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Rajarata University of Sri Lanka
Kandy

**RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES**

**B.Sc. (General) Degree in Applied Sciences
First Year – Semester II Examination – November / December 2016**

CHE 1302 – PHYSICAL CHEMISTRY I

Time: Three (3) hours

Answer any **Five (5)** questions.

The use of a non-programmable calculator is permitted.

Atmospheric Pressure = 10^5 N m^{-2}

Avogadro Number (N_A) = $6.023 \times 10^{23} \text{ mol}^{-1}$

Planck Constant (h) = $6.63 \times 10^{-34} \text{ J s}$

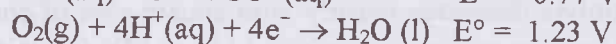
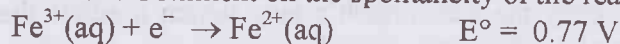
Universal Gas Constant (R) = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Velocity of Light (c) = $3 \times 10^8 \text{ m s}^{-1}$

(1) (a) Define “Standard redox potential” of an electrode.

(05 Marks)

(b) Given the two half reactions for the oxidation of iron (II) by oxygen in acidic solution. Write the net chemical reaction and calculate the Gibbs free energy change and equilibrium constant. Comment on the spontaneity of the reaction.

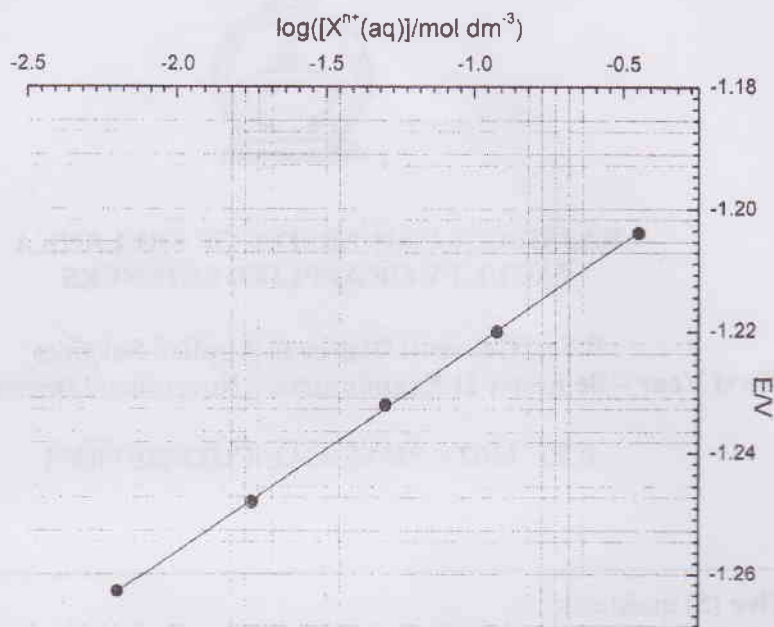


(40 Marks)

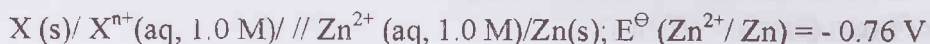
(c) An electrochemical cell contains Pb electrodes in equal volume solutions of Pb^{2+} of 0.432 M and Pb^{2+} 0.00015 M concentration. Write the spontaneous half-reaction at each electrode and the overall cell process. What will be the cell potential when the cell is first connected to a potentiometer? What will happen to the cell potential as current is allowed to flow?

(20 Marks)

(d) Figure below summarizes the result of an experiment, in which the redox potential of a metal, X, was measured at different concentrations of its ions, $\text{X}^{n+}(\text{aq})$ at the temperature 298 K.



- Calculate the charge on the metal ion.
- What is the standard potential of X?
- What is the EMF of the cell shown below?



(35 Marks)

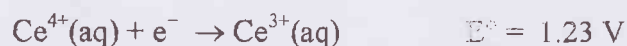
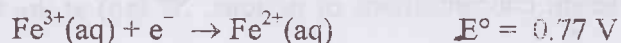
- (2) (a) The resistances of two different aqueous solutions of the salt MX, were measured at 25 °C in a conductivity cell having a cell constant equal to 18.72 m⁻¹. When the concentration of MX solution was 0.00050 mol dm⁻³ the cell resistance was 2622 ohms. When the concentration was changed to 0.0050 mol dm⁻³ the resistance was found to be 270.4 ohms. Assume that solutions of MX obey the Kohlrausch's law, which predicts that the molar conductivity for a strong electrolyte decreases linearly with square root of concentration. Use the above data to find the limiting molar conductivity (Λ^∞) of MX (in units of mS m² mol⁻¹).

