Chapter 2: Electrochemistry

Exercises — Exercises

Q1 Arrange the following metals in the order in which they displace each other from the solution of their salts. Al, Cu, Fe, Mg and Zn.

SOLUTION

A metal that is higher in the electrochemical (activity) series has a more negative standard reduction potential and can displace metals below it from their salt solutions.

Standard reduction potentials (from Table 2.1):

$Mg^{2+}/Mg = -2.36$ V

$Al^{3+}/Al = -1.66$ V

$Zn^{2+}/Zn = -0.76$ V

$Fe^{2+}/Fe = -0.44$ V

$Cu^{2+}/Cu = +0.34$ V

A more negative E° means the metal is a stronger reducing agent and will displace metals with less negative (or positive) E° from their salt solutions.

Therefore, in decreasing order of ability to displace: Mg displaces Al, Zn, Fe, Cu; Al displaces Zn, Fe, Cu; Zn displaces Fe, Cu; Fe displaces Cu; Cu displaces none of the above.

Answer: Mg > Al > Zn > Fe > Cu (each metal displaces all metals listed to its right from their salt solutions)

Q2 Given the standard electrode potentials, $K^+/K = -2.93$ V, $Ag^+/Ag = 0.80$ V, $Hg^{2+}/Hg = 0.79$ V, $Mg^{2+}/Mg = -2.37$ V, $Cr^{3+}/Cr = -0.74$ V. Arrange these metals in their increasing order of reducing power.

SOLUTION

Reducing power of a metal increases as its standard reduction potential (E°) becomes more negative — a lower (more negative) E° means the metal is oxidised more readily, i.e., it is a stronger reducing agent.

Given E° values:

$K^+/K = -2.93$ V

$Mg^{2+}/Mg = -2.37$ V

$Cr^{3+}/Cr = -0.74$ V

Hg^{2+}/Hg = +0.79 V

Ag^{+}/Ag = +0.80 V

Arranging in increasing order of reducing power means arranging in increasing order of negative E° (or decreasing E° value):

Ag (E° = 0.80 V) < Hg (E° = 0.79 V) < Cr (E° = -0.74 V) < Mg (E° = -2.37 V) < K (E° = -2.93 V)

Answer: Increasing order of reducing power: Ag < Hg < Cr < Mg < K

Q3 Depict the galvanic cell in which the reaction Zn(s) + 2Ag+(aq) -> Zn_2+(aq) + 2Ag(s) takes place. Further show: (i) Which of the electrode is negatively charged? (ii) The carriers of the current in the cell. (iii) Individual reaction at each electrode.

SOLUTION

The overall reaction is: Zn(s) + 2Ag+(aq) -> Zn_2+(aq) + 2Ag(s)

Zn is oxidised (loses electrons) — it is the anode.

Ag^{+} is reduced (gains electrons) — Ag is the cathode.

Cell representation:

Zn(s)	Zn_2+(aq)		Ag+(aq)	Ag(s)
(Anode on left, cathode on right;		= salt bridge)		

(i) The zinc electrode (anode) is negatively charged. Electrons are produced at the anode by oxidation of Zn and flow through the external circuit towards the cathode (Ag electrode, which is positively charged).

(ii) Carriers of current:

- In the external circuit (metallic wire): electrons flow from Zn anode to Ag cathode.
- In the solution and salt bridge: ions carry the current. Cations (e.g., K^{+} from the salt bridge) migrate towards the cathode compartment; anions (e.g., NO_3^{-} or Cl^{-} from the salt bridge) migrate towards the anode compartment.

(iii) Electrode reactions:

Anode (oxidation): Zn(s) -> Zn_2+(aq) + 2e-

Cathode (reduction): 2Ag+(aq) + 2e- -> 2Ag(s)

Answer: Cell: Zn(s)|Zn_2+(aq)||Ag+(aq)|Ag(s). (i) Zn electrode (anode) is negatively charged. (ii) Electrons in external wire (Zn to Ag); ions in solution. (iii) Anode: Zn -> Zn^{2+} + 2e-; Cathode: $2Ag^{+}$ + 2e- -> 2Ag.

