefficient and the density of the meat are assigned as h and  $\rho$ , respectively. The heat leaving at time t is q (W). A is the surface area.  
Derive the time t to frozen the meat: (10 %)



4. Write down the equations and explain the physical meanings of the following transport phenomenon laws: (9%)
- Momentum transfer: Newton's law of viscosity
  - Heat transfer: Fourier's law of heat conduction
  - Mass transfer: Fick's law of diffusion

5. As shown in Fig. 3, for flow of a liquid through a heat-exchange tube,  $L$  is the tube length,  $D$  is the tube diameter,  $T_0$  is the entering temperature,  $T_s$  is the surface temperature,  $v$  is the liquid velocity (assuming uniform),  $\rho$  and  $C_p$  are the density and specific heat of the fluid, respectively,  $h$  is the heat transfer coefficient between the surface and the fluid, and  $St$  is the Stanton number. Show that the exit temperature ( $T_L$ ) is:

$$T_L = T_s + (T_0 - T_s) \exp\left[-St \left(\frac{4L}{D}\right)\right] \quad (7\%)$$

6. As shown in Fig. 4, for flow of a liquid metal through a circular tube, the velocity and temperature profiles at a particular axial location may be approximated as being uniform and parabolic, respectively. That is,  $u(r) = C_1$  and  $T(r) - T_s = C_2 [1 - (r/r_0)^2]$ , where  $C_1$  and  $C_2$  are constants. Let  $T_s$  be the surface temperature,  $T_m$  be the mean temperature,  $h$  be the heat transfer coefficient between the surface and the fluid, and  $k$  be the thermal conductivity of the fluid. What are the values of the convection heat transfer coefficient  $h$  and the Nusselt number  $Nu_D$  at this location? (8%)

Hint: Wall heat flux  $q/A = h(T_s - T_m)$ ;  $u_m = C_1$ ;  $T_m = \frac{2}{u_m r_0^2} \int_0^{r_0} u T r dr$ .

7. The diagram and nomenclature of a single pass counterflow tube heat exchanger are shown in Fig. 5.

- (a). Letting  $U$  be the overall heat transfer coefficient between the two fluids, show that the heat flux ( $q/A$ ) is:

$$q/A = U \Delta T_{lm}; \text{ where } \Delta T_{lm} = (\Delta T_2 - \Delta T_1) / \left(\ln \frac{\Delta T_2}{\Delta T_1}\right) \quad (5\%)$$



(b). A counterflow tube heat exchanger is used to cool the lubricating oil for a large industrial gas turbine engine. The flow rate of cooling water through the inner tube ( $D_i = 25$  mm) is 0.2 kg/s ( $C_p = 4178$  J/kg °K), while the flow rate of oil through the outer annulus ( $D_o = 45$  mm) is 0.1 kg/s ( $C_p = 2131$  J/kg °K). The oil and water enter at temperatures of 100 and 30°C, respectively. Assuming the overall heat transfer coefficient (based on the inner tube) may be taken as  $U = 37.8$  W/m<sup>2</sup> °K, how long must the tube be made if the outlet temperature of the oil is to be 60°C? (8%)

Hint: 1 W = 1 J/s.

8. The diffusion coefficient or mass diffusivity for a gas ( $D_{AB}$ ) may be experimentally measured in an Arnold cell as shown in Fig.6. The narrow tube, which is partially filled with pure liquid A, is maintained at a constant temperature and pressure. Gas B, which flows across the open end of the tube, has a negligible solubility in liquid A and is also chemically inert to A. Component A vaporizes and diffuses into the gas phase; the rate of vaporization of A is expressed in terms of the molar mass flux,  $N_A$ .

(a). Assuming a steady-state process, no chemical production of A, and diffusion occurs in the  $z$  direction only, show that the mass molar flux of A in the  $z$  direction ( $N_{A,z}$ ) is:

$$N_{A,z} = \frac{cD_{AB}}{z_2 - z_1} \ln \frac{(1 - y_{A2})}{(1 - y_{A1})} \quad (5\%)$$

Hint:  $\frac{d}{dz} N_{A,z} = 0$ ;  $N_{A,z} = -cD_{AB} \frac{dy_A}{dz} + y_A(N_{A,z} + N_{B,z})$ ;  $N_{B,z} = 0$ ;

$y_A$  is the molar fraction of A in the gas phase,  $y_A = P_A/P$ ;  $c$  is the concentration of the gas,  $c = P/RT$ .