(30 Marks)

- (b) Sketch a conductometric titration curve for the titration of 0.1 mol dm⁻³ 50.0 mL of HCl acid with 0.1 mol dm⁻³ 60.0 mL NaOH in a burette. Explain the variation of the shape of the curve.

(20 Marks)

- (c) 25 mL of a Fe²⁺ analyte is titrated with 0.02 mol dm⁻³ Ce⁴⁺ titrant. Both are in 0.05 mol dm⁻³ H₂SO₄. The standard reduction potentials are:



- What is the potential half-way to the equivalence point?

(ii) What is the potential at the equivalence point?

* Derive the equation(s) that you may use in the calculation parts (i) and (ii).

(35 Marks)

(d) Sketch the titration curves for the above titration for (i) direct E vs. V; (ii) 1st derivative, $\Delta E/\Delta V$ vs. V and (iii) 2nd derivative $\Delta^2 E/\Delta V^2$ vs. V on the same diagram.

(15 Marks)

(3) (a) For each property listed below, indicate whether it is an intensive thermodynamic property, extensive thermodynamic property or a path property.

(i) Volume (ii) Heat (iii) Molar Thermal Capacity (iv) Helmholtz free energy

(20 Marks)

(b) State clearly under what conditions, if any, and to what type of systems the following expressions can be applied.

(i) $PV^\gamma = \text{const.}$ (ii) $dG = VdP - SdT$ (iii) $dG > 0$ (iv) $dU = nC_{V,m}dT$

(20 Marks)

(c) Write down (no proof is required) the Maxwell relationships which can be derived from the following fundamental thermodynamic equations.

(i) $dA = -SdT - PdV$ (ii) $dG = VdP - SdT$

(15 Marks)

(d) Starting from the fundamental equation for internal energy, derive the following thermodynamic equation of state for pressure:

$$P = T \left(\frac{\partial P}{\partial T} \right)_V - \left(\frac{\partial U}{\partial V} \right)_T$$

(25 Marks)

(e) Starting from the above equation in 3(d), prove that for an ideal gas $(\partial U/\partial V)_T = 0$.

(20 Marks)

(4) (a) What do you understand by the compressibility factor (Z) of a gas? Briefly explain the dependence of Z on pressure for real gases.

(20 Marks)

(b) Write down the virial equation of state for a real gas defining symbols used. What is the physical basis of the second virial coefficient – B(T)?

(20 Marks)

(c) State the alternative expression of the second law of thermodynamics in relation to an isolated system (or the universe).

(15 Marks)

(d) Briefly explain the physical basis of entropy.

(20 Marks)

(e) In a certain process, 1.5 kJ of heat is absorbed by the system at 400 K. If the entropy change for the process equals 4.2 J K^{-1} , indicate whether the process is reversible-equilibrium, spontaneous or non-spontaneous. Give reason(s) for your answer.

(25 Marks)

- (5) (a) What is meant by the mean molar translational kinetic energy of an ideal gas at 25 °C? Calculate the mean translational kinetic energy for one molecule of the same gas at the same temperature.

(20 Marks)

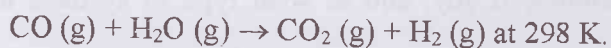
- (b) With the use of equations, define the terms “root mean square velocity”, “most probable velocity” and “mean velocity” of a collection of gas molecules.

(20 Marks)

- (c) Draw a graph for the Maxwell-Boltzmann distribution of velocities for a diatomic ideal gas, and indicate the three types of velocities mentioned in part 5(b) above. Give reason(s) as to why the mean velocity is not equal to the most probable velocity.

(20 Marks)

- (d) Calculate the standard free energy change for the following reaction



	$\Delta H^\circ_{f, 298} / \text{kJ mol}^{-1}$	$S^\circ_{298} / \text{J K}^{-1} \text{mol}^{-1}$
CO (g)	-110.5	197.9
CO ₂ (g)	-393.5	213.6
H ₂ O (g)	-241.8	188.7
H ₂ (g)		130.6

(30 Marks)

- (e) State whether the reaction considered in part (d) above, would occur spontaneously or not under the given conditions.

(10 Marks)

- (6) (a) Write down the basic assumptions of the kinetic molecular theory of gases.

(20 Marks)

- (b). Calculate the number of vibrational degrees of freedom for a polyatomic molecule containing N number of atoms.

(20 Marks)

- (c) Write down the van der Waals equation of state defining symbols used. Briefly explain how this equation accounts for the behaviour of real gases. Estimate the pressure exerted by 0.1 mol of C₂H₆ occupying 22.4 L at 273 K, assuming it behaves as a van der Waals gas ($a = 5.49 \text{ L}^2 \text{ atm mol}^{-2}$; $b = 6.38 \text{ L mol}^{-1}$ and $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$).

(45 Marks)

- (d) Briefly explain the free energy and bound energy parts of a system.

(15 Marks)

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