

**Birla Institute of Technology and Science, Pilani, Rajasthan 333031**  
**Mid Term Examination 1<sup>st</sup> Semester, 2023-2024**

**CHEM F327: ELECTROCHEM FUNDA & APPL**  
**Time: 90 mins.**

**(OPEN Book)**

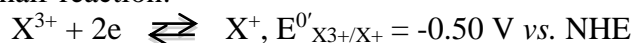
**Max. Marks: 60**  
**Date: 10.10.2023**

**Instructions to the students:**

1. There are **THREE** questions in all. Attempt all the questions.
2. Start answering each question on a fresh page. **Answer all parts of a question together.**
3. Write brief answers to the point with proper justifications.
4. Do not exchange your calculator, book etc.
5. All the standard reduction potential values are given in a separate sheet.

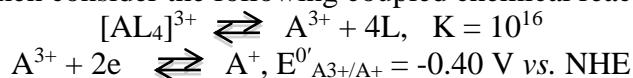
**Q. 1. (a)** Consider the reduction of a species O at a cathode:  $O + ne \rightleftharpoons R$ . Where,  $n$  represent number of electron and aqueous solution of 0.1 M  $K_2SO_4$  was used as an electrolyte. Three-electrode cell systems, where, platinum cathode, platinum anode, and SCE reference electrode were used in the electrochemical reaction. The solution was stirred continuously. **(I)** Derive the current-potential relationship under the following conditions for a system where R is initially present at a concentration  $C_R^*$  and  $C_O^* = 0$ . Consider both O and R soluble. **[5]**

**(b)** Consider the Nernstian half-reaction:



The  $i$ - $E$  curve for a solution at 25 °C containing 2.0 mM  $X^{3+}$  and 1.0 mM  $X^+$  in excess electrolyte shows  $i_{l,c} = 4.0 \mu\text{A}$  and  $i_{l,a} = -2.4 \mu\text{A}$ . **(I)** Calculate the value of  $E_{1/2}$  (V vs. NHE)? **(II)** Sketch the expected “**log plot of  $i$ - $E$  curve**” for the system. **[3+2]**

**(c)** An example of a coupled chemical reaction is given below. If a homogeneous process, fast enough to be considered always in thermodynamic equilibrium (a reversible process), is coupled to a Nernstian electron-transfer reaction, then consider the following coupled chemical reactions.



Where,  $[AL_4]^{3+}$  = metal complex,  $A^{3+}$  = free metal ion, L = free, neutral ligand. For a solution at 25 °C containing only 2.0 mM  $A^{3+}$  and 0.1 M L in excess inert electrolyte. Bulk concentration of  $[AL_4]^{3+}$  is 2.0 mM and  $m_{A^{3+}}/m_{[AL_4]^{3+}} = 1.20$ . Assume,  $m_O$  is the same for  $A^{3+}$  and  $[AL_4]^{3+}$ . **(I)** Derive the current-potential relationship under these conditions. **(II)** What is the value of  $E_{1/2}$  (V vs. NHE)? **[4+2]**

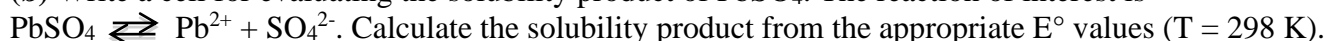
**(d)** A solution of volume 50 cm<sup>3</sup> contains  $2.5 \times 10^{-2}$  M  $Fe^{3+}$  and  $1 \times 10^{-2}$  M  $Sn^{4+}$  in 0.5 M HCl. This solution is examined by voltammetry at a Pt disk electrode of area 0.2 cm<sup>2</sup>. At the rotation rate employed, both  $Fe^{3+}$  and  $Sn^{4+}$  have mass-transfer coefficients,  $m$ , of  $10^{-3}$  cm/s. The limiting current for the reduction of  $Fe^{3+}$  under these conditions is 0.0482  $\mu\text{A}$ . A current-potential scan is taken from +1.5 to -0.50 V vs. NHE. **(I)** Sketch the  $i$ - $E$  curve that would be obtained within the potential window. Mention all the possible electrochemical reactions in the  $i$ - $E$  curve. Assume that no changes in the bulk concentrations of  $Fe^{3+}$  and  $Sn^{4+}$  occur during this scan and that all electrode reactions are Nernstian. **[4]**

