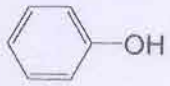
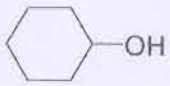
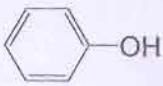
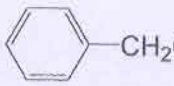
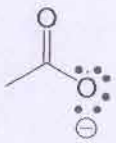
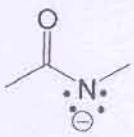
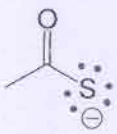
1. (Total: 21 points)

i) Arrange the compounds in each set in order of the referred properties (from the least to the most). (Each 4 points, total 12 points)

(a)   CH_3COOH Acidity

(b)    Acidity

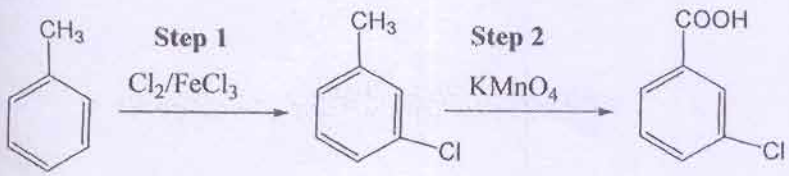
(c)    Nucelophilicity

ii) Give explanation for your result in set (b). (9 points)

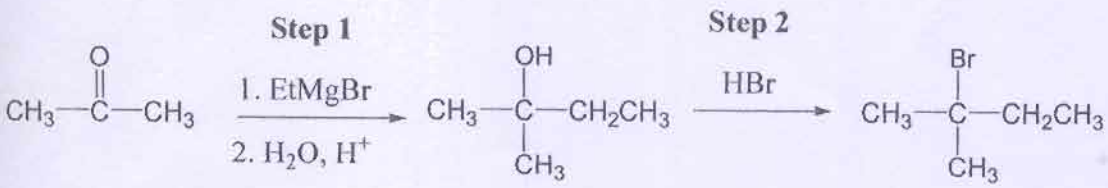
2. (Total: 15 points)

In each of the following syntheses there is at least one incorrect step. Identify the incorrect steps and explain what is wrong with each. (Each 5 points)

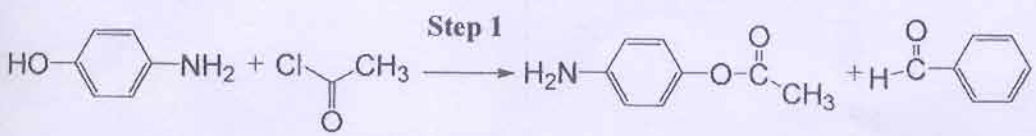
(a)



(b)

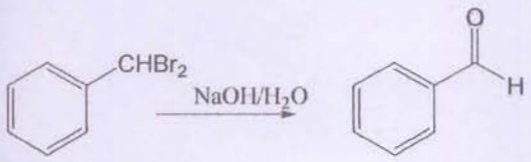


(c)



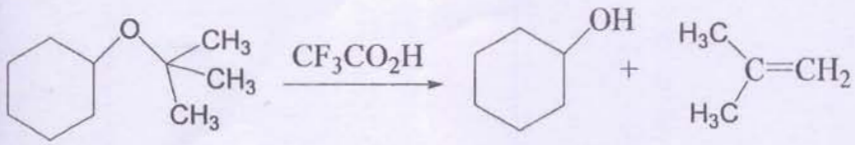
3. (Each 6 points, total 24 points) Write down the mechanistic steps involved in the following reaction.

(a)

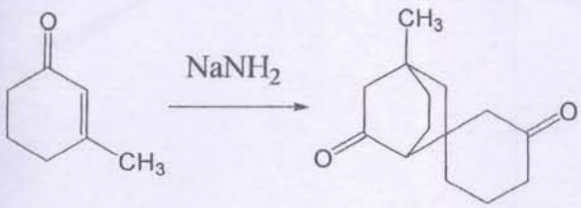


(b)

(c)



(d)



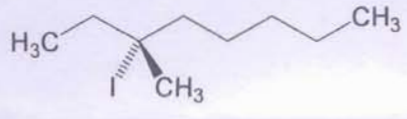
4. Multiple choices (each 2 points, total 40 points)

1. ( ) Consider the three isomeric alkanes n-hexane, 2,3-dimethylbutane, and 2-methylpentane. Which of the following correctly lists these compounds in order of increasing boiling point? a) 2,3-dimethylbutane < 2-methylpentane < n-hexane, b) 2-methylpentane < n-hexane < 2,3-dimethylbutane, c) 2-methylpentane < 2,3-dimethylbutane < n-hexane, d) n-hexane < 2-methylpentane < 2,3-dimethylbutane, e) n-hexane < 2,3-dimethylbutane < 2-methylpentane.