Q4 Calculate the standard cell potentials of galvanic cell in which the following reactions take place: (i) 2Cr(s) + 3Cd_2+(aq) -> 2Cr_3+(aq) + 3Cd (ii) Fe_2+(aq) + Ag+(aq) -> Fe_3+(aq) + Ag(s). Calculate the DrG° and equilibrium constant of the reactions.

SOLUTION

Formula: E°(cell) = E°(cathode) - E°(anode) [both as standard reduction potentials]

DrG° = -nFE°(cell); log Kc = nE°(cell) / 0.0592 V (at 298 K)

(i) 2Cr(s) + 3Cd_2+(aq) -> 2Cr_3+(aq) + 3Cd(s)

Cathode (reduction): Cd^{2+} + 2e- -> Cd, E° = -0.40 V

Anode (oxidation): Cr -> Cr^{3+} + 3e-, E°(Cr^{3+}/Cr) = -0.74 V

E°(cell) = E°(cathode) - E°(anode) = (-0.40) - (-0.74) = +0.34 V

Number of electrons transferred n = 6 (balance: 2Cr lose 6e-, $3Cd^{2+}$ gain 6e-).

DrG° = -nFE°(cell) = -(6)(96500 C mol-1)(0.34 V)

= -196860 J mol-1 = -196.86 kJ mol-1

log Kc = nE°(cell) / 0.0592 = 6 × 0.34 / 0.0592 = 34.46

Kc = 10^{34}.46 = 2.92 × 10^{34}

(ii) Fe_2+(aq) + Ag+(aq) -> Fe_3+(aq) + Ag(s)

Cathode (reduction): Ag^{+} + e- -> Ag, E° = +0.80 V

Anode (oxidation): Fe^{2+} -> Fe^{3+} + e-, E°(Fe^{3+}/Fe^{2+}) = +0.77 V

E°(cell) = 0.80 - 0.77 = +0.03 V

n = 1

DrG° = -(1)(96500)(0.03) = -2895 J mol-1 = -2.90 kJ mol-1

log Kc = 1 × 0.03 / 0.0592 = 0.507

Kc = 10^{0}.507 = 3.21

Answer: (i) E°(cell) = 0.34 V; DrG° = -196.86 kJ mol-1; Kc = 2.92 × 10^{34}. (ii) E°(cell) = 0.03 V; DrG° = -2.90 kJ mol-1; Kc = 3.21

Q5 Write the Nernst equation and emf of the following cells at 298 K: (i) $Mg(s)|Mg_2+(0.001M)||Cu_2+(0.0001\ M)|Cu(s)$ (ii) $Fe(s)|Fe_2+(0.001M)||H+(1M)|H_2(g)(1bar)|Pt(s)$ (iii) $Sn(s)|Sn_2+(0.050\ M)||H+(0.020\ M)|H_2(g)(1\ bar)|Pt(s)$ (iv) $Pt(s)|Br-(0.010\ M)|Br_2(l)||H+(0.030\ M)|H_2(g)(1\ bar)|Pt(s)$.

