NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF APPLIED CHEMISTRY
BACHELOR OF SCIENCE HONOURS DEGREE
SUPPLEMENTARY EXAMINATIONS – AUGUST 2011
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 $0.153x10^5$Pa at 303K and $0.520x10^5$Pa 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*

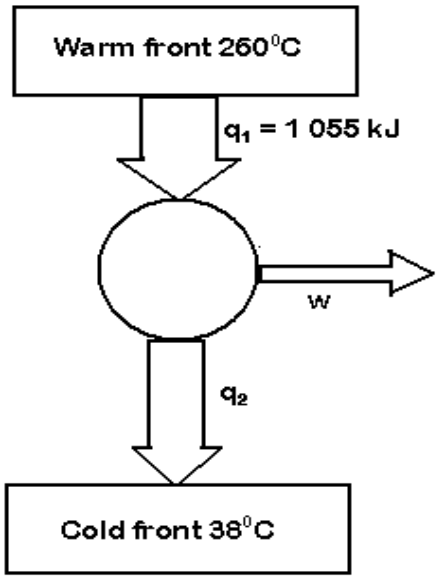
5. (a) With the aid of appropriate diagrams, state the Kelvin's and Clausius' statements of the Second Law of thermodynamics. [4 marks]

(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) If you have a heat pump of Carnot as shown below, operating between two fronts of temperatures 260^{o}C and 38^{o}C respectively, and receiving from the warm from 1 055kJ. Determine:
   (i) the entropy change of the warm front.
   (ii) the entropy change of the cold front.
   (iii) the total entropy change of the process. [12 marks]



(b) The heat capacity of gaseous argon at constant volume is 12.48 J $K^{-1}mol^{-1}$, and at constant pressure is 20.8$JK^{-1}mol^{-1.}$
   (i) Estimate the entropy change when one mole of the gas is expanded with simultaneous heating from 1dm^3 at 300K to 10dm^3 at 1200K. [4 marks]
   (ii) Estimate the entropy change when one mole of the gas is heated from 300K to 1200K at 1 atm pressure [4 marks]

7. (a) At 353K the vapour pressures of two liquids A and B which are completely miscible and form an ideal solution are 757 and 66 mmHg, respectively. For an equimolar mixture [x_A= x_B = 0.5] calculate the total vapour pressure and the mole fraction of A in the vapour phases. Assume that the mixture follows Raoult's Law. [4 marks]

(b) Calculate the estimate mole fractions (x_A, x_B, y_A, y_B) in the respective phases at equilibrium when the total pressure of the solution is 600mmHg [8 marks]

(c) Calculate the estimate mole fractions (x_A, $x_{B,}$, y_B) in the respective phases, and also the total vapour pressure when y_A (the mole fraction of A in the vapour phase at equilibrium with the liquid mixture) is fixed at 0.85. [8 marks]

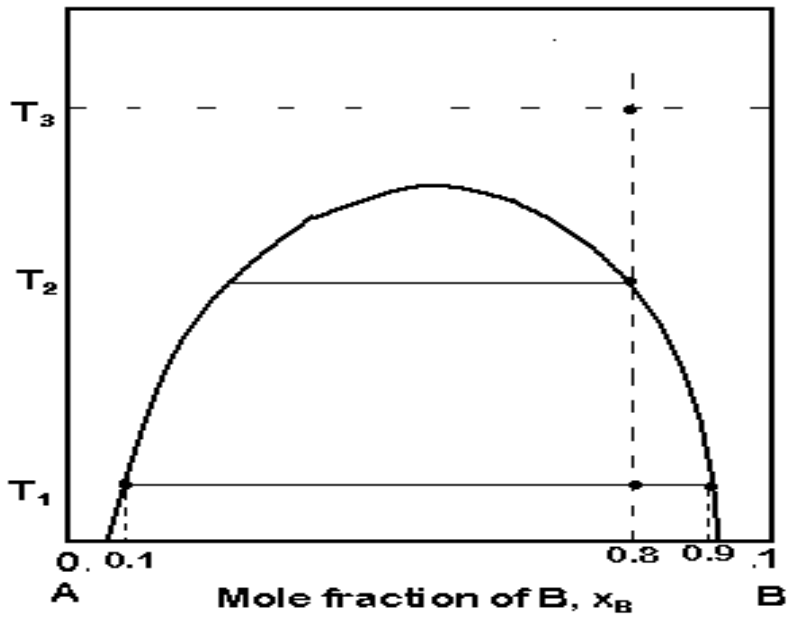
8. (a) State Kelvin's and Clausius' statements of the Second Law of Thermodynamics [4 marks]

(b) With the use of a diagram for illustrations, State and outline the four steps of a Carnot heat engine. Show all the results of work and heat and derive the carnot efficiency in terms of temperature [16 marks]

9. (a) What is an Azeotrope? [2 marks]

(b) State the two classes of azeotropic mixtures. Give an explanation for each class [6 marks]

(c) The figure below shows the phase diagram for two partially miscible liquids, A and B (which can be taken to be hexane (A) and nitrobenzene (B)). Copy the diagram and use it as you describe what will be observed when the mole fraction of B is increase from $x_B = 0$ to $x_B = 0.8$ at constant temperature T_1, and when the mixture at $x_B = 0.8$ is heated from temperature T_1 to T_3, at each significant stage giving the number, composition, and relative amounts of the phases present. [12 marks]



End of question Paper!!!