NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF APPLIED CHEMISTRY
BACHELOR OF SCIENCE HONOURS DEGREE
END OF FIRST SEMESTER EXAMINATIONS – JANUARY 2011
PHYSICAL CHEMISTRY I – SCH 2104
TIME: 3 HOURS

MATERIAL
Graph papers.

INSTRUCTIONS TO CANDIDATES

Answer ALL questions in section A and 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. (a) The standard enthalpy of reaction for the combustion of methane at 298K is:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta H^0_{rxn} = -894 kJmol^{-1}.$$

Calculate the standard enthalpy of formation of methane at the same temperature given the following information:

$\Delta H_f^0\{H_2O, (l)\} = -286.9 kJmol^{-1}$, $\Delta H_f^0\{CO_2, (g)\} = -393.5 kJmol^{-1}$, $\Delta H_f^0\{C_2H_6, (g)\} = -84.7 kJmol^{-1}$. [5 marks]

(b) The enthalpy change when water freezes at 273K is – 6 $kJmol^{-1}$. c_p for liquid water is 73.5 $JK^{-1}mol^{-1}$ and for ice 37.6$JK^{-1}mol^{-1}$. Calculate the enthalpy change when water freezes at 253K. [5 marks]

2. Give a detailed account of the first erroneous James Joule experiment to measure π_T. Your answer must include a schematic diagram of the apparatus used, the procedure, the observation, the thermodynamic implications of the observation, and the conclusion.

[10 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 assumptions used to transform the Clausius equation to the Clausius-Clapeyron equation? [2 marks]

4. 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]

SECTION B

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

5. (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]

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 $77.4JK^{-1}mol^{-1}$ and its heat capacity is $2.87JK^{-1}mol^{-1}$. (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,

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

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*** main colligative properties in the study of solutions. [8 marks]

(c) The rate of sedimentation of a recently isolated protein was monitored at 20^0C and with a rotor speed (ν) of 50 000 r.p.m.
The boundary receded as follows:

Time (t/s)	0	300	600	900	1200	1500	1800
Radius (x/cm)	6.127	6.153	6.179	6.206	6.232	6.258	6.284

Calculate the sedimentation constant and the molar mass of the protein on the basis that its partial specific volume is 0.728 cm^3g^{-1} and its diffusion coefficient is 7.62×10^{-7} cm^2s^{-1} at 20^0C, the density of the solution then being 0.9981 gcm^{-3}.

[Use $\omega = 2\pi\nu$, where ν is in cycles/second] [10 marks]

End of question Paper!!!