

**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.

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

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

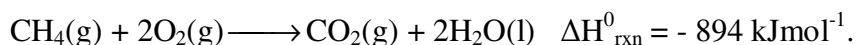
$$1 \text{ atm} = 760 \text{ torr} = 760 \text{ mmHg} = 101\,325 \text{ Pa} .$$

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

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**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:



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

$$\begin{aligned} \Delta H_f^0\{\text{H}_2\text{O}, (\text{l})\} &= -286.9 \text{ kJmol}^{-1}, \quad \Delta H_f^0\{\text{CO}_2, (\text{g})\} = - 393.5 \text{ kJmol}^{-1}, \\ \Delta H_f^0\{\text{C}_2\text{H}_6, (\text{g})\} &= - 84.7 \text{ kJmol}^{-1}. \end{aligned} \quad [5 \text{ marks}]$$

- (b)     The enthalpy change when water freezes at 273K is  $- 6 \text{ kJmol}^{-1}$ .  $c_p$  for liquid water is  $73.5 \text{ JK}^{-1}\text{mol}^{-1}$  and for ice  $37.6 \text{ JK}^{-1}\text{mol}^{-1}$ . 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  $\pi_T$ . 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°C and at atmospheric pressure are 1.0001 cm<sup>3</sup>g<sup>-1</sup> and 1.0907 cm<sup>3</sup>g<sup>-1</sup> respectively, and the latent heat of fusion of ice is 334Jg<sup>-1</sup>. Calculate the melting point of ice under a pressure of 10<sup>7</sup>Pa.

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

- (b) The vapour pressure of benzene is 0.153x10<sup>5</sup>Pa at 303K and 0.520x10<sup>5</sup>Pa at 333K. Calculate the mean latent heat of evaporation of benzene over this temperature range.

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

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

4. Antimony (m.p 630°C) and lead (m.p 326°C) form one eutectic mixture at 246°C 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°C.

[10 marks]

## **SECTION B**

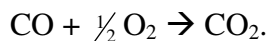
*Answer ALL THREE questions. Each question carries 20 marks*

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<sup>-1</sup>mol<sup>-1</sup> and its heat capacity is 2.87JK<sup>-1</sup>mol<sup>-1</sup>. (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<sup>0</sup>C. [3 marks]

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



The standard heats of formation of CO and CO<sub>2</sub> at 298K are -110.5 kJmol<sup>-1</sup> and -393.5 kJmol<sup>-1</sup> respectively. The heat capacities of CO, CO<sub>2</sub> and O<sub>2</sub> over the temperature range 298K to 473K are given by the equations:

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

$$c_p(\text{CO}_2) = (26.78 + 42.26 \times 10^{-3}T - 14.23 \times 10^{-6}T^2) \text{JK}^{-1}\text{mol}^{-1}$$

$$c_p(\text{O}_2) = (25.52 + 13.60 \times 10^{-3}T - 4.27 \times 10^{-6}T^2) \text{JK}^{-1}\text{mol}^{-1}$$

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<sup>0</sup>C and with a rotor speed ( $\nu$ ) 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<sup>3</sup>g<sup>-1</sup> and its diffusion coefficient is 7.62x10<sup>-7</sup> cm<sup>2</sup>s<sup>-1</sup> at 20<sup>0</sup>C, the density of the solution then being 0.9981 gcm<sup>-3</sup>.

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

***End of question Paper!!!***