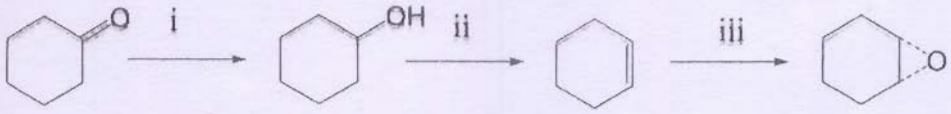
2. ( ) Which of the statements below correctly describes the chair conformations of trans-1,4-dimethylcyclohexane? a) The two chair conformations are of equal energy, b) The higher energy chair conformation contains one axial methyl group and one equatorial methyl group, c) The lower energy chair conformation contains one axial methyl group and one equatorial methyl group, d) The higher energy methyl group contains two axial methyl groups, e) the lower energy chain conformation contains two axial methyl groups.

3. ( ) Energy is _____ when bonds are formed and is _____ when bonds are broken; therefore, bond dissociation energies are always _____. a) released / consumed / exothermic, b) released / consumed / endothermic, c) consumed / released / exdothermic, d) consumed / released / endothermic, e) consumed / released / isothermic.

4. ( ) How many distinct alkene products are possible when the alkyl iodide below undergoes E2 elimination? a 1, b) 2, c) 3, d) 4, e) 5. (p.s. including geometry isomers)



There are three reagents i ~ iii required to perform the reaction scheme below



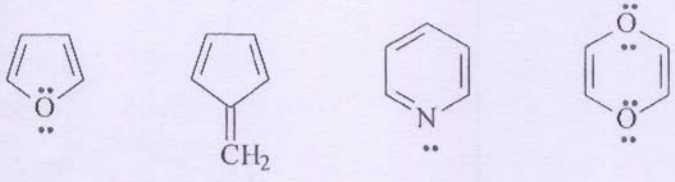
a) *m*-$ClC_6H_4CO_3H$, b) H_2/Pd, c) warm H_2SO_4/H_2O, d) PCC, CH_2Cl_2, e) $LiAlH_4$ in ether, then H_3O+, f) NaOH, heat.

5. ( ) Chose the right reagents i from the above reagent lists from a) to f).
6. ( ) Chose the right reagents ii from the above reagent lists from a) to f).
7. ( ) Chose the right reagents iii from the above reagent lists from a) to f).

Match the following groups of the bond-type to the region of infrared spectrum to which they absorb? a) 4000-2500 cm^{-1}, b) 2500-2000 cm^{-1}, c) 2000-1500 cm^{-1}, d) below 1500 cm^{-1}.

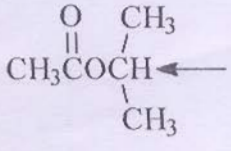
8. ( ) C-C, C-O, C-N single bonds vibrate at _____.
9. ( ) C=O, C=N and C=C bond absorptions.
10. ( ) N-H, C-H and O-H bond stretching and bending motions.
11. ( ) triple bond stretching vibrations.

12. ( ) Which statement does not describe a transition state? a) Possesses a definite geometry; b) Maximum on the potential energy diagram; c) Structure can be determined experimentally; d) Can not be isolated.
13. ( ) Which reagents react with an alkene by syn addition? I. Cl_2; II. Br_2; III. H_2/Pt; IV. OsO_4/ROOH a) I, II; b) III, IV; c) II, III; d) I, IV.
14. ( ) How many stereoisomers are possible for 2,3-butanediol? a) 1; b) 2; c) 3; d) 4.
15. ( ) Which is the best reaction condition for preparing 2-iodohexane from 1-hexene? a) I_2 / CCl_4; b) HI; c) NaI; d) HIO_4.
16. ( ) How many isomers, including stereoisomers, can be formed from the hydroxylation of 4-methylcyclohexene using osmium tetroxide? a) 2; b) 4; c) 6; d) 8.
17. ( ) Which structures are aromatic? a) II, III; b) III, IV; c) I, III; d) II, IV



I II III IV

18. ( ) How many sets of equivalent hydrogen atoms are there for 2-propanol? a) 2; b) 3; c) 4; d) 8.
19. ( ) Which is the splitting pattern for the indicated hydrogen atom? a) septet; b) quartet; c) doublet; d)



singlet.