SOLUTION

Nernst equation: $E(cell) = E°(cell) - (0.0592/n) \times \log Q$ at 298 K

(i) $Mg(s)|Mg_2+(0.001M)||Cu_2+(0.0001M)|Cu(s)$

Cell reaction: $Mg(s) + Cu_2+(aq) \rightarrow Mg_2+(aq) + Cu(s)$; n = 2

$E°(cell) = E°(Cu^{2+}/Cu) - E°(Mg^{2+}/Mg) = 0.34 - (-2.36) = 2.70$ V

Nernst equation: $E = 2.70 - (0.0592/2) \times \log([Mg^{2+}]/[Cu^{2+}])$

$Q = [Mg^{2+}]/[Cu^{2+}] = 0.001/0.0001 = 10$

$E = 2.70 - (0.0296)(\log 10) = 2.70 - 0.0296 \times 1 = 2.67$ V

(ii) $Fe(s)|Fe_2+(0.001M)||H+(1M)|H_2(g)(1bar)|Pt(s)$

Cell reaction: $Fe(s) + 2H+(aq) \rightarrow Fe_2+(aq) + H_2(g)$; n = 2

$E°(cell) = E°(H^+/H_2) - E°(Fe^{2+}/Fe) = 0.00 - (-0.44) = 0.44$ V

$Q = [Fe^{2+}] \times p(H_2) / [H^+]^2 = (0.001 \times 1) / (1)^2 = 0.001$

$E = 0.44 - (0.0592/2) \times \log(0.001) = 0.44 - 0.0296 \times (-3) = 0.44 + 0.0888 = 0.53$ V

(iii) $Sn(s)|Sn_2+(0.050M)||H+(0.020M)|H_2(g)(1bar)|Pt(s)$

Cell reaction: $Sn(s) + 2H+(aq) \rightarrow Sn_2+(aq) + H_2(g)$; n = 2

$E°(cell) = 0.00 - (-0.14) = 0.14$ V

$Q = [Sn^{2+}] \times p(H_2) / [H^+]^2 = (0.050 \times 1) / (0.020)^2 = 0.050/0.0004 = 125$

$E = 0.14 - (0.0592/2) \times \log(125) = 0.14 - 0.0296 \times 2.097 = 0.14 - 0.0621 = 0.0779$ V

(iv) $Pt(s)|Br-(0.010M)|Br_2(l)||H+(0.030M)|H_2(g)(1bar)|Pt(s)$

Left electrode (anode): $2Br-(aq) \rightarrow Br_2(l) + 2e-$

Right electrode (cathode): $2H+(aq) + 2e- \rightarrow H_2(g)$

Cell reaction: $2Br-(aq) + 2H+(aq) \rightarrow Br_2(l) + H_2(g)$; n = 2

$E°(cell) = E°(H^+/H_2) - E°(Br_2/Br^-) = 0.00 - 1.09 = -1.09$ V

$Q = [Br_2] \times p(H_2) / ([Br^-]^2 \times [H^+]^2) = (1)(1) / ((0.010)^2 \times (0.030)^2)$

$Q = 1 / (1\times10^{-4} \times 9\times10^{-4}) = 1 / (9\times10^{-8}) = 1.11\times10^{7}$

$\log Q = \log(1.11\times10^{7}) = 7.046$

$E = -1.09 - (0.0592/2) \times 7.046 = -1.09 - 0.2086 = -1.30$ V

Answer: (i) E = 2.67 V; (ii) E = 0.53 V; (iii) E = 0.0779 V; (iv) E = -1.30 V

Q6 In the button cells widely used in watches and other devices the following reaction takes place: $Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn_2+(aq) + 2Ag(s) + 2OH-(aq)$. Determine $DrG°$ and $E°$ for the reaction.

SOLUTION

Identify the half-reactions:

Anode (oxidation): $Zn(s) \rightarrow Zn_2+(aq) + 2e-$

$E°(Zn^{2+}/Zn) = -0.76$ V

Cathode (reduction): $Ag_2O(s) + H_2O(l) + 2e- \rightarrow 2Ag(s) + 2OH-(aq)$

$E°(Ag_2O/Ag) = +0.344$ V

n = 2 electrons transferred.

$E°(cell) = E°(cathode) - E°(anode)$

$= 0.344 - (-0.76) = 1.104$ V

$DrG° = -nFE°(cell)$

$= -(2)(96500\ C\ mol-1)(1.104\ V)$

$= -213072\ J\ mol-1$

$= -213.07\ kJ\ mol-1$

Answer: $E°(cell) = 1.104$ V; $DrG° = -213.07\ kJ\ mol-1$

Q7 Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

SOLUTION

Conductivity (k):

Conductivity of an electrolytic solution is the conductance of a unit volume (1 cm^3 or 1 m^3) of solution held between two electrodes of unit cross-sectional area placed unit distance apart.

It equals the inverse of resistivity: k = 1/rho.

SI unit: S m-1 (or commonly S cm-1).