(b). The Arnold evaporating cell, having a cross-sectional area of 0.82 cm<sup>2</sup>, was operated at 297 °K and 1.013×10<sup>5</sup> Pa pressure. The length of the diffusion path was 15.0 cm. If 0.0445 cm<sup>3</sup> of ethanol was evaporated in 10 hr of steady-state operation, what should be the value of the mass diffusivity of ethanol in air? (8%)

Hint: At 297 °K, the vapor pressure of ethanol is 6.931×10<sup>3</sup> Pa and its density is 0.789 g/cm<sup>3</sup>; Molecular weight of ethanol is 46 g/mol;  $R = 8.314$  Pa.m<sup>3</sup>/mol °K; 1 Pa = 1 Nt/m<sup>2</sup>.



Table I

Variable	Symbol	Dimensions
Tube diameter	$D$	$L$
Fluid density	$\rho$	$M/L^3$
Fluid viscosity	$\mu$	$M/Lt$
Fluid heat capacity	$c_p$	$Q/MT$
Fluid thermal conductivity	$k$	$Q/LT$
Velocity	$v$	$L/t$
Heat-transfer coefficient	$h$	$Q/L^2T$

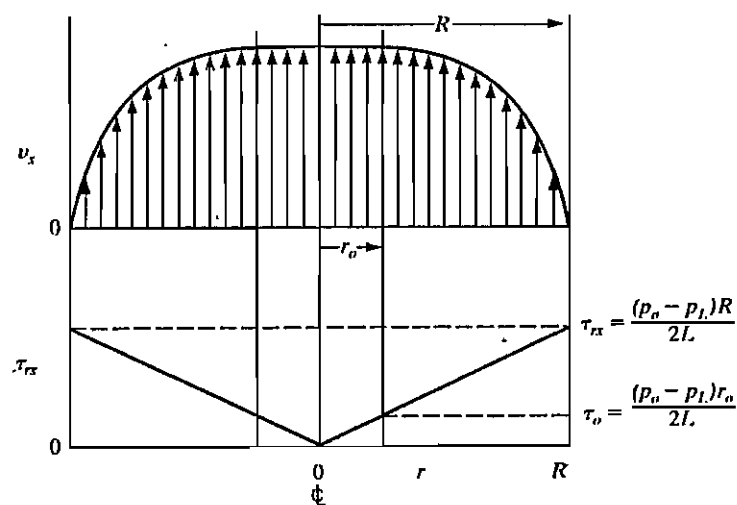
Table II

Variable	Symbol	Dimensions
Significant length	$L$	$L$
Fluid density	$\rho$	$M/L^3$
Fluid viscosity	$\mu$	$M/Lt$
Fluid heat capacity	$c_p$	$Q/MT$
Fluid thermal conductivity	$k$	$Q/LT$
Fluid coefficient of thermal expansion	$\beta$	$1/T$
Gravitational acceleration	$g$	$L/t^2$
Temperature difference	$\Delta T$	$T$
Heat-transfer coefficient	$h$	$Q/L^2T$

Table III

Variable	Symbol	Dimensions
tube diameter	$D$	$L$
fluid density	$\rho$	$M/L^3$
fluid viscosity	$\mu$	$M/Lt$
fluid velocity	$v$	$L/t$
fluid diffusivity	$D_{AB}$	$L^2/t$
mass-transfer coefficient	$k_c$	$L/t$

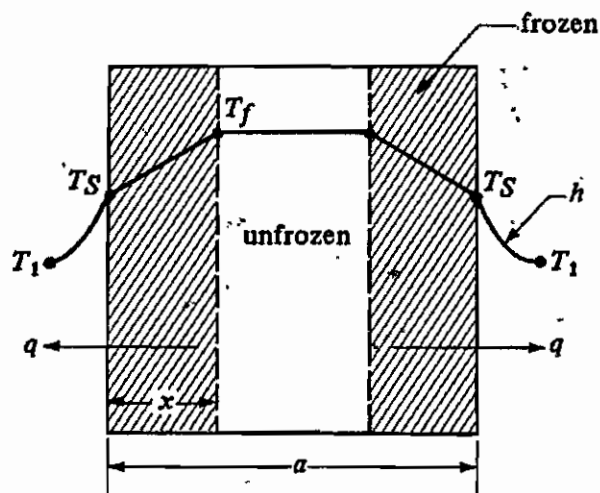
Fig.1



Velocity profile and shear diagram for flow of a Bingham plastic fluid in a pipe.



