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DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR

Session: Spring 2016-17 Exam: Midterm Exam No. of Students: 700

Subject No.: CY11001 Subject Name: Chemistry Time: 2hrs. Full Marks:40

PLEASE READ THE INSTRUCTIONS GIVEN BELOW BEFORE ANSWERING THE PAPER
(This question paper contains 4 pages, including this page)

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1. This Question Paper has TWO parts (i.e., PART-A and PART-B). Make sure that each of you have received both, PART-A and PART-B of the Question Paper.
2. Answer ALLquestions.
3. ALL QUESTIONS OF PART- A and PART-B SHOULD BE ANSWERED SERIALLY.
4. ANSWERS OF PART-A MUST BE WRITTEN TOGETHER.
5. LEAVE A PAGE BLANK IN THE ANSWER SCRIPT IN BETWEEN THE ANSWERS OF PART-A and THE ANSWERS OF PART-B.
6. ANSWER SCRIPTS SUBMITTED WITHOUT FOLLOWING THE INSTRUCTION No.3, No. 4 and No. 5 MAY NOT BE EVALUATED

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1. All symbols used in the question paper have their usual meaning
2. Mention the sign convention used.
3. Clearly state whether you are using reduction or, oxidation potential in electrochemistry.
4. No credit will be given without workout being shown wherever necessary.

[Supplied Data: $k = 1.38 \times 10^{-23}$ J K^{-1}; $R = 8.314$ J $K^{-1}mol^{-1}$; 1 bar = 1×10^5 Pa; 1 Faraday = 96,500 C mol^{-1}; 1 atm = 760 Torr]

PART – A

Q1. Write the correct option/ options (A/B/C/D) in the Answer Script **....(1 × 10 = 10)**

(i) Which of the following statements is correct for an ideal gas

(A) $\left(\frac{\partial H}{\partial V}\right)_T = 0; \left(\frac{\partial U}{\partial V}\right)_T \neq 0;$ **(B)** $\left(\frac{\partial H}{\partial V}\right)_T = 0; \left(\frac{\partial U}{\partial V}\right)_T = 0;$

(C) $\left(\frac{\partial H}{\partial V}\right)_T \neq 0; \left(\frac{\partial U}{\partial V}\right)_T = 0;$ **(D)** $\left(\frac{\partial H}{\partial V}\right)_T \neq 0; \left(\frac{\partial U}{\partial V}\right)_T \neq 0$

(ii) Activity of a '***m***' molal solution of $FeCl_3$ electrolyte is

(A) $9(\gamma_\pm\ m)^4$; **(B)** $(\gamma_\pm\ m)^4$; **(C)** $(\gamma_\pm\ m^4)$; **(D)** $27(\gamma_\pm\ m)^4$

(iii) Which of the following expressions is correct for a closed system involved in expansion-compression work?

(A) $dH = TdS + VdP$; **(B)** $dH = TdS - PdV$; **(C)** $dH = TdS - VdP$; **(D)** $dH = TdS + PdV$

(iv) Which of the following relations is true for the mixing of two ideal gases?

(A) $(\partial\ \Delta_{mix}G/\partial P)_T = 0$; **(B)** $\Delta_{mix}G = 0$; **(C)** $\Delta_{mix}A = 0$; **(D)** $(\partial\Delta_{mix}G/\partial T)_P = 0$

(v) At the triple-point in the phase diagram of a pure substance the vapour pressures are related as

(A) $p_{solid} = p_{liq} \neq p_{vap}$; **(B)** $p_{solid} \neq p_{liq} = p_{vap}$; **(C)** $p_{solid} \neq p_{liq} \neq p_{vap}$; **(D)** $p_{solid} = p_{liq} = p_{vap}$

(vi) Which of the following expression does not represent the chemical potential (μ_i) of a component i in a homogeneous mixture:

(A) $\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,nj\neq i}$; **(B)** $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,nj\neq i}$; **(C)** $\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,nj\neq i}$; **(D)** $\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,nj\neq i}$

(vii) What will be the thermal efficiency of a Carnot heat engine that receives 500 kJ of heat per cycle from a high temperature heat reservoir at 627 °C and rejects heat to a low temperature heat reservoir at 27 °C?

(A) 0.333; **(B)** 0.6; **(C)** 0.4; **(D)** 0.6667

(viii) In what proportion of mole fraction (x) should hexane and heptane be mixed to obtain the highest value of entropy of mixing (ΔS_{mix})?