20. ( ) Although all of the following compounds are of similar molecular weight, one of them is much higher boiling than the others. Which one? (a) tetrahydrofuran, (b) 1-butanol, c) methyl propyl ether, (d) 1,2-propanediol.

1. Consider the three distinct isomers of dichlorobenzene. To which symmetry group does each belong? Which can have a dipole moment? (10%)

2. The decomposition of N_2O_5

$$2N_2O_5 = 4NO_2 + O_2$$

is studied by measuring the concentration of oxygen as a function of time, and it is found that

$$\frac{d[O_2]}{dt} = (1.5\times10^{-4}\,s^{-1})[N_2O_5]$$

at constant temperature and pressure. Under these conditions, the reaction goes to completion to the right. What is the half-life of the reaction under these conditions? (5%)

The rate constants for this gas reaction $1/2N_2O_5 = 2NO_2 + 1/2O_2$ are as follows:

T/K	273	298	308	318	328	338
$k/10^{-5}\ s^{-1}$	0.0787	3.46	13.5	49.8	150	487

What are the values of the activation energy and the pre-exponential factor? (10%)

3. A mole of an ideal monoatomic gas is allowed to expand adiabatically and reversibly from 22.7 L mol^{-1} at 1 bar and 0 °C to a volume of 45.4 L mol^{-1}, the pressure drops to 0.315 bar. What is the final temperature, and how much work is done on this monoatomic gas? (10%)

4. What is the value of the nuclear magneton? Calculate the ratio of the number of protons in the upper spin state to that in the lower spin statein a magnetic field of 2 T at room temperature and 1 mK (10^{-3} K). (10%)

5. What is the molar volume of $N_2(g)$ at 500 K and 600 bar according to (*a*) the ideal gas law and (*b*) the virial equation? (*c*) Explain the difference. The virial coefficient *B* of $N_2(g)$ at 500 K is 0.0169 L mol^{-1}. (10%)

6. Toluene is vaporized at its boiling point, 111 °C. The heat of vaporization at this temperature is 361.9 J g^{-1}. For the vaporization of toluene, calculate (*a*) the work per mole, (*b*) the heat absorbed per mole, (*c*) the change in molar internal energy, (*d*) the change in molar Gibbs energy, and (*e*) the change in molar entropy. (20%)

7. Show that the total degeneracy g_{total} of the energy levels of the hydrogenlike atom is n^2 by writing out the possible quantum numbers for $n = 1$, 2, 3, and 4. (10%)