Fig.2



Temperature profile during freezing.

Fig.3

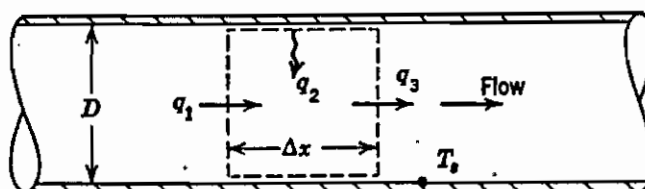


Fig.4

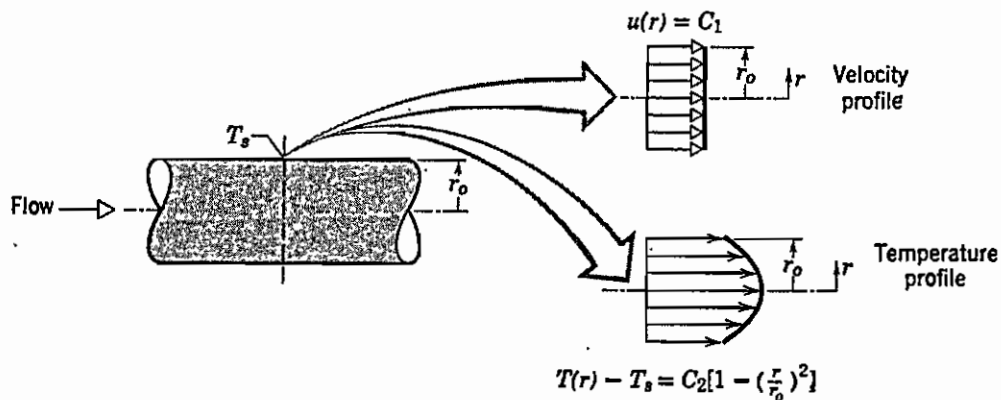




Fig.5

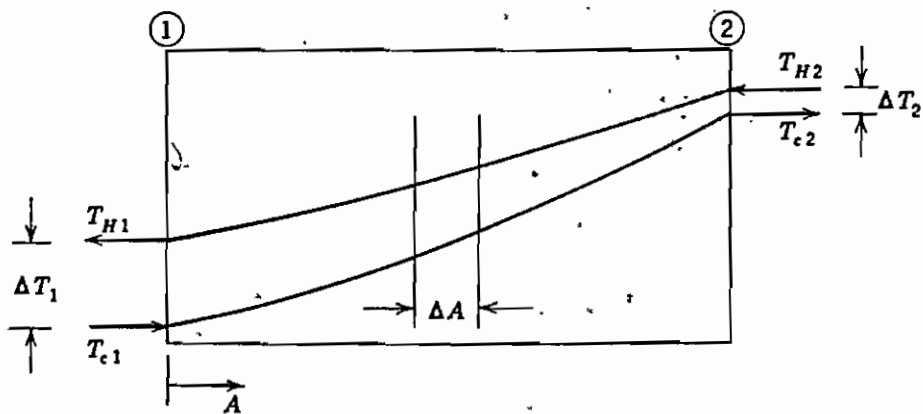
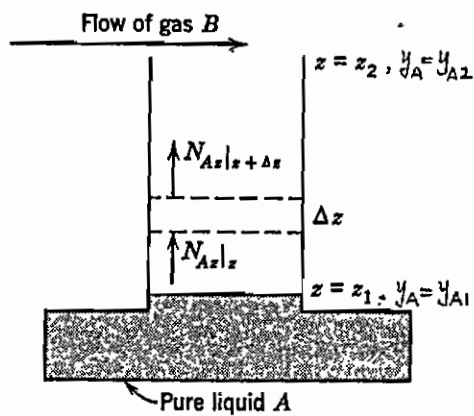


Fig.6





1. (20 %)

(a) Explain the concept of the viscoelastic deformation, stress relaxation, and viscoelastic creep behaviors of the polymeric materials. (10 %).

