ELECTROCHEMISTRY

1. Given that the standard potentials (E°) of Cu^{2+}/Cu and Cu^{+}/Cu are 0.34 V and 0.522 V respectively, the E° of Cu^{2+}/Cu^{+} is :

(1) +0.158 V (2) 0.182 V

(3) –0.182 V (4) –0.158 V

2. The equation that is incorrect is -

(1) $\left(\Lambda_m^0\right)_{NaBr} - \left(\Lambda_m^0\right)_{NaI} = \left(\Lambda_m^0\right)_{KBr} - \left(\Lambda_m^0\right)_{NaBr}$

(2) $\left(\Lambda_m^0\right)_{H_2O} = \left(\Lambda_m^0\right)_{HCl} + \left(\Lambda_m^0\right)_{NaOH} - \left(\Lambda_m^0\right)_{NaCl}$

(3) $\left(\Lambda_m^0\right)_{KCl} - \left(\Lambda_m^0\right)_{NaCl} = \left(\Lambda_m^0\right)_{KBr} - \left(\Lambda_m^0\right)_{NaBr}$

(4) $\left(\Lambda_m^0\right)_{NaBr} - \left(\Lambda_m^0\right)_{NaCl} = \left(\Lambda_m^0\right)_{KBr} - \left(\Lambda_m^0\right)_{KCl}$

3. What would be the electrode potential for the given half cell reaction at pH = 5 ?_____

$2H_2O \rightarrow O_2 + 4H^{\oplus} + 4e^-$; E^0_{red} = 1.23 V

(R = 8.314 J mol^{-1} K^{-1} ; Temp = 298 K; oxygen under std. atm. pressure of 1 bar)

4. For an electrochemical cell

$Sn(s) \mid Sn^{2+}$ (aq,1M)$||Pb^{2+}$ (aq,1M)$|Pb(s)$

the ratio $\frac{[Sn^{2+}]}{[Pb^{2+}]}$ when this cell attains equilibrium is _____.

(Given $E^0_{Sn^{2+}|Sn} = -0.14V$,

$E^0_{Pb^{2+}|Pb} = -0.13V, \frac{2.303RT}{F} = 0.06$)

5. 108 g of silver (molar mass 108 g mol^{-1}) is deposited at cathode from $AgNO_3$(aq) solution by a certain quantity of electricity. The volume (in L) of oxygen gas produced at 273 K and 1 bar pressure from water by the same quantity of electricity is _____.

6. Amongst the following, the form of water with the lowest ionic conductance at 298 K is:

(1) distilled water

(2) water from a well

(3) saline water used for intravenous injection

(4) sea water

7. 250 mL of a waste solution obtained from the workshop of a goldsmith contains 0.1 M $AgNO_3$ and 0.1 M AuCl. The solution was electrolyzed at 2 V by passing a current of 1 A for 15 minutes. The metal/metals electrodeposited will be :-

$\left(E^0_{Ag^+/Ag} = 0.80V, E^0_{Au^+/Au} = 1.69V\right)$

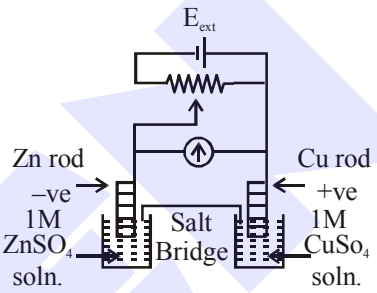
(1) only silver

(2) only gold

(3) silver and gold in equal mass proportion

(4) silver and gold in proportion to their atomic weights

8.



$E^o_{Cu^{2+}|Cu} = +0.34V$

$E^o_{Zn^{2+}|Zn} = -0.76V$

Identify the incorrect statement from the options below for the above cell :

(1) If E_{ext} > 1.1 V, Zn dissolves at Zn electrode and Cu deposits at Cu electrode

(2) If E_{ext} > 1.1 V, e^- flows from Cu to Zn

(3) If E_{ext} = 1.1 V, no flow of e^- or current occurs

(4) If E_{ext} < 1.1 V, Zn dissolves at anode and Cu deposits at cathode

9. The photoelectric current from Na (work function, w_0 = 2.3 eV) is stopped by the output voltage of the cell

$Pt(s)|H_2(g, 1bar)|HCl(aq., pH = 1)|AgCl(s)|Ag(s)$

The pH of aq. HCl required to stop the photoelectric current from K(w_0 = 2.25eV), all other conditions remaining the same, is ___$\times 10^{-2}$ (to the nearest integer).

Given, $2.303\frac{RT}{F} = 0.06V; E^0_{AgCl|Ag|Cl^-} = 0.22V$

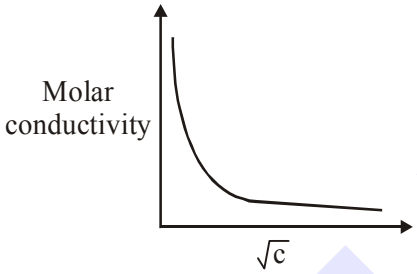
10. An acidic solution of dichromate is electrolyzed for 8 minutes using 2A current. As per the following equation

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

The amount of Cr^{3+} obtained was 0.104 g. The efficiency of the process(in%) is
(Take : F = 96000 C, At. mass of chromium = 52)
_____.

