

PROBLEMS OF

ELECTROCHEMISTRY

1. For a cell involving one electron, $E^\circ_{\text{cell}} = \underline{0.59 \text{ V}}$ at 298 K, the equilibrium constant for the cell reaction is

$$2.303 RT$$

[Given that $\frac{\quad}{F} = \underline{0.059 \text{ V}}$ at $T = 298 \text{ K}$]

(a) 1.0×10^{30}

(b) 1.0×10^2

(c) 1.0×10^5

(d) 1.0×10^{10}

$$\log K = 10$$

$$K = 10^{10}$$

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~~$$\Delta G = \Delta G^\circ + RT \ln Q$$~~

$$\Delta G^\circ = - RT \ln K$$

$$\Rightarrow + nF E_{\text{cell}}^\circ = + RT \ln K$$

$$\Rightarrow E_{\text{cell}}^\circ = \frac{2.303 RT}{nF} \log K$$

$$0.59 = \frac{0.0591 n F}{1} \log K$$

eq 3 x 2 + eq 1

2. Following limiting molar conductivities are given as :

$\lambda_{m(H_2SO_4)}^\circ = x \text{ Scm}^2 \text{ mol}^{-1}$; $\lambda_{m(K_2SO_4)}^\circ = y \text{ Scm}^2 \text{ mol}^{-1}$

- eq 2
divide by 2
① ②

$\lambda_{m(CH_3COOK)}^\circ = z \text{ Scm}^2 \text{ mol}^{-1}$; λ_{m}° (in $\text{S cm}^2 \text{ mol}^{-1}$)
for CH_3COOH will be

(a) $x - y + 2z$ (b) $x + y - z$

(c) $x - y + z$

~~(d)~~ $\frac{(x-y)}{2} + z$

$\lambda_{m(H_2SO_4)}^\circ = 2\lambda_{mH^+}^\circ + \lambda_{mSO_4^{2-}}^\circ$
 $\lambda_{m(K_2SO_4)}^\circ = 2\lambda_{mK^+}^\circ + \lambda_{mSO_4^{2-}}^\circ$
- ② ④

$\lambda_{m(CH_3COOK)}^\circ = \lambda_{mCH_3COO^-}^\circ + \lambda_{mK^+}^\circ$
② ③

$\lambda_{mCH_3COOH}^\circ = \lambda_{mCH_3COO^-}^\circ + \lambda_{mH^+}^\circ$ - ?

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3. During the electrolysis of molten sodium chloride, the time required to produce 0.10 mol of chlorine gas using a current of 3 amperes is

$$\underline{1F = 96500C}$$

- (a) 55 minutes (b) 110 minutes
(c) 220 minutes (d) 330 minutes



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$$(1\text{mole}e^- = 1F)$$

$$\underline{1\text{mol}} \rightarrow \underline{2\text{mole}e^-} = \underline{2F}$$

$$\underline{Q = I \times t}$$

$$\underline{0.10 Cl_2} \rightarrow \underline{0.2F}$$

$$0.2 \times 96500 = 3 \times t$$

$$t = \underline{110\text{min}}$$

4. The pressure of H_2 required to make the potential of H_2 electrode zero in pure water at 298 K is

(a) 10^{-10} atm (b) 10^{-4} atm

(c) 10^{-14} atm (d) 10^{-12} atm

$$H^+ = 10^{-7}$$

$$pH = 7$$

$$-\log H^+ = 7$$

$$H^+ = 10^{-7}$$

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$$E = E^\circ - \frac{0.0591}{n} \log \frac{P_{H_2}}{[H^+]^2}$$

