

Indian Institute of Technology Kharagpur
Department of Chemistry

R

Spring 2011-2012 Mid-semester Exam Time: 2 Hrs No. of Students: 700
Subject No: CY11001 Full Marks: 30 Subject Name: Chemistry (1st Year)

Instructions:

- (a) Attempt ALL the questions.
- (b) All parts of a question MUST be answered together.
- (c) Numerical results MUST be reported in SI units.
- (d) Explicitly mention the sign convention used.
- (e) Clearly state whether you are using oxidation or reduction potentials in electrochemistry.
- (f) The question paper contains TWO pages.

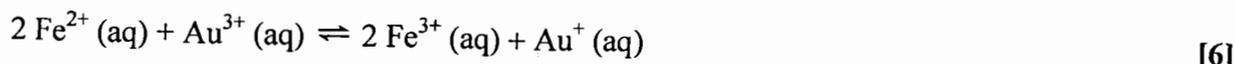
[Supplied Data: $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; 1 Faraday = 96,500 C mol⁻¹]

- Q1.** (a) For air at temperatures near 25°C and pressure in the range of 0 bar to 50 bar, the Joule–Thomson coefficient (μ_{JT}) can be considered as 0.2 K bar⁻¹. Estimate the final temperature of air if 58 g of air at 25°C and 50 bar undergoes Joule–Thomson throttling to a final pressure of 1 bar. [2]
- (b) Calculate ΔG for isothermal compression of 30.0 g of water from 1.0 bar to 100.0 bar at 25°C. Consider V is independent of P in this range and density of water in this range is 0.997 g/cm³. [2]
- (c) For Mercury, given that α (expansion coefficient) = $1.82 \times 10^{-4} \text{ K}^{-1}$ and κ (isothermal compressibility) = $3.87 \times 10^{-5} \text{ atm}^{-1}$ at 20 °C; find out $\left(\frac{\partial \delta}{\partial V}\right)_T$ in SI unit. [2]
- (d) In the gas-phase reaction $A + 2B \rightarrow 3C + 2D$, it was found that when 2.00 mol A, 1.00 mol B, and 3.00 mol D were mixed and allowed to come to equilibrium at 25°C, the resulting mixture contained 0.79 mol C at a total pressure of 1.00 bar. Calculate (i) K_x , (ii) K_p and (iii) ΔG_r^0 . The symbols carry usual meaning. Assume the gases are ideal.

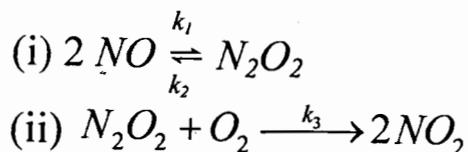
[2+1+1]

[P.T.O.]

- Q2. (a) Standard reduction potentials (E^0) for the electrodes Au^+ / Au , $\text{Au}^{3+} / \text{Au}$, and $\text{Fe}^{3+} / \text{Fe}^{2+}$ are 1.69 V, 1.40 V and 0.77 V, respectively. Calculate the standard cell potential (E^0_{cell}) and the equilibrium constant for the following reaction at 298 K



- (b) For the reaction, $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$, the following mechanism has been suggested.



Show that

$$\frac{d}{dt} [\text{NO}_2] = \frac{A[\text{NO}]^2[\text{O}_2]}{1 + B[\text{O}_2]}, \quad \text{where } A = 2 k_1 k_3 / k_2 \text{ and } B = k_3 / k_2. \quad [4]$$

- Q3. (a) The vapour pressure of solid ammonia in torr is found to obey the equation:

$$\ln P = -4124.4 / T - 1.81630 \ln T + 34.4834, \quad (\text{T is in Kelvin})$$

Use the Clausius-Clapeyron equation to determine the molar enthalpy of sublimation of ammonia at 170 K. [3]

- (b) 2 moles of an ideal gas occupying 44.8 litres volume 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]

- (c) 2 moles of an ideal monatomic gas initially at 1 atm and 300 K are put through the following cycle consisting of 3 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 by 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 **Step-III** of the cycle (given: molar heat capacity of the gas, $C_p = 2.5R$).

[2+2=4]