

## NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY DEPARTMENT OF APPLIED CHEMISTRY <br> BACHELOR OF SCIENCE HONOURS DEGREE SUPPLEMENTARY EXAMINATIONS - AUGUST 2010 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.

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

## SECTION A

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

1. (a) Write the Phase rule and define the three terms in it.
[7 marks]
(b) What is the difference between a component and a constituent? Use a simple example to show this difference.
[3 marks]
2. (a) Name the four simple types of processes used in thermodynamic studies and for each type state the variable held constant.
[8 marks]
(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?
[2 marks]
3. (a) The standard enthalpy of reaction for the combustion of methane at 298 K is

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\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}) \quad \Delta \mathrm{H}_{\mathrm{rxn}}^{0}=-894 \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 .
[5 marks]
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
(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.
(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) Estimate the melting point of ice under a pressure of 350 atm . The densities of ice and water at 273.15 K and 1 atm pressure are $\rho_{\mathrm{l}}=0.9917 \mathrm{gcm}^{-3}$ and $\rho_{\mathrm{w}}=0.9998$ $\mathrm{gcm}^{-3}$, respectively. The latent heat of fusion, $\Delta \mathrm{H}_{\text {fus }} / \mathrm{m}=333.5 \mathrm{~J} \cdot \mathrm{~g}^{-1}$. If we assume that $\Delta \mathrm{H}_{\text {fus }}$ and the densities are practically constant over the pressure range, with

$$
\begin{aligned}
& V=m / \rho \\
& \frac{\Delta P}{\Delta T}=\frac{\Delta H_{t}}{T \Delta V_{t}}
\end{aligned}
$$

(b)

At 273.15 K the enthalpy change of fusion of water is $6 \mathrm{kJmol}^{-1}$ and the corresponding volume change $-1.6 \times 10^{-6} \mathrm{~m}^{3} \mathrm{~mol}^{-1}$. Estimate the temperate at which ice will melt at 1000 atm pressure (use $1 \mathrm{~atm}=10^{5} \mathrm{pa}$ )
[5 marks]
(c) Derive the Clausius-Clapeyron equation from the Clausius equation $\frac{d P}{d T}=\frac{\Delta H_{t}}{T \Delta V_{t}}$.

Use the liquid-vapour boundary and mention the assumptions.
[10 mark]
6. (a) At 298 K the vapour pressures of two liquids A and B which are completely miscible and form an ideal solution are 0.20 atm and 0.35 atm , respectively. For a mixture $\left[\mathrm{x}_{\mathrm{A}}=0.4\right.$ ] calculate the total vapour pressure and the mole fraction of A in the vapour phases.
(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 0.30 atm

> [8 marks]
(b) Calculate the estimate mole fractions ( $\mathrm{x}_{\mathrm{A}}, \mathrm{x}_{\mathrm{B}}, \mathrm{y}_{\mathrm{B}}$ ) in the respective phases, and also the total vapour pressure when $\mathrm{y}_{\mathrm{A}}$ (the mole fraction of A in the vapour phase at equilibrium with the liquid mixture) is fixed at 0.85 .
7. (a) 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 $\mathrm{z}_{\mathrm{A}}=a$ is reduced from $\mathrm{P}_{1}$ to $\mathrm{P}_{5}$ 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

(b) Write the Phase rule and define each of the three variable terms in it
[8 marks]
(c) What is a constituent in a system?
[2 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]

## End of question Paper!!!