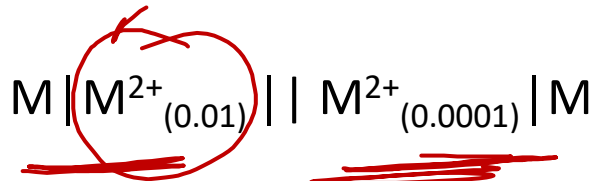
$$0 = 0 - \frac{0.0591}{2} \log \frac{P_{H_2}}{(10^{-7})^2}$$

$$\log \frac{P_{H_2}}{10^{-14}} = 0$$

$$P_{H_2} = 10^{-14} \text{ atm}$$

5. Calculate emf of the following cell at 25°C if value of E°_{cell} is 4 V

(Given $\frac{RT}{F} \ln 10 = 0.06$) :



- (a) 3.94 V (b) 4.06 V (c) 2.03 V (d) 8.18 V

$E = E^\circ - \frac{0.0591}{n} \log \frac{10^{-2}}{10^{-4}}$

$M \rightarrow M^{+2}$

$\Rightarrow E = 4 - \frac{0.0591}{2} \log 10^2$

$= 4 - 0.0591$

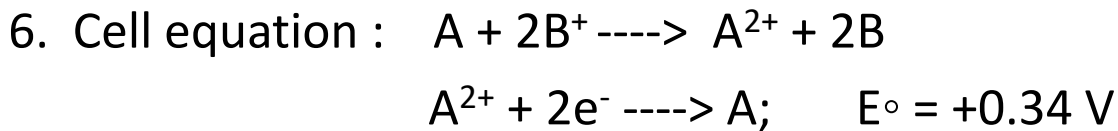
$= 3.94 \text{ V}$

$\log m^n = n \log m$

$\left[\frac{4 - 0.0591 \times 2}{2} \right]$

... AIIMS 2019

$\log 10 = 1$



And $\log_{10} K = 15.6$ at 300 K for all reactions.

Find E° for $B^+ + e^- \rightleftharpoons B$

$2.303 RT$

[Given that $\frac{\quad}{nF} = 0.059$ at 300K]

Handwritten notes:

$$E = E_{\text{cell}} - \frac{0.059}{n} \log Q$$

$$E^\circ_{\text{cell}} = \frac{0.059}{2} \log K$$

$$E^\circ_{\text{cell}} = \frac{0.059}{2} \times 156$$

- (a) 0.80 V (b) 1.26 V (c) -0.54 V (d) +0.94 V

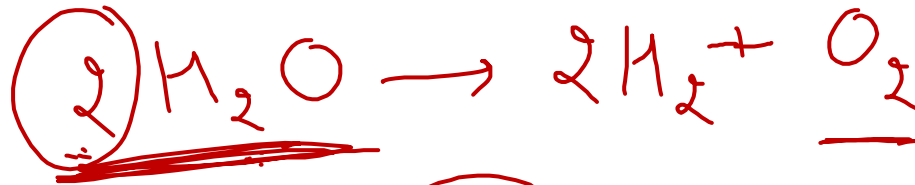
Handwritten equation: $E_{\text{cell}} = E_{B^+/B} - E_{A^{2+}/A}$

