NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF APPLIED CHEMISTRY
BACHELOR OF SCIENCE HONOURS DEGREE
END OF FIRST SEMESTER EXAMINATIONS – FEBRUARY 2010
PHYSICAL CHEMISTRY I – SCH 2104
TIME: 3 HOURS

MATERIAL
Graph papers.

INSTRUCTIONS TO CANDIDATES

Answer ALL questions in section A and Any Three questions in Section B. Answer each question on a FRESH page.

$R = 8.314 JK^{-1} mol^{-1} = 0.08206 dm^3 atm K^{-1} mol^{-1}$

$F = eN_A = 9.6500 \times 10^4 C mol^{-1}$; $N_A = 6.022 \times 10^{23} mol^{-1}$

1 atm = 760 torr = 760mmHg = 101 325 Pa .

$\ln x = 2.3026 \log_{10} x$

SECTION A *Answer ALL questions. Each question carries 10 marks (Total 40)*

1. Calculate the heat of formation of propane gas from its elements
   (a) at constant pressure
   (b) at constant volume
   given that at 298K and 1 atm pressure:
   Heat of combustion of propane = $-2220 kJmol^{-1}$
   Heat of formation of water = $-286.0 kJmol^{-1}$
   Heat of formation of carbon dioxide = $-393.5 kJmol^{-1}$
   [Assume ideal behaviour for the gases] [10 marks]

2. (a) The heat capacity of gaseous argon at constant pressure is $20.8 JK^{-1}mol^{-1}$. Estimate the entropy change when one mole of argon is heated from 300K to 1200K at 1 atm pressure. [4 marks]

   (b) Calculate the entropy change when one mole of cadmium vapour at 1 atm pressure is heated from 1040K to 1100K and subsequently compressed to a pressure of 6 atm. You may assume that the vapour follows perfect gas behaviour.
   c_v [Cd(g)] $= 12.5 JK^{-1}mol^{-1}$ [4 marks]

   (c) Calculate the thermodynamic efficiency of a heat engine operating between the temperatures 600K and 400K [2 marks]

3. (a) The specific volumes of water and ice at 0^0C and at atmospheric pressure are 1.0001 cm^3g^{-1} and 1.0907 cm^3g^{-1}, respectively, and the latent heat of fusion of ice is $334Jg^{-1}$. Calculate the melting point of ice under a pressure of 10^7Pa.

[$\frac{\Delta T}{\Delta P} = \frac{T_f \Delta V}{\Delta H_f}$] [4 marks]

(b) The vapour pressure of benzene is 0.153×10^5Pa at 303K and 0.520×10^5Pa at 333K. Calculate the mean latent heat of evaporation of benzene over this temperature range.

[$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$] [4 marks]

(c) What are the two assumption used to transform the Clausius equation to the Clausius-Clapeyron equation [2 marks]

4. The saturated vapour pressures of benzene and toluene are both given by the equation,

$$\log P^* = \frac{-0.05223A}{T} + B$$

where T is the thermodynamic temperature and A and B have the following values:

	A	B
Benzene	32 295K	9.7795
Toluene	39 198K	10.4549

Assuming that mixtures benzene and toluene form ideal solutions calculate the molar percentage of benzene in
(a) a mixture which boils at 97^0C under an external pressure of 1 atm, and
(b) the initial condensate formed on distilling this mixture

[10 marks]

SECTION B

*Answer **ONLY THREE** questions. Each question carries 20 marks*

5. (a) With the aid of appropriate diagrams, state the Kelvin's and Clausius' statements of the Second Law of thermodynamics. [4 marks]

(b) What is the thermodynamic definition of entropy?
Use the Carnot cycle to prove that entropy is a state function. [8 marks]

(c) Entropy can be used as a criterion for spontaneous change and equilibrium. By first writing the Clausius inequality state how it is used [4 marks]

(d) Use an example on spontaneous cooling to illustrate the Clausius inequality [4 marks]

6. (a) (i) State the Third law of Thermodynamics [3 marks]

(ii) Calculate the entropy of liquid mercury at its melting point, 234.1K. The standard entropy of mercury (at 298.2K) is $77.4 JK^{-1}mol^{-1}$ and its heat capacity is $2.87 JK^{-1}mol^{-1}$. (Assume the heat capacity of mercury is constant in the temperature range 234.1K to 298.2K) [4 marks]

(b) Use the Trouton's rule to predict the molar enthalpy of vaporization of Carbon tetrachloride given that it boils at 76.1^0C [3 marks]

(c) Calculate the standard enthalpy change at 473K for the reaction,

$CO + \frac{1}{2} O_2 \rightarrow CO_2$.

