Class 12 Chemistry · Chapter 2: Electrochemistry

Answer key and marking scheme · 20 marks · about 40 minutes · based on NCERT

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1. Given E°/V: $Na^+|Na$ −2.71, $Mg^{2+}|Mg$ −2.36, $Al^{3+}|Al$ −1.66, $Zn^{2+}|Zn$ −0.76. The strongest reducing agent among the four metals in aqueous solution is [1]

(a) Zn (b) Na
(c) Mg (d) Al

Answer: (b) The lower the standard electrode potential, the stronger the metal as a reducing agent; sodium has the lowest E° of the four.

2. Given E°/V: $Ag^+|Ag$ 0.80, $Cu^{2+}|Cu$ 0.34, $Ni^{2+}|Ni$ −0.25, $Au^{3+}|Au$ 1.40. Which metal can liberate hydrogen from 1 M HCl under standard conditions? [1]

(a) Ag (b) Cu
(c) Au (d) Ni

Answer: (d) Only a metal with a negative E° reduces H^+ (E° = 0.00 V) to H_2; of the four, only nickel has a negative E°.

3. Two hydrogen electrodes, each with H_2 at 1 bar, dip in buffer solutions of pH 2 and pH 5 and are joined by a salt bridge. At 298 K (2.303RT/F = 0.059 V) the emf of the cell is [1]

(a) 0.413 V (b) 0.177 V
(c) 0.295 V (d) 0.118 V

Answer: (b) Each electrode has E = −0.059 pH. The pH 5 electrode (lower E) is the anode: Ecell = (−0.059 × 2) − (−0.059 × 5) = 0.059 × 3 = 0.177 V. 0.413 V adds the two pH values; 0.295 V uses pH 5 alone.

4. At 298 K, the electrode potential of a copper rod in 0.010 M $CuSO_4$ is ($E°(Cu^{2+}|Cu)$ = 0.34 V; take 2.303RT/F = 0.059 V) [1]

(a) 0.222 V (b) 0.399 V
(c) 0.311 V (d) 0.281 V

Answer: (d) $E = E° - (0.059/2) \log(1/[Cu^{2+}]) = 0.34 - 0.0295 \times \log 100 = 0.34 - 0.059 = 0.281$ V. Adding the term gives 0.399 V; using log 10 gives 0.311 V; dropping the 2 gives 0.222 V.

5. Given $E°(Al^{3+}|Al) = -1.66$ V and $E°(Ni^{2+}|Ni) = -0.25$ V, the standard emf of the cell $Al(s) \mid Al^{3+}(aq) \parallel Ni^{2+}(aq) \mid Ni(s)$ is [1]

(a) −1.41 V (b) 1.41 V
(c) 1.91 V (d) 2.82 V

Answer: (b) E°cell = E°right − E°left = −0.25 − (−1.66) = 1.41 V. E° is intensive: the factor 2 or 3 in the balanced equation does not multiply it.

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6. Sodium metal cannot be obtained by electrolysing aqueous NaCl. Give the reason, and state how sodium is obtained by electrolysis. [2]

In aqueous solution water (H^+, E° 0.00 V) is reduced in preference to Na^+ (E° −2.71 V), so H_2 is evolved at the cathode, not sodium. Sodium is got by electrolysing molten (fused) NaCl: $Na^+ + e^- \rightarrow Na$ at the cathode, with Cl_2 at the anode.

- water is reduced before Na^+ (higher E°), giving H_2 (1)
- electrolysis of fused NaCl, $Na^+ + e^- \rightarrow Na$ (1)

7. State the two conditions iron needs in order to rust, and write the formula of rust. [2]

Rusting needs both water (moisture) and air (oxygen). Rust is hydrated ferric oxide, $Fe_2O_3{\cdot}xH_2O$.