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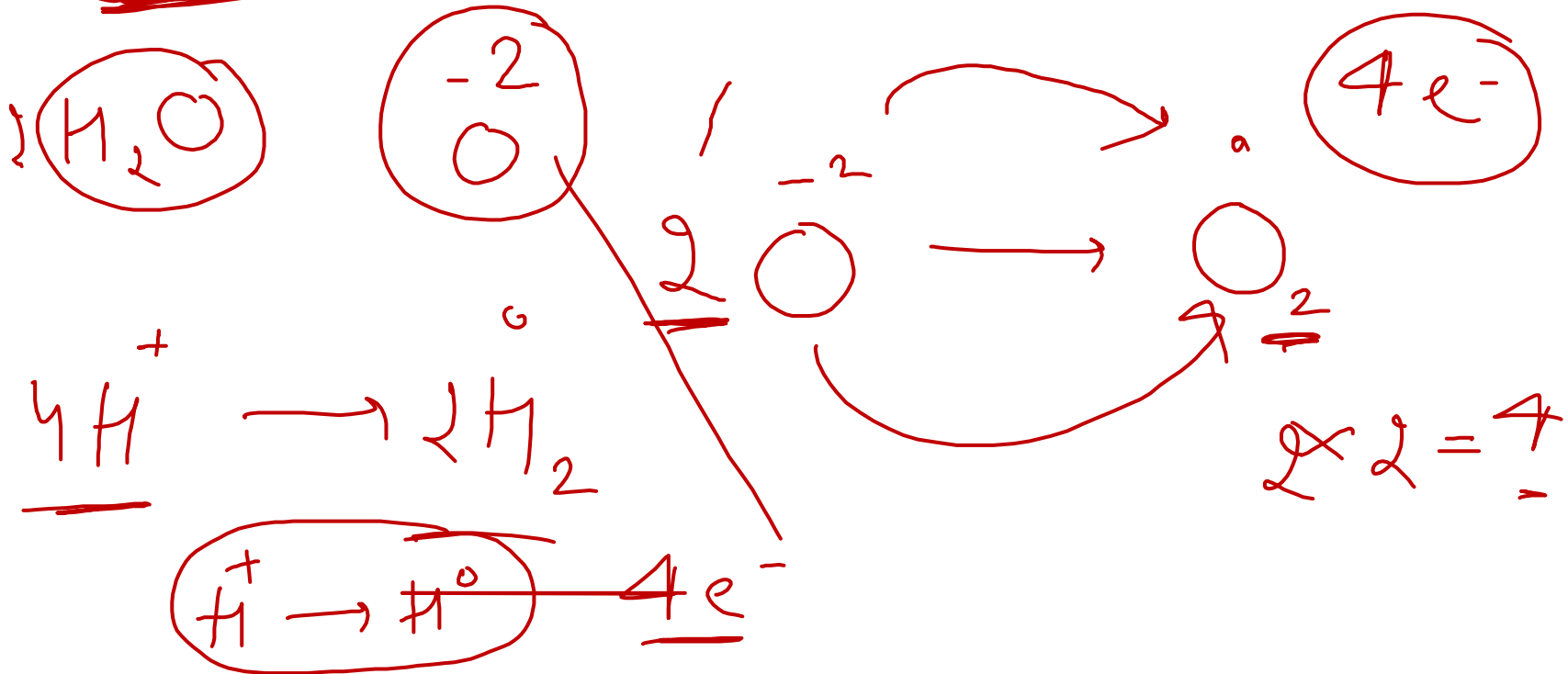
7. Time taken to completely decompose 36 g of water by passing 3A current is

- (a) 35.8 hr (b) 40 hr (c) 51.8 hr (d) 22.5 hr

$$\frac{4 \text{ mole } e^-}{4F}$$



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$$\underline{36 \text{ g}} \rightarrow \underline{4F} \quad \underline{4 \times 96500 \text{ C}}$$

$$Q = I \times t$$

$$4 \times 96500 = 3 \times \underline{t}$$

8. A conductivity cell has a cell constant of 0.5 cm^{-1} . This cell when filled with 0.01 M NaCl solution has a resistance of 384 ohms at 25°C . Calculate the equivalent conductance of the given solution.

$$K = G \frac{l}{A}$$

$$K = \frac{l}{R} \frac{l}{A}$$

$$= \frac{1}{384} \times 0.5$$

- (a) $130.2 \Omega^{-1} \text{ cm}^2 (\text{g eq})^{-1}$ (b) $137.4 \Omega^{-1} \text{ cm}^2 (\text{g eq})^{-1}$
 (c) $154.6 \Omega^{-1} \text{ cm}^2 (\text{g eq})^{-1}$ (d) $169.2 \Omega^{-1} \text{ cm}^2 (\text{g eq})^{-1}$

$$\frac{l}{A} = 0.5 \text{ cm}^{-1}$$

$$M = 0.01$$

$$R = 384 \Omega$$

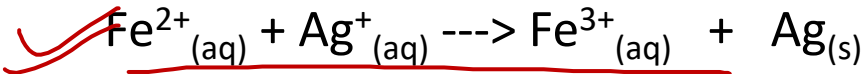
$$N = 0.01$$

$$\Lambda_{\text{eq}} = \frac{K \times 1000}{N}$$

$$K = G \frac{l}{A}$$

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9. Calculate the standard cell potential (in V) of the cell in which following reaction takes place.