Numerically: $k = G \times (l/A) = G \times G^*$ where $G^* = l/A$ is the cell constant.

Molar conductivity (Lm):

Molar conductivity is the conductance of the volume of solution containing one mole of electrolyte, kept between two electrodes of unit distance apart with sufficient area of cross section.

$Lm = k / c$ (c in mol m-3 gives Lm in S m_2 mol-1; alternatively, Lm (S cm_2 mol-1) = k(S cm-1) × 1000 / c(mol L-1)).

Variation with concentration:

Conductivity (k):

Conductivity decreases with decrease in concentration (dilution) for both strong and weak electrolytes.

On dilution, the number of ions per unit volume decreases, so the conductance of that unit volume decreases.

Molar conductivity (Lm):

Molar conductivity increases with decrease in concentration (dilution) for both strong and weak electrolytes.

Although k decreases on dilution, the volume V of solution containing one mole of electrolyte increases. The increase in V more than compensates the decrease in k, so Lm = k × V increases.

For strong electrolytes (e.g., KCl, NaCl):

Lm increases slowly and nearly linearly with c^0.5: Lm = Lm° - A sqrt(c) (Debye-Hückel-Onsager equation).

Lm° (limiting molar conductivity at zero concentration) can be obtained by extrapolating the Lm vs c^0.5 plot to c = 0.

For weak electrolytes (e.g., CH_3COOH):

Lm increases steeply on dilution, especially near low concentrations, because the degree of dissociation alpha increases sharply.

Lm° cannot be obtained by extrapolation; it is calculated using Kohlrausch's law: Lm° = n+ l°+ + n- l°-.

Answer: Conductivity (k) = conductance of unit-volume solution; decreases on dilution (fewer ions per unit volume). Molar conductivity (Lm) = k/c; increases on dilution. Strong electrolytes: slow increase (Lm = Lm° - A*sqrt(c)); weak electrolytes: steep increase due to increased dissociation.

Q8 The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm-1. Calculate its molar conductivity.

SOLUTION

Given:

Concentration c = 0.20 mol L-1

Conductivity k = 0.0248 S cm-1

Using the relation:

Lm (S cm_2 mol-1) = k (S cm-1) × 1000 (cm_3 L-1) / c (mol L-1)

Lm = 0.0248 × 1000 / 0.20

= 24.8 / 0.20

= 124.0 S cm_2 mol-1

Answer: Molar conductivity Lm = 124.0 S cm_2 mol-1

Q9 The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500 Ohm. What is the cell constant if conductivity of 0.001M KCl solution at 298 K is 0.146 × 10-3 S cm-1.

SOLUTION

Given:

R = 1500 ohm

k = 0.146 × 10-3 S cm-1 = 1.46 × 10-4 S cm-1

The cell constant G* is related to resistance and conductivity by:

G* = R × k

G* = 1500 ohm × 1.46 × 10-4 S cm-1

= 1500 × 0.000146 cm-1

= 0.219 cm-1

Answer: Cell constant G* = 0.219 cm-1

Q10 The conductivity of sodium chloride at 298 K has been determined at different concentrations: Concentration/M: 0.001, 0.010, 0.020, 0.050, 0.100; 10^2 × k / S m-1: 1.237, 11.85, 23.15, 55.53, 106.74. Calculate Lm for all concentrations and draw a plot between Lm and $c^{0.5}$. Find the value of Lm°.

SOLUTION

From the table header '10^2 × k / S m-1', we have: k (S m-1) = given value / 100.

Convert to S cm-1: k (S cm-1) = k (S m-1) / 100.

Molar conductivity: Lm (S cm_2 mol-1) = k (S cm-1) × 1000 / c (mol L-1).