8. According to Table 1 what are the equilibrium constants for the following reactions at 25 °C? (15%)

(a) $H^+(ao) + Li(s) = Li^+(ao) + 1/2H_2(g)$

(b) $2H^+(ao) + Pb(s) = Pb^{2+}(ao) + H_2(g)$

(c) $3H^+(ao) + Au(s) = Au^{3+}(ao) + 3/2H_2(g)$

Table 1 Standard Electrode Potentials at 25 °C

Electrode	E°/V	*Electrode Reaction*
$F^- \mid F_2(g) \mid Pt$	2.87	$\frac{1}{2}F_2(g) + e^- = F^-$
$Au^{3+} \mid Au$	1.50	$\frac{1}{3}Au^{3+} + e^- = \frac{1}{3}Au$
$Pb^{2+} \mid PbO_2 \mid Pb$	1.455	$\frac{1}{2}PbO_2 + 2H^+ + e^- = \frac{1}{2}Pb^{2+} + H_2O$
$Cl^- \mid Cl_2(g) \mid Pt$	1.3604	$\frac{1}{2}Cl_2(g) + e^- = Cl^-$
$H^+ \mid O_2(g) \mid Pt$	1.2288	$H^+ + \frac{1}{4}O_2(g) + e^- = \frac{1}{2}H_2O$
$Ag^+ \mid Ag$	0.7992	$Ag^+ + e^- = Ag$
$Fe^{3+}, Fe^{2+} \mid Pt$	0.771	$Fe^{3+} + e^- = Fe^{2+}$
$I^- \mid I_2(s) \mid Pt$	0.5355	$\frac{1}{2}I_2 + e^- = I^-$
$Cu^+ \mid Cu$	0.521	$Cu^+ + e^- = Cu$
$OH^- \mid O_2(g) \mid Pt$	0.4009	$\frac{1}{4}O_2(g) + \frac{1}{2}H_2O + e^- = OH^-$
$Cu^{2+} \mid Cu$	0.3394	$\frac{1}{2}Cu^{2+} + e^- = \frac{1}{2}Cu$
$Cl^- \mid Hg_2Cl_2(s) \mid Hg$	0.268	$\frac{1}{2}Hg_2Cl_2 + e^- = Hg + Cl^-$
$Cl^- \mid AgCl(s) \mid Ag$	0.2224	$AgCl + e^- = Ag + Cl^-$
$Cu^{2+}, Cu^+ \mid Pt$	0.153	$Cu^{2+} + e^- = Cu^+$
$Br^- \mid AgBr(s) \mid Ag$	0.0732	$AgBr + e^- = Ag + Br^-$
$H^+ \mid H_2(g) \mid Pt$	0.0000	$H^+ + e^- = \frac{1}{2}H_2(g)$
$D^+ \mid D_2(g) \mid Pt$	−0.0034	$D^+ + e^- = \frac{1}{2}D_2(g)$
$Pb^{2+} \mid Pb$	−0.126	$\frac{1}{2}Pb^{2+} + e^- = \frac{1}{2}Pb$
$Sn^{2+} \mid Sn$	−0.140	$\frac{1}{2}Sn^{2+} + e^- = \frac{1}{2}Sn$
$Ni^{2+} \mid Ni$	−0.250	$\frac{1}{2}Ni^{2+} + e^- = \frac{1}{2}Ni$
$Cd^{2+} \mid Cd$	−0.4022	$\frac{1}{2}Cd^{2+} + e^- = \frac{1}{2}Cd$
$Fe^{2+} \mid Fe$	−0.440	$\frac{1}{2}Fe^{2+} + e^- = \frac{1}{2}Fe$
$Zn^{2+} \mid Zn$	−0.763	$\frac{1}{2}Zn^{2+} + e^- = \frac{1}{2}Zn$
$OH^- \mid H_2(g) \mid Pt$	−0.8279	$H_2O + e^- = \frac{1}{2}H_2(g) + OH^-$
$Mg^{2+} \mid Mg$	−2.37	$\frac{1}{2}Mg^{2+} + e^- = \frac{1}{2}Mg$
$Na^+ \mid Na$	−2.714	$Na^+ + e^- = Na$
$Li^+ \mid Li$	−3.045	$Li^+ + e^- = Li$

Quantity	Symbol	Value
Planck constant	h	6.626×10^{-34} J s
$h/2\pi$	$\hbar$	1.055×10^{-34} J s
Elementary charge	e	1.602×10^{-19} C
Proton mass	m_p	1.673×10^{-27} kg
Gas constant	R	8.315 J K^{-1} mol^{-1}
		8.315×10^{-2} L bar K^{-1} mol^{-1}
Nuclear g factor	g_N	5.585 for ^1H nucleus

Prob. #1 A tank contains 800 gal of water in which 200 lb of salt is dissolved. Two gallons of fresh water runs in per minute, and 2 gal of the mixture in the tank, kept uniform by stirring, runs out per minute. How much salt is left in the tank after 5 hours (20%)

Prob. #2 The following matrix is Hermitian ? Skew-Hermitian ? Unitary ? Find their eigenvalues and eigenvectors (20%)