Given that

$E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = x \text{ V}$

$E^{\circ}_{\text{Fe}^{2+}/\text{Fe}} = y \text{ V}$

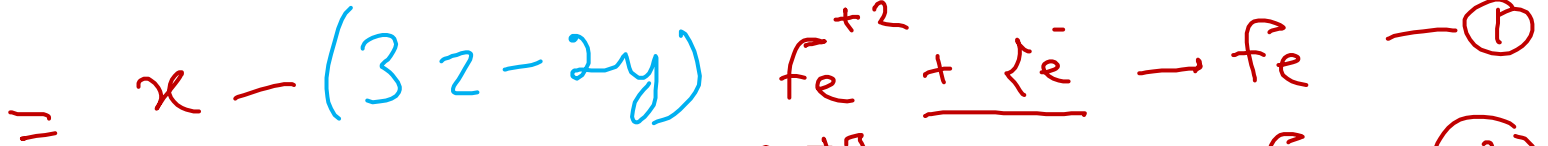
$E^{\circ}_{\text{Fe}^{3+}/\text{Fe}} = z \text{ V}$

$E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = ?$
 $3z - 2y$

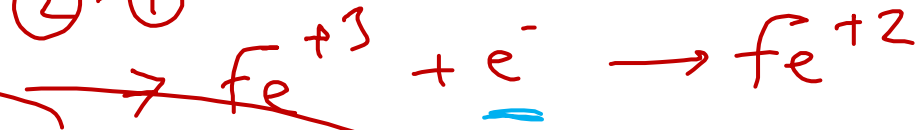
- (a) $x-z$ (b) $x-y$ (c) $x+2y-3z$ (d) $x+y-z$

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$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$



$(2) - (1)$



$x - 3z + 2y$

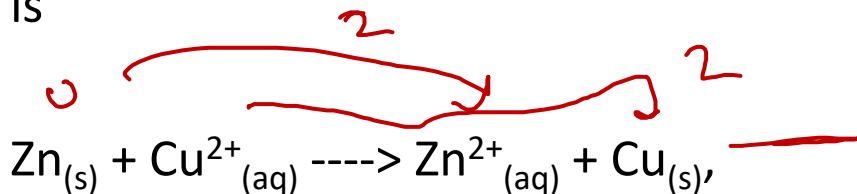
$\Delta G^{\circ}_3 = \Delta G^{\circ}_2 - \Delta G^{\circ}_1$

$$\Delta G^{\circ}_3 = \Delta G^{\circ}_2 - \Delta G^{\circ}_1$$

$$-1F \varepsilon^{\circ} = -3Fz - (-2Fy)$$

$$\varepsilon^{\circ} = 3z - 2y$$

10. The standard Gibbs energy for the given cell reaction in kJ mol^{-1} at 298 K is



$E^\circ = 2\text{V}$ at 298 K

(Faraday's constant, $F = 96000 \text{ C mol}^{-1}$)

- (a) -192 (b) 192 (c) ~~384~~ (d) 384

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$$\begin{aligned}
 \Delta G^\circ &= -nFE^\circ_{\text{cell}} \\
 &= -2 \times 96000 \times 2 \\
 &= -384 \text{ kJ/mol}
 \end{aligned}$$

11. Consider the statements S1 and S2:

S1 : Conductivity always increases with decrease in the concentration of electrolyte.

vol ↑
no of ions per unit vol ↓

S2 : Molar conductivity always increases with decrease in the concentration of electrolyte.