(b) Explain the influence of temperature on the mechanical properties of polymeric materials (5%)

(c) Sketch schematic the relaxation modulus-temperature plots for the almost totally crystalline isotactic polystyrene, the lightly crosslinked atactic polystyrene, and the amorphous polystyrene, respectively. (5%)

2. (15 %)

Demonstrate the structure and properties of the polymer crystal by using the fringed-micelle, chain folded, and spherulite models, respectively.

3. (15%)

The wear resistance of a steel gear is to be improved by hardening its surface. This is to be accomplished by increasing the carbon content within an outer surface layer as a result of carbon diffusion into the steel; the carbon is to be supplied from an external carbon-rich gaseous atmosphere at an elevated and constant temperature. The initial carbon content of the steel is 0.2 wt%, whereas the surface concentration is to be maintained at 1.00 wt%. In order for this treatment to be effective, a carbon content of 0.6 wt% must be established at a position 0.75 mm below the surface. Specify an appropriate heat treatment in terms of temperature and time for temperatures between 900 °C and 1050 °C. Use data in Table 1 for the diffusion of carbon in  $\gamma$ -iron.


**Table 1** A Tabulation of Diffusion Data

Diffusing Species	Host Metal	$D_0(m^2/s)$	Activation Energy $Q_d$		Calculated Values	
			$kJ/mol$	$eV/atom$	$T(^{\circ}C)$	$D(m^2/s)$
Fe	$\alpha$ -Fe (BCC)	$2.8 \times 10^{-4}$	251	2.60	500	$3.0 \times 10^{-21}$
					900	$1.8 \times 10^{-15}$
Fe	$\gamma$ -Fe (FCC)	$5.0 \times 10^{-5}$	284	2.94	900	$1.1 \times 10^{-17}$
					1100	$7.8 \times 10^{-16}$
C	$\alpha$ -Fe	$6.2 \times 10^{-7}$	80	0.83	500	$2.4 \times 10^{-12}$
					900	$1.7 \times 10^{-10}$
C	$\gamma$ -Fe	$2.3 \times 10^{-5}$	148	1.53	900	$5.9 \times 10^{-12}$
					1100	$5.3 \times 10^{-11}$
Cu	Cu	$7.8 \times 10^{-5}$	211	2.19	500	$4.2 \times 10^{-19}$
Zn	Cu	$2.4 \times 10^{-5}$	189	1.96	500	$4.0 \times 10^{-18}$
Al	Al	$2.3 \times 10^{-4}$	144	1.49	500	$4.2 \times 10^{-14}$
Cu	Al	$6.5 \times 10^{-5}$	136	1.41	500	$4.1 \times 10^{-14}$
Mg	Al	$1.2 \times 10^{-4}$	131	1.35	500	$1.9 \times 10^{-13}$
Cu	Ni	$2.7 \times 10^{-5}$	256	2.65	500	$1.3 \times 10^{-22}$

Source: E. A. Brandes and G. B. Brook (Editors), *Smithells Metals Reference Book*, 7th edition, Butterworth-Heinemann, Oxford, 1992.

#### 4. (20%)

固體之生成與反應過程，主要包括擴散(Diffusion)、固相反應(Solid state reaction) 及燒結 (Sintering) 等程序。試比較說明各程序之主要反應機構及相關能量變化等特性。

#### 5. (20%)

試繪圖並詳細說明固體燒結過程中，包括那五種主要之物質輸送機構。

#### 6.

試解釋下列名詞

- (1) 主級鍵結 (Primary bonding) (3%)
- (2) 過冷液體 (Supercooled liquids) (3%)
- (3) 高溫腐蝕 (High temperature corrosion) (4%)





1. (25 %)

