

## NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY DEPARTMENT OF APPLIED CHEMISTRY BACHELOR OF SCIENCE HONOURS DEGREE END OF FIRST SEMESTER EXAMINATIONS - APRIL/MAY 2009 PHYSICAL CHEMISTRY I - SCH 2104 TIME: 3 HOURS

## INSTRUCTIONS TO CANDIDATES

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

$$
\begin{aligned}
& \mathrm{R}=8.314 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}=0.08206 \mathrm{dm}^{3} \mathrm{~atm} \mathrm{~K} \\
& \mathrm{~F} \mathrm{~mol}^{-1} \\
& \mathrm{~F}=\mathrm{eN}_{\mathrm{A}}=9.6500 \times 10^{4} \mathrm{C} \mathrm{~mol}^{-1} ; \mathrm{N}_{\mathrm{A}}=6.022 \times 10^{23} \mathrm{~mol}^{-1} \\
& 1 \mathrm{~atm}=760 \text { torr }=760 \mathrm{mmHg}=101325 \mathrm{~Pa} . \\
& \ln \mathrm{x}=2.3026 \log _{10} \mathrm{X}
\end{aligned}
$$

## 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 298 K is

$$
\mathrm{CH}_{4}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \Delta \mathrm{H}_{\mathrm{rxn}}^{0}=-8940 \mathrm{kJmol}^{-1} .
$$

Calculate the standard enthalpy of formation of methane at the same temperature given the following information:
$\Delta \mathrm{H}_{\mathrm{f}}^{0}\left\{\mathrm{H}_{2} \mathrm{O},(\mathrm{l})\right\}=-286.9 \mathrm{kJmol}^{-1}, \Delta \mathrm{H}_{\mathrm{f}}^{0}\left\{\mathrm{CO}_{2},(\mathrm{~g})\right\}=-393.5 \mathrm{kJmol}^{-1}$,
$\Delta \mathrm{H}_{\mathrm{f}}{ }^{0}\left\{\mathrm{C}_{2} \mathrm{H}_{6},(\mathrm{~g})\right\}=-84.7 \mathrm{kJmol}^{-1}$. [5 marks]
(b) The enthalpy change when water freezes at 273 K is $-6 \mathrm{kJmol}^{-1} . \mathrm{c}_{\mathrm{p}}$ for liquid water is $73.5 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}$ and for ice $37.6 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}$. Calculate the enthalpy change when water freezes at 253 K .
2. (a) Name the four simple types of processes used in thermodynamic studies and for each type state the variable held constant.
(b) No actual process is reversible but reversibility is a limit which actual processes can be made to approach by choice of experimental conditions. What is a reversible process?
3. (a) Write the Phase rule and define the three terms in it.
(b) What is the difference between a component and a constituent? Use a simple example to show this difference.
4. (a) Using a graph, show through the relationship of chemical potential and temperature how the freezing and boiling temperatures of a liquid change when a non-volatile solute is added to it. The solid dissolves neither in the solid solvent nor the vapour [4 marks]
(b) State the other two colligative properties (apart from the two referred to in the first part of the question) and for one of them name the analytical method in which it is utilized.
[3 marks]
(c) Estimate the concentration of a carbohydrate in a dilute standard solution that has an osmotic pressure of 2.47 atm at 303 K , given that the solution behaves ideally.
[3 marks]

## SECTION B

Answer ONLY THREE questions. Each question carries 20 marks
5. (a) 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.
[17 marks]
(b) What was wrong with wrong with Joules apparatus?
[ 2 marks]
(c) What is do we mean by Joule- Thompson effect?
6. (a) If you have a heat pump of Carnot as shown below, operating between two fronts of temperatures $260^{\circ} \mathrm{C}$ and $38^{\circ} \mathrm{C}$ respectively, and receiving from the warm from 1055 kJ . 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 $12.48 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$, and at constant pressure is $20.8 \mathrm{JK}^{-1} \mathrm{~mol}^{-1 .}$.
(i) Estimate the entropy change when one mole of the gas is expanded with simultaneous heating from $1 \mathrm{dm}^{3}$ at 300 K to $10 \mathrm{dm}^{3}$ at 1200 K .
[4 marks]
(ii) Estimate the entropy change when one mole of the gas is heated from 300 K to 1200 K at 1 atm pressure
[4 marks]
7. (a) At 353 K 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 $\left[\mathrm{x}_{\mathrm{A}}=\mathrm{x}_{\mathrm{B}}=0.5\right.$ ] calculate the total vapour pressure and the mole fraction of A in the vapour phases. Assume that the mixture follows Raoult's Law.
(b) Calculate the estimate mole fractions $\left(\mathrm{x}_{\mathrm{A}}, \mathrm{x}_{\mathrm{B}}, \mathrm{y}_{\mathrm{A}}, \mathrm{y}_{\mathrm{B}}\right)$ in the respective phases at equilibrium when the total pressure of the solution is 600 mmHg [8 marks]
(c) Calculate the estimate mole fractions $\left(\mathrm{x}_{\mathrm{A}}, \mathrm{x}_{\mathrm{B}}, \mathrm{y}_{\mathrm{B}}\right)$ 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 $\mathrm{T}_{1}$, and when the mixture at $\mathrm{x}_{\mathrm{B}}=0.8$ 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!!!