Calculations:

c = 0.001 mol L-1: k = 1.237/100 S m-1 = 0.01237 S m-1 = 1.237×10-4 S cm-1

Lm = 1.237×10-4 × 1000 / 0.001 = 123.7 S cm_2 mol-1; $c^{0.5}$ = 0.0316 (mol

L-1)^0.5

c = 0.010 mol L-1: k = 11.85/100 S m-1 = 0.1185 S m-1 = 1.185×10-3 S cm-1
Lm = 1.185×10-3 × 1000 / 0.010 = 118.5 S cm$_2$ mol-1; c^0.5 = 0.1000

c = 0.020 mol L-1: k = 23.15/100 S m-1 = 0.2315 S m-1 = 2.315×10-3 S cm-1
Lm = 2.315×10-3 × 1000 / 0.020 = 115.75 S cm$_2$ mol-1; c^0.5 = 0.1414

c = 0.050 mol L-1: k = 55.53/100 S m-1 = 0.5553 S m-1 = 5.553×10-3 S cm-1
Lm = 5.553×10-3 × 1000 / 0.050 = 111.1 S cm$_2$ mol-1; c^0.5 = 0.2236

c = 0.100 mol L-1: k = 106.74/100 S m-1 = 1.0674 S m-1 = 1.0674×10-2 S cm-1
Lm = 1.0674×10-2 × 1000 / 0.100 = 106.74 S cm$_2$ mol-1; c^0.5 = 0.3162

Summary table:

c(M)	c^0.5	Lm (S cm$_2$ mol-1)
0.001	0.0316	123.70
0.010	0.1000	118.50
0.020	0.1414	115.75
0.050	0.2236	111.06
0.100	0.3162	106.74

Plot: Lm vs c^0.5 gives a straight line (Debye-Hückel-Onsager equation: Lm = Lm° - A*sqrt(c)).
Extrapolating the straight line to c^0.5 = 0 (i.e., c = 0) gives the y-intercept = Lm°.
From linear fit of these data: Lm° ≈ 124.0 S cm$_2$ mol-1.
(Check via Kohlrausch: Lm°(NaCl) = l°(Na^+) + l°(Cl^-) = 50.1 + 76.3 = 126.4 S cm$_2$ mol-1.)

Answer: Lm values: 123.70, 118.50, 115.75, 111.06, 106.74 S cm$_2$ mol-1 (at c = 0.001, 0.010, 0.020, 0.050, 0.100 M respectively). Lm° ≈ 124.0 S cm$_2$ mol-1 (from graph extrapolation; Kohlrausch value = 126.4 S cm$_2$ mol-1)

Q11 Conductivity of 0.00241 M acetic acid is 7.896 × 10-5 S cm-1. Calculate its molar conductivity. If Lm° for acetic acid is 390.5 S cm₂ mol-1, what is its dissociation constant?

SOLUTION

Step 1: Calculate molar conductivity Lm.

c = 0.00241 mol L-1, k = 7.896 × 10-5 S cm-1

Lm = k × 1000 / c = (7.896 × 10-5 × 1000) / 0.00241

= 0.07896 / 0.00241 = 32.76 S cm₂ mol-1

Step 2: Find degree of dissociation alpha.

alpha = Lm / Lm° = 32.76 / 390.5 = 0.0839

Step 3: Calculate dissociation constant Ka.

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Ka = c × alpha² / (1 - alpha)

= 0.00241 × (0.0839)² / (1 - 0.0839)

= 0.00241 × 0.007039 / 0.9161

= 1.697 × 10-5 / 0.9161

= 1.85 × 10-5 mol L-1

Answer: Lm = 32.76 S cm₂ mol-1; dissociation constant Ka = 1.85 × 10-5 mol L-1

Q12 How much charge is required for the following reductions: (i) 1 mol of Al^{3+} to Al? (ii) 1 mol of Cu^{2+} to Cu? (iii) 1 mol of MnO_4^- to Mn₂+?

SOLUTION

Charge Q = n × F, where n = moles of electrons transferred, F = 96500 C mol-1.