The van der Waals equation of state describes real gases more accurately than does the ideal gas law:-

$$(P + an^2/V^2)(V - nb) = nRT$$

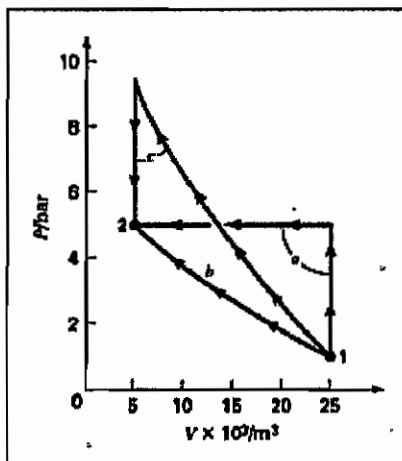
The symbols  $a$  and  $b$  represents parameters that have different constant values for different substances. The symbol  $R$  is molar gas constant. Derive formulas for the critical temperature and critical molar volume for a gas obeying the van der Waals equation of state.

2. (25 %)

Air is compressed from an initial condition of 1 bar and 298.15 K(25 °C) to a final state of 5 bar and 298.15K(25 °C) by three different mechanically reversible processes in a closed system:

- Heating at constant volume followed by cooling at constant pressure.
- Isothermal compression.
- Adiabatic compression followed by cooling at constant volume.

Assume air to be an ideal gas with the constant heat capacities,  $C_v = (5/2)R$  and  $C_p = (7/2)R$ . Calculate the work required, heat transferred, and the changes in internal energy and enthalpy of the air for each process.





3. (25%)

One mole of an ideal gas is compressed isothermally but irreversibly at 130°C from 2.5 bar to 6.5 bar in a piston/cylinder device. The work required is 30% greater than the work of reversible, isothermal compression. In the process, the heat transferred from the gas during compression flows to a heat reservoir at 25°C. Calculate

- (a) the minimum work required for the compression operation. (6%)
- (b) the entropy change of the gas. (6%)
- (c) the entropy change of the heat reservoir. (6%)
- (d) the total entropy change of the process. (7%)

4. (25%)

Ethyl alcohol and *n*-hexane are put into an evacuated, isothermal chamber. After equilibrium is established at 75°C, it is observed that two liquid phases and a vapor phase are in equilibrium. One of the liquid phases contains 9.02 mol% *n*-hexane. Activity coefficients for the *n*-hexane-ethyl alcohol liquid mixtures can be represented by the following equation

$$RT \ln \gamma_i = 8.163x_i^2 \text{ kJ/mol}$$

Compute

- (a) the equilibrium composition of the coexisting liquid phase. (9%)
- (b) the system pressure at equilibrium. (8%)
- (c) the more fraction of the vapor phase. (8%)

Data Vapor pressure equations (*T* in K, *P* in bar)

$$n\text{-Hexane: } \ln P^{\text{vap}} = \frac{-3570.58}{T} + 10.4575$$

$$\text{Ethyl alcohol: } \ln P^{\text{vap}} = \frac{-4728.98}{T} + 13.4643$$



1. The first-order homogeneous gaseous decomposition  $A \rightarrow 3R$  is carried out in an isothermal batch reactor at 2 atm with 30% inerts present, and the volume increases by 70% in 20 min. In a constant-volume reactor, find the time required for the pressure to reach 8 atm if the initial pressure is 5 atm, 2 atm of which consist of inerts. (20%)
2. The irreversible reaction  $A + B = AB$  has been studied kinetically, and the rate of formation of product has been found to be well correlated by the following rate equation:

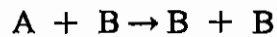
$$r_{AB} = kC_A^2 \quad \text{independent of } C_B$$

Please derive the reaction mechanism by this rate expression and start with two-step reversible model. The chemistry of the reaction suggests that the intermediate consists of an association of reactant molecules and that a chain reaction does not occur. (20%)

3. Please explain the following terms: (20%)
  - (a) rate-limiting step
  - (b) reactive distillation
  - (c) holding time and space time
  - (d) recycle reactor and semibatch reactor



4. The feed contains 99% A, 1% B. The desired product is to consist of 10% A, 90% B. The transformation of A into B takes place by means of the elementary reaction

