

## DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR

Session: Autumn 2016-17

Exam: Midterm Exam

No. of Students: 670

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)

- 1. This Question Paper has <u>TWO</u> 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. <u>ALL QUESTIONS OF PART- A and PART-B SHOULD BE ANSWERED SERIALLY.</u>
- 4. ANSWERS OF PART-A MUST BE WRITTEN TOGETHER.
- 5. <u>LEAVE A PAGE BLANK IN THE ANSWER SCRIPT IN BETWEEN</u> 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

- 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 atm = 760 Torr]

## Q1. Write the correct option (a/b/c/d) in the Answer Script

 $....(1 \times 10 = 10)$ 

(i) Chemical potential  $\mu_i$  of a component i in a homogeneous mixture can be defined as:

(a) 
$$\mu_i = \left(\frac{\partial G}{\partial n}\right)_{T,P,n_i}$$
; (b)  $\mu_i = \left(\frac{\partial H}{\partial n}\right)_{T,P,n_i}$ ; (c)  $\mu_i = \left(\frac{\partial A}{\partial n}\right)_{T,P,n_i}$ ; (d)  $\mu_i = \left(\frac{\partial U}{\partial n}\right)_{T,P,n_i}$ 

(ii) What will be the activity for 'm' molal solution of an AB<sub>2</sub> electrolyte?

- (a)  $(\gamma_{\pm} m^3)$ ;
- (b)  $(\gamma_{\pm} m)^3$ ; (c)  $4(\gamma_{\pm} m)^3$ ;
- (d)  $(\gamma_{\pm} m_{+}^{3})$

(iii) Which of the following statements is always true for a liquid mixture of two components A and B in equilibrium with a mixture of their vapours?

(a)  $\mu_A(1) = \mu_B(1)$  and  $\mu_A(g) = \mu_B(g)$ ;

**(b)**  $\mu_A(1) = \mu_A(g) = \mu_B(1) = \mu_B(g)$ 

(c)  $\mu_A(1) = \mu_A(g)$  and  $\mu_B(1) = \mu_B(g)$ ;

(d)  $\mu_{A}(1) \neq \mu_{A}(g) \neq \mu_{B}(1) \neq \mu_{B}(g)$ 

(iv) Which of the following is a reversible process?

(a) Melting of ice at 0°C and 1 atm.;

- **(b)** Melting of ice at 25°C and 1 atm.;
- (c) Evaporation of water at 25°C and 1 atm.
- (d) Freezing of water at  $-10^{\circ}$ C and 1 atm.

(v) At inversion temperature of a gas, the value of Joule-Thomson coefficient  $(\mu_{JT})$  will be:

- (a)  $\mu_{JT} = 0$ ;
- (b)  $\mu_{JT} > 0$ ;
- (c)  $\mu_{JT} < 0$ ;

(d)  $\mu_{JT} \approx \infty$ 

(vi) What will happen to the chemical potential of O<sub>2</sub> when 1.0 mole of O<sub>2</sub> gas is added to a container that already contained 1.0 mole of O<sub>2</sub> gas?

- (a)  $\mu$  (O<sub>2</sub>) will increase;
- (b)  $\mu$  (O<sub>2</sub>) will decrease;
- (c)  $\mu$  (O<sub>2</sub>) will remain unchanged

(vii) Which one is the correct condition for spontaneous reaction in an electrochemical cell

(a)  $\Delta G_{T.P} < 0$ ,  $E_{cell} > 0$ ;

**(b)**  $\Delta G_{T,P} > 0$ ,  $E_{cell} < 0$ 

(c)  $\Delta G_{T,V} < 0$ ,  $E_{cell} < 0$ ;

(d)  $\Delta G_{T.P} = 0$ ,  $E_{cell} = 0$ 

(viii) What fraction of the total quantity of heat  $(q_h)$  taken from the source that is at temperature  $T_h$  can be converted into work in a reversible cyclic process? ( $\Delta T$  is the temperature difference between the source and the sink)

- (a)  $\Delta T \times T_h$ ;
- **(b)**  $\Delta T / T_h$ ;
- (c) zero;
- (d)  $T_h / \Delta T$ .