11. an oxidation-reduction reaction in which 3 electrons are transferred has a ΔG^o of 17.37 kJ mol^{-1} at 25°C. The value of E^o_{cell} (in V) is _____ $\times 10^{-2}$
(1 F = 96,500 C mol^{-1})

12. The variation of molar conductivity with concentration of an electrolyte (X) in aqueous solution is shown in the given figure.



The electrolyte X is :
(1) CH_3COOH (2) KNO_3
(3) HCl (4) NaCl

13. For the disproportionation reaction $2Cu^+(aq) \rightleftharpoons Cu(s) + Cu^{2+}(aq)$ at 298 K, ln K (where K is the equilibrium constant) is _____ $\times 10^{-1}$.
Given

$$(E^0_{Cu^{2+}/Cu^+} = 0.16V \quad E^0_{Cu^+/Cu} = 0.52V \quad \frac{RT}{F} = 0.025)$$

14. Potassium chlorate is prepared by the electrolysis of KCl in basic solution

$$6OH^- + Cl^- \rightarrow ClO_3^- + 3H_2O + 6e^-$$

If only 60% of the current is utilized in the reaction, the time (rounded to the nearest hour) required to produce 10 g of $KClO_3$ using a current of 2 A is_____.
(Given : F = 96,500 C mol^{-1} molar mass of $KClO_3$=122 $gmol^{-1}$)

15. For the given cell ;
$Cu(s)|Cu^{2+}(C_1M)||Cu^{2+}(C_2M)|Cu(s)$ change in Gibbs energy (ΔG) is negative, if :

(1) $C_1 = 2C_2$ (2) $C_2 = C1/\sqrt{2}$

(3) $C_1 = C_2$ (4) $C_2 = \sqrt{2}C_1$

SOLUTION

1. NTA Ans. (1)

Sol.

	E^0	ΔG^0
$Cu^{2\oplus} + 2e^{\oplus} \longrightarrow Cu$	0.34	$= -2F\ (0.34)$
$Cu^{\oplus} + e^{\oplus} \longrightarrow Cu$	0.522	$= -F\ (0.522)$
$Cu^{2\oplus} + e^{\oplus} \longrightarrow Cu^{+}$		

$\Delta G^0 = -2F\ (0.34) - (-F(0.522) = -F\ (0.68 - 0.522) = -F\ (0.158)$

$$E^0 = \frac{-F(0.158)}{-F} = 0.158V$$

2. NTA Ans. (1)

Sol. Option (1) is incorrect.

According to Kohlrausch's law correct expression is

$$\left(\Lambda_m^0\right)_{NaBr} - \left(\Lambda_m^0\right)_{NaI} = \left(\Lambda_m^0\right)_{KBr} - \left(\Lambda_m^0\right)_{KI}$$

The other statements are correct.

3. NTA Ans. (–0.93 to –0.94)

Sol. $2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$; $E^0_{red.} = 1.23V$

From nernst equation

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln Q$$

at 1 bar & 298 K

$$\frac{2.303RT}{F} = 0.059$$

pH = 5 $\Rightarrow [H^+] = 10^{-5}$ M

$E^\circ_{oxidation} = -1.23$ volt

$$E_{cell} = -1.23 - \frac{0.059}{4}\log[H^+]^4$$

$$E_{cell} = -1.23 - \frac{0.059}{4}\log(10^{-5})^4$$

$= -1.23 + 0.059 \times 5 = -0.935$ V

4. NTA Ans. (2.13 to 2.17)

Sol. Cell reaction is :

$Sn(s) + Pb^{+2}(aq) \longrightarrow Sn^{+2}(aq) + Pb(s)$

Apply Nernst equation :

$$E_{cell} = E^0_{cell} - \frac{0.06}{2}\log\frac{\left[Sn^{+2}\right]}{\left[Pb^{+2}\right]} \quad ...(1)$$

$E^0_{cell} = -0.13 + 0.14 = 0.01$ V

At equilibrium : $E_{cell} = 0$

Substituting in (1)

$$0 = 0.01 - \frac{0.06}{2}\log\frac{\left[Sn^{+2}\right]}{\left[Pb^{+2}\right]}$$

$$\Rightarrow \quad \frac{1}{3} = \log\frac{\left[Sn^{+2}\right]}{\left[Pb^{+2}\right]}$$

$$\Rightarrow \quad \frac{\left[Sn^{+2}\right]}{\left[Pb^{+2}\right]} = 2.15$$

5. NTA Ans. (5.66 to 5.68)

Sol. gm eq. of Ag = $\frac{108}{108} = 1$

gm eq. of $O_2(g) = 1$

Volume of $O_2(g) = 22.7 \times \frac{1}{4}$ = 5.675 litre

6. NTA Ans. (1)

Sol. Distilled water have lowest ionic conductance.