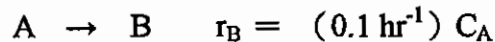


with rate constant  $k=2$  liter/ (mol.min.) . The concentration of active materials is

$$C_{A0} + C_{B0} = C_A + C_B = C_0 = 1 \text{ mol./liter}$$

What reactor holding time will yield a product in which  $C_B=0.9$  mol./liter (a) in a plug flow reactor, (b) in a mixed reactor, and (c) in a minimum-size setup without recycle. (20%)

5. 200 gram moles of B are to be produced hourly from a feed consisting of a saturated solution of A ( $C_{A0} = 1$  mol./liter) in a mixed flow reactor. The reaction is



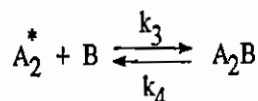
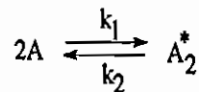
Cost of reactant at  $C_{A0} = 1$  mol./liter is 0.2/ (mol.A) . Cost of reactor including installation, auxiliary equipment, instrumentation, overhead, labor, depreciation, etc., is 0.02/ (hr-liter) .

What reactor size, feed rate, and conversion should be used for optimum operations? (20%)



1. (20 points)

If the nonelementary reaction  $2A + B = A_2B$  includes the following elementary reversible reactions, derive the rate law for  $-r_A$ .



What is the relationship among  $r_A$ ,  $r_B$ , and  $r_{A_2B}$ ?

2. (14 points)

The frequency of flashing of fireflies as a function of temperature is given below.

Temperature ( $^{\circ}\text{C}$ )	21.0	25.0	30.0
Flashes per min.	9.0	12.16	16.2

What is the activation energy and frequency factor for the frequency of flashing of fireflies? What is the frequency of flashing of fireflies at  $50^{\circ}\text{C}$ ?

3. (16 points)

At 580 nm, which is the wavelength of its maximum absorption, the complex  $\text{FeSCN}^{2+}$  has a molar absorptivity of  $7.00 \times 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$ . Calculate

(a) the absorbance of a  $2.50 \times 10^{-5} \text{ M}$  solution of the complex at 580 nm in a 1.00-cm cell.

(b) the absorbance of a solution in which the concentration of the complex is twice that in (a).

(c) the transmittance of the solutions described in (a) and (b).

(d) the absorbance of a solution that has half the transmittance of that described in (a).

4. (15 points)

Calculate  $\Delta H_{\text{tot}}$  and  $\Delta S_{\text{tot}}$  when two copper blocks, each of mass 10 kg, one at 373 K and the other at 273 K, are placed in contact in an isolated container. The specific heat capacity of copper is  $0.385 \text{ J/K-g}$  and may be assumed constant over the temperature range involved.

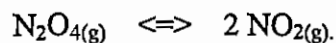


5. (15 points)

The emf of the cell  $\text{Ag} \mid \text{AgI}_{(s)} \mid \text{AgI}_{(aq)} \mid \text{Ag}$  is 0.9509 V at 298 K. Assuming  $\text{AgI}_{(aq)}$  is an ideal solution. Calculate (a) the solubility product of AgI and (b) its solubility.

6. (20 points)

$\text{N}_2\text{O}_4$  is 18.46 per cent dissociated at 298 K and 1 bar in the equilibrium

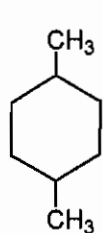


Assuming the gases are perfect. Calculate (a) K at 298 K, (b)  $\Delta_r G^\circ$ , (c) K at 373 K given that  $\Delta_r H^\circ = 57.2$  kJ/mole over the temperature range.

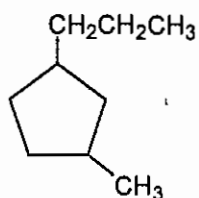


1. (10%)

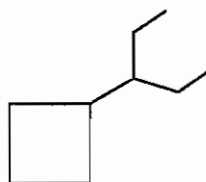
Give IUPAC names for the following cycloalkanes:



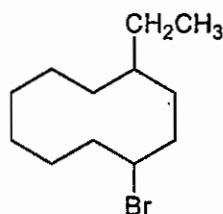
(a)



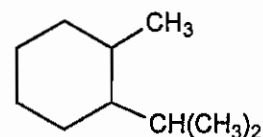
(b)