The standard heats of formation of CO and CO_2 at 298K are -110.5 $kJmol^{-1}$ and -393.5 $kJmol^{-1}$, respectively. The heat capacities of CO, CO_2 and O_2 over the temperature range 298K to 473K are given by the equations:

$$c_p (CO) = (26.53 + 7.70 \times 10^{-3}T - 1.17 \times 10^{-6} T^2)\ JK^{-1}mol^{-1}$$

$$c_p (CO_2) = (26.78 + 42.26 \times 10^{-3}T - 14.23 \times 10^{-6} T^2) JK^{-1}mol^{-1}$$

$$c_p (O_2) = (25.52 + 13.60 \times 10^{-3}T - 4.27 \times 10^{-6} T^2) JK^{-1}mol^{-1}$$

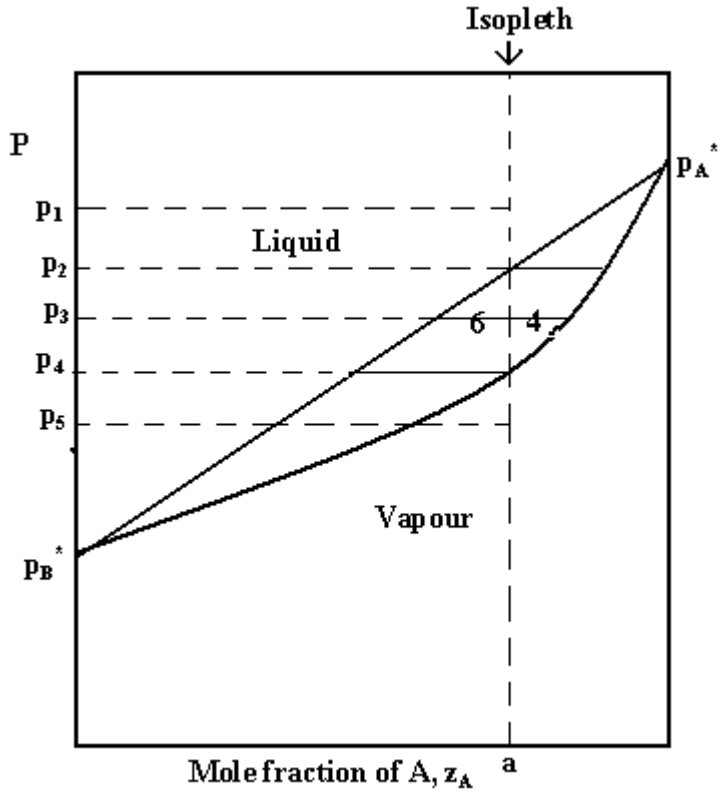
where T is the thermodynamic temperature [10 marks]

7. (a) What is a Colligative property [2 marks]

(b) State the four colligative property [8 marks]

(c) The figure below is a pressure – composition diagram a mixture of two volatile liquids A and B. Copy the diagram and use it as you describe in detail what will be observed when the pressure of a system of composition $z_A = a$ is reduced from P_1 to P_5 along the Isopleth, At each pressure indicated give the number of phases, the equilibrium composition of the phases (use notation of your choice), and the relative amounts of the phases

[10 marks]



8. (a) Pure benzene freezes at 5.40^0C and a solution of 0.223g of phenyl acetic acid ($C_6H_5CH_2COOH$) in 4.4g of benzene freezes at 4.47^0C. The latent heat of fusion of benzene is 9.89kJmol^{-1}. Calculate the apparent relative molecular mass of phenyl acetic acid and constant on the result

$$[\ \Delta T = \frac{RT_f^2}{\Delta H_f}.\frac{n_B}{n_A + n_B}\ ]$$ [6 marks]

(b) The osmotic pressure (against pure water) of a solution containing 1g of sucrose and *y* g of glucose in 1 kg of water at 25^0C is 0.3 x 10^5 Nm^{-2}. Calculate *y*, assuming ideal behaviour

[4 marks]

(c) Antimony (m.p 630^0C) and lead (m.p 326^0C) form one eutectic mixture at 246^0C which is 81 mole percent lead, but do not form any solid solutions. Draw a temperature – composition diagram, assuming that the liquidus lines are linear, and label each region indicating which phases are in equilibrium under the conditions that the regions represent. For a mixture containing 50 mole percent lead determine, (a) the temperature at which solid first crystallizes out, (b) the nature and proportion of solid in the mixture at 300^0C [10 marks]

End of question Paper!!!