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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

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

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## 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  $\text{FeCl}_3$  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)  $(\partial \Delta_{\text{mix}}G/\partial P)_T = 0$ ; (B)  $\Delta_{\text{mix}}G = 0$ ; (C)  $\Delta_{\text{mix}}A = 0$ ; (D)  $(\partial \Delta_{\text{mix}}G/\partial T)_P = 0$
- (v) At the triple-point in the phase diagram of a pure substance the vapour pressures are related as  
 (A)  $p_{\text{solid}} = p_{\text{liq}} \neq p_{\text{vap}}$ ; (B)  $p_{\text{solid}} \neq p_{\text{liq}} = p_{\text{vap}}$ ; (C)  $p_{\text{solid}} \neq p_{\text{liq}} \neq p_{\text{vap}}$ ; (D)  $p_{\text{solid}} = p_{\text{liq}} = p_{\text{vap}}$
- (vi) Which of the following expression does not represent the chemical potential ( $\mu_i$ ) of a component  $i$  in a homogeneous mixture:  
 (A)  $\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_{j \neq i}}$ ; (B)  $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j \neq i}}$ ; (C)  $\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j \neq i}}$ ; (D)  $\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j \neq i}}$
- (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  $627^\circ\text{C}$  and rejects heat to a low temperature heat reservoir at  $27^\circ\text{C}$ ?  
 (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 ( $\Delta S_{\text{mix}}$ )?  
 (A)  $x_{\text{hexane}} = 0.4$ ,  $x_{\text{heptane}} = 0.6$ ; (B)  $x_{\text{hexane}} = 0.6$ ,  $x_{\text{heptane}} = 0.4$ ;  
 (C)  $x_{\text{hexane}} = 0.5$ ,  $x_{\text{heptane}} = 0.5$ ; (D)  $x_{\text{hexane}} = 0.25$ ,  $x_{\text{heptane}} = 0.75$
- (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 ( $\Delta S$ ) 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  $\alpha$  is the isobaric expansion coefficient.

[3]

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

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

If  $C_{P,m}$  and  $\mu_{JT}$  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  $-10^\circ\text{C}$  is converted into ice at  $-10^\circ\text{C}$  and 1 atm. State whether the process is reversible or irreversible. Calculate the value of  $\Delta S_{\text{sys}}$ , assuming  $C_{P,m}$  values of water and ice in the temperature range  $-10^\circ\text{C}$  to  $0^\circ\text{C}$  are  $75 \text{ JK}^{-1}\text{mol}^{-1}$  and  $38 \text{ JK}^{-1}\text{mol}^{-1}$ , respectively.  $\Delta_{\text{fus}} H = 6006 \text{ J mol}^{-1}$ .

[4]



**Q4. (a)** In a fuel cell, methane gas undergoes the same reaction as the combustion process to produce  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(l)$  and generate electricity. Calculate the maximum electrical work that can be obtained from 1 mole of methane gas at  $25^\circ\text{C}$ , if  $\Delta_f G^\circ$  values of  $\text{CH}_4(g)$ ,  $\text{CO}_2(g)$ , and  $\text{H}_2\text{O}(l)$  at  $25^\circ\text{C}$  are given to be  $-50.8$ ,  $-394.5$ , and  $-237.3 \text{ kJ mol}^{-1}$ , respectively.

[2]

**(b)** For the reaction:  $\text{U}(s) + \frac{3}{2}\text{H}_2(g) \leftrightarrow \text{UH}_3(s)$ ; the equilibrium pressure of  $\text{H}_2(g)$  over solid uranium and uranium hydride ( $\text{UH}_3$ ) at  $500 \text{ K}$  is  $1.04 \text{ Torr}$ . Calculate the standard Gibbs energy of formation of  $\text{UH}_3(s)$  at  $500 \text{ K}$ . Assume that the  $\text{H}_2$  gas behaves like an ideal gas at this low pressure.

[4]

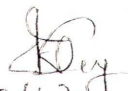
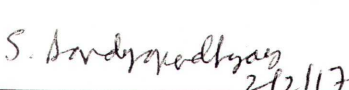
**(c)** Determine the standard electrode potential of a cell for which the total reaction is as follows:



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

[4]

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Signatures of the Paper Setters