**Q. 2. (a)** Consider the following electrochemical cell. Assume that all systems are aqueous.

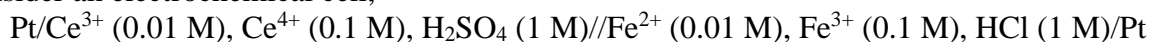


Write all the cathode and anode reactions and their emf for the above cell. Are the reactions spontaneous? Justify your answer in one line.

**(b)** Write a cell for evaluating the solubility product of  $PbSO_4$ . The reaction of interest is



(c) Consider an electrochemical cell,



Calculate  $K_{\text{rxn}}$  for the overall reaction involved in the cell. Calculate the potential of each electrode vs. NHE.

(d) For an electrochemical cell,  $\text{Cu}/\text{Au}/\text{Fe}^{2+}, \text{Fe}^{3+}, \text{H}^+//\text{Cl}^-/\text{AgCl}/\text{Ag}/\text{Cu}'$  would the cell potential be independent of the identity of Au as long as Au is chemically inert? Use electrochemical potentials to prove your point.

(e) Identify the type of junction potentials for the following situation and show the movement of ions in the junction potential.  $\text{KNO}_3 (0.01 \text{ M})/\text{NaOH} (0.1 \text{ M})$  [5+4+4+4+3]

**Q. 3. (a)** The production and disappearance of H atom are given below.



Derive the experimentally observed Tafel equation from the above two reactions ( $V = a + b \log I$ , where,  $V =$  overpotential,  $a$  and  $b$  are constants,  $I =$  current). Show all the steps clearly. [4]

(b) The following data and the plot (figure 1) were obtained for the reduction of species R to  $\text{R}^-$  (one step one electron process) in a stirred solution at a  $0.1 \text{ cm}^2$  electrode; the solution contained  $0.01 \text{ M R}$  and  $0.01 \text{ M R}^-$ . All approximations are applicable in the reduction reaction.

$\eta$ (mV)	-100	-120	-150	-500	-600
$i$ ( $\mu\text{A}$ )	45.9	62.6	100	965	965

Calculate the following parameters. (I)  $k^0$ , (II)  $\alpha$ , (III)  $R_{\text{ct}}$ , and (IV)  $m_0$  [3+2+2+3]

(c) Justify, “when  $iR_s$  (voltage drop) is small one should prefer to use two-electrode system than three-electrode system to determine  $i-E$  curve”. [3]

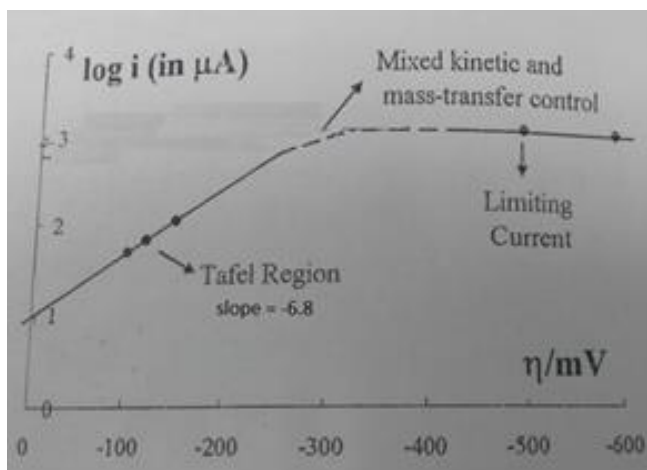


figure 1

(d) In case of one-step, one-electron processes show that  $j_0 \propto k^0$  (where,  $j_0 =$  exchange current density &  $k^0 =$  standard rate constant), assuming the reaction is at equilibrium at null current. [3]

\*\*\*\*\*END\*\*\*\*\*