(ix) Which one of the following fundamental equations is/ are applicable for any open system?

(a) dG = VdP - SdT;

- **(b)**  $dG = VdP SdT + \Sigma \mu_i dn_i$ ;
- (c)  $dG = PdV + TdS + \Sigma \mu_i dn_i$ ;
- (d)  $dG = PdV SdT + \Sigma \mu_i dn_i$

(x)  $\Delta S > 0$  is a condition for spontaneity for which of the following systems:

- (a) Closed system;
- **(b)** Open system:
- (c) Isolated system;
- (d) All systems

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

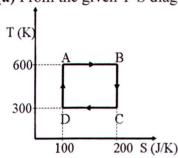
Q2. (a) Show that:

$$U = G - P \left( \frac{\partial G}{\partial P} \right)_{T} - T \left( \frac{\partial G}{\partial T} \right)_{P}$$

- **(b)** Prove the following relation:  $\left(\frac{\partial H}{\partial V}\right)_T = -V^2 \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial (T/V)}{\partial V}\right)_P$
- (c) Two moles of an ideal gas at 45 °C are compressed adiabatically and reversibly from 75.0 litres to 20.0 litres. Calculate q, w,  $\Delta U$ , and  $\Delta H$  for the process. [Given:  $C_V = 2.5 R$  for the gas].

$$\dots[2+3+5=10]$$

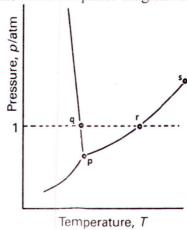
Q3. (a) From the given T-S diagram (ABCD) of a reversible Carnot engine shown below, find the



- (i) Net work delivered by the engine in each cycle
- (ii) Heat taken from the source in each cycle
- (iii)  $\Delta S_{sink}$  in each cycle

$$\dots[1+1+2=4]$$

- (b) Calculate the following for a liquid whose vapour pressure (in **Torr**) between 15 °C and 35 °C fits the expression:  $\log(p_i) = 8.750 \frac{1625}{T}$ .
- (i) The enthalpy of vaporization (in kJ mol<sup>-1</sup>) of the liquid; (ii) The normal boiling point (in K) ....[2+2=4]
- (c) Label the points (p, q, r, s) shown in the phase diagram of a one component system



....
$$\left[\frac{1}{2} \times 4 = 2\right]$$

- Q4. (a) For the following reaction at 25  $^{\circ}$ C and 1 atm, the Gibbs energy change is + 2.90 kJ mol<sup>-1</sup>. C (s, graphite)  $\rightarrow$  C (s, diamond)

  Densities of graphite and diamond at 25  $^{\circ}$ C are 2.25 and 3.51 g cm<sup>-3</sup> respectively.
  - (i) Will increase in pressure favour the conversion of graphite to diamond? Justify your answer.
  - (ii) If your answer in part (i) is yes, then calculate the maximum pressure necessary to make this reaction spontaneous at 25  $^{\circ}$ C. ....[2 + 2 = 4]
  - (b) For the galvanic cell:  $Pt \mid H_2(g, P_{H2}) \mid HCl(aq, a_{H+}) \mid O_2(g, P_{O2}) \mid Pt$
  - (i) Write the half-cell as well as complete cell reactions.
  - (ii) If the standard state Gibbs energy of formation ( $\Delta_f G^o$ ) of  $H_2O(I)$  is -237.13 kJ mol<sup>-1</sup>. Calculate the EMF of the cell in the standard state.
  - (iii) Calculate the equilibrium constant of the overall cell reaction at 298 K. ....[2 + 2 + 2 = 6]

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