7. Official Ans. by NTA (4)

Sol. As voltage is '2V' so both Ag^+ & Au^+ will reduce and their equal gm equivalent will reduce so

gmeq Ag = gmeq of Au

$$\frac{Wt_{Ag}}{E_{qwt_{Ag}}} = \frac{Wt_{Au}}{E_{qwt_{Au}}}$$

So $$\frac{wt_{Ag}}{wt_{Au}} = \frac{E_{qwt_{Ag}}}{E_{qwt_{Au}}} = \frac{At\,wt_{Ag}}{Atwt_{Au}}$$

8. Official Ans. by NTA (1)

Sol. $E^o_{cell} = 0.34 - (-0.76)$

= 1.10 volt

If $E_{ext} > 1.10$ volt

Cu $\rightarrow$ Anode

Zn $\rightarrow$ Cathode

If $E_{ext} = 1.10$ volt

Zn $\rightarrow$ Anode

Cu $\rightarrow$ Cathode

9. Official Ans. by NTA (58)
Official Ans. by ALLEN (142)

Sol. $\frac{1}{2}H_2 \rightarrow H^+ + e^{\ominus}$

$e^{\ominus} + AgCl_{(s)} \rightarrow Ag_{(s)} + Cl^{\ominus}$

$\frac{1}{2}H_2 + AgCl_{(s)} \rightarrow H^+_{(aq)} + Ag_{(s)} + Cl^{\ominus}_{(aq)}$

$$E = \varepsilon^0 - \frac{.06}{1}\log\frac{\left[H^+\right]\left[Cl^{\ominus}\right]}{P_{H_2}^{\frac{1}{2}}}$$

$$E = 0.22 - .06\log\frac{\left(10^{-1}\right)\left(10^{-1}\right)}{1^{\frac{1}{2}}}$$

E = 0.22 + .12 = .34 volt

$\Rightarrow$ total energy of photon will be (for Na)
= 2.3 + 0.34 = 2.64 eV

10. Official Ans. by NTA (60)

Sol. Moles of $e^{\ominus} = \left(\frac{8\times60\times2}{96000}\right)$

Using stoichiometry; theoritically

$$\frac{n_{e^{\ominus}}\text{ used}}{6} = \frac{n_{cr^{+3}}\text{ produced}}{2}$$

$$\Rightarrow n_{cr^{+3}}\text{produced} = \frac{2}{6}\times\frac{8\times60\times2}{96000}$$

$$= \frac{0.02}{6}$$

$\Rightarrow$ $wt_{cr^{+3}}$ theoritically produced

$$= \left(\frac{0.02}{6}\times52\right)g$$

$$\Rightarrow \%\text{ efficiency} = \frac{0.104g}{\left(\frac{0.02\times52}{6}\right)g}\times100$$

= 60%

11. Official Ans. by NTA (6)

Sol. $\Delta G^\circ = -AFE^\circ = -3\times96500\times E^\circ$

$\Rightarrow$ $E^\circ = -6\times10^{-2}$ V

12. Official Ans. by NTA (1)

Sol. Its a weak electrolyte hence : CH_3COOH

13. Official Ans. by NTA (144.00)

Sol. $Cu^+ \longrightarrow Cu^{2+} + e^-$

$Cu^+ + e^- \longrightarrow Cu(s)$

$2Cu^+ \longrightarrow Cu^{2+} + Cu$

$E^o_{cell} = E^o_{Cu^+/Cu} - E^o_{Cu^{2+}/Cu^+}$

= 0.52 – 0.16

= 0.36 V

At equilibrium $\rightarrow E_{cell} = 0$

$$E^o_{cell} = \frac{RT}{nF}\ln K$$

$$\ln K = \frac{E^o_{cell}\times nF}{RT}$$

$$\ln K = \frac{0.36\times1}{0.025}$$

$= 14.4 = 144 \times 10^{-1}$

14. Official Ans. by NTA (11.00)

15. Official Ans. by NTA (4)

Sol. $\Delta G = -n\,F\,E_{cell}$

ΔG is negative, if E_{cell} is positive

Anode : $Cu(s) \longrightarrow Cu^{+2}(C_1) + 2e^- : E^\circ$

Cathode : $Cu^{+2}(C_2) + 2e^- \longrightarrow Cu(S) : -E^\circ$

Cell reaction : $Cu^{+2}(C_2) \longrightarrow Cu^{+2}(C_1)$ $E^\circ_{cell} = 0$

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log Q$$

$$E_{cell} = 0 - \frac{2.303RT}{nF}\log\left(\frac{C_1}{C_2}\right)$$

$$E_{cell} > 0 : \text{ if } \frac{C_1}{C_2} < 1 \Rightarrow C_1 < C_2$$