- water and oxygen (air) both needed (1)
- $Fe_2O_3{\cdot}xH_2O$ (1)

8. Distinguish a primary battery from a secondary battery, naming one example of each. [2]

A primary battery reacts only once and cannot be recharged, e.g. the dry cell or the mercury cell. A secondary battery can be recharged by passing current through it in the opposite direction and used again, e.g. the lead storage battery or the nickel–cadmium cell.

- primary: used once, not rechargeable, with an example (1)
- secondary: recharged by reverse current, with an example (1)

9. For the lead storage battery while it is being discharged, write (i) the anode reaction, (ii) the cathode reaction, and (iii) explain why the density of the electrolyte can be used to tell how far the battery has run down. [3]

(i) Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$. (ii) Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$. (iii) Overall $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$: sulphuric acid is used up and water formed, so the acid becomes more dilute and its density falls as the battery discharges.

- anode reaction (1)
- cathode reaction (1)
- H_2SO_4 consumed and water formed, so density falls (1)

10. Using E°/V: MnO_4^-/Mn^{2+} 1.51, Cl_2/Cl^- 1.36, Pb^{2+}/Pb −0.13, Ni^{2+}/Ni −0.25, Fe^{2+}/Fe −0.44, Zn^{2+}/Zn −0.76, answer with a reason from E°cell: (i) Why is dilute HCl not used to acidify the solution in a titration with $KMnO_4$? (ii) A nickel-plated stirrer is left in $Pb(NO_3)_2$ solution. What forms on its surface? (iii) Can zinc be recovered from a $ZnSO_4$ effluent by adding scrap iron? [3]

(i) MnO_4^- reduced, Cl^- oxidised: E°cell = 1.51 − 1.36 = +0.15 V, positive, so MnO_4^- oxidises Cl^- to Cl_2 and part of the $KMnO_4$ is used up on the acid, spoiling the titre. (ii) Pb^{2+} reduced, Ni oxidised: E°cell = −0.13 − (−0.25) = +0.12 V, positive, so the nickel dissolves as Ni^{2+} and a layer of lead deposits on the stirrer. (iii) Zn^{2+} reduced, Fe oxidised: E°cell = −0.76 − (−0.44) = −0.32 V, negative, so iron cannot displace zinc and no zinc is recovered.

- (i) E°cell = +0.15 V, Cl^- is oxidised by MnO_4^- (1)
- (ii) E°cell = +0.12 V, lead deposits and nickel dissolves (1)
- (iii) E°cell = −0.32 V, no reaction, zinc not recovered (1)

11. Chloroacetic acid, $ClCH_2COOH$, has $K_a = 1.29 \times 10^{-3}$ mol L^{-1} at 298 K. Given $\lambda°(H^+) = 349.6$ and $\lambda°(ClCH_2COO^-) = 40.4$ S cm^2 mol^{-1}, calculate for its 0.010 M solution the degree of dissociation (1 − α cannot be neglected), the molar conductivity and the conductivity. [3]

$K_a = c\alpha^2/(1-\alpha)$: $0.010\alpha^2 + 1.29 \times 10^{-3}\alpha - 1.29 \times 10^{-3} = 0$, so $\alpha = [-1.29 \times 10^{-3} + \sqrt{(1.66 \times 10^{-6} + 5.16 \times 10^{-5})}]/0.020 = 0.30$. $\Lambda°m = \lambda°(H^+) + \lambda°(ClCH_2COO^-) = 349.6 + 40.4 = 390.0$ S cm^2 mol^{-1} (Kohlrausch); $\Lambda m = \alpha\Lambda°m = 0.30 \times 390.0 = 117$ S cm^2 mol^{-1}. $\kappa = \Lambda m \times c/1000 = 117 \times 0.010/1000 = 1.17 \times 10^{-3}$ S cm^{-1}.

- $\alpha = 0.30$ from the quadratic in $K_a = c\alpha^2/(1-\alpha)$ (1)
- $\Lambda°m = 390.0$ and $\Lambda m = 117$ S cm^2 mol^{-1} (1)
- $\kappa = 1.17 \times 10^{-3}$ S cm^{-1} (1)

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