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

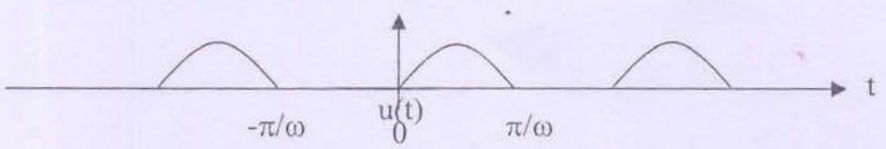
Prob. #3 (a) Make the plots of the two functions h(t) & x(t), their Fourier Transform and their convolution at time. Graph the Fourier Transform of their convolution to prove Convolution theorem (10%)

$$h(t) = \text{rect}(t), \quad x(t) = \text{rect}(t), \; -T_o < t < T_o$$

(b) Find the Fourier transform of f(t). Show the details. (10%)

$$f(t) = \begin{cases} t & \text{if } -1 < t < 1 \\ 0 & \text{otherwise} \end{cases}$$

Prob. #4. 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%)



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

Prob. #5. (a) Find the volume of the tetrahedron with vertices (0,2,1), (4,3,0), (6,6,5), (4,7,8) (10%)

(b) Find the directional derivative of f at P in the direction of a (10%)

$f = 4x^2 + y^2 + 9z^2$, P: (2,4,0), a = [-2, -4, 3]

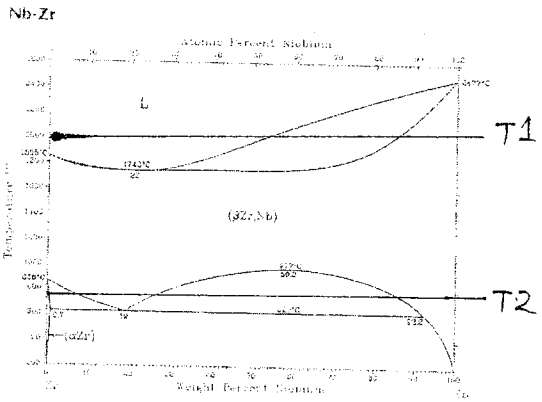
國立中山大學９７學年度碩士班招生考試試題

科目：熱力學【材光系碩士班乙組】

請於答案卷上依序作答，並清楚標明題號及運算推導過程

熱力

1. What is the phase rule? And derive the phase rule according to the thermodynamic equilibrium conditions. (15%)
2. The melting point of gallium is 30 °C at 1 atm. The densities of solid and liquid gallium are 5.885 and 6.08 g/cm^3, respectively. The heat of melting of gallium is 80 J/g. Please calculate the melting point of gallium at 0.8 atm pressure. Atomic weight of gallium is 69.72 g. (20%)
   1 cm^3.atm = 0.1013 Joule
3. One mole of a monoatomic ideal gas, in the initial state T= 273 K, P= 1 atm, is subjected to the following three processes, each of which is conducted reversibly:
   (a) A doubling of its volume at constant pressure,
   (b) Then a doubling of its pressure at constant volume,
   (c) then a return to the initial state along the path $P = 6.643 * 10^{-4} V^2 + 0.6667$
   Calculate the heat and work effects, which occur during each of the three processes. (20%)
4. (a) What is the enthalpy of pure, liquid aluminum at 1000 K ? (use pure, solid aluminum at 298 K as the reference state) (10%)
   (b) An electric resistance furnace is used to melt pure aluminum at the rate of 100 kg per hour. The furnace is fed with solid aluminum at 298 K. The liquid aluminum leaves the furnace at 1000 K. What is the minimum electric power rating (kw) of the furnace? (10%)
   Data for aluminum:
   Atomic weight = 27 g/mol
   Heat capacity of solid = 26 J/mol.K
   Heat capacity of liquid = 29 J/mol.K
   Melting point = 932 K
   Heat of fusion = 10700 J/mol
5. Calculate ΔU and ΔS when 0.5 mole of liquid water at 273 K is mixed with 0.5 mole of liquid water at 373 K, and the system is allowed to reach equilibrium in an adiabatic enclosure. (heat capacity of water = 77 J/mol.K; and heat capacity of ice = 38 J/mol.K) 15%
6. According to the following phase diagram, plot the free energy diagrams at temperature T1 and T2. (10%)



Electric Fields (40%)

1. A line of charge with linear charge density (charge per unit length) λ produces an electric field $\vec{E}$ at a distance r. The length of this line is L.
   (a) Please find the electric field $\vec{E}$. Not that $\vec{E}$ is a vector.
   (b) What happen to $\vec{E}$ if $L >> r$?
   (c) What happen to $\vec{E}$ if $r >> L$?