(A) $x_{heaxane} = 0.4, x_{heptane} = 0.6$; **(B)** $x_{heaxane} = 0.6, x_{heptane} = 0.4$;

(C) $x_{heaxane} = 0.5, x_{heptane} = 0.5$; **(D)** $x_{heaxane} = 0.25, x_{heptane} = 0.75$

(ix) To experience cooling under Joule-Thomson expansion, the gas must have the initial temperature set at

(A) Above the upper inversion temperature; **(B)** Between the upper and lower inversion temperatures;

(C) Below the lower inversion temperature; **(D)** Any temperature

(x) The lowering of the chemical potential of a species in an ideal mixture (vapor or liquid) is a consequence of

(A) Enthalpy of mixing; **(B)** Change in volume on mixing;

(C) Entropy of mixing; **(D)** Le Châtelier's principle

PART – B

ANSWERS OF Part B should begin on new Page in the Answer Script

Q2. (a) Two moles of an ideal gas occupying volume of 44.8 litres at 273 K and 1 atm pressure have been expanded reversibly and isothermally. Calculate the final volume of the gas if the heat absorbed during the process is 3 kJ.

[3]

(b) Two moles of an ideal monatomic gas initially at 1 atm and 300 K are put through the following cycle consisting of three steps, all of which are reversible.

Step-I: Isothermal compression to 2 atm.
Step-II: Isobaric temperature change to 400 K
Step-III: Return to the initial state following the path P = a + bT, where a, b are constants.

(i) Sketch the cycle on a P-T diagram.
(ii) Calculate the entropy change (**ΔS**) associated with each of the three steps of the cycle (given: molar heat capacity of the gas, C_P=2.5R).

[2 + 3 =5]

(c) The vapour pressure of solid ammonia in torr is found to obey the equation:

$$\ln P = -\frac{4124.4}{T} - 1.82 \ln T + 34.48$$

Use the Clausius-Clapeyron equation to determine the molar enthalpy of sublimation of ammonia at 170 K.

[2]

Q3. (a) For a real gas with molar volume and molar enthalpy of V_m and H_m, respectively, show: $\left(\frac{\partial H_m}{\partial P}\right)_T = V_m(1 - \alpha T)$, where α is the isobaric expansion coefficient.

[3]

(b) For a van der Waals gas, the compressibility factor Z is given by

$Z = 1 + \frac{(b - a/RT)P}{RT}$, where a and b are constants.

If $C_{P,m}$ and μ_{JT} are the molar heat capacity and Joule-Thomson coefficient of the gas, respectively, then show that $C_{P,m} \times \mu_{JT} = \left(\frac{RT^2}{P}\right)\left(\frac{\partial Z}{\partial T}\right)_P$.

[3]

(c) Two moles of supercooled water at – 10 °C is converted into ice at – 10 °C and 1 atm. State whether the process is reversible or irreversible. Calculate the value of ΔS_{sys}, assuming $C_{P,m}$ values of water and ice in the temperature range −10 °C to 0 °C are 75 $JK^{-1}mol^{-1}$ and 38 $JK^{-1}mol^{-1}$, respectively. $\Delta_{fus}H = 6006\ J\,mol^{-1}$.

[4]

Q4. (a) In a fuel cell, methane gas undergoes the same reaction as the combustion process to produce CO_2 (g) and $H_2O(l)$ and generate electricity. Calculate the maximum electrical work that can be obtained from 1 mole of methane gas at 25 °C, if $\Delta_f G^\circ$ values of $CH_4(g)$, $CO_2(g)$, and $H_2O(l)$ at 25 °C are given to be −50.8, −394.5, and −237.3 kJ mol^{-1}, respectively.

[2]

(b) For the reaction: $\mathbf{U}(s) + \frac{3}{2}\mathbf{H_2}(g) \leftrightarrow \mathbf{UH_3}(s)$; the equilibrium pressure of H_2 (g) over solid uranium and uranium hydride (UH_3) at 500 K is 1.04 Torr. Calculate the standard Gibbs energy of formation of UH_3 (s) at 500 K. Assume that the H_2 gas behaves like an ideal gas at this low pressure.

[4]

(c) Determine the standard electrode potential of a cell for which the total reaction is as follows:

$$\boldsymbol{Co^{3+}(aq.) + 3Cl^{-}(aq.) + 3Ag(s) \rightarrow 3AgCl(s) + Co(s)}$$

[Given: $E^\circ_{(AgCl/Ag,\,Cl^-)} = +0.22$ V; $E^\circ_{(Co^{3+}/\,Co^{2+})} = +1.81$ V; $E^\circ_{(Co^{2+}/\,Co)} = -0.28$ V]

[4]

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21/2/17 S. Bandyopadhyay 21/2/17

Signatures of the Paper Setters