(i) $Al^{3+} + 3e^- \rightarrow Al$

3 electrons per Al^{3+} ion; for 1 mol Al^{3+}: n = 3 mol e-

Q = 3 × 96500 = 289500 C = 2.895 × 10^5 C

(ii) $Cu^{2+} + 2e^- \rightarrow Cu$

2 electrons per Cu^{2+} ion; for 1 mol Cu^{2+}: n = 2 mol e-

Q = 2 × 96500 = 193000 C = 1.93 × 10^5 C

(iii) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

5 electrons per MnO_4^- ion; for 1 mol MnO_4^-: n = 5 mol e-

Q = 5 × 96500 = 482500 C = 4.825 × 10^5 C

Answer: (i) 2.895 × 10^5 C (3F); (ii) 1.930 × 10^5 C (2F); (iii) 4.825 × 10^5 C (5F)

Q13 How much electricity in terms of Faraday is required to produce (i) 20.0 g of Ca from molten $CaCl_2$? (ii) 40.0 g of Al from molten Al_2O_3?

SOLUTION

(i) Ca from molten $CaCl_2$:

Cathode reaction: $Ca^{2+} + 2e^- \rightarrow Ca$

Molar mass of Ca = 40 g mol-1

Moles of Ca = 20.0 / 40 = 0.5 mol

Electrons required = 2 mol e- per mol Ca

Electricity = 0.5 × 2 = 1.0 F

(ii) Al from molten Al_2O_3:

Cathode reaction: $Al^{3+} + 3e^- \rightarrow Al$

Molar mass of Al = 27 g mol-1

Moles of Al = 40.0 / 27 = 1.481 mol

Electrons required = 3 mol e- per mol Al

Electricity = 1.481 × 3 = 4.444 F ≈ 4.4 F

Answer: (i) 1.0 F (ii) 4.4 F

Q14 How much electricity is required in coulomb for the oxidation of (i) 1 mol of H_2O to O_2? (ii) 1 mol of FeO to Fe_2O_3?

SOLUTION

(i) Oxidation of 1 mol H_2O to O_2:

Half-reaction: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

This shows 4 electrons are released per 2 mol H_2O, i.e., 2 electrons per mol H_2O.

For 1 mol H_2O: n = 2 mol e-

Q = 2 × 96500 = 193000 C = 1.93×10^5 C

(ii) Oxidation of 1 mol FeO to Fe_2O_3:

In FeO: Fe is in +2 oxidation state. In Fe_2O_3: Fe is in +3 oxidation state.

Half-reaction: $Fe^{2+} \rightarrow Fe^{3+} + e^-$ (one electron lost per Fe atom)

For 1 mol FeO (1 mol Fe^{2+}): n = 1 mol e-

Q = 1 × 96500 = 96500 C

Answer: (i) 1.93×10^5 C (2F) (ii) 96500 C (1F)

Q15 A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

SOLUTION

Given:

Current I = 5 A

Time t = 20 min = 20 × 60 = 1200 s

Step 1: Calculate charge passed.

Q = I × t = 5 × 1200 = 6000 C

Step 2: Cathode reaction: Ni_2+(aq) + 2e- -> Ni(s)

n = 2 electrons per Ni atom

Step 3: Moles of Ni deposited.

mol Ni = Q / (n × F) = 6000 / (2 × 96500) = 6000 / 193000 = 0.03109 mol

Step 4: Mass of Ni.

Molar mass of Ni = 58.7 g mol-1

mass = 0.03109 × 58.7 = 1.82 g

Answer: Mass of Ni deposited = 1.82 g

Q16 Three electrolytic cells A, B, C containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

SOLUTION

Since all cells are in series, the same charge Q passes through each cell.

Step 1: Find charge Q from the silver deposited.

Cathode reaction in B: Ag+(aq) + e- -> Ag(s); n = 1, M(Ag) = 108 g mol-1

mol Ag = 1.45 / 108 = 0.01343 mol

Q = mol Ag × n × F = 0.01343 × 1 × 96500 = 1295.9 C

Step 2: Time of electrolysis.

t = Q / I = 1295.9 / 1.5 = 863.9 s ≈ 864 s ≈ 14.4 min

Step 3: Mass of Cu deposited (cell C).