v ↑

$$\Lambda_m = K \times \frac{V}{A}$$

$$l = 1 \text{ cm}$$

$$A = 1 \text{ cm}^2$$

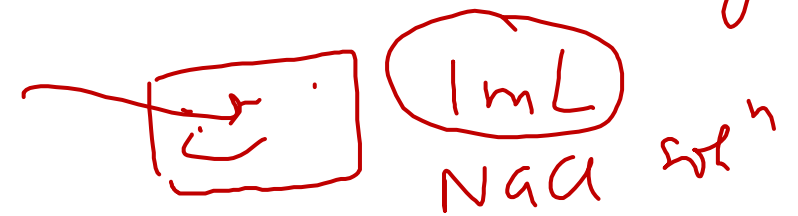
The correct option among the following is

- (a) Both S1 and S2 are wrong
- (b) Both S1 and S2 are correct
- (c) S1 is wrong and S2 is correct
- (d) S1 is correct and S2 is wrong

$K = \frac{G l}{A}$

$K = G$ of one unit (ml)

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limiting molar conductivity

NaCl

$$\lambda_m^{\circ}(\text{NaCl}) = \lambda_{\text{Na}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ}$$

~~$$\lambda_m^{\circ} \text{CaCl}_2 = \lambda_m^{\circ} \text{Ca}^{2+} + 2\lambda_m^{\circ} \text{Cl}^-$$~~

~~$$\lambda_m^{\circ} \text{CH}_3\text{COOH} = \lambda_m^{\circ} \text{CH}_3\text{COO}^- + \lambda_m^{\circ} \text{H}^+$$~~

(1+2-3)

①

$$\lambda_m^{\circ} \text{CH}_3\text{COONa} = \lambda_m^{\circ} \text{CH}_3\text{COO}^- + \lambda_m^{\circ} \text{Na}^+$$

②

$$\lambda_m^{\circ} \text{HCl} = \lambda_m^{\circ} \text{H}^+ + \lambda_m^{\circ} \text{Cl}^-$$

$$\lambda_m^{\circ} \text{NaCl} = \lambda_{\text{Na}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ}$$

12.

How long (approximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66 g of diborane? (Atomic weight of B = 10.8 u)

