Model Answer Dr / M.M. El-Rabiei

Fayoum university Faculty of science Chemistry department



Electro-Analytical chemistry Ex. B.Sc.Geo.Bot.&Bio/ Chem.students 1st. semester



Part .1. Electro- Analytical part.

- 1- the answer must be include the definition of
 - a) Migration transport under potential gradient dE / dx
 - b) Diffusion Transport under concentration gradient. dC / dx
 - c) Convection Transport under density gradient. dw/ dx

$$2- Cd == Cd ++ +2e -$$

 $E_{befor} = E^{o} + 0.0591 / 2 Log [Cd^{++}]$

 $= 0.34 + 0.0591/2 \log 10^{-3}$ = 0.34 - 0.088 = 0.251 V

$$Cd^{++} + Y^{4-} = CdY^{2-}$$

$$K_{f} = [CdY^{2-}] / [Cd^{++}][Y^{-4}]$$

$$[Cd^{++}] = [CdY2-]/K_f [Y^{-4}]$$

 $E_{after} = 0.34 + 0.0591 / 2 \text{ Log } [\text{CdY}^{2-}] / \text{K}_{f} . [\text{Y}^{4-}] \\= 0.34 + 0.0591 / 2 \text{ Log } [0.001] / 10^{8} . [0.1 - 0.001]$

3- Ag / AgCl / Cl⁻ / H⁺ inter/ lass membrane / H⁺_{ext}/ Cl⁻ / Hg₂Cl₂ / Hg

Reference electrode is $Ag / AgCl / Cl^{-1}$ $E_{ref.} = E^{0} - 0.0591 \log [Cl^{-1}]$ $E_{cell} = (E_{ref 1} + E_{m1}) - (E_{ref 2} + E_{m2})$ If $E_{ref 1} = E_{ref 2}$

$$E_{cell} = E_{m1} - E_{m2}$$

$$E_{m1} = K_1 + 0.0591 \log a_1$$

$$E_{m2} = K_2 + 0.0591 \log a_2$$

$$E_{cell} = K_1 + 0.0591 \log a_1 - K_2 - 0.0591 \log a_2$$

$$E_{cell} = K + 0.0591 \log a_1$$

$$= K - 0.0591 \text{ pH}$$

Where $K = K_1 - K_2 - 0.0591 \log a_2$

If the two reference electrode are $Ag / AgCl / Cl^{-}$ and the SEC.

$$K = K_1 - K_2 + E_{SEC} - E_{Ag/AgCl} - 0.0591 \log a_2$$

4- The Answer should be includes.

$$RH_{2x} + xM^{2+} = RM_x + 2xH^+$$

 Ca^{++} ISE the ion exchanger is aliphatic di ester of phosphoric acid dissolved in a polar solvent. The chain lengths about 8 – 16 carbon atoms.

The internal aqueous solution contain fixed concentration of CaCl₂

The reference electrode is Ag / AgCl / Cl⁻

The equilibrium at each interface represented as

$$[(RO)_2 POO]_2 Ca = 2 (RO)_2 POO^- + Ca^{++}$$

The potential of the electrode is given by the equation

 $E = K + 0.0591/2 \log Ca^{++}$

The CaISE described is reported to be independent of pH range between 5.5-11

5- Dropping mercury electrode (DME)

Composition: mercury resevoir – capillary attached. Drops fall from the resevoir at constant rate usually between 5-30 drop / min. life time 5 - 30 sec / drop. Voltage scaning rate 50-200 mV / min.

Change in potential of DME can be neglected compared to life time.

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The current measured obtained under practically potentiostatic condition.

i.e. **D.***C polarography*.

Reference electrode S.C.E or Ag / AgCl / Cl⁻ or Hg/ Hg₂SO₄ / SO₄⁻⁻ or Pt.

Polarogram. I vs. E curve.

Supporting electrolyte KCl.

Polarographic wave result from the reaction

$$Cd^{2+} + 2e^{-} + 2Hg = Cd(Hg)$$

Sharpe increase in current at \ge -2 V

Residual current i_r / migration current i_m / diffusion current i_d / limiting current i_L

$$i_L = i_d + i_m + i_r$$