(c)



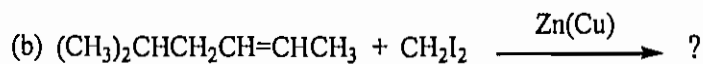
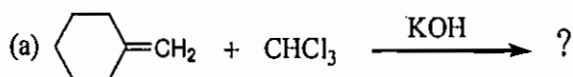
(d)



(e)

2. (10%)

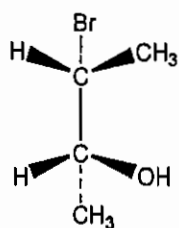
What product would you expect from the following reactions?



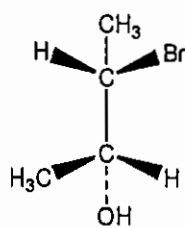
3. (10%)

Assign R,S configurations to each chirality center in the following molecules.

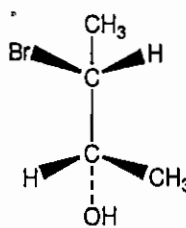
Which are enantiomers, and which are diastereomers?



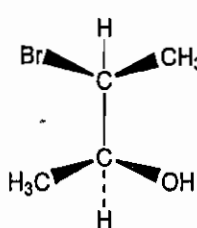
(a)



(b)



(c)



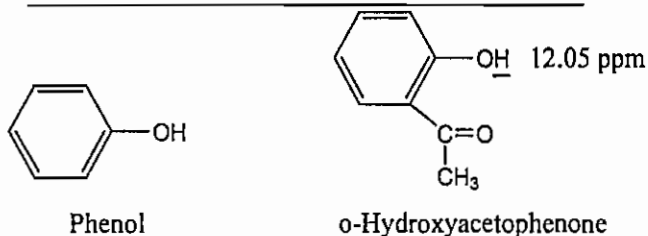
(d)



4. (10%)

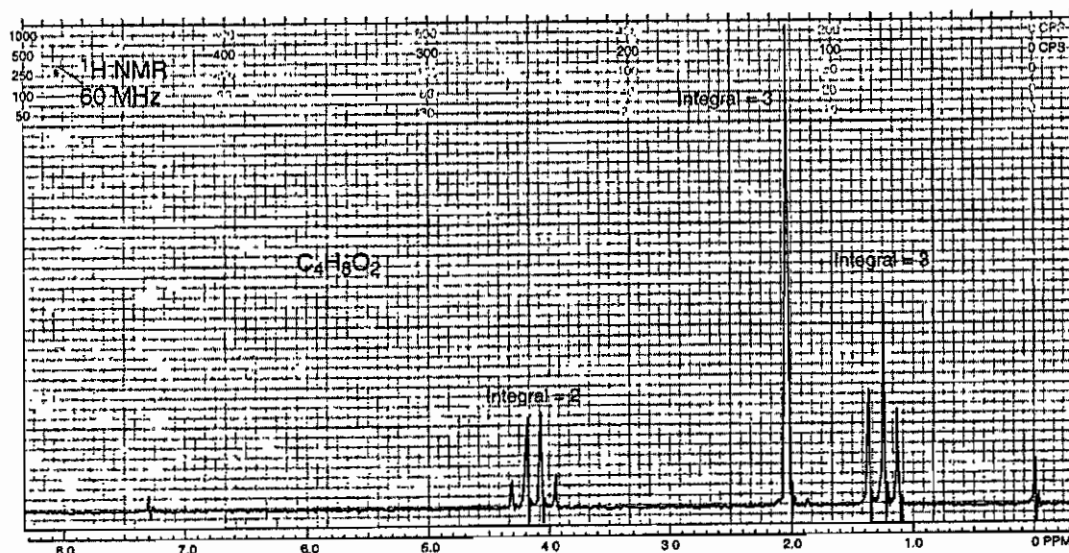
The position of the OH resonance of phenol varies with concentration in solution, as the following table shows. On the other hand, the hydroxyl proton of ortho-hydroxyacetophenone appears at 12.05 ppm and does not show any great shift upon dilution. Explain.