- (a) 6.4 hours (b) 0.8 hours (c) 3.2 hours (d) 1.6 hours



$$\underline{12 \times 96500} = \underline{100 \times t}$$

$$(10 \times 2) + 6$$

$$= 27.66 \text{ g}$$

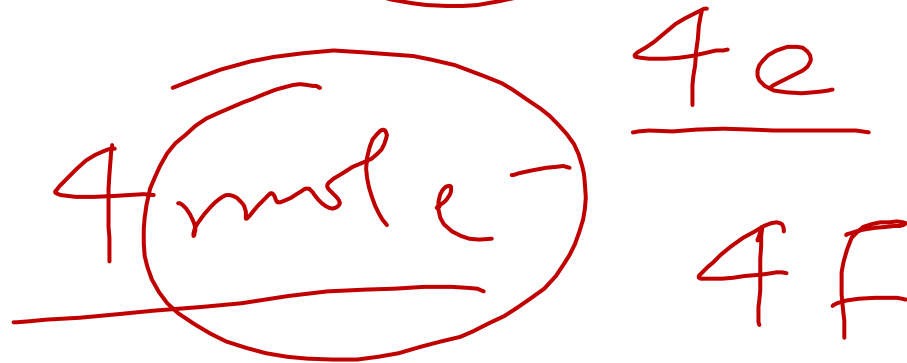
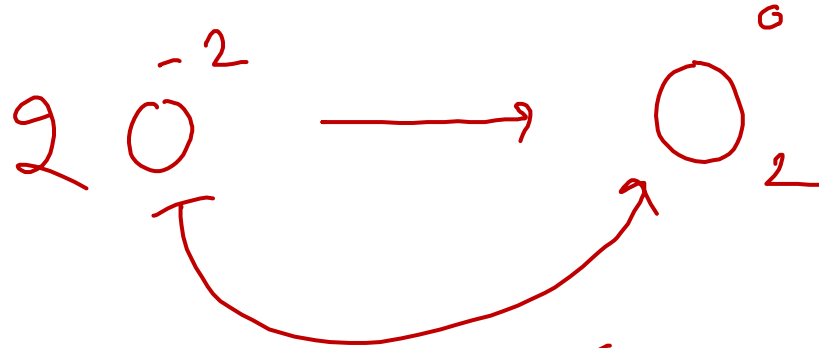
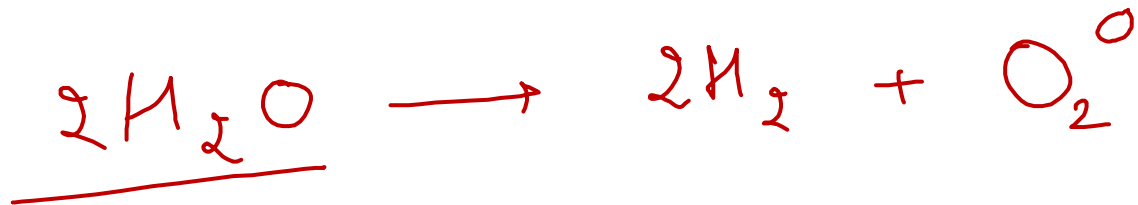
→ 1 mol

3 mol O₂



12F

1 mol



13. Given :

$$E^\circ_{\text{Cl}_2/\text{Cl}^-} = 1.36 \text{ V},$$

-1.36

$$E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}$$

+0.74

$$E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V},$$

-1.33

$$E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V}$$

-1.51

itself gets oxidised

Among the following, the strongest reducing agent is

(a) Cr^{3+}

(b) Cl^-

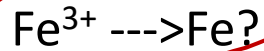
(c) Cr

(d) Mn^{2+}

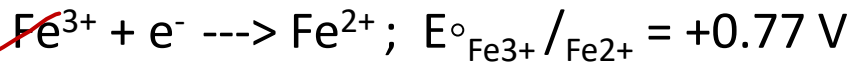
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14. What is the standard reduction potential (E°) for



Given that :



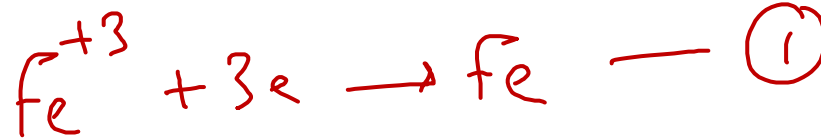
- (a) +0.057 V (b) +0.30 V (c) -0.30 V (d) -0.057 V