Principle of a Three-level Laser (60%)

2. When a photon with suitable energy ($h\nu = E_2 - E_1$) hits an exited atom at energy level E_2, it can stimulate an electron to transit to the lower level E_1 and emit another photon. The emitted photon has exactly the same frequency, phase, polarization, and propagation direction as the incident photon. Such a phenomenon is the so-called stimulated emission. If more electrons are in the exited state E_2 than in the ground state E_1, photons are more likely to stimulated emission than to be absorbed. Such a condition is called population inversion. If a **laser** is to operate continuously, both populating the upper level and depopulating the lower level are important, because accumulation of too many atoms (or molecules) in the lower level can end the population inversion and consequently stop the laser action. The excitation of atoms (or molecules) to produce a population inversion is called pumping. The excitation energy pumps electrons from the ground state to a short-lived highly excited level E_3. The atoms (or molecules) drop quickly to a metastable upper level E_2. The laser transition then takes these atoms (or molecules) to the ground state E_1. Such a laser system is called "a three-level system". The degree of amplification is measured as **gain**, which is the increase in intensity I when a light beam passes a laser medium, and is expressed as $G = {dI / dx}/{I}$. The intensity after the light beam travels a distance x within this medium can then be written as $I(x) = I_o e^{Gx}$, where I_o is the initial intensity at $x = 0$. The ruby laser is an optically pumped three-level laser, in which the energy between the ground level and the excited level is 2.254 eV, and the energy between the ground level and the metastable level is 1.784 eV.
   (a) Determine the wavelength of the pumping light, and that of the laser light for the ruby laser.
   (b) If the power output is $10mW$, how many photons of this light does the ruby laser emit each second?
   (c) If the gain, G, at the central wavelength is $0.001/cm$ in the ruby, what is the traveling distance for a light beam within the ruby in order to be amplified 100 times?
   (d) One way to get the light to pass through a long length of the laser medium is by putting mirrors on both sides of the laser medium. The light is bounced back and forth between the two mirrors and makes many passes through the laser medium. Thus, the traveling distance for a light beam is enlarged. These two mirrors, together with the laser materials in between, form an optical resonant cavity. Assume that the length of resonant cavity is $150mm$ and the overall gain of the ruby is $0.001/cm$. If one of the cavity mirrors reflects all the light that impinges on it, please determine the minimum required reflectance of the other mirror.
   (e) Continued from (d), it is interesting to notice that the laser power is higher inside the cavity than outside. If the output power is $10mW$, what is the power inside the cavity?

(1) When considering the stress-strain curve of a material during tensile test, some people like to use the change in the length of the specimen to represent the strain of the specimen, and some people like to use the change in the cross section of the specimen to represent the strain of the specimen. (a) Do you expect any difference exist between the stress-strain curves construct under these two ways? Justify your answer! (b) Which way you would like to use? Why? 10 points

(2) Give schematic drawing(s) of possible point defect(s) in ceramics. 8 points

(3) Steel specimens with the average grain size of 50μ and 100 μ have yield strength of 250MPa and 200MPa respectively. To what would be the grain size have to be changed to give a yield strength of 300MPa? 10 points

(4) Describe how a silicon single crystal with several inches diameter is produced? 10 points

(5) Titanium has a hexagonal crystal system. Draw the unit cell of Ti which has two atoms in one unit cell. 8 points

(6) The diffusivity of any element increases when the temperature increases. Explain the reason for this. Give your answer without any equation! 10 points

(7) Slip and twinning are two different ways that a material responses to plastic deformation. Explain the difference of the character of these two deformation modes. 10 points

(8) Use electron band structure to explain what is (a) a conductor, (b) a semiconductor, and (c) an insulator. 6 points

(9) Indexing the first four peaks (counted from low angle) of the diffraction pattern of (a) fcc, and (b) bcc polycrystalline crystals by using an X-ray diffractometer. 8 ponts

(10) Explain the following terms (a) constitutional supercooling, (b) peritectic reaction, and (c) interface controlled growth of second phase. 12 points

(11) Part of the Mn-Ge phase diagram is shown below. Give the name, amount (in wt%) , and composition of the phase(s) that exist for a Mn-38wt% Ge alloy at (a) 965°C, (b) 836°C, (c) 756°C, and (d) 580°C. 8 points