Cu_2+(aq) + 2e- -> Cu(s); n = 2, M(Cu) = 63.5 g mol-1

mol Cu = Q / (2 × F) = 1295.9 / (2 × 96500) = 6.715 × 10-3 mol

mass Cu = 6.715 × 10-3 × 63.5 = 0.4264 g ≈ 0.4263 g

Step 4: Mass of Zn deposited (cell A).

Zn_2+(aq) + 2e- -> Zn(s); n = 2, M(Zn) = 65.4 g mol-1

mol Zn = Q / (2 × F) = 6.715 × 10-3 mol

mass Zn = 6.715 × 10-3 × 65.4 = 0.4391 g ≈ 0.4390 g

Answer: Time = 864 s (≈ 14.4 min); mass of Cu deposited = 0.4263 g; mass of Zn deposited = 0.4390 g

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Q17 Using the standard electrode potentials given in Table 2.1, predict if the reaction between the following is feasible: (i) Fe_3+(aq) and I-(aq) (ii) Ag+(aq) and Cu(s) (iii) Fe_3+(aq) and Br-(aq) (iv) Ag(s) and Fe_3+(aq) (v) Br_2(aq) and Fe_2+(aq).

SOLUTION

A reaction is feasible (spontaneous) if E°(cell) = E°(cathode) - E°(anode) > 0.

Relevant standard reduction potentials from Table 2.1:

$E°(I_2/I^-)$ = 0.54 V, $E°(Fe^{3+}/Fe^{2+})$ = 0.77 V, $E°(Ag^+/Ag)$ = 0.80 V

$E°(Cu^{2+}/Cu)$ = 0.34 V, $E°(Br_2/Br^-)$ = 1.09 V

(i) Fe_3+(aq) + I-(aq):

Fe^{3+} is the oxidant (cathode): Fe^{3+} + e- -> Fe^{2+}; E° = 0.77 V

I^- is the reductant (anode): $2I^-$ -> I_2 + 2e-; $E°(I_2/2I^-)$ = 0.54 V

E°(cell) = 0.77 - 0.54 = +0.23 V > 0: FEASIBLE

Reaction: $2Fe_3$+(aq) + 2I-(aq) -> $2Fe_2$+(aq) + I_2(s)

(ii) Ag+(aq) + Cu(s):

Ag^+ is the oxidant (cathode): Ag^+ + e- -> Ag; E° = 0.80 V

Cu is the reductant (anode): Cu -> Cu^{2+} + 2e-; $E°(Cu^{2+}/Cu)$ = 0.34 V

E°(cell) = 0.80 - 0.34 = +0.46 V > 0: FEASIBLE

Reaction: 2Ag+(aq) + Cu(s) -> 2Ag(s) + Cu_2+(aq)

(iii) Fe_3+(aq) + Br-(aq):

Fe^{3+} is the oxidant (cathode): Fe^{3+} + e- -> Fe^{2+}; E° = 0.77 V

Br^- is the reductant (anode): $2Br^-$ -> Br_2 + 2e-; $E°(Br_2/Br^-)$ = 1.09 V

E°(cell) = 0.77 - 1.09 = -0.32 V < 0: NOT FEASIBLE

Fe^{3+} cannot oxidise Br^- under standard conditions.

(iv) Ag(s) + Fe_3+(aq):

Fe^{3+} is the oxidant (cathode): Fe^{3+} + e- -> Fe^{2+}; E° = 0.77 V

Ag is the reductant (anode): Ag -> Ag^+ + e-; $E°(Ag^+/Ag)$ = 0.80 V

E°(cell) = 0.77 - 0.80 = -0.03 V < 0: NOT FEASIBLE

Ag is not oxidised by Fe^{3+} under standard conditions.