$$\Delta G_2^\circ + \Delta G_3^\circ = \Delta G_1^\circ$$

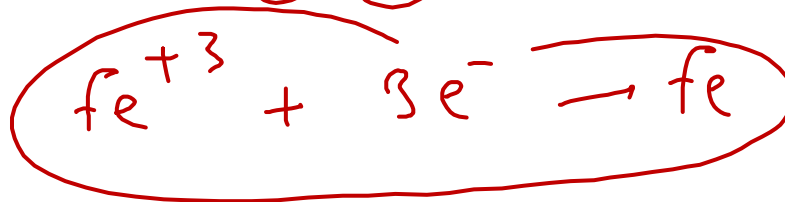
$$-2F(-0.47)$$

$$+ (-1F(+0.77))$$

$$= -3F E^\circ$$



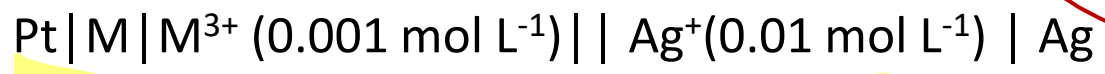
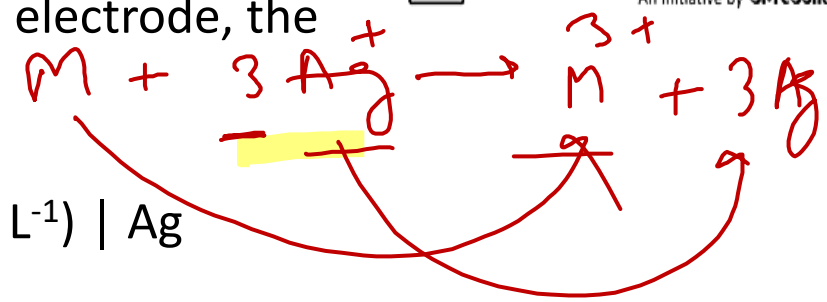
$$(2) + (3) = 1$$



$$-\frac{0.17}{3} = \underline{0.057 \text{ V}}$$

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15. To find the standard potential of M^{3+}/M electrode, the following cell is constituted:



The emf of the cell is found to be 0.421 volt at 298 K. The standard potential of half reaction $M^{3+} + 3e^- \rightarrow M$ at 298 K will be

(Given $E^\circ_{Ag^+/Ag}$ at 298 K = 0.80 Volt)

$$E_{cell} = E_{Ag^+/Ag} - E_{M^{3+}/M}$$

- (a) 0.32 Volt (b) 0.66 Volt (c) 0.38 Volt (d) 1.28 Volt

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0.421

$$E_{cell} = E_{cell}$$

$$0.421 = \frac{0.0591}{3} \log \frac{10}{(10^{-2})^3}$$

0.427

0.424 =

16.

What will occur if a block of copper metal is dropped into a beaker containing a solution of 1 M ZnSO_4 ?

- (a) The copper metal will dissolve with evolution of oxygen gas.
- (b) The copper metal will dissolve with evolution of hydrogen gas.
- (c) No reaction will occur.
- (d) The copper metal will dissolve and zinc metal will be deposited.

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17. Oxidation of succinate ion produces ethylene and carbon dioxide gases. On passing 0.2 Faraday electricity through an aqueous solution of potassium succinate, the total volume of gases (at both cathode and anode) at STP (1 atm and 273 K) is

- (a) 8.96 L (b) 4.48 (c) 6.72 L (d) 2.24 L

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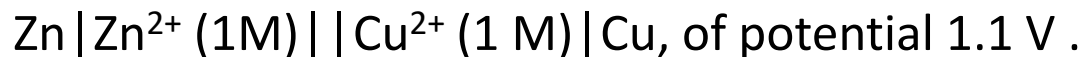
18.

Two Faradays of electricity are passed through a solution of CuSO_4 . The mass of copper deposited at the cathode is (at. Mass of Cu=63.5 amu) :

(a) 2 g (b) 127 g (c) 0 g (d) 63.5 g

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19. A variable, opposite external potential (E_{ext}) is applied to the cell :



When $E_{\text{ext}} < 1.1\text{ V}$ and $E_{\text{ext}} > 1.1\text{ V}$, respectively electron flow from

- (a) anode to cathode and cathode to anode
- (b) cathode to anode and anode to cathode
- (c) cathode to anode in both cases
- (d) anode to cathode in both cases.

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20. At 298 K, the standard reduction potentials are 1.51 V for $\text{MnO}_4^- | \text{Mn}^{2+}$, 1.36 V for $\text{Cl}_2 | \text{Cl}^-$, 1.07 V for $\text{Br}_2 | \text{Br}^-$ and 0.54 V for $\text{I}_2 | \text{I}^-$.

At pH = 3, permanganate is expected to oxidize

$$\left[\frac{RT}{F} = 0.059\text{V} \right]$$

(a) Cl^- , Br^- and I^- (b) Cl^- and Br^- (c) Br^- and I^- (d) I^- only

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