Concentration w/v in CCl <sub>4</sub>	$\delta$ (ppm)
100 %	7.45
20%	6.75
10%	6.45
5 %	5.95
2 %	4.88
1%	4.37



5. (10%)

The following compound, with the formula C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>, is an ester. Give its structure and assign the chemical shift values.







6. (10%)

Draw structures of all products expected from monochlorination at room temperature of:

- (a) isohexane  
 (b) 2,2-dimethylbutane  
 (c) 2,2,4-trimethylpentane

7. (10%)

A hydrocarbon was found to have a molecular weight of 80-85. A 10.02 mg sample took up 8.40 ml of  $H_2$  gas measured at  $0^\circ C$  and 760 mmHg pressure. Ozonolysis yields only HCHO and HCOCHO. What was the hydrocarbon?

8. (10%)

Which of the following compounds could give rise to each of the infrared spectra shown below:

Tetrahydrofuran

3-buten-2-ol

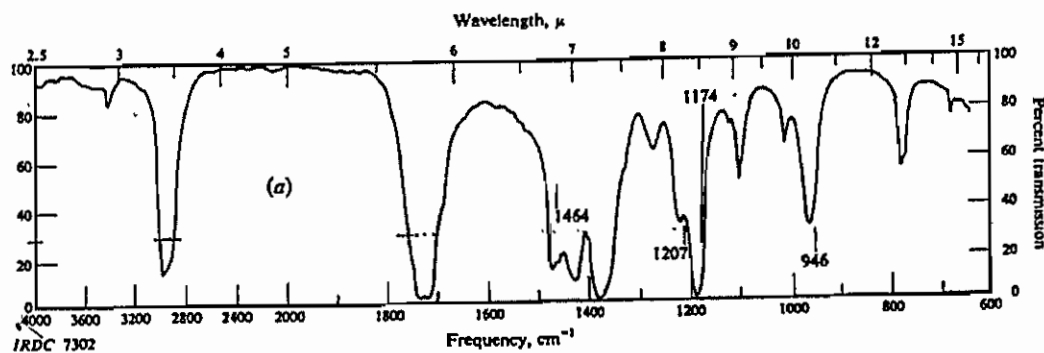
Propionic acid

Isobutyraldehyde

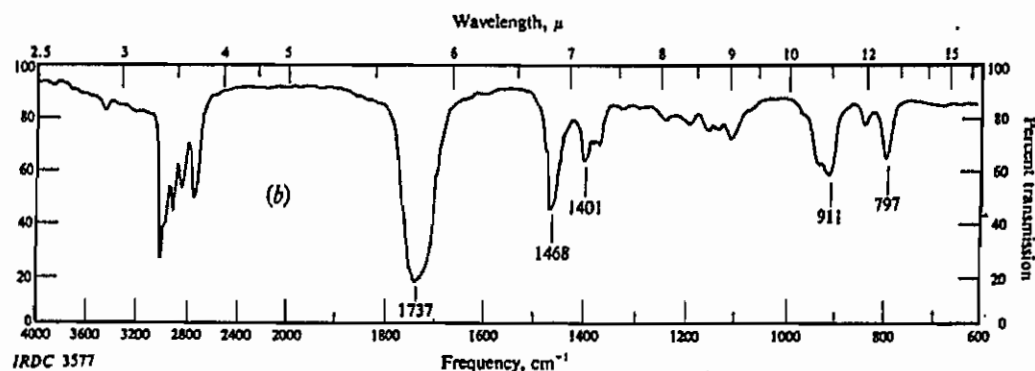
2-butanone

Aniline

(a)



(b)





9.(10%)

Predict the major products formed when isopropylbenzene reacts with the following reagents.

- (a).  $\text{Br}_2$  and  $\text{FeBr}_3$
- (b). hot, concd.  $\text{KMnO}_4$
- (c).  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$
- (d). 1 equivalent of  $\text{Br}_2$  and light.

10. (10%)

Poly(vinyl alcohol), a hydrophilic polymer used in aqueous adhesive, is made by polymerizing vinyl acetate and then hydrolyzing the ester linkages.

- (a). give the structures of poly(vinyl acetate) and poly(vinyl alcohol).
- (b). why is poly(vinyl alcohol) made by this circuitous route?  
why not just polymerize vinyl alcohol?