(v) $Br_2(aq) + Fe_2+(aq)$:

Br_2 is the oxidant (cathode): $Br_2 + 2e- \rightarrow 2Br^-$; $E° = 1.09$ V

Fe^{2+} is the reductant (anode): $Fe^{2+} \rightarrow Fe^{3+} + e-$; $E°(Fe^{3+}/Fe^{2+}) = 0.77$ V

$E°(cell) = 1.09 - 0.77 = +0.32$ V > 0: FEASIBLE

Reaction: $Br_2(aq) + 2Fe_2+(aq) \rightarrow 2Br-(aq) + 2Fe_3+(aq)$

Answer: (i) Feasible: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ ($E°cell = +0.23$ V). (ii) Feasible: $2Ag^+ + Cu \rightarrow 2Ag + Cu^{2+}$ ($E°cell = +0.46$ V). (iii) Not feasible ($E°cell = -0.32$ V). (iv) Not feasible ($E°cell = -0.03$ V). (v) Feasible: $Br_2 + 2Fe^{2+} \rightarrow 2Br^- + 2Fe^{3+}$ ($E°cell = +0.32$ V).

Q18 Predict the products of electrolysis in each of the following: (i) An aqueous solution of $AgNO_3$ with silver electrodes. (ii) An aqueous solution of $AgNO_3$ with platinum electrodes. (iii) A dilute solution of H_2SO_4 with platinum electrodes. (iv) An aqueous solution of $CuCl_2$ with platinum electrodes.

SOLUTION

In electrolysis, the cation with the highest reduction potential is preferentially reduced at the cathode (most easily reduced); the anion with the lowest reduction potential (easiest to oxidise) is preferentially oxidised at the anode.

(i) Aqueous $AgNO_3$ with silver electrodes:

Ions in solution: Ag^+, NO_3^-, H_2O (H^+, OH^-).

Cathode: $Ag+(aq) + e- \rightarrow Ag(s)$. Ag^+ is preferentially reduced ($E° = +0.80$ V >> 0.00 V for H^+).

Product at cathode: Ag metal deposited.

Anode: Silver electrode is active. $Ag(s) \rightarrow Ag+(aq) + e-$ (oxidation of the electrode itself, $E° = 0.80$ V) is easier than oxidation of NO_3^- or water.

Product at anode: Silver electrode dissolves ($Ag \rightarrow Ag^+$). Concentration of $AgNO_3$ remains constant.

(ii) Aqueous $AgNO_3$ with platinum electrodes:

Ions in solution: Ag^+, NO_3^-, H_2O.

Cathode: $Ag+(aq) + e- \rightarrow Ag(s)$ is preferentially reduced.

Product at cathode: Ag metal deposited.

Anode: Pt is an inert electrode. NO_3^- is very stable and not easily oxidised. Water is oxidised preferentially:

$2H_2O \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Product at anode: O_2 gas evolved.

(iii) Dilute H_2SO_4 with platinum electrodes:

Ions in solution: H^+, SO_4^{2-}, H_2O.

Cathode: $H^+(aq) + e^- \rightarrow 1/2\ H_2(g)$ (or $2H^+ + 2e^- \rightarrow H_2$). H^+ is preferentially reduced over water.

Product at cathode: H_2 gas evolved.

Anode: SO_4^{2-} is very stable (very high E° required to oxidise it). Water is oxidised preferentially:

$2H_2O \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Product at anode: O_2 gas evolved.

Net result: Water is decomposed (H_2 at cathode, O_2 at anode); H_2SO_4 concentration increases.

(iv) Aqueous $CuCl_2$ with platinum electrodes:

Ions in solution: Cu^{2+}, Cl^-, H_2O.

Cathode: $Cu_2+(aq) + 2e^- \rightarrow Cu(s)$. Cu^{2+} is preferentially reduced (E° = +0.34 V >> 0.00 V for H^+).

Product at cathode: Cu metal deposited.

Anode: Cl^- is preferentially oxidised (lower discharge potential / overvoltage effect; E° for Cl^-/Cl_2 = 1.36 V) over water (E° = 1.23 V, but due to overpotential, Cl^- is discharged first from concentrated Cl^- solutions).

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Product at anode: Cl_2 gas evolved.

Answer: (i) Ag deposits at cathode; Ag electrode dissolves at anode (active electrode). (ii) Ag deposits at cathode; O_2 evolves at anode. (iii) H_2 at cathode; O_2 at anode. (iv) Cu deposits at cathode; Cl_2 evolves at anode.